STUDIES ON THE CARBONYLATION OF ALKYNES

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123	c	Yields based on ...	% yields based on ...
133	a		add 1 x ⊙
140	a	P-I	Pd-I
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189	c	PhC CPh	PhC≡CPh
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ABSTRACT

The reaction between acetylenes and carbon monoxide in n-butanol solution in the presence of a palladium iodide/sodium iodide catalyst has been investigated.

Acetylene, methyl-, butyl- and phenylacetylene reacted readily at atmospheric pressure to yield mixtures of esters. Substituted acrylates, succinates, maleates and fumarates were the major products; the monoesters which were formed were, in the main, non-linear.

The effect of various additives on the product spectrum was examined, thus hydrogen chloride enhanced the yield of monoester in most cases, whilst air and other oxidising agents lowered it. Possible mechanistic routes were investigated by isotopic labelling and other techniques.

Dimethylacetylene and diphenylacetylene reacted less readily, and it was necessary to employ elevated pressures to bring about carbonylation. The products then included esters and lactones.

CHAPTER ONE

Literature Survey

C O N T E N T S

1.1. INTRODUCTION

1.2. CARBONYLATION OF ACETYLENE IN THE PRESENCE OF COMPOUNDS OF THE FOLLOWING METALS

(i) Nickel

(ii) Iron

(iii) Cobalt

(iv) Palladium

1.3. CARBONYLATION OF MONOALKYLACETYLENES IN THE PRESENCE OF COMPOUNDS OF THE FOLLOWING METALS

(i) Nickel

(ii) Iron

(iii) Cobalt

(iv) Palladium

1.4. CARBONYLATION OF MONOARYLACETYLENES IN THE PRESENCE OF COMPOUNDS OF THE FOLLOWING METALS

(i) Nickel

(ii) Cobalt

(iii) Palladium

1.5. CARBONYLATION OF DIALKYLACETYLENES IN THE PRESENCE OF COMPOUNDS OF THE FOLIOWING METALS

(i) Nickel

(ii) Iron

(iii) Cobalt

1.6. CARBONYLATION OF DIARYLACETYLENES IN THE PRESENCE OF COMPOUNDS OF THE FOLLOWING METALS

(i) Nickel

(ii) Palladium

1.7. REFERENCES

1.1. INTRODUCTION

The reaction of acetylene with carbon monoxide in the presence of a metal catalyst was explored during the 2nd World War by W.Reppe[1]. The reaction was of interest because it offered a route to industrially important acrylate esters.

Reppe found that nickel(II) compounds effectively catalysed the reaction, and since then nickel has been most frequently used in investigations of alkyne carbonylation. However, the catalytic power of other transition metals has also been reported. The present work has been concerned with reactions catalysed by palladium.

A detailed review of carbonylation reactions has been given by C.B.Lines[2] and relevant reviews have been published[3, 4, 5]. It is therefore proposed to survey those aspects of the carbonylation of acetylenic hydrocarbons which are particularly relevant to the investigations to be described in later chapters.

1.2. CARBONYLATION OF ACETYLENE IN THE PRESENCE OF COMPOUNDS OF THE FOLLOWING METALS

(i) Nickel: Reppe[1] discovered two reactions leading to acrylate esters during his war-time work. The first was a stoicheiometric reaction between acetylene and nickel tetracarbonyl carried out in water in the presence of acid.

$$4HC{\equiv}CH + Ni(CO)_4 + 4H_2O + 2HCl \xrightarrow{40^\circ C,\ \text{Atmospheric pressure}} H_2C{=}CH{-}COOH + NiCl_2 + [H_2] \quad \ldots\ldots\ldots\ldots\ldots 1.$$

An exothermic reaction started after a short induction period. Water could be replaced by alcohols, thiols, amines and organic acids, when esters, thioesters, amides and mixed anhydrides respectively were formed. Hydrogen was not liberated as such, but various reduced by-products were found, such as propionic acid, pent-3-enoic acid and tetrahydrobenzoic acid.

The second type of reaction was a catalytic carbonylation using nickel(II) salts and carbon monoxide under pressure. It was presumed to proceed via the formation of nickel carbonyl:

$$HC{\equiv}CH + CO + ROH \xrightarrow[150^\circ C,\ 30\ \text{atmos.}]{Ni^{(II)},\ H^{\oplus}} H_2C{=}CH{-}COOR \quad \ldots\ldots\ldots 2.$$

Again, a variety of solvents could be used. Reppe found that the most effective catalyst was a complex formulated as $NiBr_2(PPh_3)_2BuBr$. The presence of an acid was desirable. By-products of the reaction were the pent-3-enoate, pentanoate, β-butoxypropionate, fumarate and tetrahydrophthalate esters.

Since the publication of Reppe's results, a number of workers have investigated carbonylation reactions, thus Ehrreich et al.[6] examined a stoicheiometric reaction of acetylene and nickel carbonyl. Bhattacharyya & Sen[7] found that iron, cobalt and especially nickel, when employed as the halides supported on silica gel or as 'naphthenates', catalysed the formation of methyl acrylate from carbon monoxide, acetylene and methanol at 15 atmospheres pressure.

Chiusoli and his co-workers[8, 9, 10, 11] have discovered another reaction apparently involving the insertion of an acetylene unit during the carbonylation of allylic compounds such as allyl chloride or allyl alcohol. They used nickel tetracarbonyl as a catalyst, and carbon monoxide was taken up at atmospheric pressure. Chiusoli and Merzoni[12] described a reaction using Raney nickel in the presence of thiourea, or nickel chloride in the presence of iron powder and basic magnesium carbonate to give 2,5-diunsaturated esters:

$$H_2C{=}CH{-}CH_2{-}Cl + HC{\equiv}CH + CO + ROH \xrightarrow{\text{Nickel Compound}} H_2C{=}CH{-}CH_2{-}CH{=}CH{-}COOR + [HCl] \quad \ldots\ldots\ldots\ldots 3.$$

The reactions proceeded when a variety of substituted allyl compounds[8, 9, 11, 13] and acetylenes (v.i) were used.

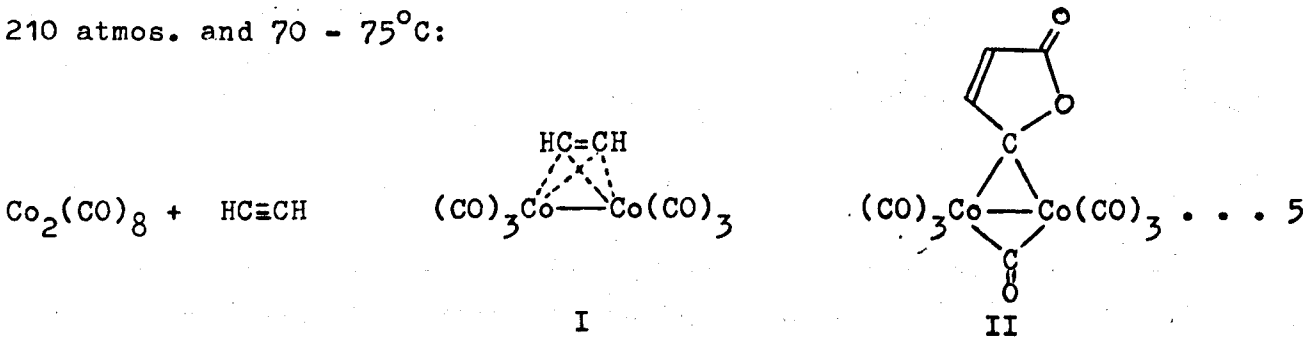
Chiusoli et al.[14] have also effected a reaction between phenyl iodide, acetylene and carbon monoxide:

$$PhI + HC{\equiv}CH + 2CO + HX + ROH \xrightarrow[-IX]{Ni(CO)_4,\ 130^{\circ}C,\ 30\ \text{atmos.}} Ph{-}CO{-}CH_2{-}CH_2{-}COOR \quad \ldots\ldots\ldots\ldots\ldots\ldots 4.$$

(ii) Iron: W.Reppe[1] attempted to react acetylene with iron pentacarbonyl, however the reaction only proceeded with difficulty, and it was necessary to add small amounts of preformed ester to achieve a moderate yield of acrylate.

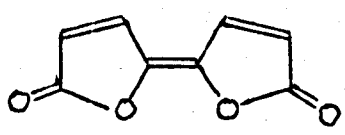
(iii) Cobalt: Various workers have treated acetylene with carbon monoxide in the presence of cobalt compounds and have observed ketones and lactones amongst the products. Thus Pino and Miglierina[15] used dicobalt octacarbonyl as a catalyst at 100°C and a pressure of 200 - 300 atmos. and obtained dimethyl succinate as the main product together with acrylate, fumarate, carbomethoxysuccinate and 4-ketoheptanedioate esters and cyclopent-2-enone. In later work[16, 17], Pino and his co-workers observed the formation of acrylate and succinate esters and cyclopentenone, with traces of fumarate, muconate, hex-3-enedioate and 4-ketohexanoate esters and cyclopentanone, when acetylene was treated with carbon monoxide at high pressure in the presence of a dicobalt octacarbonyl catalyst.

Sternberg et al.[18] obtained a complex (II) by treating the acetylene / cobalt carbonyl complex (I) with carbon monoxide at 210 atmos. and 70 - 75°C:



Since Sternberg and his co-workers used a lower temperature than Pino et al. (v.s.), II may be the precursor of the ester compounds observed by the latter workers. II may also be an intermediate in the formation of the lactones described by Albanesi et al.[19] and Sauer et al.[20] (v.i.).

The formation of bicyclic lactones 'bifurandiones' III and IV has been reported independently by two groups of workers.



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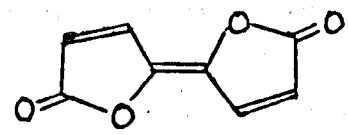
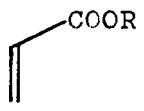


IV

Albanesi and Tovaglieri[19] studied the reaction of carbon monoxide with acetylene, using dicobalt octacarbonyl as catalyst in an acetone / acetic anhydride solution at 100°C and 180 atmos. pressure and obtained cis- and trans-bifurandione. Sauer et al.[20] used

cobalt salts in a wide variety of inert solvents at pressures ranging from 100 - 1000 atmos. and temperatures of 90 - 120°C. They also obtained mixtures of III and IV, but were able to control the relative proportions to some extent by a suitable choice of solvents. They extended their work to a number of substituted acetylenes (v.i.).

(iv) Palladium: The use of palladium chloride, palladium sulphate or palladium / charcoal, in the presence of iodine or hydrogen iodide to catalyse the carbonylation of acetylene at atmospheric pressure, was described by Jacobsen and Spathe[21]. Using the appropriate alcohol as solvent, they obtained lower aliphatic esters of acrylic, propionic maleic, fumaric and succinic acids, V - IX respectively:



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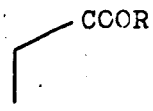

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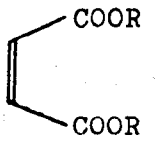
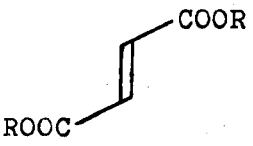
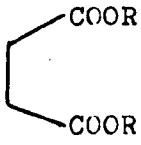


VII



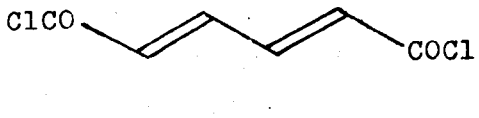
VIII



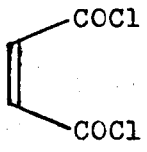
IX

A similar reaction, catalysed by sodium tetraiodopalladate(II) was independently discovered in 1962 by W.T.Dent and R.Long at I.C.I., Billingham[22]. The effects of varying the experimental conditions in this reaction was the subject of an investigation by Lines and Long[2, 23], the results of which are described elsewhere (Chapter 2.1 (i), (ii)). In brief, Lines and Long obtained the same five esters as Jacobsen and Spathe as principal products, and found that added halogen acid increased the amount of unsaturated monoester formed. Hopes that the reaction would form the basis of a useful commercial route to acrylates were not realised, though the ability of palladium to bring about carbonylation at atmospheric pressure was an attractive feature.

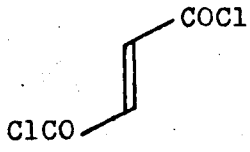
Tsuji[24] described a similar reaction in which acetylene at 5 atmos. in contact with palladium chloride in ethanol treated with carbon monoxide at 80 atmos. at 50°C for 12 hours, gave mainly diethyl maleate. However, Tsuji and his co-workers[25] also described a reaction in which acetylene and carbon monoxide with palladium chloride or bisbenzonitrilepalladium(II) chloride in benzene gave trans,trans-muconyl, maleyl and fumaryl chlorides X, XI and XII respectively:



X



XI



XII

Chiusoli et al.[26, 27] observed a similar reaction in which palladium chloride in the presence of thiourea acted as a catalyst rather than simply as a reagent. The solvent was methanol, and the following esters were formed: dimethyl maleate and cis,cis-muconate(XIII) with traces of fumarate and the other isomers of muconate esters.

XIII

1.3. CARBONYLATION OF MONOALKLACETYLENES IN THE PRESENCE OF COMPOUNDS OF THE FOLLOWING METALS.

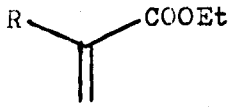
(i) Nickel: W.Reppe[1] investigated the catalytic carbonylation of hexylacetylene (oct-1-yne). In aqueous acetic acid containing nickel(II) ions under a carbon monoxide pressure of 30 atmos., hexylacetylene gave α-hexylacrylic acid (α-methyleneoctanoic acid) in fair yield.

Jones, Shen and Whiting[28] have studied the stoicheiometric reaction of butylacetylene (hex-1-yne) with nickel tetracarbonyl in acidified ethanol which gave the non-linear acrylate derivative,XIV.

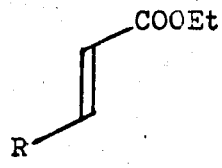
$$4BuC{\equiv}CH + Ni(CO)_4 + 4EtOH + 2HCl \xrightarrow{55^{\circ}C} H_2C{=}CBu{-}COOEt + NiCl_2 + [H_2] \quad \ldots\ldots\ldots 6.$$

XIV

Methyl and ethylacetylenes[29] have also been studied under the conditions used by Jones et al. Both linear (XVI) and non-linear (XV)



XV



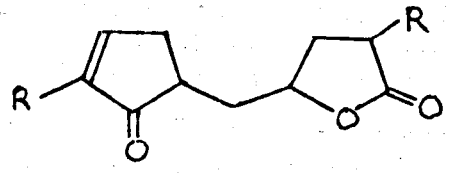
XVI

esters were obtained, though the non-linear form predominated in both cases.

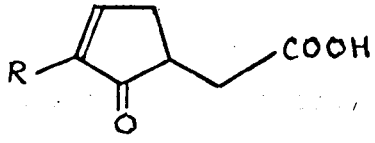
A more detailed study of methylacetylene was undertaken by Happel and Marsel[30]. They used nickel tetracarbonyl first as a stoicheiometric reagent, then as a catalyst, with methylacetylene and carbon monoxide in approximately equal amounts, a pressure ranging from 1 - 4 atmos. and a temperature of 45 - 80°C. The presence of some form of acid such as hydrogen chloride was necessary and a number of lower alcohols were found to be suitable both as reactants and solvents. Methacrylate ester, the major product, was formed in good yield.

Methylacetylene was further examined as a source of methacrylate esters by Sakakibara and his co-workers[31, 32]. They studied reactions with both catalytic and stoicheiometric amounts of nickel compounds and found that the stoicheiometric reaction would only proceed at atmospheric pressure if a proportion of acetylene were included in the reactant gases. The catalytic reaction was carried out in the presence of either bis(triphenylphosphine)nickel bromide, or nickel tetracarbonyl and a compound containing reactive hydrogen, such as concentrated hydrochloric acid. Pressures of 15 - 25 atmos. and temperatures of 150 - 290°C were required. The chief by-products were crotonate and isobutyrate esters, methacrylic acid and acetone. Sakakibara and his co-workers[32] showed that the reaction rate was dependent on the methylacetylene concentration. High concentrations of methylacetylene favoured reaction, whilst high concentrations of carbon monoxide apparently had an inhibiting effect.

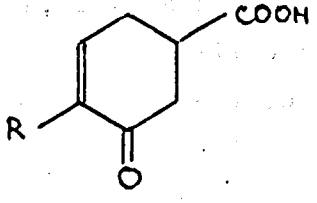
Chiusoli and his co-workers[33, 34, 35] investigated the reaction between acetylenes, allyl chloride and carbon monoxide, and found cyclic ketones amongst the products



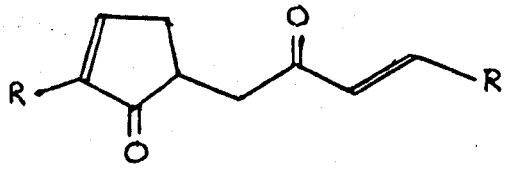
XVII



XVIII



XIX



XX

Monosubstituted acetylenes (R-C≡CH), carbon monoxide and allyl chloride (or substituted allyl chloride) were reacted in the presence of nickel tetracarbonyl in aqueous acetone. In the case of methylacetylene, XVII, XIX and XX (R=Me) were formed. Butyl- and hexylacetylene gave XVII, XVIII and XIX (R=Bu,C_6H_{13}).

(ii) Iron: Reppe and Vetter[36] have reported that methylacetylene, when treated with iron pentacarbonyl in aqueous alkali gave 2,5-dimethylhydroquinone.

(iii) Cobalt: Sternberg et al.[18] have treated propylacetylene with carbon monoxide at 70°C and 190 atmos. in the presence of dicobalt octacarbonyl. A complex formulated as $Co_2(CO)_9PrC{\equiv}CH$, was obtained. The structure of the complex was assumed to be analogous to that of II, which had been prepared from acetylene, but definite proof of the structure was lacking.

Sauer et al.[20] extended their studies on the formation of bifurandiones, III and IV, to monosubstituted acetylenes. Methyl- or butylacetylene with carbon monoxide in the presence of cobalt gave the analogous lactones. The substances, which were mixtures of isomers, had ill defined melting points. Three positional isomers are possible, each existing in cis- and trans- forms. Similar work has been carried out by Albanesi[37]. Using methylacetylene and carbon monoxide in acetone / acetic anhydride in the presence of cobalt octacarbonyl at 100°C and 235 atmos., he obtained three isomers of dimethylbifurandione.

(iv) Palladium: Tsuji[24] has reported the formation of diethyl citraconate when methylacetylene and carbon monoxide at 80 atmos. in ethanol were held overnight at 50°C in the presence of a catalytic amount of palladium chloride.

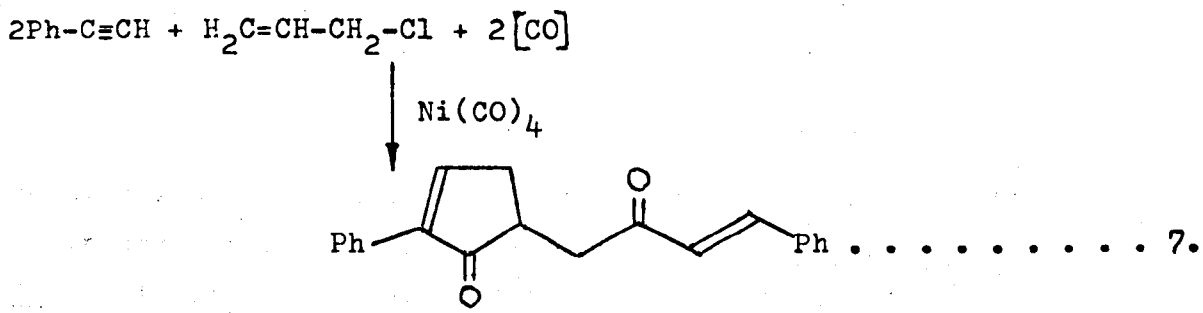
1.4. CARBONYLATION OF MONOARYLACETYLENES IN THE PRESENCE OF COMPOUNDS OF THE FOLLOWING METALS

(i) Nickel: The carbonylation of phenylacetylene was reported by Reppe[1]. Using the 'catalytic' method with a nickel(II) salt, and carbon monoxide at 30 atmos., the non-linear product was formed. Using water as a solvent, atropic acid was obtained; with alcohols, amines, thiols and organic acids the corresponding esters, amides, thioesters and mixed anhydrides were formed.

Jones and his co-workers[28] and Clarkson[29] have carried out

reactions using stoicheiometric amounts of phenylacetylene and nickel carbonyl in aqueous ethanol. Both obtained ethyl atropate as a principal product.

Chiusoli et al.[33, 35, 38] applied the stoicheiometric reaction with nickel carbonyl to a mixture of phenylacetylene and allyl chloride and obtained XX (where R=Ph) as the major product, in contrast with their work on alkylacetylenes.



. . . . . 7.

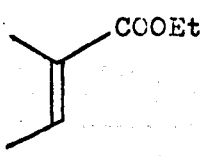
Analogous products were obtained using substituted allyl chlorides.

(ii) Cobalt: Sauer et al.[20] have observed the formation of substituted bifurandiones from phenylacetylene or 2-naphthylacetylene and carbon monoxide at 90-120°C and 100-1000 atmos. in the presence of cobalt compounds. Mixtures of isomers were obtained.

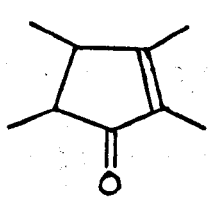
(iii) Palladium: J.Tsuji[24] has reported the dicarbonylation of phenylacetylene by treatment with carbon monoxide at 80 atmos. and 50°C for 12 hours in the presence of palladium chloride. Diethyl phenylmaleate was obtained.

1.5. CARBONYLATION OF DIALKYLACETYLENES IN THE PRESENCE OF COMPOUNDS OF THE FOLLOWING METALS.

(i) Nickel: Jones, Shen and Whiting[39] reacted dibutylacetylene (dec-5-yne) with nickel tetracarbonyl in aqueous ethanolic acetic acid at 65 - 75°C. The reaction was exothermic, and α,β—dibutylacrylic acid was obtained in 40% yield. A cis-orientation was inferred for the butyl groups. Using a similar reaction, but with dimethylacetylene (but-2-yne) in a solvent consisting of aqueous ethanol, R.Clarkson[29] obtained ethyl tiglate XXI and 2, 3, 4, 5-tetramethylcyclopent-2-enone XXII.

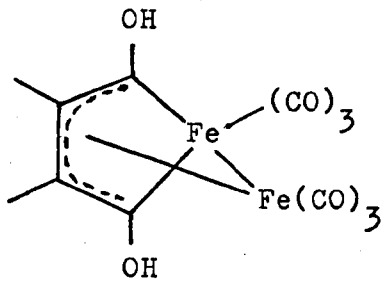


XXI



XXII

(ii) Iron: When dimethylacetylene was treated with iron pentacarbonyl in aqueous alkali[40] a complex, for which structure XXIII was proposed, was obtained:

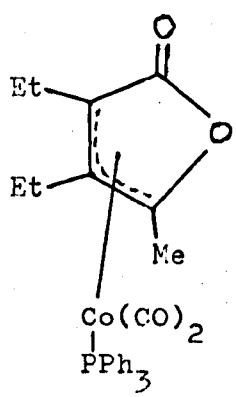


XXIII

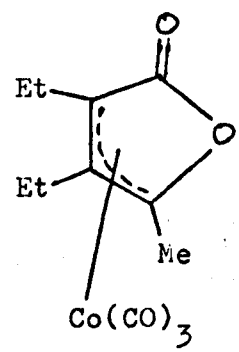
The complex was presumed to be an intermediate in the formation of hydroquinones under similar conditions[36].

(iii) Cobalt: Sauer et al.[20] studied the reaction of diethylacetylene (hex-3-yne) with carbon monoxide at high pressures and temperatures in the presence of a cobalt salt such as the acetate. Cis- and trans-tetraethylbifurandione were obtained in much the same way that bifurandiones had been obtained from acetylene and monosubstituted acetylenes.

R.F.Heck[41] obtained a π-allylic lactone complex XXIV by the interaction of diethylacetylene and acetylcobalt tetracarbonyl at 0°C in the presence of triphenylphosphine. In the absence



XXIV



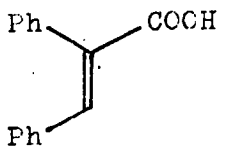
XXV

of the phosphine, a complex presumed on the basis of infrared spectroscopy to be XXV was formed, but it was too unstable to isolate.

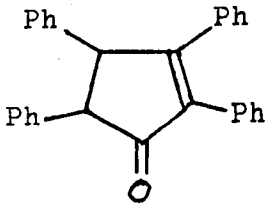
1.6. CARBONYLATION OF DIARYLACETYLENES IN THE PRESENCE OF COMPOUNDS OF THE FOLLOWING METALS

(i) Nickel: The carbonylation of diphenylacetylene was investigated

by W.Reppe[1]. Using carbon monoxide at 30 atmos. in the presence of nickel(II) and a solvent consisting of a mixture of water, acetic acid and acetone, the main product was α-phenylcinnamic acid, XXVI. A stoicheiometric reaction with diphenylacetylene and

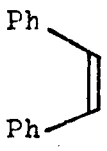


XXVI

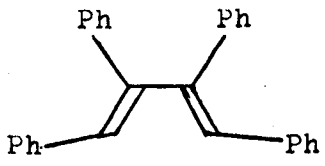


XXVII

nickel tetracarbonyl was carried out by Jones and his co-workers[39], the solvent being aqueous ethanol and acetic acid. α-Phenylcinnamic acid was obtained in 40% yield. A very similar reaction was carried out by Clarkson[29], who obtained a 59% yield of the acid (XXVI) with 5% of its ethyl ester, 20% of 2,3,4,5-tetraphenylcyclopent-2-enone (XXVII) and small amounts of the olefins XXVIII and XXIX:



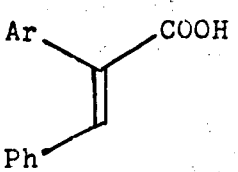
XXVIII



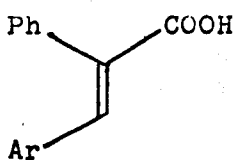
XXIX

Mueller and MacArtor[42] carried out a stoicheiometric reaction in ethanolic benzene, and obtained ethyl α-phenylcinnamate in good yield. However, when they repeated the experiment in ethanolic dioxan, the main product was the cyclic ketone XXVII with only small amounts of ester present.

Bird and Briggs[43] have studied the stoicheiometric carbonylation of a series of acetylenes, Ar-C≡C-Ph (where Ar- is a <u>meta</u>- or <u>para</u>-substituted phenyl group) they obtained two series of acids, XXX and XXXI from the reactions, and were able to obtain a Hammett-type



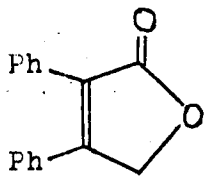
XXX



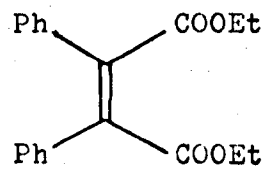
XXXI

correlation between $\log\frac{[XXXI]}{[XXX]}$ and the appropriate σ-constants of the substituents.

(ii) Palladium: Tsuji and Nogi[44] carbonylated diphenylacetylene at 100°C using carbon monoxide at 100 atmos. in the presence of palladium chloride or palladium / charcoal in methanol or ethanol and 10% hydrogen chloride. The main product was 2,3-diphenylcrotonolactone (XXXII) with traces of α-phenylcinnamate



XXXII



XXXIII

ester (XXVI) and diphenylmaleate (XXXIII). A low hydrogen chloride concentration favoured the formation of the monoester.

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CHAPTER TWO

Studies on the Carbonylation of Acetylene

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- (ii) The Results of Lines & Long
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2.1. INTRODUCTION

The carbonylation of acetylene with a palladium catalyst in alcoholic solution has been studied in detail by C.B.Lines and R.Long [1,2]. The main findings of this work will be summarised, since the present work is, in the main, a direct continuation.

(i) The Standard Reaction: Lines & Long chose to regard the following set of experimental conditions as 'standard' in order to provide a point of reference for other experiments:

n-Butanol was selected as reactant & solvent because its boiling point (117°C) permitted a convenient reaction temperature of 75°C to be achieved. The catalyst employed was sodium tetraiodopalladate(II), Na_2PdI_4 which was prepared *in situ* by mixing palladium iodide (4 m mols) and sodium iodide (8 m mols) in butanol (1 mol). The two reactant gases, carbon monoxide and acetylene, were passed through the well stirred solution at a rate of three litres per hour each. The duration of the experiment was 7 hours.

A typical set of results from the standard reaction is given in table 2.1.

For the purpose of providing a valid comparison with work using other acetylenes, a typical set of Lines' 'standard' results is given in the form of percentage yields based on acetylene. The values are misleadingly low since the gaseous reactant was only partially converted and the composition of the exhausted gases was not known. Yields were as follows: butyl acrylate, 4.5; propionate, 2.3; dibutyl maleate, 1.3; fumerate, 3.1 and succinate, 4.4%. The overall yield of recognised products was thus about 16% and the productivity of the catalyst (i.e. mols of product/moles of catalyst) = 40.

(ii) The Results of Lines & Long: It was found that the above conditions favoured a reaction between acetylene, carbon monoxide and butanol, yielding mainly the butyl esters of acrylic and propionic acids, and the dibutyl esters of maleic, fumaric & succinic acids, corresponding to 'B', 'C', 'E', 'G', 'F' respectively in the chromatogram, (fig.2.1.). Dibutyl succinate and butyl acrylate were the major products.

It was shown that palladium bromide/sodium bromide and palladium chloride/sodium chloride mixtures were, by contrast, very poor carbonylation catalysts. The addition of anhydrous hydrogen halides (HCl,HBr,HI) increased the yield of butyl acrylate whilst decreasing the amount of dibutyl succinate produced; a typical set of results with HCl is given in table 2.1.

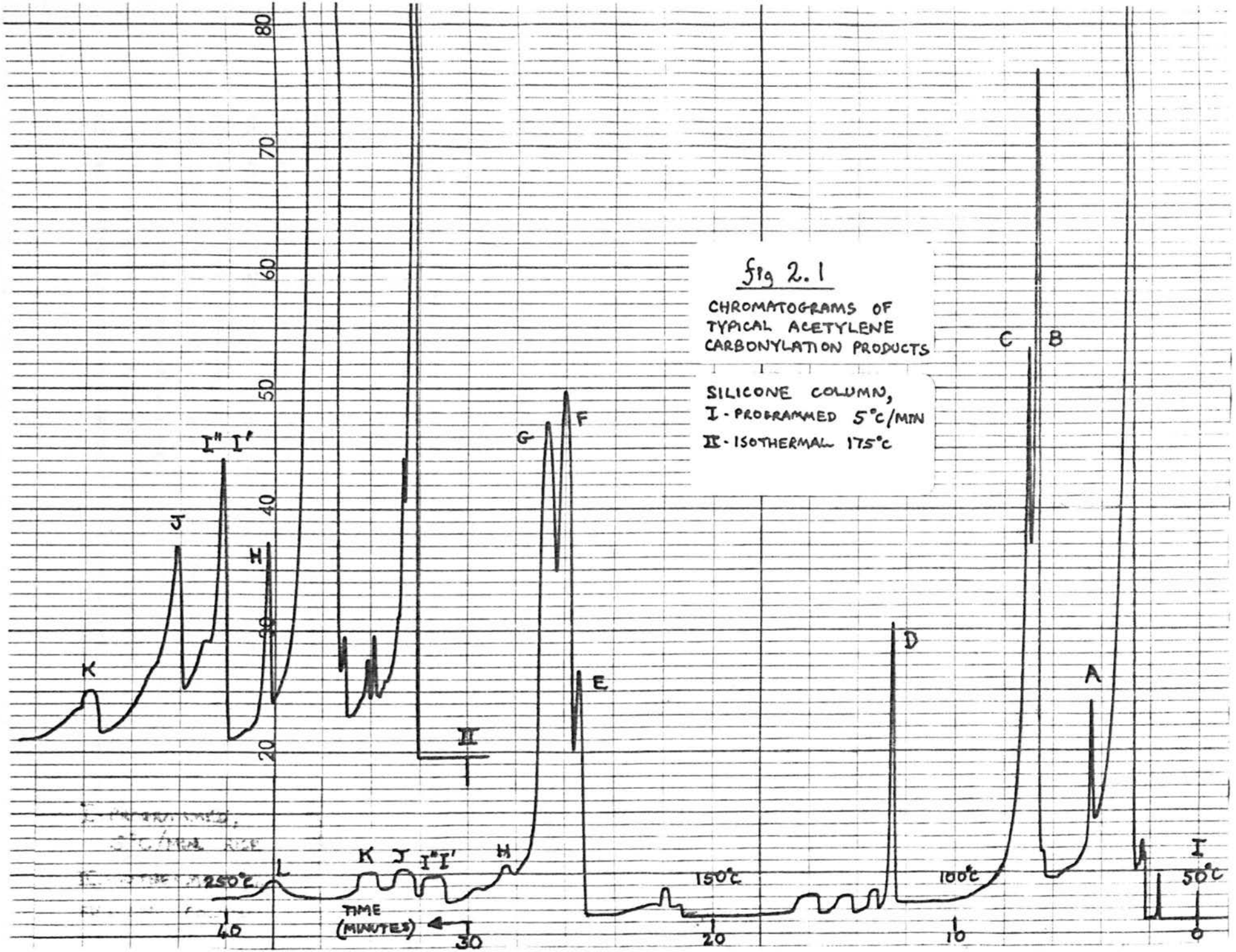


Fig 2.1

CHROMATOGRAMS OF TYPICAL ACETYLENE CARBONYLATION PRODUCTS

SILICONE COLUMN,
I - PROGRAMMED 5°C/MIN
II - ISOTHERMAL 175°C

Increasing the concentration of the catalytic species did not result in a proportionate increase in conversion of reactant gases to esters. Variation of the ratios of the reactant gases from the standard conditions resulted in an overall decrease in the production of esters. Observations on the ratio of moles of acetylene to moles of carbon monoxide consumed in the formation of the five ester products, suggested that carbon monoxide exercises a controlling role in the carbonylation reaction.

Experiments designed to show whether any of the ester products was the precursor of any other, demonstrated that butyl acrylate was not carbonylated to dibutyl succinate, and that succinate & acrylate did not interact to yield fumarate & propionate under the reaction conditions.

Dibutyl maleate underwent isomerisation to fumarate to some extent, especially in the presence of hydrogen chloride. The addition of less than 40 m mols of dibutyl fumarate resulted in a low conversion of acetylene whilst 40 m mols or more caused complete suppression of the reaction.

The formation of butyl acrylate and dibutyl maleate was reduced when the carbonylation was carried out in butanol-O-d, whilst the production of dibutyl succinate & dibutyl fumarate was enhanced.

Lines & Long observed seven minor products in typical reaction mixtures, and identified one of them by infrared spectroscopy & mass spectrometry as an unspecified isomer of dibutyl hexenedioate.

(iii) The Objectives of the Present Work: It was hoped that a continued study of the carbonylation of acetylene would yield further information about the mechanism by which the reaction proceeds and about the identities of the minor products.

2.2. CARBONYLATION OF ACETYLENE UNDER A VARIETY OF CONDITIONS

(i) Carbonylation Under Neutral Conditions: It had been shown that the concentration of butyl acrylate in the reaction mixture reached a maximum and then began to fall. Due to experimental difficulties the weight of the reaction mixture was not determined during the progress of the reaction, and hence it was not possible to decide whether the amount of acrylate actually fell, or only apparently did so as the other components rose. A series of reactions was carried out for periods of 1, 3, 5 and 7 hours respectively, and the amount of each ester present was deduced from the weight increase and

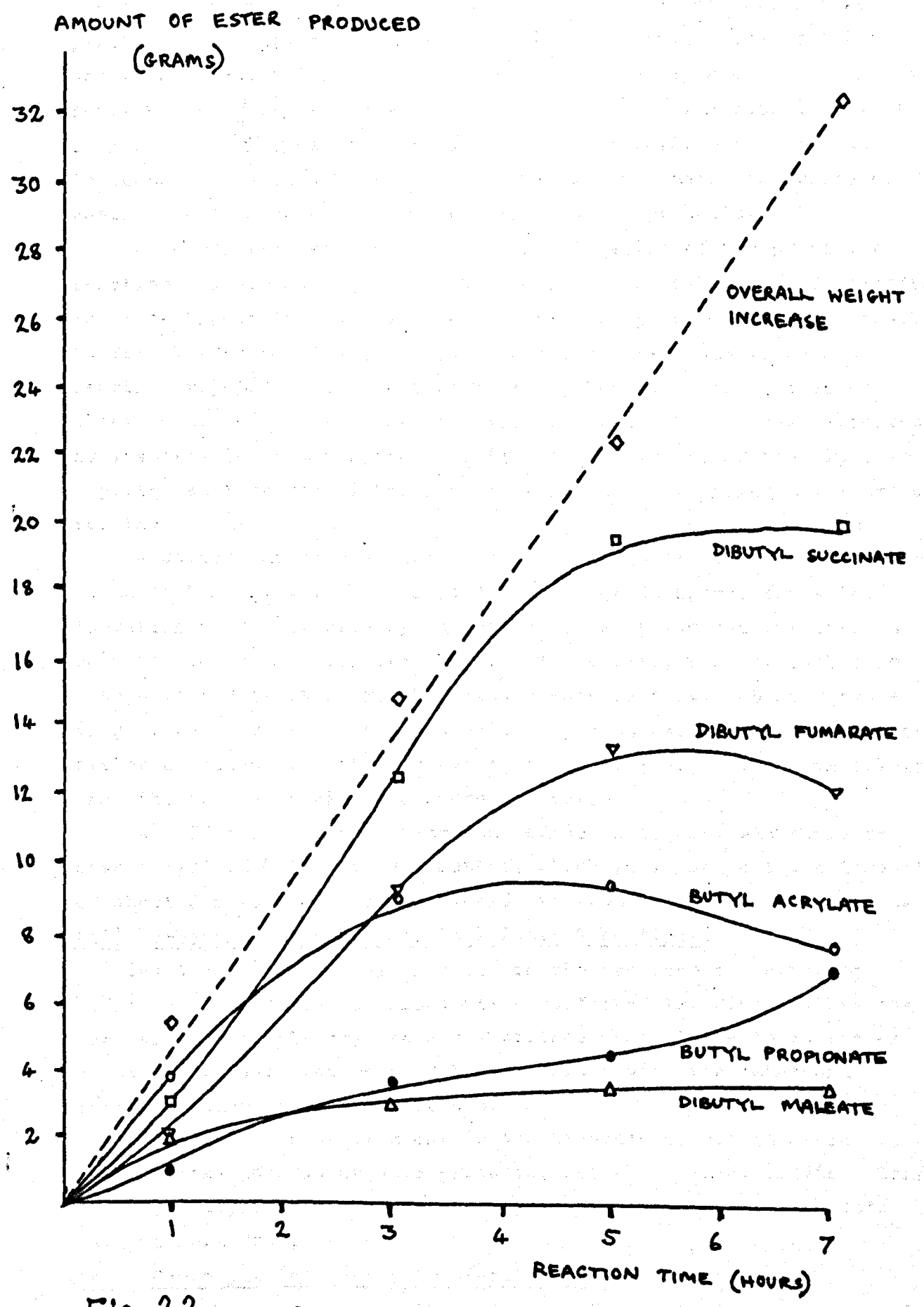


Fig. 2.2. REACTION 2.1. :

A CARBONYLATION REACTION CARRIED OUT UNDER NEUTRAL CONDITIONS WITH THE PRODUCT ANALYSES SHOWN IN GRAMS.

chromatographic analyses. The weight of each ester in grams was plotted against reaction time (fig.2.2.). In the case of butyl acrylate, the curve reached a maximum. The amounts of other esters continued to increase in a non linear fashion. The overall weight increased linearly with time (at 4.6 g/h, fig.2.2.) and since an increase in the rate of stirring caused an increased conversion of gases, a diffusion controlled mechanism seems probable.

Attempts were made to measure the variation of the pH of the reaction mixture during the carbonylation of acetylene. Titrimetric and potentiometric methods were unsatisfactory, but it proved possible to follow the 'pH' using universal indicator paper, and to obtain readings reproducible to within half a 'pH' unit. The values so obtained may not correspond to a true pH, since a non-aqueous solvent is involved (although exchange with the bound-water of the paper is expected to take place) but may be regarded as providing a measure of relative acidity.

A carbonylation was carried out under the 'standard' conditions of Lines & Long, but allowed to continue for 18 hours, the ester formation being followed by gas chromatography and acidity changes being followed as described above. The acidity reading fell from 6 to 4 in the first hour, then slowly rose to 5 over about 7 hours (fig.2.3.), suggesting that an acidic species was generated and then either consumed or destroyed during the reaction. It seems likely that the acidic species was hydrogen iodide.

A 0.03 m solution of hydrogen iodide in butanol was found to have a 'pH' of 4 by the same method, which would suggest the formation of about 2 m mols of hydrogen iodide in the carbonylation reaction.

(ii) Carbonylation Under Acidic & Basic Conditions:

(a) A reaction was carried out in the presence of anhydrous hydrogen chloride (10 m moles) which confirmed the finding that the formation of butyl acrylate was increased, whilst the formation of dibutyl succinate was reduced by comparison with the 'standard' reaction under neutral conditions.

(b) A reaction carried out in the presence of sodium hydroxide (10 m moles) gave no organic products, and the characteristic colour of the catalyst solution was destroyed, a heavy brown precipitate being thrown down.

(iii) Carbonylation in the Presence of Oxidising Agents:

(a) Following the fortuitous observation during the carbonylation

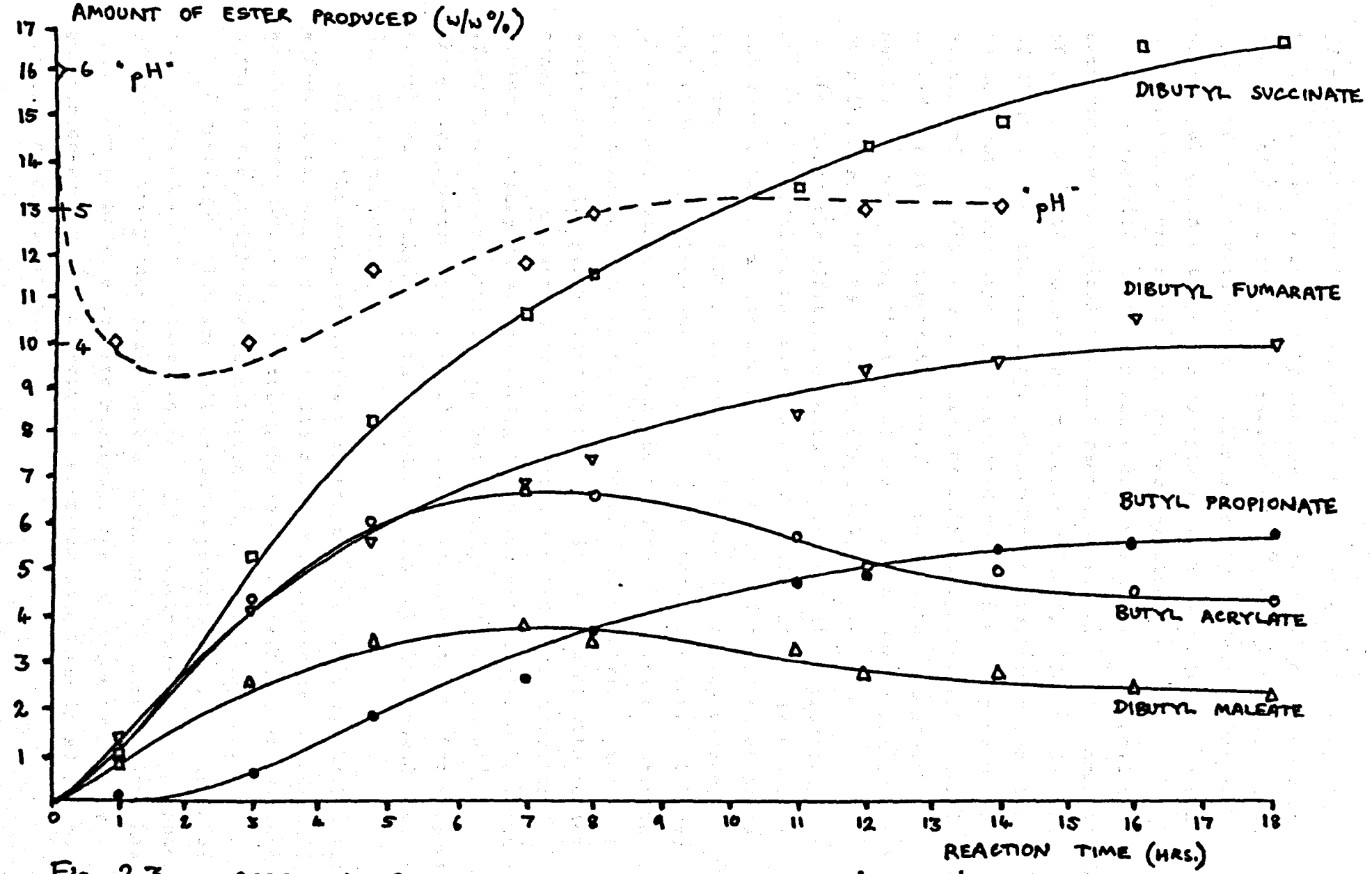


Fig. 2.3. REACTION 2.2. : A CARBONYLATION REACTION UNDER 'STANDARD' CONDITIONS WITH AN EXTENDED REACTION TIME.

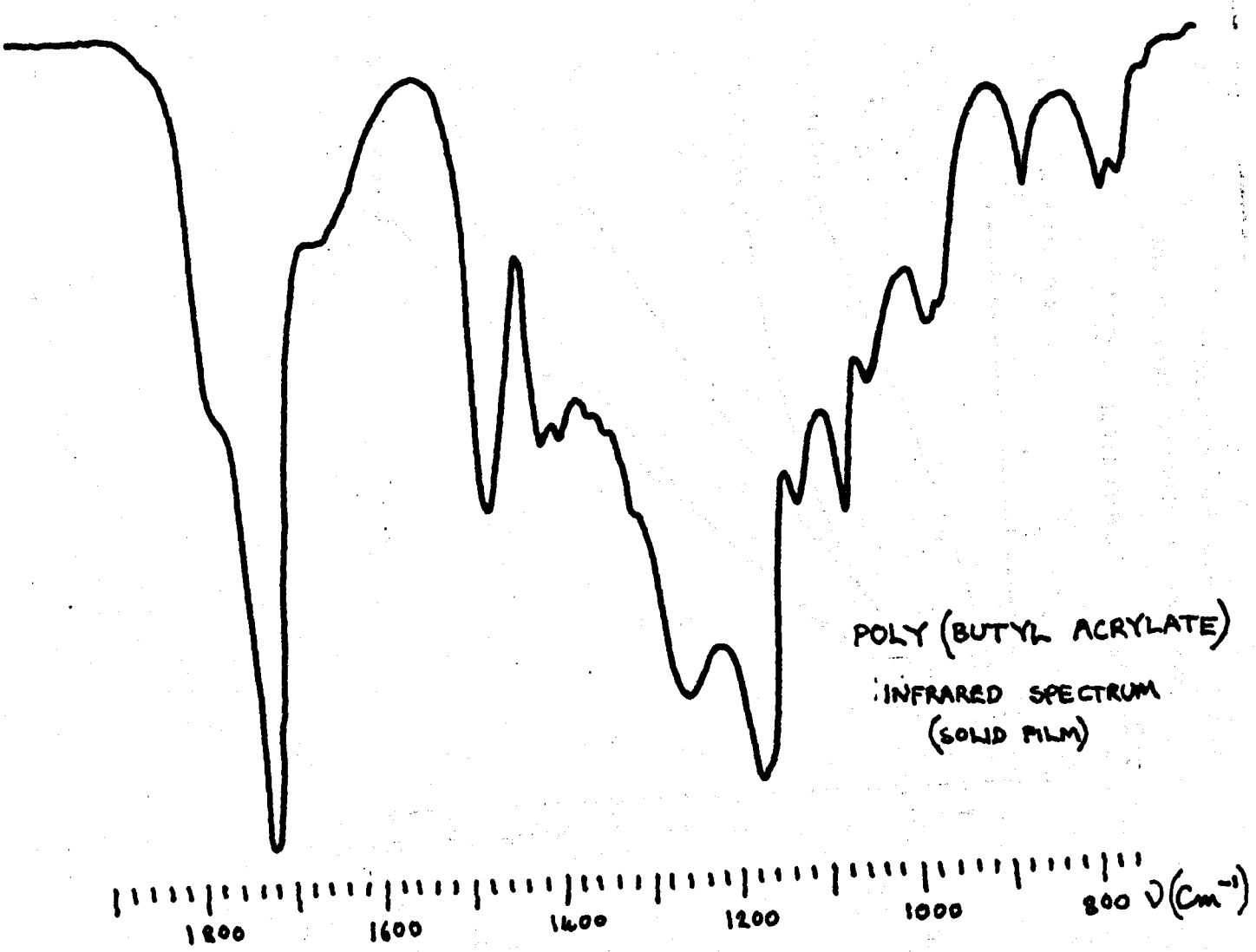
of methylacetylene (cf chapter 3.3 (i)), that overall conversion to products was increased by the presence of air, and in view of the work of Chiusoli and his co-workers [3,4], which suggested that hydrogenated products could be eliminated by the passage of air during palladium catalysed carbonylations, it was decided to pass air through an otherwise standard carbonylation.

The overall weight increase (16g.) was somewhat reduced by comparison with typical standard reactions (18 g) and the amount of butyl acrylate produced was markedly reduced. The production of dibutyl succinate and butyl propionate was certainly less than in the typical reaction, but saturated products were by no means eliminated. With the exception of butyl acrylate, which still showed a maximum concentration before the reaction was stopped, and butyl propionate, the rate of production of esters was constant over the period of the reaction (fig. 2.4.).

(b) Since the addition of acid had the effect of promoting monoester formation, and air had the contrary effect, it was of interest to study a reaction in the presence of hydrogen chloride and air. The weight increase (9 g.) was considerably reduced, whilst butyl acrylate was the predominant ester product. A heavy black deposit was obtained, and the solution lost its characteristic wine red colour. Extraction of the residue with water yielded a white solid (1.2 g.) which gave an analysis consistent with sodium chloride. Extraction of the remaining solid with chloroform yielded a sticky substance (0.1 g.) the infrared spectrum of which (fig. 2.5.) was identical with that of poly(butyl acrylate)[5]. The n.m.r. spectrum (fig. 2.5.) was also consistent with the polymeric structure. Analysis of the residual black material showed that it was palladium iodide.

(c) In the methylacetylene work (cf chapter 3.3(i)), the beneficial effect of air was ascribed to its ability to reoxidise palladium(0) which formed during the reaction, hence the addition of an oxidising agent in the acetylene carbonylation might be advantageous.

Copper(II) salts are well known to promote the reoxidation of palladium, as in the Wacker process [6], but their use in the presence of terminal acetylenes could well be hazardous. Benzoquinone has been shown to be an effective reoxidant for palladium by Moiseev and his co-workers [7], accordingly reactions have been tried in the presence of benzoquinone.


POLY (BUTYL ACRYLATE)
INFRARED SPECTRUM
(SOLID FILM)
1800
1600
1400
1200
1000
800
ν (Cm⁻¹)

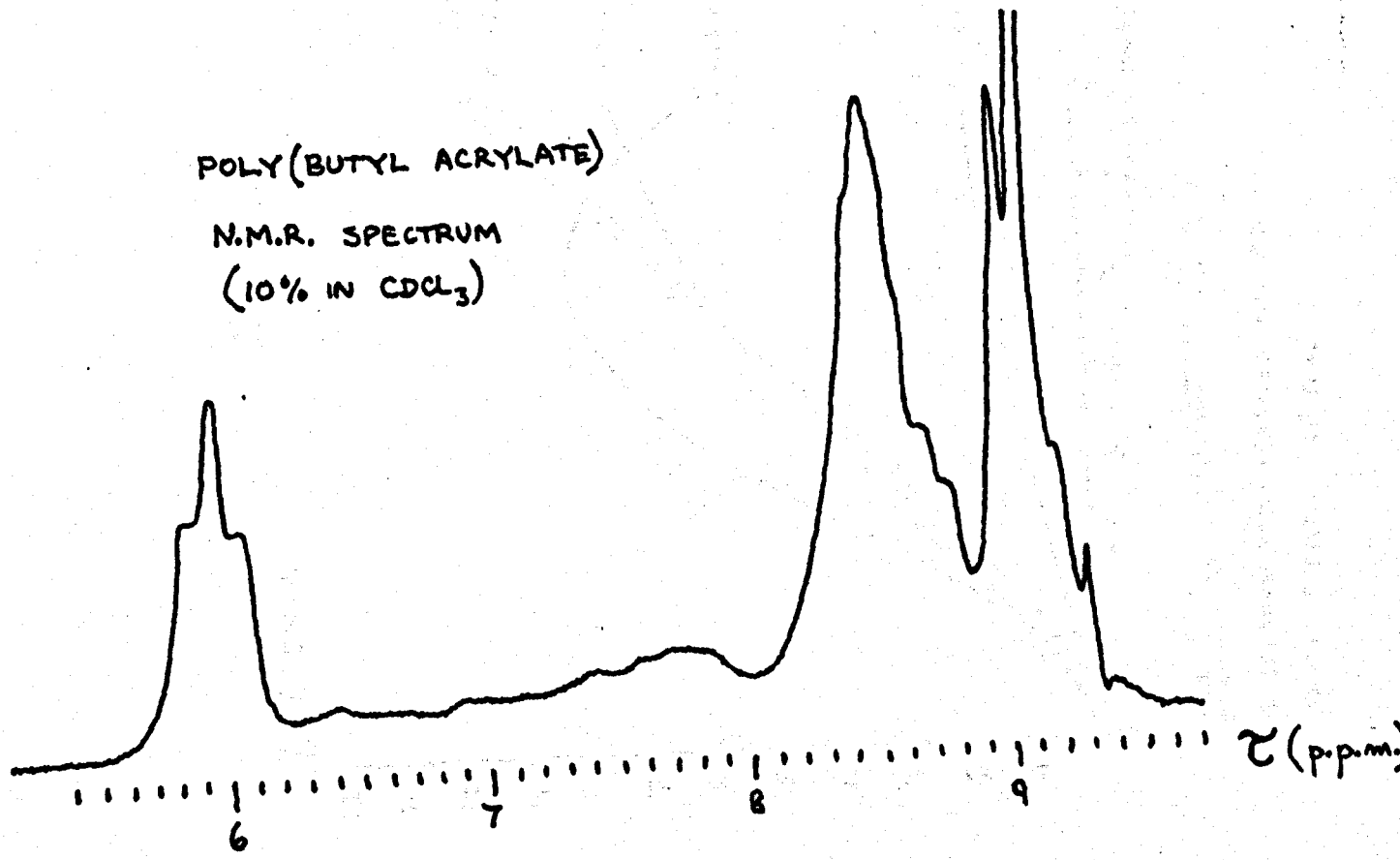

POLY (BUTYL ACRYLATE)
N.M.R. SPECTRUM
(10% IN CDCl3)
6
7
8
9
τ (p.p.m.)

Fig 2.5

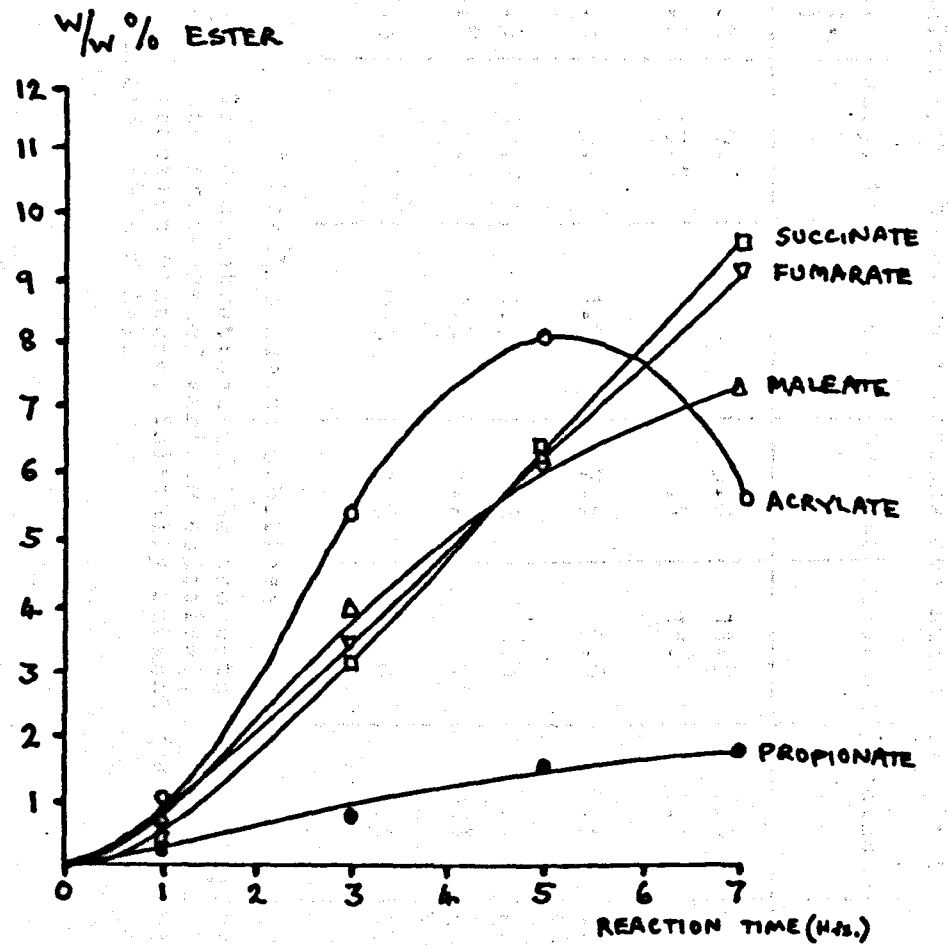


Fig 2.4. REACTION 2.4. :

A CARBONYLATION REACTION CARRIED OUT IN THE PRESENCE OF AIR.

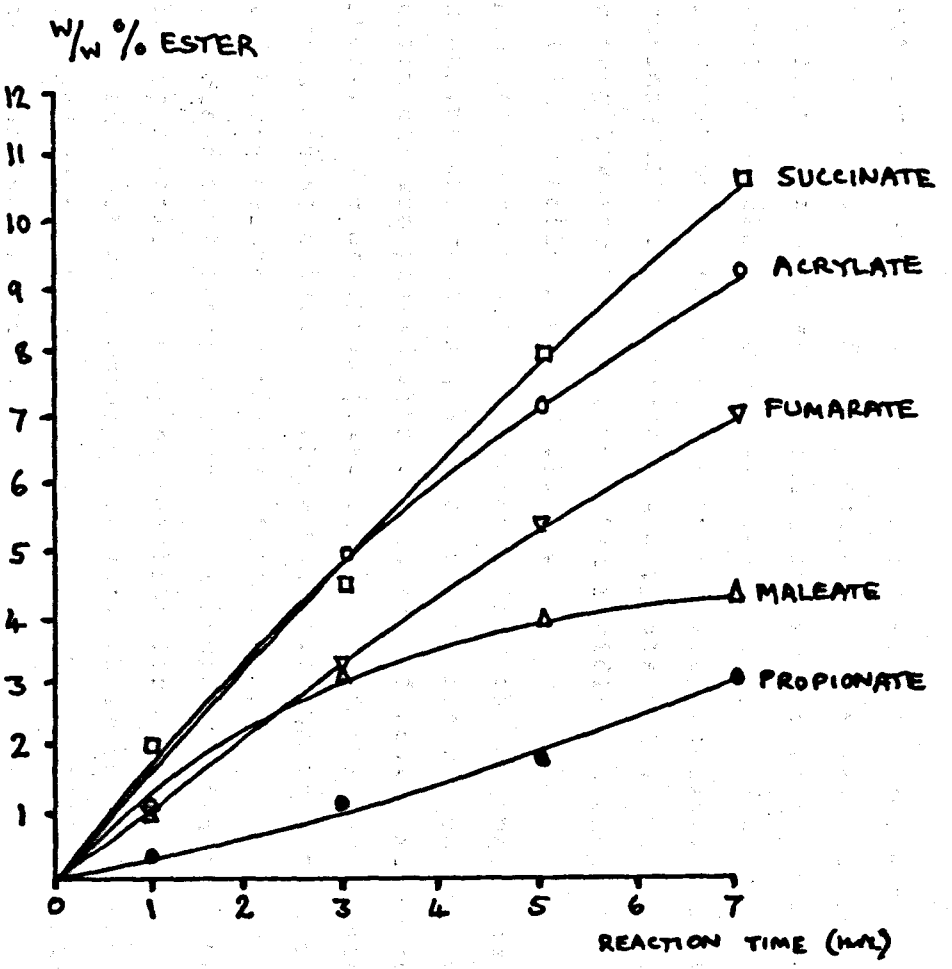


Fig 2.8. REACTION 2.9.

A CARBONYLATION REACTION CARRIED OUT IN THE PRESENCE OF HYDROGEN.

Initially a reaction was carried out with benzoquinone present and no air passing. The final product spectrum was not greatly different from that observed in the standard reaction, except that the proportion of dibutyl succinate was reduced. However, the rates of formation of the esters were markedly changed, thus the concentrations of butyl propionate & acrylate and dibutyl succinate remained very low for 5 hours, and then rapidly increased towards the end of the reaction, (cf fig.2.6.).

Since the above reaction suggested that the benzoquinone was consumed during the reaction, a further reaction was carried out, during which air was passed with the object of reoxidising the benzoquinone. The analyses (fig. 2.7.) showed that succinate was the predominant ester, but there was still an induction period of about 5 hours before a rapid reaction began.

It is clear that benzoquinone has a profound effect on the carbonylation reactions, delaying reaction for a period of several hours. When reaction commences however, it is rapid. Compared with the standard reaction, such reactions show relatively low yields of saturated products.

Results from the above reactions are summarised in table 2.1.:

Rn. No.	Wt. Inc. (g)	Acrylate	Propionate	Maleate	Fumarate	Succinate	Additive
*	18.4	9.6	5.0	5.0	11.7	16.9	-
*	20.7	19.7	4.9	8.4	13.6	9.2	HCl (10 m mol)
2.4.	16.2	5.7	1.9	7.5	9.6	9.3	Air (1-1.5 l/h)
2.5.	8.3	12.7	1.9	7.2	5.1	4.1	Air & HCl
2.7.	8.8	6.2	1.5	4.7	7.0	5.3	Quinone (5.4 g.)
2.8.	5.3	2.6	0.5	3.6	5.0	6.5	Quinone (2.5 g.) & Air

* Results due to C.B.Lines[1]

Table 2.1: The concentrations of the products of carbonylation of acetylene in the presence of various additives, expressed as a W/W% of the total reaction mixture, initially butanol (60 g.) containing palladium iodide (4 m mols).

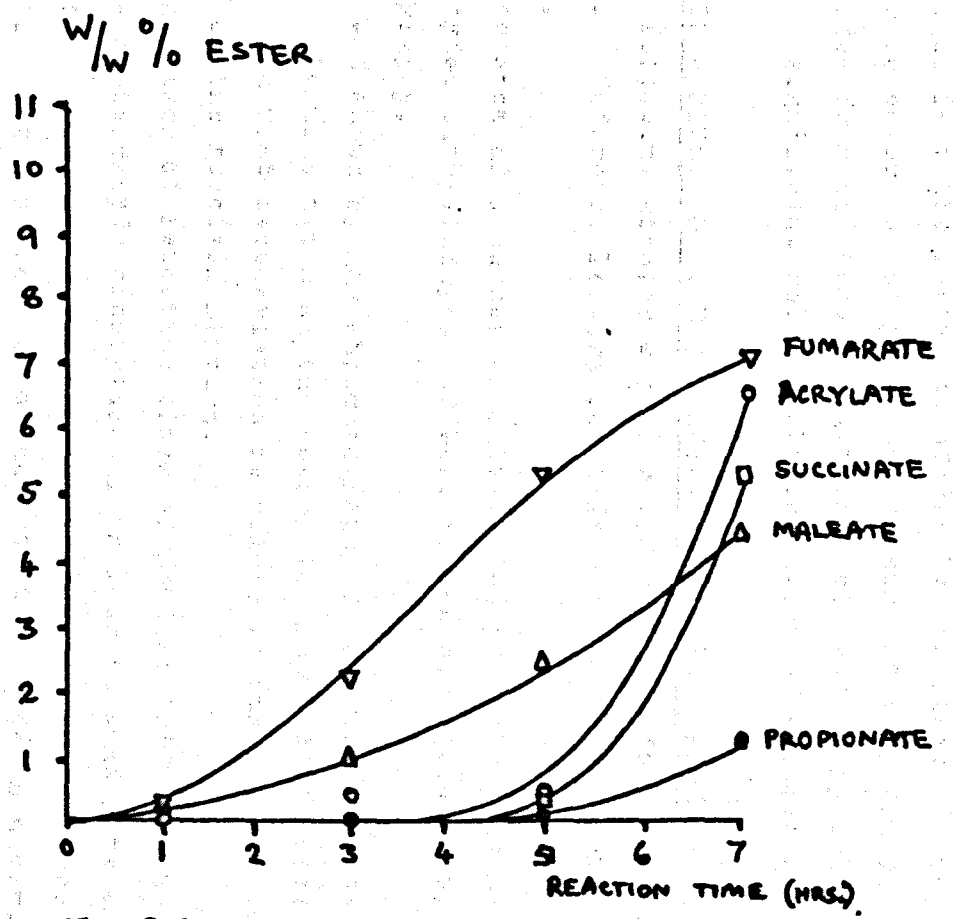


Fig. 2.6, REACTION 2.7.

A CARBONYLATION REACTION CARRIED OUT IN THE PRESENCE OF BENZOQUINONE.

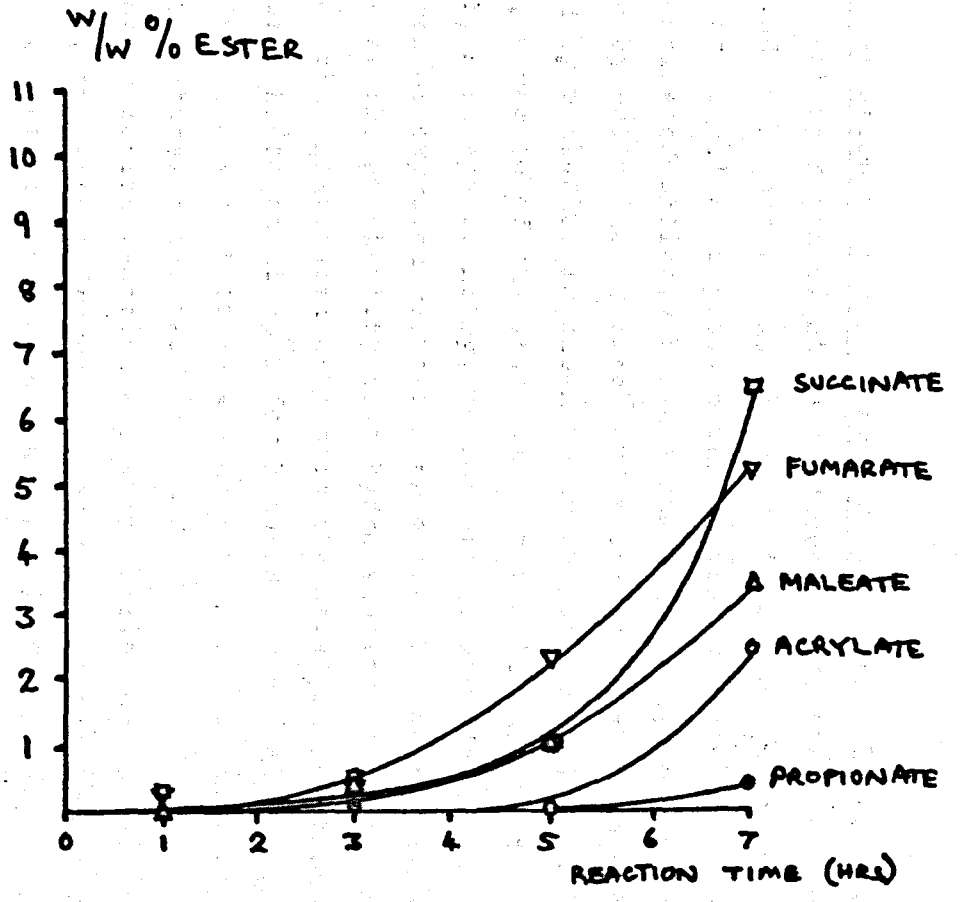


Fig. 2.7, REACTION 2.8.

A CARBONYLATION REACTION CARRIED OUT IN THE PRESENCE OF BENZOQUINONE AND AIR.

(iv) Carbonylation in the Presence of Hydrogen: Although it was possible that hydrogen might be produced during the reaction and be involved in heterogenious or homogenious hydrogenation of the unsaturated species to produce the saturated products observed, it was considered unlikely because homogenious hydrogenation catalysed by palladium is rare[8] and heterogenious hydrogenation catalysed by palladium is known to be inhibited by iodide ion[9]. Moreover, a sample of the vent gases from a 'standard' reaction proved, by mass spectrometry, to contain no significant amounts of hydrogen or expected reduction products such as ethylene.

To test the possibility that hydrogenation takes place, a mixture of the unsaturated esters in the catalyst solution was treated with hydrogen at 75°C for 7 hours. No saturated esters were produced, although there was some isomerisation of dibutyl maleate to dibutyl fumarate.

A carbonylation reaction was then carried out under standard conditions, but with hydrogen passing at 1.8 litres per hour. The product distribution was not altered in favour of the saturated products, in fact the formation of dibutyl succinate (along with the fumarate ester was slightly suppressed (cf fig. 2.8.). It can be concluded from the above result that elementary hydrogen does not play a significant role in the formation of saturated species.

2.3. MINOR PRODUCTS OF THE CARBONYLATION OF ACETYLENE

The following studies were carried out on a few typical reaction mixtures. Reference letters identify peaks in the chromatogram, fig. 2.1.

(i) The absence of a number of anticipated products such as acetaldehyde, butyraldehyde and benzene was demonstrated by gas chromatography.

(ii) 'A' was shown by gas chromatography to be butyl iodide. It had the same retention times as the authentic compound on three different columns. In most carbonylation reactions it was present to about 0.5 W/W% of the reaction mixture.

(iii) Comparison of retention times of product 'D' with those of authentic acetaldehyde dibutylacetal on four columns gave excellent agreement. The n.m.r. spectra of the two materials were also identical. It was present to the extent of 2-3% in neutral reaction

mixtures, but rising to 6.5% under acid conditions (Rn. 2.3.) and 4% in the extended reaction (Rn. 2.2. cf table 2.2.).

(iv) 'H' was not identified, however as shown by table 2.2., it was never present to more than ca. 2% of the reaction mixture.

(v) Dibutyl adipate was shown by gas chromatography to be absent from the reaction mixture. A fraction was obtained by preparative scale gas chromatography, containing the three major higher products, 'I', 'J' and 'K'. Peaks 'H' & 'L' were excluded. The fraction was hydrogenated over platinum, and the product was shown by gas chromatography on four columns to be homogenious. Gas chromatography showed the product to be identical to dibutyl adipate, as did the infrared and n.m.r. spectra. There are seven substances which could arise in the reaction and give rise to adipate ester on hydrogenation, namely cis- and trans-hex-2-enedioate, cis- and trans-hex-3-enedioate and cis,cis-, trans,trans- and cis,trans-muconate esters.

(a) 'I' was separated by preparative chromatography. Its infrared spectrum, fig.2.9, was very similar to that of authentic dibutyl trans-hex-3-enedioate , and its n.m.r. spectrum, fig. 2.10., showed signals, (4.2-4.4τ, 7.0τ) characteristic of that substance. However it also showed signals (3.5-4.2τ, & 6.7-7.7τ) similar to those quoted by N. Schamp[10] for dimethyl cis-hex-2-enedioate. In the ultraviolet region (fig. 2.9.) 'I' showed a λ_{MAX}^{MeOH} = 214 n.m., ε_{MAX} = 6,000, suggesting a high proportion of a conjugated component. The ultraviolet spectrum of the trans-hex-2-enedioate ester (which should be fairly similar to that of the cis-ester) had a similar λ_{MAX} with an ε_{MAX} of 13,000 (see (b) below). The mass spectrum of 'I' has been examined by C.B.Lines[1], it showed a parent peak & fragmentation pattern consistent with it being a hexenedioate ester.

Gas chromatography with higher resolution showed that 'I' consisted of two major components in comparable amounts. One 'I'' was shown to be dibutyl trans-hex-3-enedioate by comparison of its retention times on four columns with those of the authentic compound. The other 'I''was compared with an impure sample of dibutyl cis-hex-2-enedioate giving identical retention times on two columns. It was thus concluded that fraction 'I' was a mixture of dibutyl trans-hex-3-enedioate and cis-hex-2-enedioate.

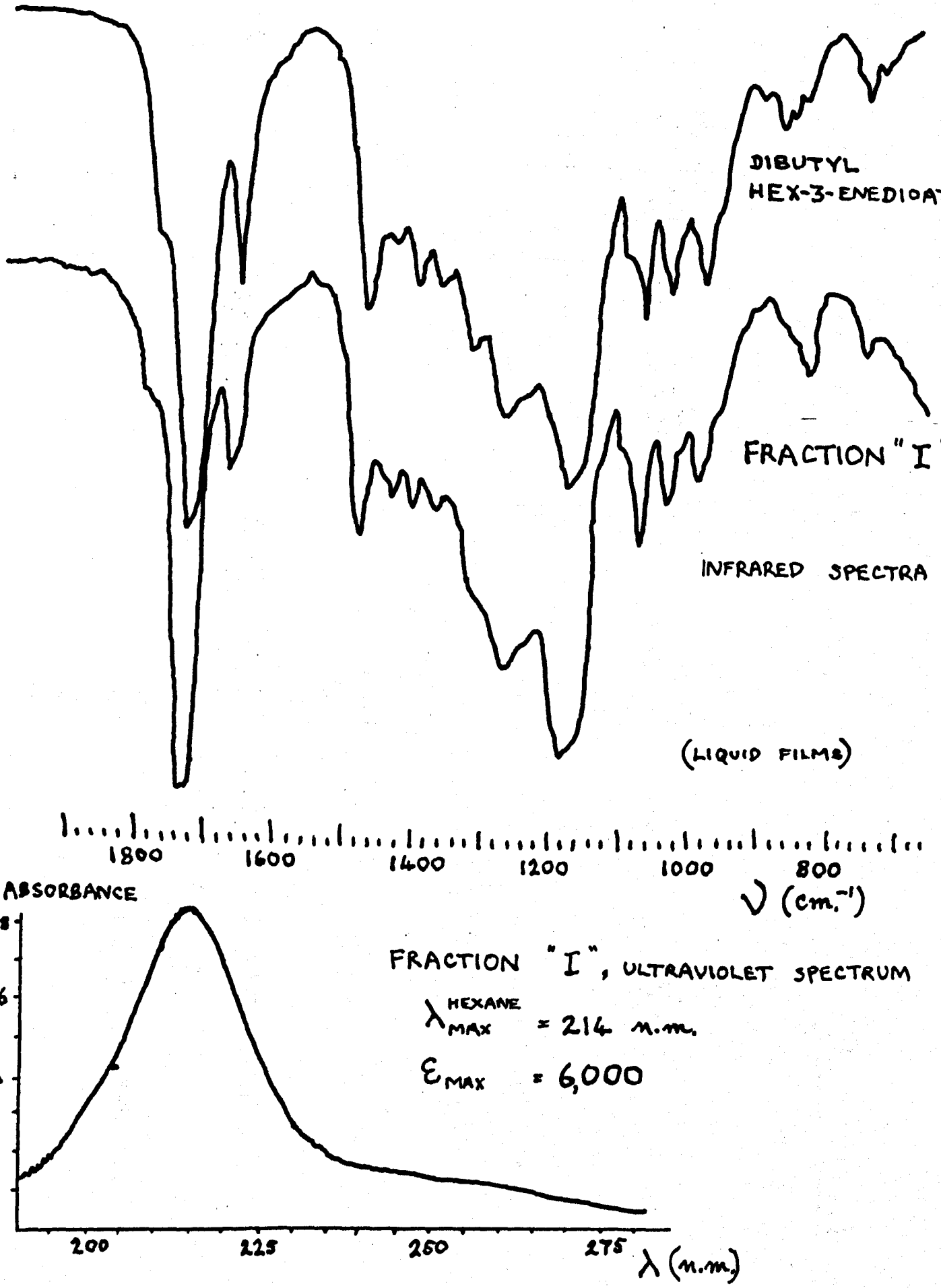

DIBUTYL
HEX-3-ENEDIOATE
FRACTION "I"
INFRARED SPECTRA
(LIQUID FILMS)
1800
1600
1400
1200
1000
800
ν (cm.⁻¹)
ABSORBANCE
0·8
0·6
0·4
0·2
200
225
250
275
λ (n.m.)
FRACTION "I", ULTRAVIOLET SPECTRUM
λ MAX HEXANE = 214 n.m.
ε MAX = 6,000

Fig. 2.9

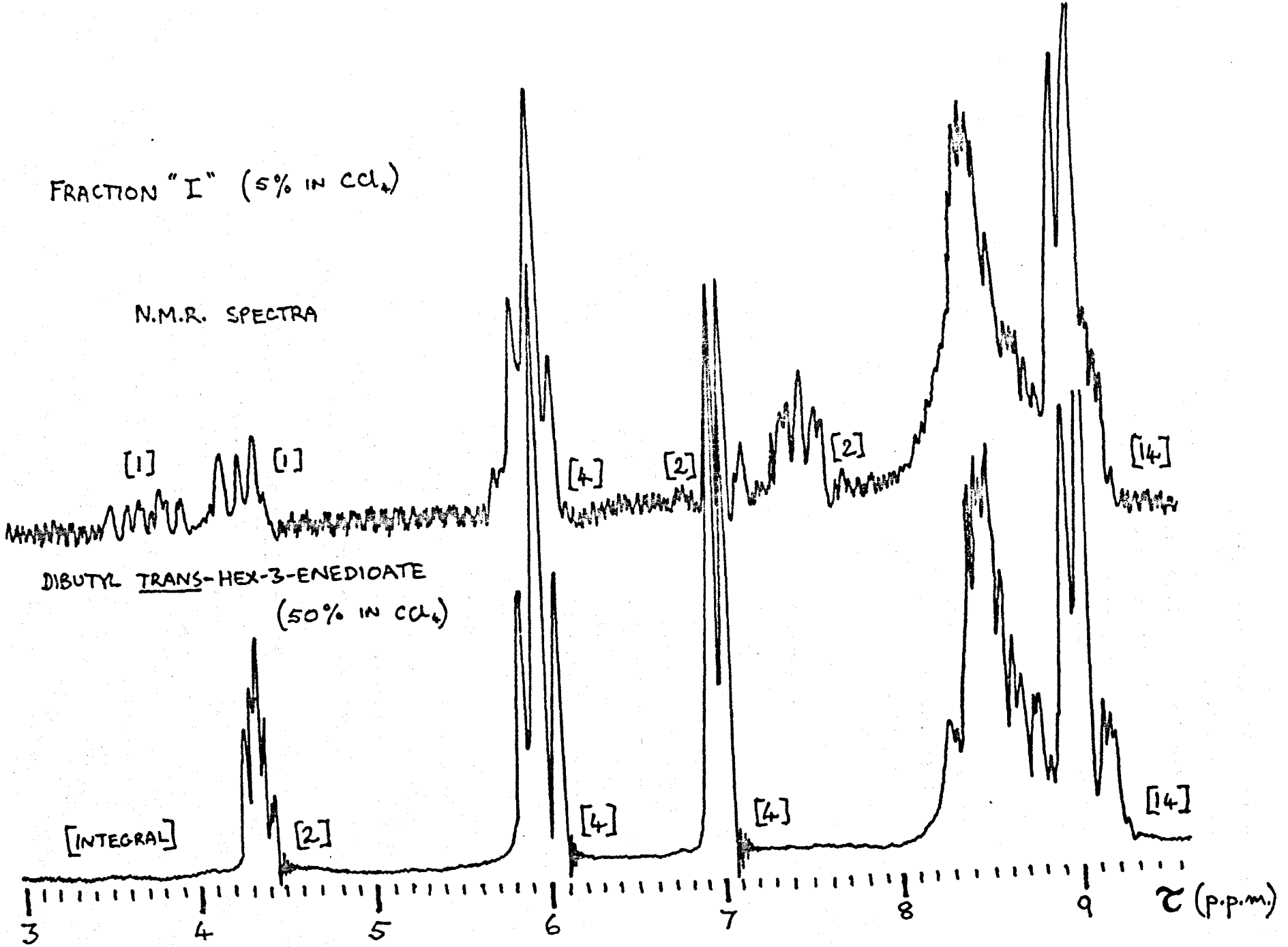

FRACTION "I" (5% IN CCl_4)
N.M.R. SPECTRA
[1]
[1]
[4]
[2]
[2]
[14]
DIBUTYL TRANS-HEX-3-ENEDIOATE
(50% IN CCl_4)
[INTEGRAL]
[2]
[4]
[4]
[14]
3
4
5
6
7
8
9
τ (p.p.m.)

Fig. 2.10

(b) 'J' was separated by preparative scale gas chromatography. It had the same retention times on 4 columns as a sample of authentic dibutyl trans-hex-2-enedioate, and its infrared and n.m.r. spectra were identical to those of the authentic compound.

In view of the observed ultraviolet properties of the mixture 'I' (see (a) above) it is interesting to note the data of the trans-hex-2-enedioate ester:

$$\lambda_{MAX}^{MeOH} = 211 \text{ n.m.}, \varepsilon_{MAX} = 13{,}000$$

(c) 'K' was isolated by gas chromatography and proved to have identical infrared and n.m.r. spectra, and retention times on 4 columns, to an authentic sample of dibutyl trans, trans-muconate. The n.m.r. data agreed well with that given by Elvidge & Ralph[11] for the dimethyl ester, and consideration of the published data precluded the possibility that 'K' was, or contained significant amounts of, the other muconate stereoisomers.

Quantitative analyses of the 4 major non-vic- diesters are given in table 2.2. It is significant that the hex-2-enedioate ester predominates, except in the case where a reaction was carried on for an extended period (rn.2.), when muconate became the major C_6 diester, thus lending support to the belief that muconate might be formed from a hexenedioate. Tsuji & Imamura[12] have described a reaction whereby diethyl hex-3-enedioate was oxidised to the muconate ester by palladium chloride: a π-allyl complex is formed initially, and can react with carbon monoxide or a base to yield diethyl trans,trans-muconate and palladium metal. However, exposure of dibutyl hex-3-enedioate to carbon monoxide in a solution containing the palladium iodide catalyst used in the present work for 5 hours, did not give rise to any dibutyl muconate detectable by gas chromatography.

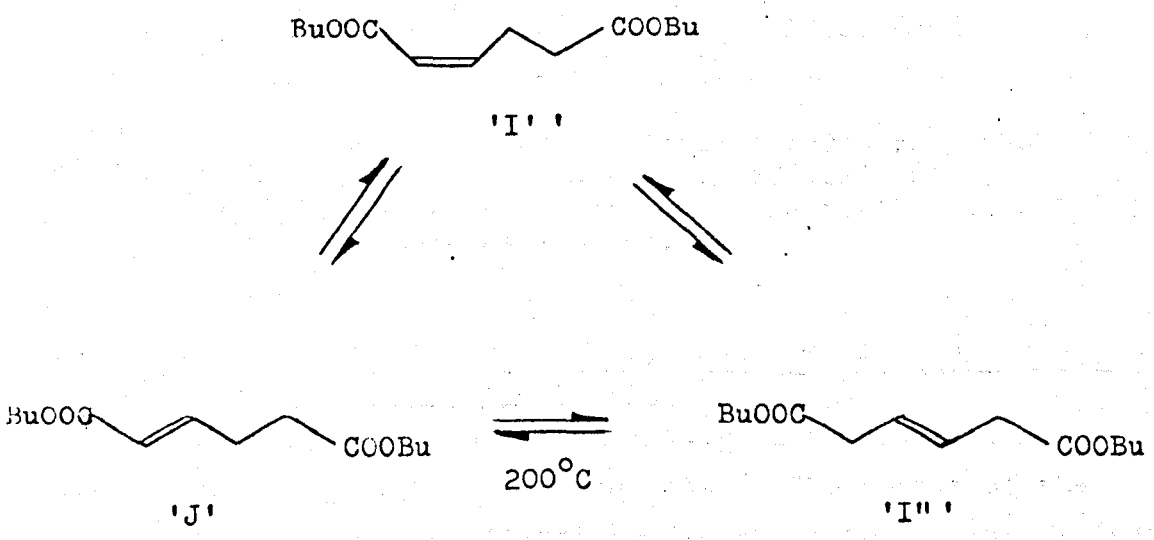
A larger amount of dibutyl trans-hex-2-enedioate was produced in the acid reaction (rn.3.) than in standard carbonylations, whilst only small amounts of products of higher retention time than dibutyl fumarate were obtained from carbonylation carried out in the presence of hydrogen (rn.9.), or benzoquinone and air (rn.8.). Carbonylation of acetylene-d_2 (rn.16.cf. Chapter 2.4 (viii)) also gave only small amounts of higher products (cf table 2.2.).

Some work involving the addition of butyl acrylate to a methylacetylene reaction mixture (cf Chapter 3.5 (v)), led to the

belief that hex-2-enedioate esters were formed directly from acrylate and acetylene during carbonylation.

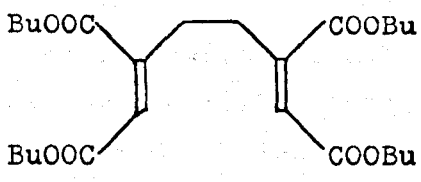
It is possible to envisage formation of an equilibrium mixture of hexenedioates from any isomer, possibly with oxidation of hex-3-enedioate to muconate ester, palladium(II) compounds being well known to catalyse the equilibration of olefins[13]. It is interesting to note that a sample of dibutyl trans-hex-3-enedioate which had been stored for a period of 2 years was found to have been converted to a mixture containing approximately equal amounts of trans-hex-2-enedioate and trans-hex-3-enedioate with some cis-hex-2-enedioate.

A sample which had been heated at 200°C for 3 hours in a sealed tube proved (by gas chromatography and n.m.r. spectroscopy) to have been substantially (70%) converted to the trans-hex-2-enedioate isomer.



(vi) 'L' (Kovats retention index $I^{SE.30}_{230^{o}}$ = 1995) was isolated by preparative gas chromatography. Its mass spectrum gave a parent peak of $\frac{m}{e}$ = 482.288, $C_{26}H_{42}O_8$ requires 482.288, with major fragments at $\frac{m}{e}$ = 408 & 308.

Structure I was suggested as being consistent with the mass spectrum and mode of formation:



I

However, the infrared spectrum (ν= 3050, 1730, 1180 cm^{-1}) gave no evidence of unsaturation, and the assignment of a structure must remain tentative. As shown in table 2.2., the concentration of 'L' never rises above ca. 1% W/W.

Reaction Number	'D'	'H'	'I"'	'I''	'J'	'K'	'L'	Conditions
*	3.0	1.8	3.6	2.5	5.4	4.2	0.9	Neutral
2.1.	2.9	1.2	3.0	2.3	4.6	1.4	0.6	Neutral
2.2.	4.1	2.0	3.9	3.2	6.0	7.0	0.8	Neutral, 18 hour rn.
2.3.	6.5	1.8	3.7	3.0	5.8	1.8	0.5	Acid present
2.10.	2.2	1.0	3.5	3.0	4.5	2.9	0.3	Acrylate present
2.11.	2.0	0.8	2.5	1.5	3.1	2.9	0.2	Acrylate & air present
2.9.	1.5	1.2	1.3	0.5	2.3	1.4	0.2	Hydrogen passing
2.8.	1.5	0.3	0.2	-	0.6	-	-	Benzoquinone & air present
2.16.	2.9	0.2	0.6	0.4	1.6	0.3	-	DC:CD used

* Reaction carried out by C.B.Lines[1]

Table 2.2: The amounts of minor products formed during the carbonylation of acetylene under a variety of conditions, expressed as W/W% of the reaction mixtures, initially Butanol (60 g.) containing palladium iodide (4 m mols).

2.4. MISCELLANEOUS REACTIONS DESIGNED TO ELUCIDATE ASPECTS OF THE MECHANISM OF CARBONYLATION REACTIONS

The mechanism by which palladium catalysed carbonylation proceeds is obscure in a number of respects. The object of the following experiments was to attempt to discriminate between different plausible pathways to the products. Thus to follow the fate of, for example, product butyl acrylate, butyl methacrylate was incorporated in the reaction mixture and the products obtained were screened for the presence of an additional methyl group.

(i) Reaction of the Catalyst with Carbon Monoxide: C.B.Lines[1] has shown that when carbon monoxide was passed into a solution of the palladium iodide catalyst in butanol, no organic species were produced.

However when a sodium tetraiodopalladate(II) solution was shaken with carbon monoxide for about 20 minutes, its characteristic wine-red colour changed to blood red. The ultraviolet spectrum of the blood red solution showed an intense band at λ_{MAX}^{BuOH} = 257 n.m. ε_{MAX} = 85,000, which however decreased in intensity over a few hours,

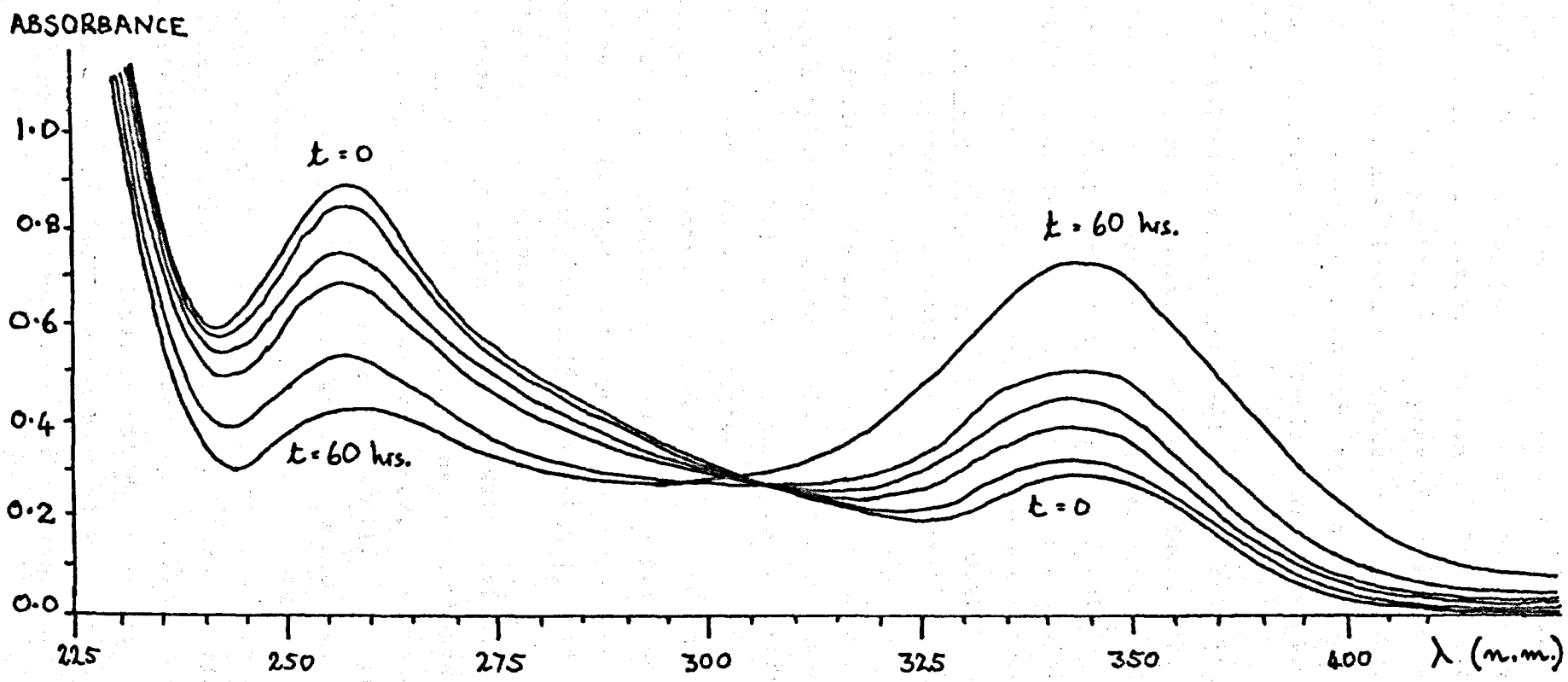


Fig. 2.11 :

ULTRAVIOLET SPECTRA OF Na_2PdI_4 SOLUTION AFTER EXPOSURE TO CARBON MONOXIDE

(8×10^{-5} M IN BUTANOL, 10 mm. SILICA CELLS, TIME, t, SINCE EXPOSURE = 0·0, 0·1, 0·3, 1·0, 20·0, 60·0 hrs.)

whilst a band at λ_{MAX}^{BuOH} = 344, characteristic of Na_2PdI_4 solutions increased to ε_{MAX} = 100,000, the reaction was apparently complete after 60 hours (cf. fig. 2.11.). It was concluded that a chemical reaction took place initially, being presumably either the displacement of an iodo- ligand or ligands by a carbonyl moiety or formation of a penta- or higher coordinate complex. The product was unstable and reverted to the tetraiodopalladate(II) complex in a few hours.

A similar solution could be obtained by shaking palladium iodide in butanol under carbon monoxide for several days; the undissolved black residue gave a correct analysis for palladium iodide. It was therefore presumed that a complex of the type $I_2Pd(CO)_n$ was formed.

Attempts to isolate a palladium species from the above reaction mixtures using thin layer chromatography were not successful.

(ii) Reaction of the Catalyst with Acetylene: C.B.Lines[1] has shown that no organic species detectable by gas chromatography was produced when acetylene was passed through solutions of the catalyst.

However, following the observations that a rapid reaction takes place between butylacetylene and sodium tetraiodopalladate(II) solution (cf. Chapter 4.), it was proposed to re-investigate the possibility of a reaction with acetylene.

The ultraviolet spectral changes taking place in a catalyst solution in butanol in contact with excess acetylene were followed by ultraviolet spectroscopy over a period of 20 hours. The spectra showed that the Pd-I charge-transfer band at λ_{MAX} = 344 diminished in intensity over the period.

When a catalyst solution was shaken with acetylene for 5 days and subjected to thin layer chromatography, using benzene as the mobile phase, a single spot, R_F = 0.86 was obtained. A product was isolated by column chromatography as a thick yellow oil. In the ultraviolet it showed a very broad absorption, with λ_{MAX} = 200 n.m. The infrared spectrum (fig.2.12.) was very similar to that obtained from the reaction of butylacetylene with the catalyst solution (cf. Chapter 4.4 (i)) having an absorption band at 1735 cm^{-1}. Since ignition of the oil yielded no metallic residue, assignment of the band as a coordinated acetylene stretch[20] was ruled out and it was ascribed to a carbonyl group. The spectrum also showed a band at 2910 cm^{-1}, a typical aliphatic C-H stretching frequency. The product was probably a

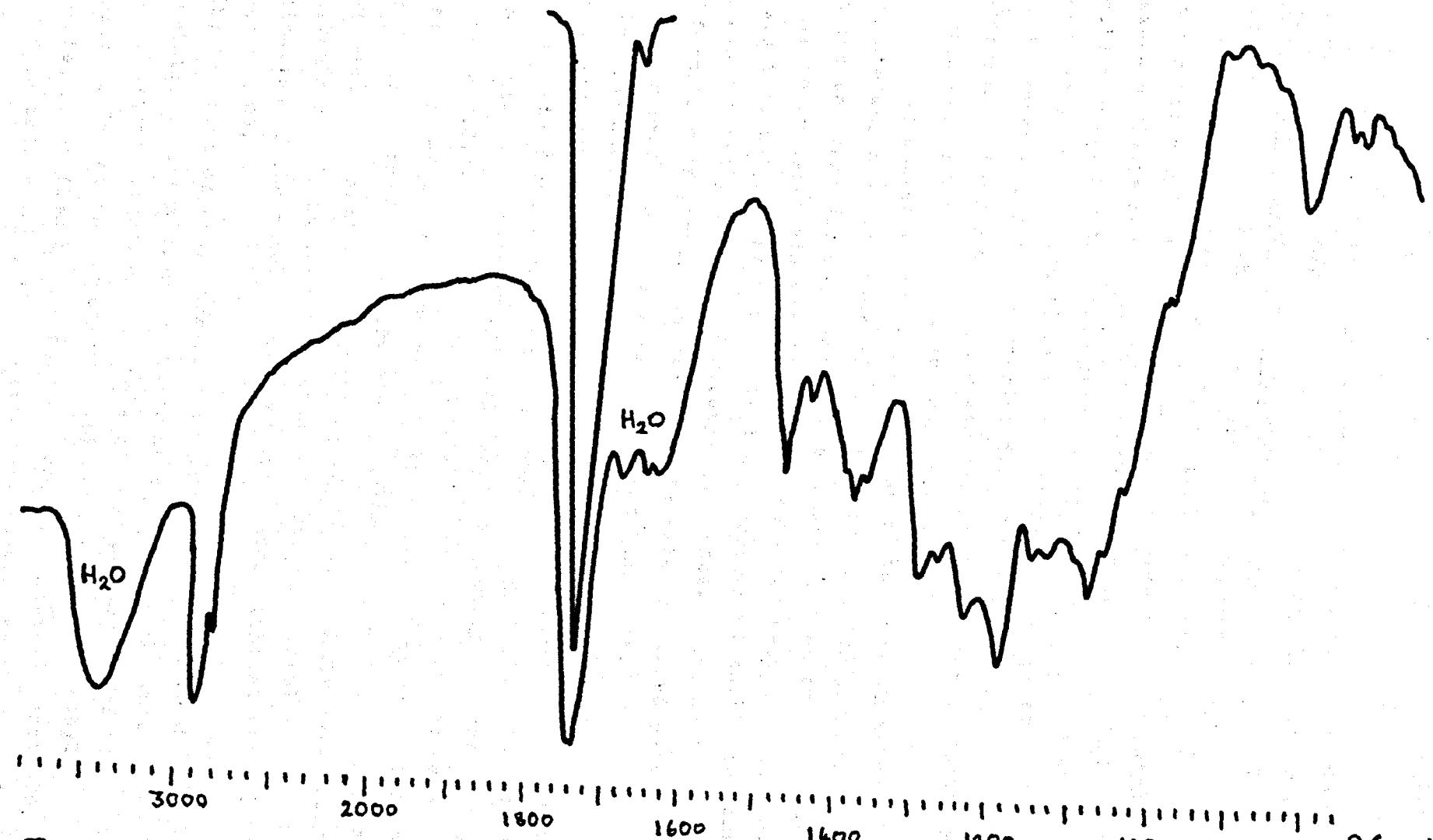


Fig. 2.12, THE PRODUCT FROM THE INTERACTION OF H-C≡C-H WITH Na_2PdI_4 IN BUTANOL (KBr disc)

condensation product of acetylene with or without the participation of butanol (which might account for the strong aliphatic bands).

(iii) Carbonylation in the Presence of Various Esters: It is obvious from section 2 (i) that butyl acrylate undergoes further reaction as carbonylation proceeds. It is believed, (cf. section 3 (v)) that butyl acrylate plays a part in the formation of dibutyl hex-2-enedioate and possibly the other C_6 diesters. Such a reaction could account for the whole loss of acrylate ester. When the standard reaction conditions were modified by the presence of air and hydrogen chloride, polymerisation of the acrylate ester was observed. However no polymer was detected when carbonylation was carried out under the standard conditions.

It was suspected in an early phase of the work that butyl acrylate was the precursor of the other major ester products: propionate by reduction, succinate by carbonylation and fumarate & maleate by carbonylation followed by dehydrogenation. C.B.Lines[1] showed that butyl acrylate may be the precursor of butyl propionate, but was not the precursor of dibutyl succinate. The evidence for the formation of propionate via acrylate ester required substantiation and it was proposed to investigate allied reactions.

(a) The addition of butyl acrylate to otherwise standard reactions with or without air passing did not lead to any increase in the amount of propionate formed, nor were the amounts of products with retention times greater than that of dibutyl fumarate greatly changed (cf. table 2.2.). However the amounts of diesters formed were markedly reduced in both cases. It is apparent that the diesters are not formed from butyl acrylate by carbonylation. The lowering of the yields of diester may possibly be due to a lower solubility of carbon monoxide in the ester solution than in butanol, or to the modification of the catalyst by acrylate ligands (though its colour was unchanged).

(b) Addition of ethyl acrylate to an otherwise standard carbonylation, with a view to observing chemically distinct products of its subsequent reaction, led to a reduced conversion of acetylene. In addition, 25% of the added compound was converted to ethyl propionate, identified by gas chromatography. Diethyl succinate was not detected, showing that transesterification reactions did not take place under the reaction conditions used.

Reaction No	Added Ester (g)	Air (l/h)	Weight (g)	Butyl Acrylate	Butyl Propionate	Dibutyl Maleate	Dibutyl Fumarate	Dibutyl Succinate
•	-	0	18.4	9.6	5.0	5.0	11.7	16.9
2.10.	Butyl Acrylate (4)	0	19.7	[13.8]	4.4	2.1	6.7	9.2
2.4.	-	1-1.5	16.2	5.7	1.9	7.5	9.6	9.3
2.11.	Butyl Acrylate (4)	1-1.5	13.8	[7.0]	1.6	5.6	6.3	5.0
2.31.	Ethyl Acrylate (10)	0	10.0	5.7	3.4	4.4	7.4	8.2
2.12.	Butyl Methacrylate (3)	0	18.2	8.7	6.8	2.6	12.4	21.0
2.13.	Butyl Methacrylate (4.7)	1-1.5	14.7	9.9	2.9	4.6	7.9	8.1
2.14.	Dibutyl Maleate (5)	1-1.5	12.4	5.9	1.1	[9.3]	8.1	6.8
2.15.	Dibutyl Pyrotartrate (1.7)	0	14.6	9.8	5.0	3.2	10.2	15.6
2.32.	Dibutyl Citraconate (9.6)	0	5.6	1.4	0.2	0.0	5.9	7.1
2.33.	Dibutyl Mesaconate (9.6)	0	9.4	3.6	0.6	0.0	11.6	15.0

• Result due to C.D.Lines[1]

Table 2.3. The concentrations of products from carbonylations carried out in the presence of various esters expressed as W/W% of the reaction mixture, initially butanol (60 g) containing palladium iodide (4 m mols)

(c) Addition of butyl methacrylate to otherwise standard reactions with or without the passage of air, did not result in the formation of butyl isobutyrate or diesters bearing a methyl group, nor any significant amounts of new 'higher' products.

The amounts of diesters formed were not reduced significantly by comparison with standard reactions.

(d) Addition of dibutyl maleate to a standard reaction in the presence of a stream of air, did not result in an increased amount of dibutyl succinate, nor was any new 'higher' product formed.

(e) The presence of dibutyl pyrotartrate did not result in any significant change in the proportions of the products, nor was any dehydrogenation product such as dibutyl mesaconate detectable.

(f) The presence of dibutyl citraconate in a reaction mixture resulted in a conversion much lower than that observed under standard conditions. The formation of butyl acrylate and propionate and dibutyl maleate was greatly reduced. No pyrotartrate ester was detected, but about 32% isomerisation to dibutyl mesaconate was observed.

(g) The presence of dibutyl mesaconate did not inhibit the carbonylation as much as the citraconate ester, but again the monoesters and dibutyl maleate were greatly reduced relative to the other products. No pyrotartrate or citraconate esters were detected by gas chromatography. Analysis revealed 95% of the mesaconate ester unchanged at the end of the reaction.

(iv) The Attempted Interaction of Butyl Acrylate with Carbon Monoxide:

To confirm Lines'[1] conclusion that butyl acrylate does not react with carbon monoxide in the presence of palladium iodide a reaction was carried out at 90°C under a carbon monoxide pressure of 80 atmospheres. No diester products were observed. In view of the possibility that the β-protons of acrylate ester are rendered labile in the presence of palladium iodide and carbon monoxide with the formation of a palladium vinyl system, butyl acrylate was exposed to carbon monoxide and the tetraiodopalladate catalyst in butanol-O-d for 12 hours. It was then separated by preparative gas chromatography, and shown by n.m.r. spectroscopy not to have exchanged any protons for deuterium. It can be concluded from the foregoing, that butyl acrylate does not react with carbon monoxide under the standard reaction conditions.

It would however appear to be the precursor of butyl propionate, since ethyl acrylate is reduced to ethyl propionate when present during carbonylation.

(v) The Attempted Reduction of Unsaturated Esters with Hydrogen Iodide and Palladium:

It was suspected that reduction of unsaturated products might be brought about by hydrogen iodide, presumed to be formed in the reaction (cf. Chapter 2.2 (i)), in combination with palladium metal. However, exposure of butyl acrylate to a mixture of palladium/charcoal and anhydrous hydrogen iodide in butanol with or without the passage of carbon monoxide did not give rise to any butyl propionate detectable by gas chromatography.

(vi) Attempted Carbonylation with a Mercury(II) Catalyst:

Mechanisms have been suggested for the palladium catalysed carbonylation of olefins, wherein carbon monoxide acts as a nucleophile and attacks the activated hydrocarbon, [14]. Mercury(II) salts are well known to activate acetylenes to nucleophilic attack [15], as in the manufacture of acetaldehyde from acetylene using a mercuric sulphate catalyst. Hence it was felt that a successful carbonylation using a mercuric iodide/sodium iodide catalyst would provide evidence in support of the nucleophilic carbon monoxide mechanism.

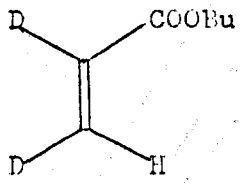
A reaction was carried out under standard conditions, but using HgI_2 (4 m mols) and NaI (8 m mols) as catalyst. No organic products whatever could be detected.

(vii) The Attempted Interaction of Acetylene with Cyanide Ion: As a further test of the nucleophilic nature of the reaction between acetylene and carbon monoxide, it was proposed to react acetylene in the presence of the catalyst with cyanide ion. Mono- and dinitriles were expected as a result of nucleophilic attack by the cyanide ion. However acetylene and sodium cyanide in the absence of palladium iodide yielded a single product which was shown by n.m.r. spectroscopy (5.78τ, triplet, 4H; 8.0-9.2τ, multiplet, 14H), its infrared spectrum (ν(cm^{-1})= 1180, 1310, 1465, 1740, 1770, 2880, 2960) & its mass spectrum ($\frac{m}{e}$ = 41, 57, 101, 147) to be dibutyl oxalate. The infrared and mass spectra were identical with those given in the literature [16, 17 resp.]. The yield of dibutyl oxalate based on acetylene was 2.3%. When the palladium iodide/sodium iodide catalyst was present in its usual concentration with the sodium cyanide only dibutyl oxalate was obtained (in slightly lower yield).

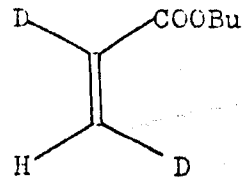
From section 4 (vi) & (vii) it would seem that a mechanism involving nucleophilic carbon monoxide, whilst not excluded, cannot be substantiated.

(viii) The Carbonylation of Acetylene-d_2 (Rn.2.16) A quantity of acetylene-d_2 was prepared and carbonylated according to the standard procedure, except that for reasons of economy, the reaction was only carried on for 5 hours. The usual range of products was obtained in rather less than the usual quantities, except that butyl propionate concentration was strikingly low, i.e. 0.5 W/W% compared with a typical 5.0%, (cf. fig. 2.13.). The products higher than dibutyl fumarate were also present only to a relatively small extent (cf. table 2.2.)

The butyl acrylate-d_2 from reaction2.16 was isolated by preparative scale gas chromatography. Its n.m.r. spectrum (fig. 2.14.) showed two multiplets, in the olefinic region, integrating as a total of 1 proton, at 3.73τ and 4.27τ. It was concluded that the two signals were due to the remaining proton in two possible geometrical isomers, II & III, II corresponding to the downfield signal, owing



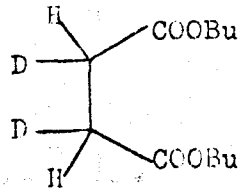
II



III

to the proximity of the deshielding carbonyl group to the proton. The two isomers integrated as II : III = 3:2, indicating that cis-addition of the -COOBu and -H groups was somewhat favoured.

The diesters from reaction2.16 were collected as a single fraction. Its n.m.r. spectrum showed very small singlets at 3.22τ, 3.85τ (corresponding to the olefinic protons in fumarate and maleate esters respectively) and a singlet at 7.50τ (corresponding to succinate ester). Comparison of the n.m.r. integrals with a gas chromatographic analysis of the sample showed that succinate, maleate and fumarate were all present as dideutero- compounds IV, V, VI respectively:



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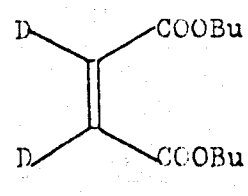

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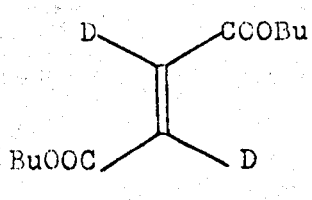

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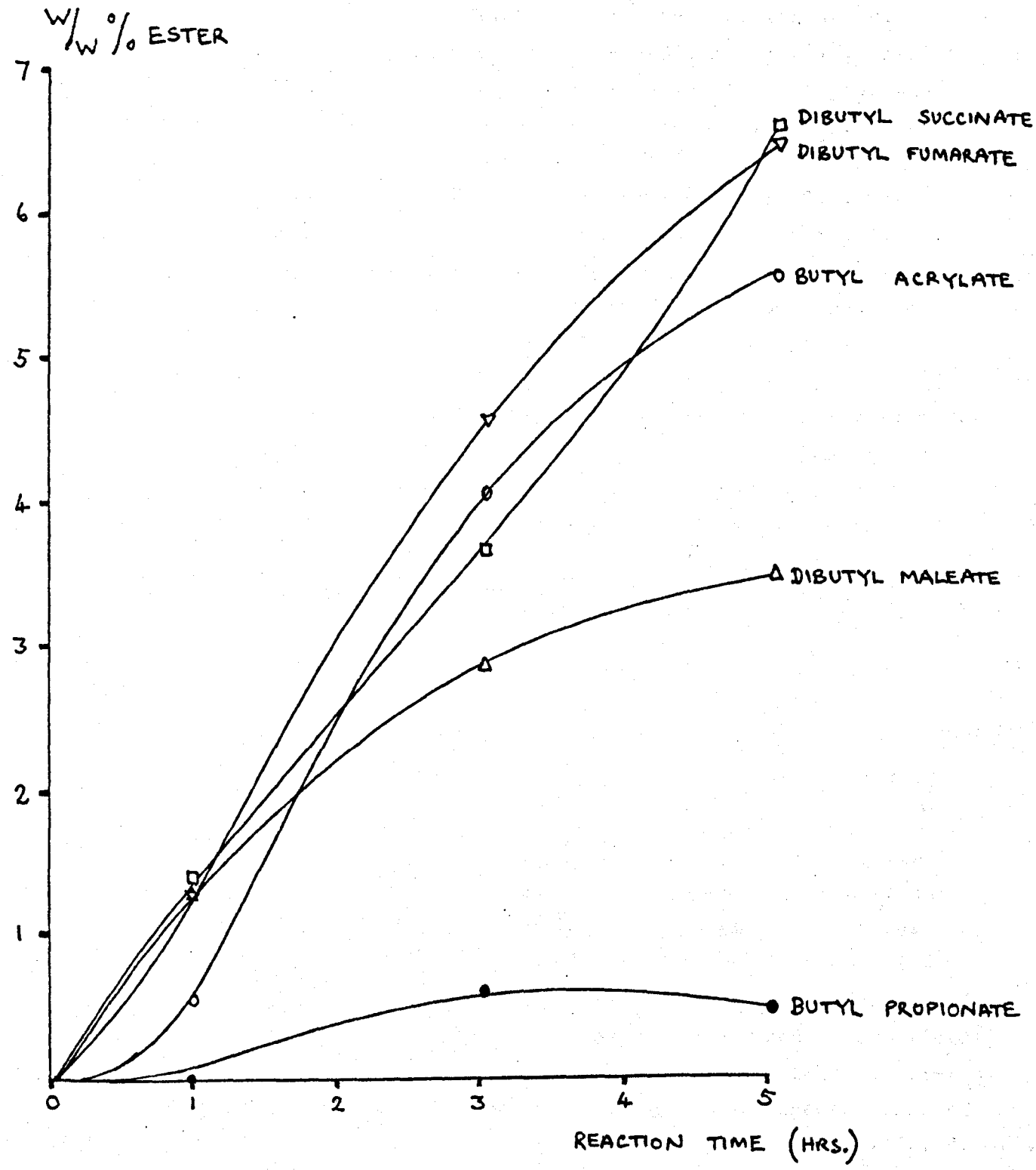


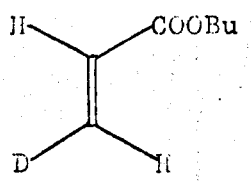
Fig. 2.13, REACTION 2.16. :

THE CARBONYLATION OF ACETYLENE-d_2

Confirmation of the above assignments was obtained by hydrogenating the mixture over platinum. The product was shown by gas chromatography to be dibutyl succinate, and its n.m.r. spectrum showed it to be dibutyl succinate-d_2, i.e. 5.94τ, triplet, 4H; 7.50τ, singlet, 2H; 8.2-9.2τ, multiplet, 14H. Except for the preference for cis-addition in monoester formation, the products were as expected.

(ix) The Products from Carbonylation in Butanol-O-d: C.B.Lines[1] carried out a number of reactions using Butanol-O-d as a solvent, and reported on certain isotope effects (cf. section 1.(ii)). It seemed desirable to isolate the products from Lines[1] reaction mixtures and observe how deuterium had become incorporated into their structures.

Butyl acrylate was obtained by preparative gas chromatography. Its n.m.r. spectrum showed a multiplet integrating as one proton in the olefinic region (fig. 2.14.), which suggested that butyl acrylate-d_1 was present in two forms, VII and VIII in the ratio



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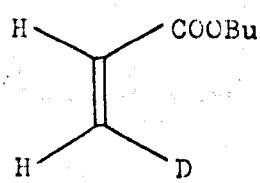

VIII

VII : VIII = 2 : 3, showing as did the previous experiment, that cis-addition across the triple bond was slightly favoured.

Dibutyl fumarate and succinate were isolated by preparative gas chromatography. The fumarate ester had infrared, n.m.r. and mass-spectra identical to those of an authentic sample and hence had not incorporated any deuterium.

The succinate ester had infrared and n.m.r. spectra identical to those of dibutyl succinate-d_2 obtained in the preceding experiment (4. (ix)). Its mass spectrum did not show a parent ion, but ions were present at $\frac{m}{e}$=159 and 103, corresponding to the expected loss of -OBu, followed by C_4H_8, from dibutyl succinate-d_2 (cf. figs 2.15., 2.16.).

The presence of deuterated dibutyl succinate and non deuterated dibutyl fumarate shows that the unsaturated diester does not arise by dehydrogenation of succinate as has been suggested, since in any such elimination reaction it is expected the heavy isotope will be retained[18].

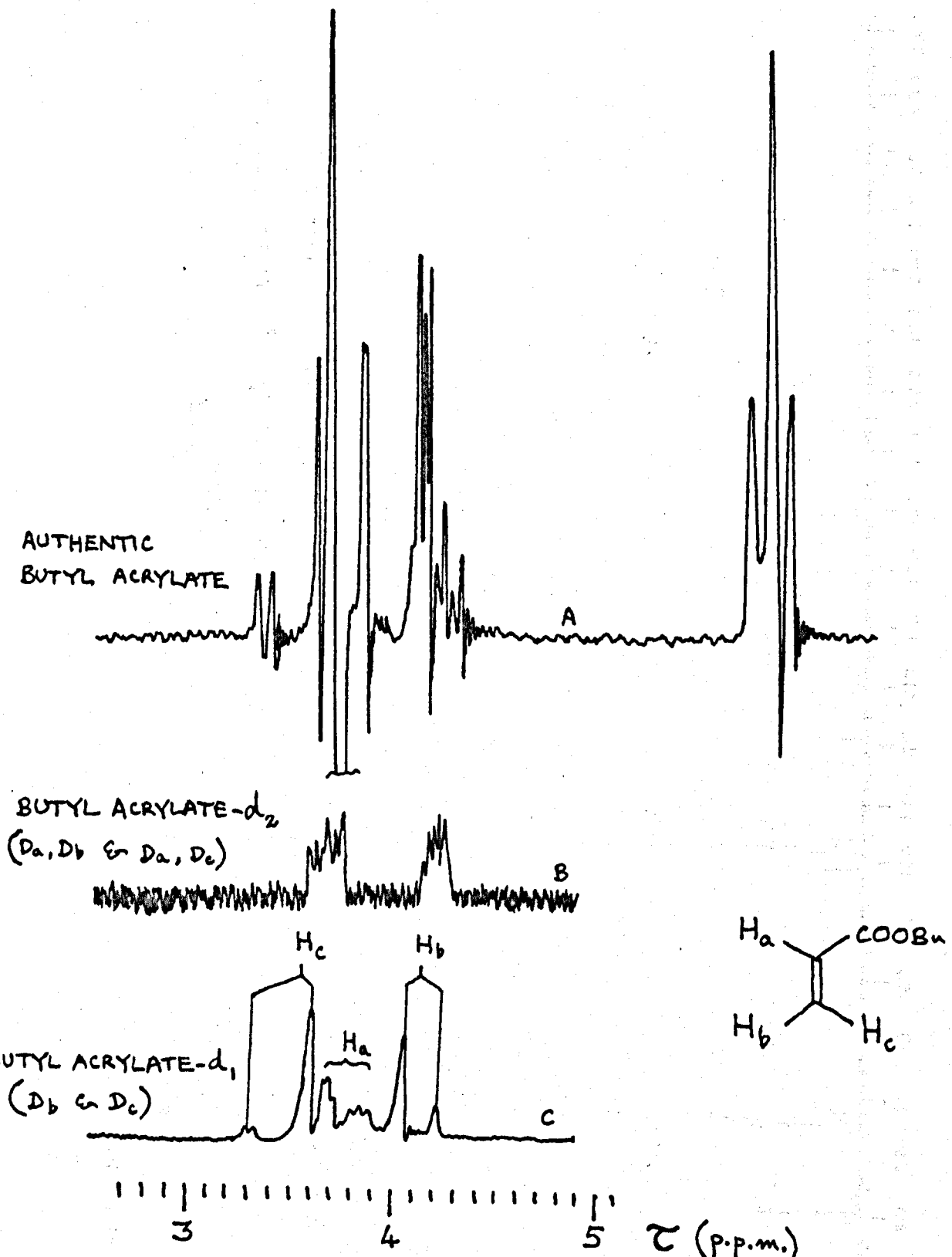

Fig 2.14₂ DEUTERATED BUTYL ACRYLATES, N.M.R. SPECTRA

(CCl_4 SOLUTIONS; A, 15%; B, 5%, 20 RUNS ACCUMULATED; C, 30%.)

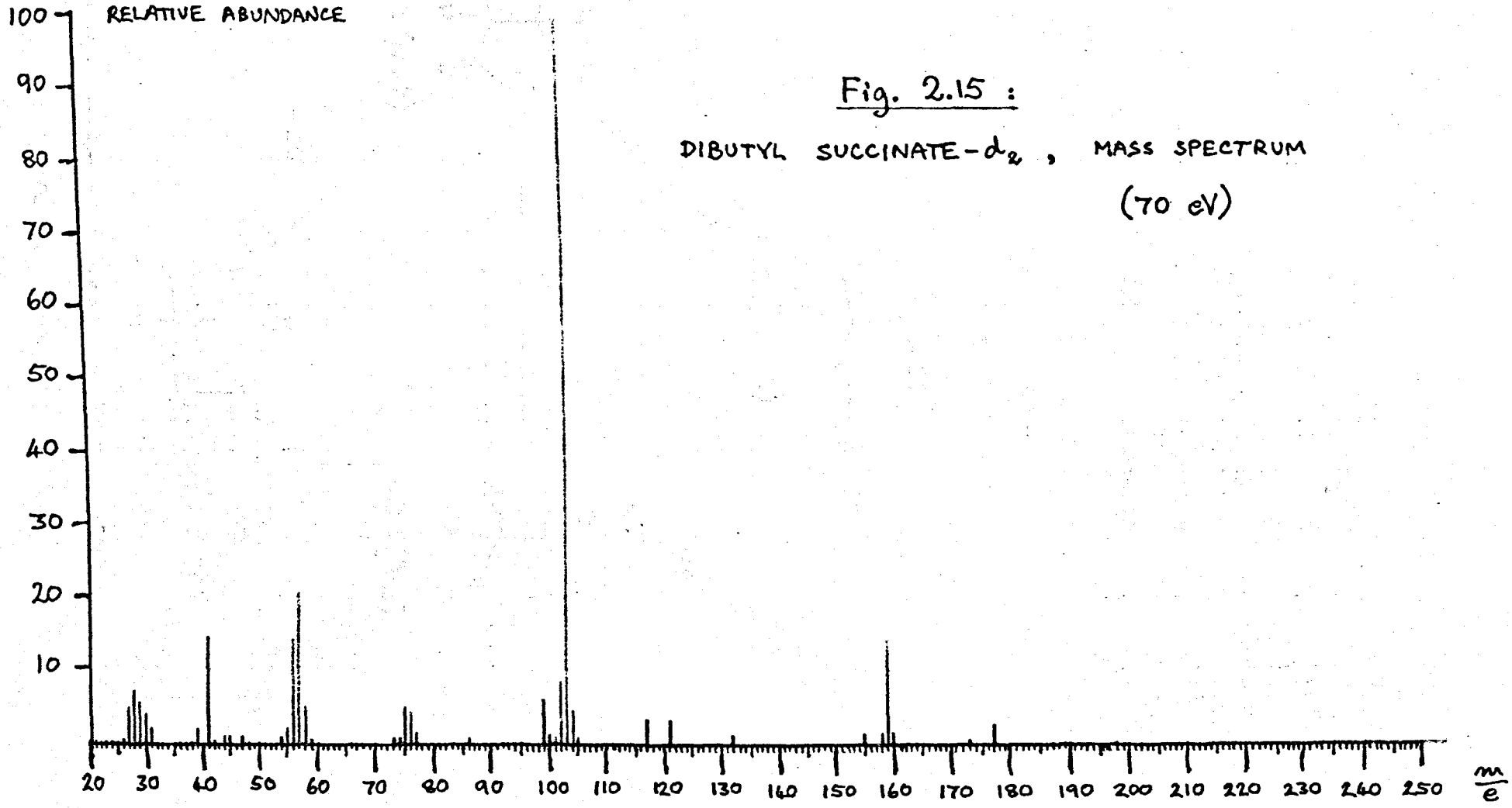

Fig. 2.15 :

DIBUTYL SUCCINATE-d_2 , MASS SPECTRUM

(70 eV)

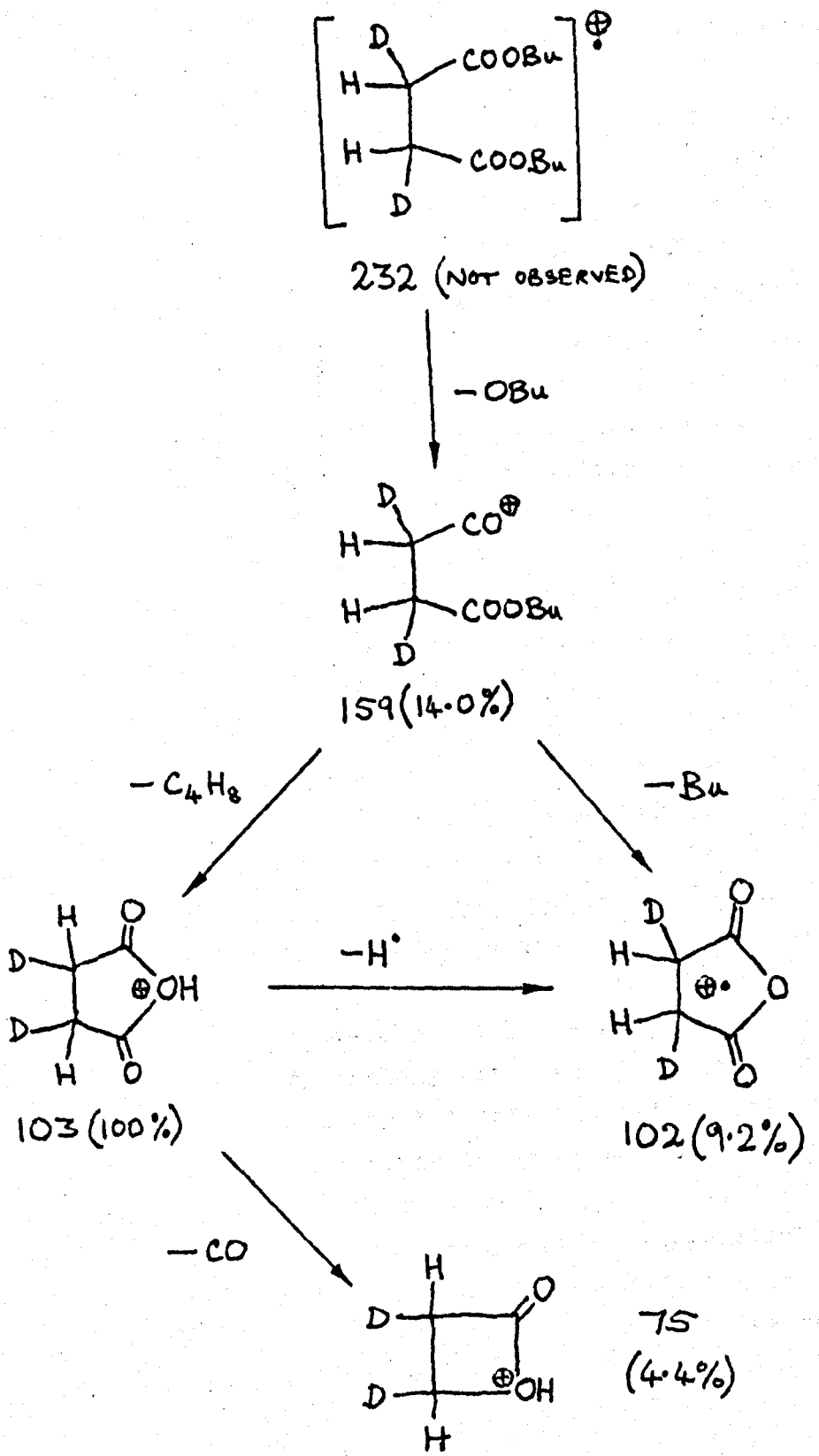

Fig 2.16: TENTATIVE FRAGMENTATION SCHEME FOR DIBUTYL SUCCINATE-d_2

2.5. ATTEMPTED CARBONYLATION USING OTHER CATALYST SYSTEMS

The literature contains many references to carbonylation catalysed by complexes of palladium, e.g. Bittler et al.[14] have used tetrakis(triphenylphosphine)palladium and tetrakis(triorthocresylphosphite)palladium for the carbonylation of olefins.

It was decided to test a number of complexes for effectiveness in promoting the carbonylation of acetylene.

(i) Bis(triphenylphosphine)palladium(II) Iodide: The complex was found to be only sparingly soluble in butanol, i.e. only 1/5 of the desired 4 m mols was taken up under the standard conditions. On passage of carbon monoxide and acetylene for 7 hours, very small amounts of ester products were detected, the analyses being as follows: butyl acrylate, 0.1%; propionate, 0.0%; dibutyl maleate, 0.6%; succinate, 0.4% and fumarate, 0.3%, indicating that the catalytic power of the complex is much lower than that of sodium tetraiodopalladate(II), even making allowance for its low solubility.

The complex was recovered (in 60% yield), unchanged as shown by infrared spectroscopy, on cooling the reaction mixture.

(ii) Bis(tributylphosphine)palladium(II) Iodide: The complex was found to be soluble to the required extent of 4 m mols in 70 mls. of butanol at 75°C. However no products could be detected by gas chromatography after passage of the reactant gases.

The complex was recovered unchanged on cooling the solution.

(iii) Bis(diphenylphosphino)ethanepalladium(II) Iodide: It is known that complexes of the type L_2PdX_2 (where L is a ligand such as a phosphine, and X is an acid anion such as iodide) exist as equilibrium mixtures of *cis*- and *trans*-forms with the *trans*-form predominating[19]. Since it is believed, by analogy with the findings of Collman & Kang[20], that the acetylene may occupy two coordination sites in a square planar complex, it was felt appropriate to observe the catalytic power of a chelated *cis*- complex. Since some measure of success had been achieved using the triphenylphosphine complex (section 4.(i)), it was decided to use the complex obtained from bis(diphenylphosphino)ethane.

The complex however was found to have a very low solubility in butanol, i.e. 1/20 of the required 4 m mols in 70 mls. at 75°C. Attempts were made to effect a carbonylation using the complex

(a) as a dilute solution in butanol,

(b) in butanol:dimethylformamide (1:2) and

(c) in butanol:toluene (1:2).

However in no case was any product detectable by gas chromatography, and the complex could always be recovered unchanged.

(iv) Palladium(II) Acetate: Palladium Acetate proved to be ineffective as a catalyst since it decomposed on gentle warming, even in glacial acetic acid solution at 40°C. No products except acetic acid were detected by gas chromatography in any of the reactions.

2.6. SUMMARY & CONCLUSIONS

Sodium tetraiodopalladate(II) constitutes a powerful carbonylation catalyst for acetylene, being greatly superior to a number of other palladium(II) compounds. However it catalyses both mono- and dicarbonylation reactions. The ratio of mono- to dicarbonylation products can be changed in favour of monoesters by the presence of acids and in favour of diesters by certain oxidising species.

It has been shown that saturated esters are produced by reduction of unsaturated esters, but a mechanism involving nucleophilic attack on the co-ordinated acetylene by carbon monoxide is not supported by the available evidence.

Dibutyl muconate and a number of hexenedioates are by-products of the reaction.

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CHAPTER THREE

Studies on the Carbonylation of Methylacetylene

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3.1. INTRODUCTION

Following the studies on the carbonylation of acetylene, it was of interest to examine the effect of substituent groups on the reactivity of the acetylenic bond. In this and subsequent chapters the results of the carbonylation of a number of acetylenes are described.

In the first instance methylacetylene was selected as the simplest monosubstituted acetylene.

3.2. EXPLORATORY REACTIONS

(i) The Carbonylation of Methylacetylene Under the Conditions Previously Used for Acetylene:

When methylacetylene was treated with carbon monoxide in exactly the same way as acetylene had been under the so-called 'standard' reaction conditions, it was observed that, in contrast with the results of using acetylene, the wine red colour of the catalyst solution had changed to a greenish yellow, and a heavy black solid had been deposited. Analysis of the solid showed that it contained 90% palladium. Gas chromatography did not reveal any products except traces of two compounds later shown to be dibutyl citraconate (0.5 W/W%) and dibutyl mesaconate (0.7 W/W%).

(ii) The Effect of Varying the Reaction Temperature:

As part of a study of varying the experimental conditions, with the object of increasing the conversion of methylacetylene, the carbonylation was investigated at a reaction temperature of 65°C. The results were markedly different from those noted in (i) above. A number of esters and other products were observed and identified, amounting to a 6% conversion of the methylacetylene. The formation of some of the products was followed by gas chromatography, (cf. fig. 3.2.). The colour change and the destruction of the catalyst were, however, still observed.

Products were identified as shown in table 3.1., letters referring to peaks in the gas chromatogram (fig. 3.1.). No evidence could be obtained for the presence of a number of expected products such as butyraldehyde, propionaldehyde, mesitylene, pseudocumene, butyl n-butyrate and dibutyl itaconate. The absence of itaconate ester tends to refute the suggestion that isomerisation of methylacetylene to allene is an essential step in the reaction, since dicarbonylation of allene would be expected to lead to itaconate ester, by analogy with the work of Tsuji & Susuki[1].

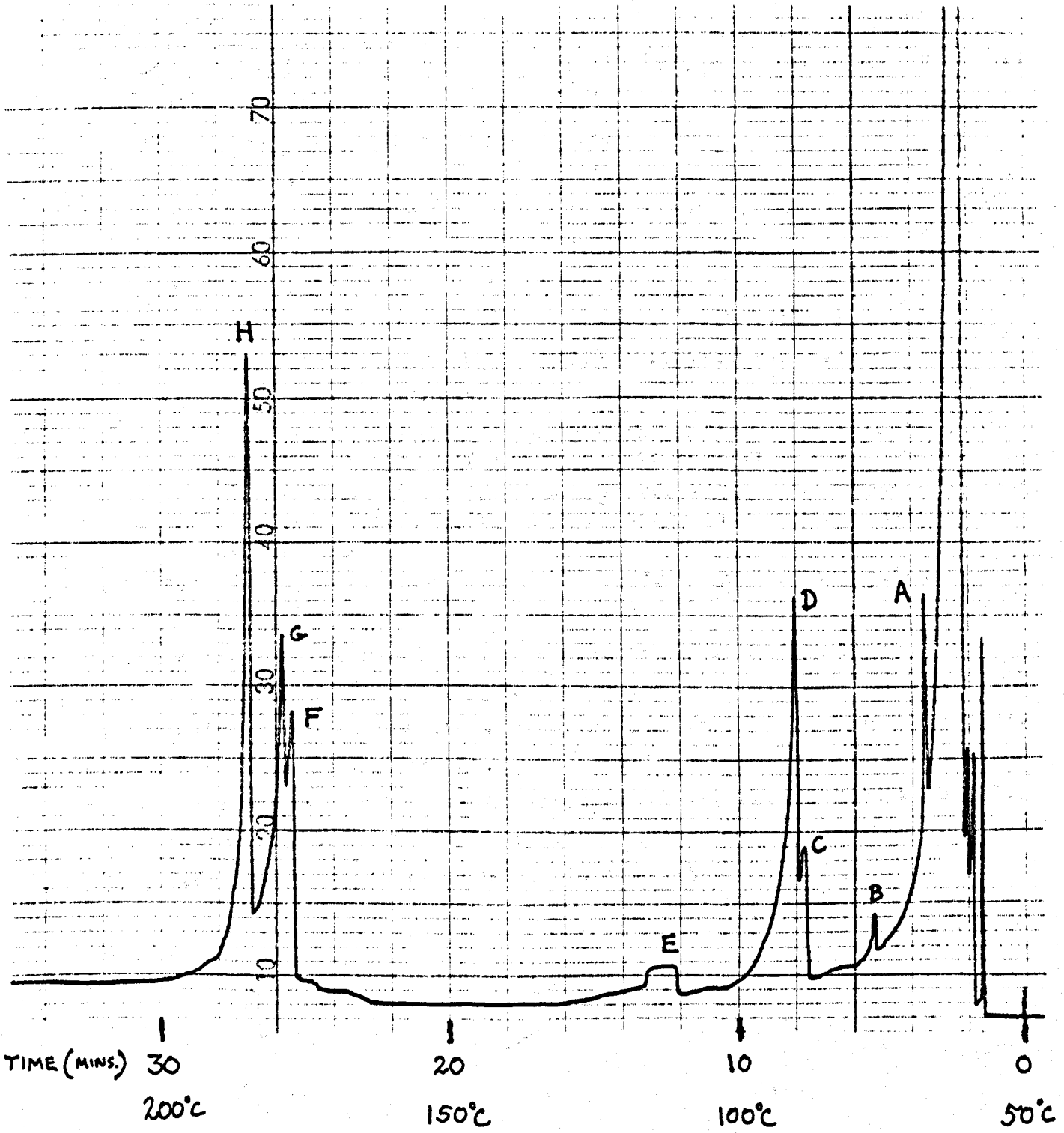


Fig 3.1 CHROMATOGRAM OF TYPICAL METHYLACETYLENE CARBONYLATION MIXTURE

(SILICONE COLUMN, PROGRAMMED TO 5°C/MIN. RISE)

Peak in Chromatogram	Identity	Means of Identification
-*	Acetone	C(3), i(2,4-dinitrophenylhydrazone)
'A'	Butyl iodide	C(3)
'B'	trans-1,2-Diiodopropene	C(3)
'C'	Butyl isobutyrate	C(3)
'D'	Butyl methacrylate	C(4), i(n.m.r.)
'E'	Butyl crotonate	C(3)
'F'	Dibutyl pyrotartrate	C(4)
'G'	Dibutyl citraconate	C(4), i(i.r., n.m.r.)
'H'	Dibutyl mesaconate	C(4), i(i.r., n.m.r.)

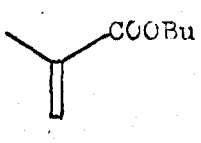
* Present in the cold-trap.

C(n) denotes comparison of the gas chromatographic retention times with those of the authentic compound on n columns.

i denotes isolation (usually by preparative gas chromatography) and identification by the spectroscopic or other methods specified.

Table 3.1. Identification of the Products from the Carbonylation of Methylacetylene.

N.B. Acetone was estimated to be present to about 2% W/W in the present and subsequent reactions. The formation of acetone from methylacetylene parallels the formation from acetylene of acetaldehyde, detected as its dibutyl acetal. It is well known that acetals are much more readily formed from aldehydes than are ketals from ketones[2]. Butyl iodide was present to about 0.5% W/W, whilst trans-1,2-diiodopropene was present to the extent of 0.2% W/W



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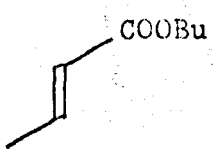

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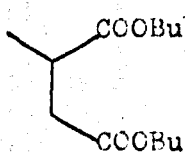
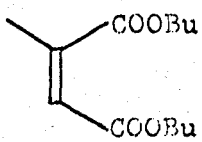
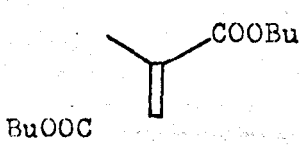


'F'



'G'



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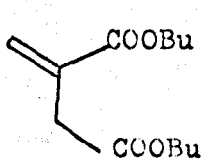


Dibutyl Itaconate

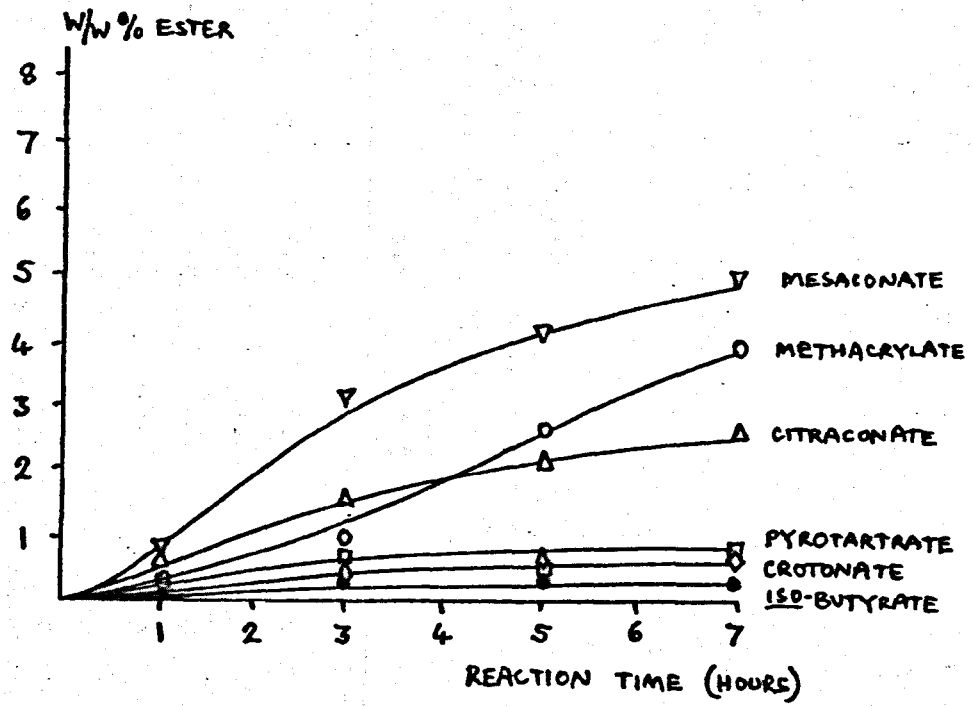


Fig. 3.2

Rm. 3.2

CARBONYLATION OF METHYLACETYLENE WITH A HIGH METHYLACETYLENE FLOW RATE

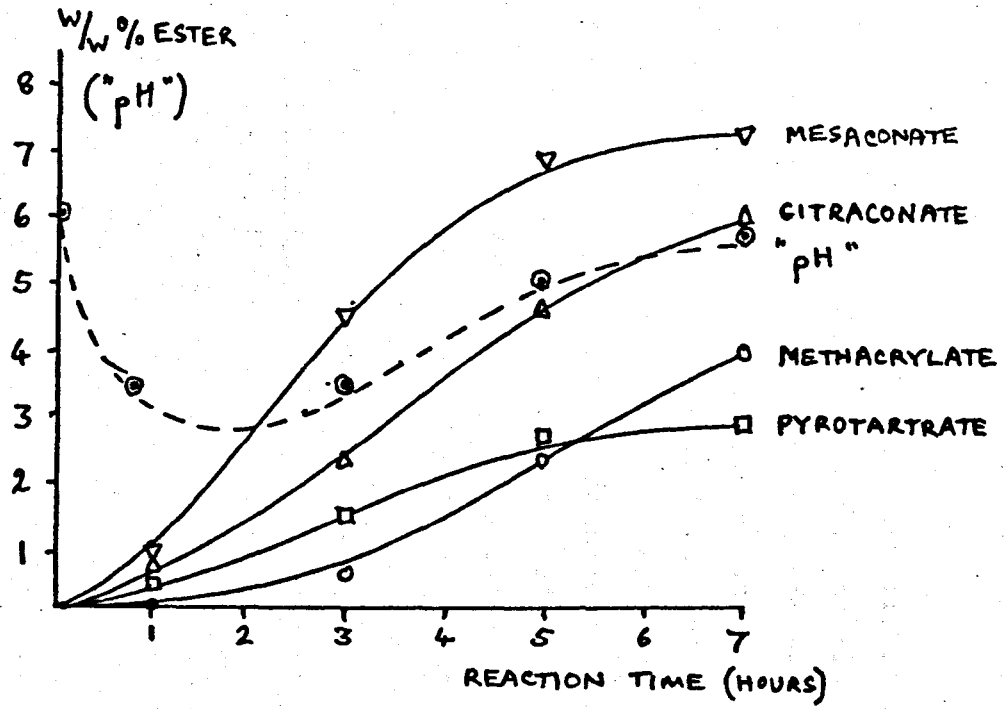


Fig. 3.3

Rm. 3.5

CARBONYLATION OF METHYLACETYLENE UNDER STANDARD CONDITIONS ; VARIATION OF "pH"

No other substances were detectable in significant amounts. It was decided that quantitive analyses would be confined to butyl methacrylate and dibutyl citraconate, mesaconate and pyrotartrate, since acetone, butyl isobutyrate and crotonate and the two iodinated compounds were only present to a very small extent, not exceeding a total of 5% W/W of the reaction mixture.

The only monoester formed in significant amounts was the non-linear isomer, consistent with the findings of many workers who have investigated the carbonylation of monosubstituted acetylenes. Methacrylate ester has been obtained as the main product of nickel catalysed carbonylation of methylacetylene by Clarkson[3], Happel & Marsel[4] and Sakakibara and his co-workers[5,6].

(iii) The Carbonylation of Methylacetylene at a Reduced Flow-Rate:

As part of the study of the variation of reaction conditions, the carbonylation of methylacetylene was examined with the gas passing at a lower flow-rate in the hope of reducing its apparent tendency to destroy the catalyst. Reactions 3.4, 3.5 and 3.6 were carried out at 65°C and with a methylacetylene flow-rate of 1.5 l/h. In reaction 3.5 the 'pH' of the solution was monitored using universal indicator paper as described in the case of acetylene (Chapter 2.2(i)). The 'pH' reading was observed to fall from 5 to about 3 in the early stages of the reaction and to slowly rise to a value of 6 at the end (fig. 3.3). The 'pH' change was more marked than in the acetylene reactions, and since methylacetylene reactions were associated with deposition of metallic palladium, it was reasonable to assume that the acidity was due to the formation of hydrogen iodide.

The results of reaction 3.5 are shown in fig. 3.3, and final analyses for the three reactions are summarised in table 3.2, together with those of reaction 3.7.

Reaction No	3.4	3.5	3.6	3.7
Temperature (°C)	65	65	65	40
Wt increase (g)	7.5	6.8	7.7	6.2
butyl methacrylate	5.6	4.0	3.5	4.8
dibutyl citraconate	4.2	6.0	4.0	2.4
dibutyl mesaconate	6.3	7.1	6.3	5.2
dibutyl pyrotartrate	2.2	2.8	2.3	0.7

Table 3.2 The Amounts of Ester Products Obtained by the Carbonylation of Methylacetylene with a Lowered Methylacetylene Flow-Rate. (Expressed as a W/W% of the Reaction Mixture, initially 60 g).

It was apparent that lowering the flow-rate of methylacetylene did not change the course of the reaction, within the limits of experimental error. This observation was not suprising since it was shown by C.B.Lines[7], in the case of acetylene, that the reaction rate was limited by the availability of carbon monoxide, due no doubt to the relative insolubility of carbon monoxide in butanol. (The solubility of acetylene in ethanol is greater than that of carbon monoxide by a factor of 30[8]. A similar difference in solubility might be expected in butanol, and the ratio is probably even higher in the case of methylacetylene).

(iv) The Standard Reaction: Since the flow-rate of methylacetylene could be halved without effecting the amounts of products in its reactions (though yields based on the acetylene are of course doubled) it was decided to 'standardise' the reaction using the above conditions to provide convenient reference data. In discussions of methylacetylene reactions, the 'standard' reaction should be taken to mean a reaction in which carbon monoxide (at 3 l/h) and methylacetylene (at 1.5 l/h) are passed into a well stirred solution of palladium iodide (4 m mols) and sodium iodide (8 m mols) in butanol (60 g) and 65°C for a period of 7 hours, (cf. reactions 3.4, 3.5 & 3.6, table 3.2).

(v) Carbonylation at Reduced Temperature: Since a considerable increase in the yield of products had been achieved by lowering the temperature to 65°C, a reaction (Rn. 3.7) was carried out with the temperature at 40°C and conditions otherwise standard. The amounts of esters so produced were slightly reduced by comparison with 'standard' reactions (cf. fig. 3.4 and table 3.2). It is noteworthy however, that the ratio of mono- to diesters was somewhat increased, and the amount of dibutyl pyrotartrate was greatly reduced.

(vi) Carbonylation for an Extended Period: During the above reactions, the formation of diesters frequently ceased after about 5 hours, whilst the production of methylacrylate ester continued rapidly. A reaction was studied over a longer period, to determine the ultimate yield of methacrylate ester.

Reaction 3.8 was carried out under 'standard' conditions, but continued for 11 hours. The results are shown in fig. 3.5; it can

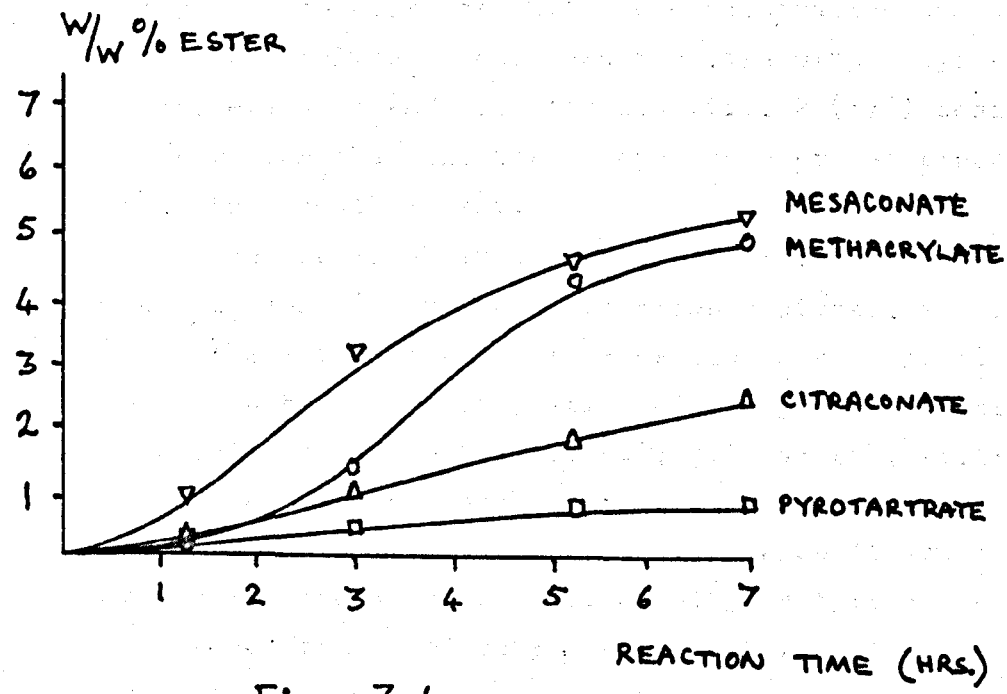


Fig. 3.4

Rm. 3:7

CARBONYLATION OF METHYLACETYLENE AT 40°C

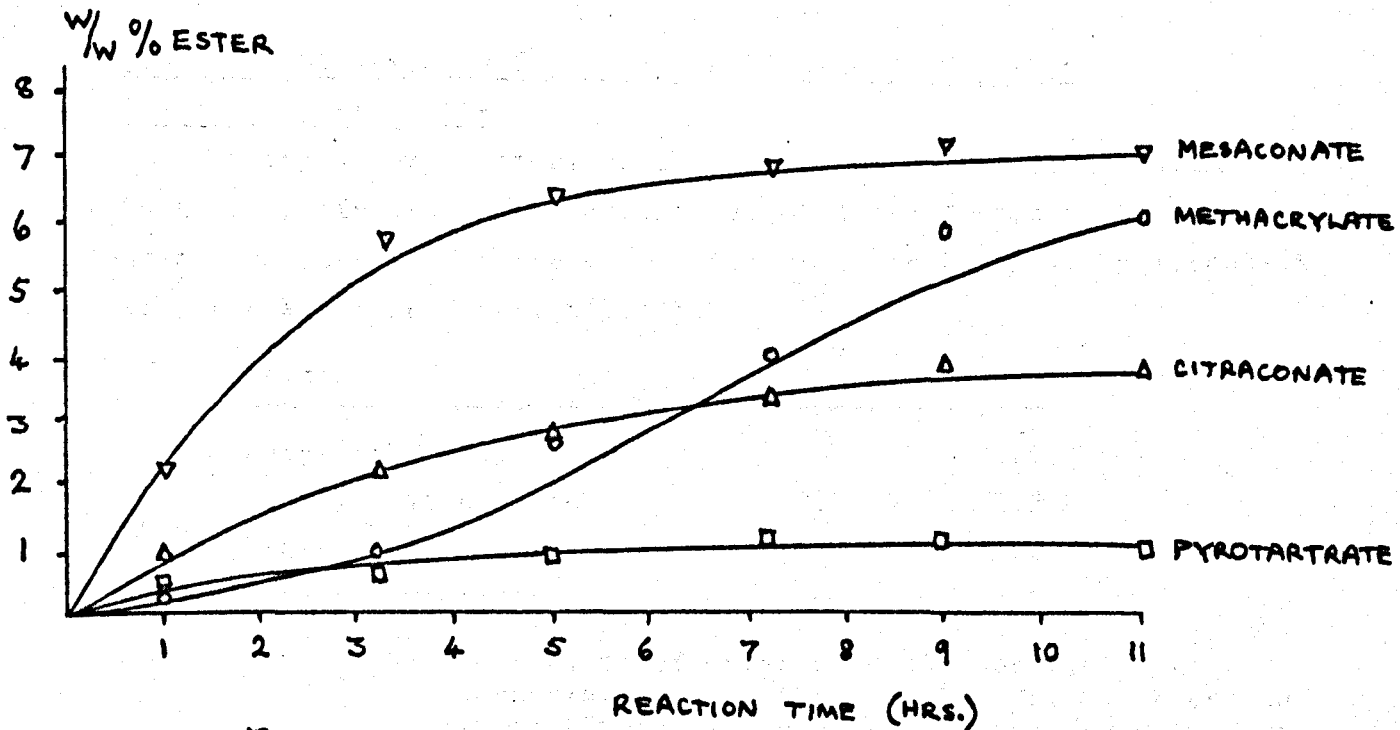


Fig. 3.5

Rm. 3.8

CARBONYLATION OF METHYLACETYLENE OVER AN EXTENDED PERIOD

be seen that butyl methacrylate continued to be produced for a limited period after the formation of diesters had ceased, though it was never present in greater amount than dibutyl mesaconate. There was no evidence that the concentration of butyl methacrylate began to decline as had been the case with butyl acrylate in the acetylene work (cf. Chapter 2.1 (ii), 2 (i)) consistent with the observation that the corresponding saturated product was present only to a small extent.

The low level at which both isobutyrate and pyrotartrate esters were present in the above reaction mixtures, was in marked contrast with the large amounts of saturated esters (propionate & succinate) produced by the carbonylation of acetylene. Evidence has been adduced (Chapter 2.4 (iii) (b); 3.5 (v) (a), (viii) (a), (b)) to support the contention that the saturated esters were produced by reduction of the unsaturates. Hence it would appear that the branched esters produced from methylacetylene are much more difficult to reduce than the acetylene products.

All the above reactions (section 3.2 (i) - (vi)) were associated with a colour change in the catalyst solution, a palladium precipitate being thrown down and the wine red colour of the catalyst changing to a greenish yellow.

3.3. CARBONYLATION IN THE PRESENCE OF OXIDISING AGENTS

(i) The Effect of Air:

During an exploratory reaction (rn.3.9), the adventitious ingress of air caused the amounts of products formed to be higher than was observed for the comparable reaction (3.1) without contact with the atmosphere (cf. table 3.3).

Reaction No	3.1	3.9
Butyl methacrylate	-	1.5
Dibutyl citraconate	0.5	2.7
Dibutyl mesaconate	0.7	4.0
Dibutyl pyrotartrate	-	1.2

Table 3.3: The Amounts of Ester Products Obtained by Carbonylation of Methylacetylene in the Presence of Air.(Expressed as a W/W% of the Reaction Mixture, initially 60 g).

It was obvious that air had a beneficial effect on the reaction.

Since it has been reported by Chiusoli and his co-workers[9,10] that the presence of a stoicheiometric amount of oxygen during the carbonylation of acetylene with a palladium chloride catalyst prevented the formation of saturated products, it was decided to investigate the effects of the presence of air during the carbonylation of methylacetylene.

(ii) Variation of the Air Flow-Rate: A series of reactions was carried out with air passing at a number of flow-rates. The results are summarised in table 3.4.

Reaction No	3.10	3.3	3.13	3.14
Air (l/h)	0.5	1.5	4.0	8.0
Weight Increase (g)	7.0	7.7	4.0	2.7
butyl methacrylate	2.0	1.7	0.0	0.0
dibutyl citraconate	3.4	5.7	2.4	1.9
dibutyl mesaconate	5.8	7.4	1.2	0.9
dibutyl pyrotartrate	1.7	2.2	0.0	0.0
Colour after 7 hours	yellow Pd^{o} ppt.	wine red	wine red	wine red

Table 3.4 The Amounts of Ester Products Obtained by Carbonylation of Methylacetylene in the Presence of Air at Various Flow-Rates, the Methylacetylene Flow-Rate being 3 l/h. (Expressed as a W/W% of the Reaction Mixture, initially 60 g).

From the above results a flow-rate of 1-1.5 l/h of air appeared to be most beneficial, and therefore was used in the following reactions when the presence of air was indicated.

(iii) Variation of the Temperature with Air Present: From a study of the effect of varying the temperature of carbonylation of methylacetylene in the presence of air, it was possible to demonstrate that a maximum overall conversion could be achieved at about 65°C (cf. fig. 3.6). It was noteworthy that the production of butyl methacrylate was apparently much higher at a lower temperature, (40°C).

(iv) Carbonylation of Methylacetylene Under 'Standard' Conditions but with Air Passing:

On the basis of the foregoing results, it was found that the best conversion of methylacetylene could be realised using the 'standard' conditions, but with air passing at 1-1.5 l/h. The results of such a reaction (Rn. 3.11) are displayed in fig. 3.7 (a). All the esters

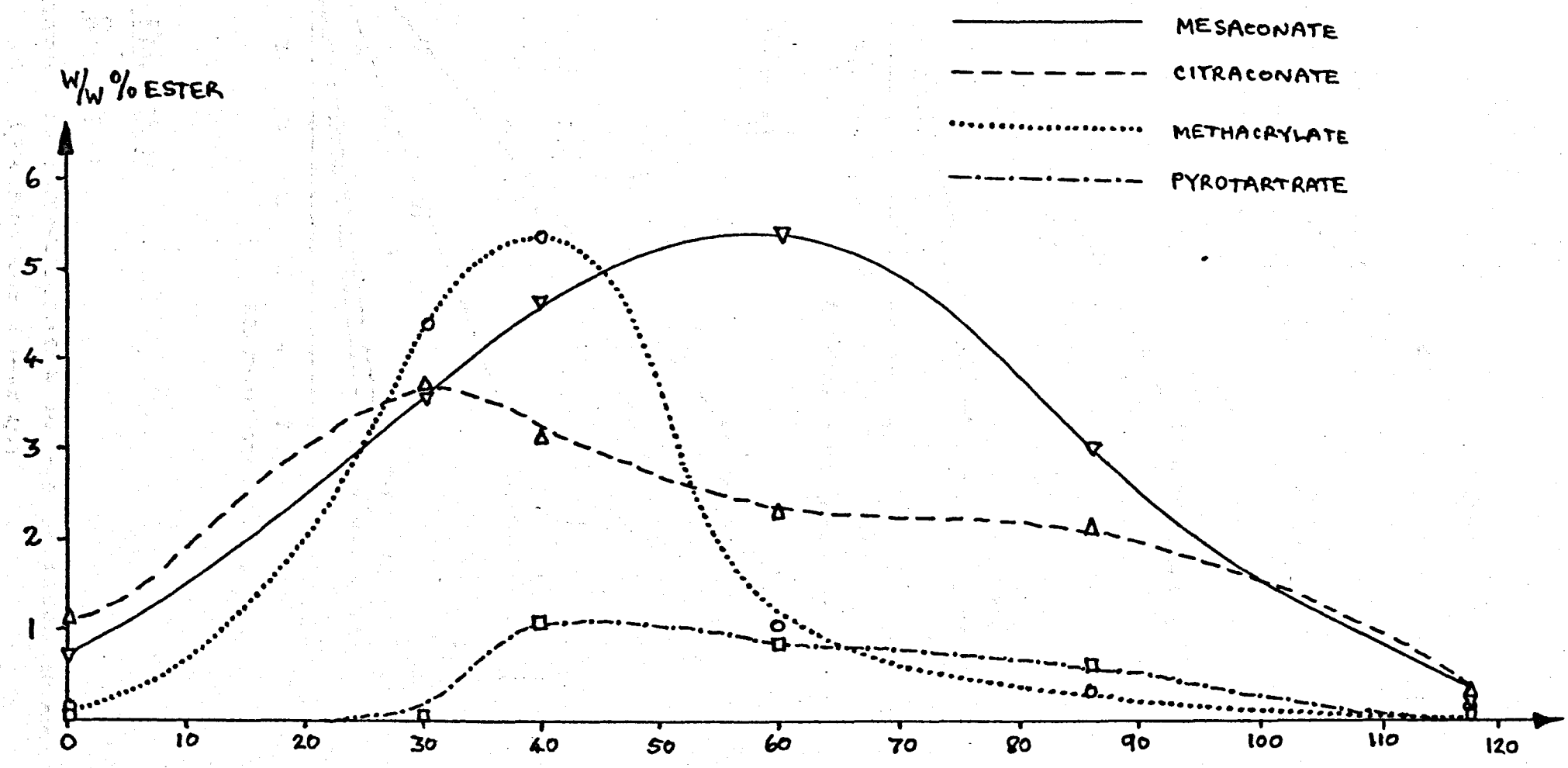
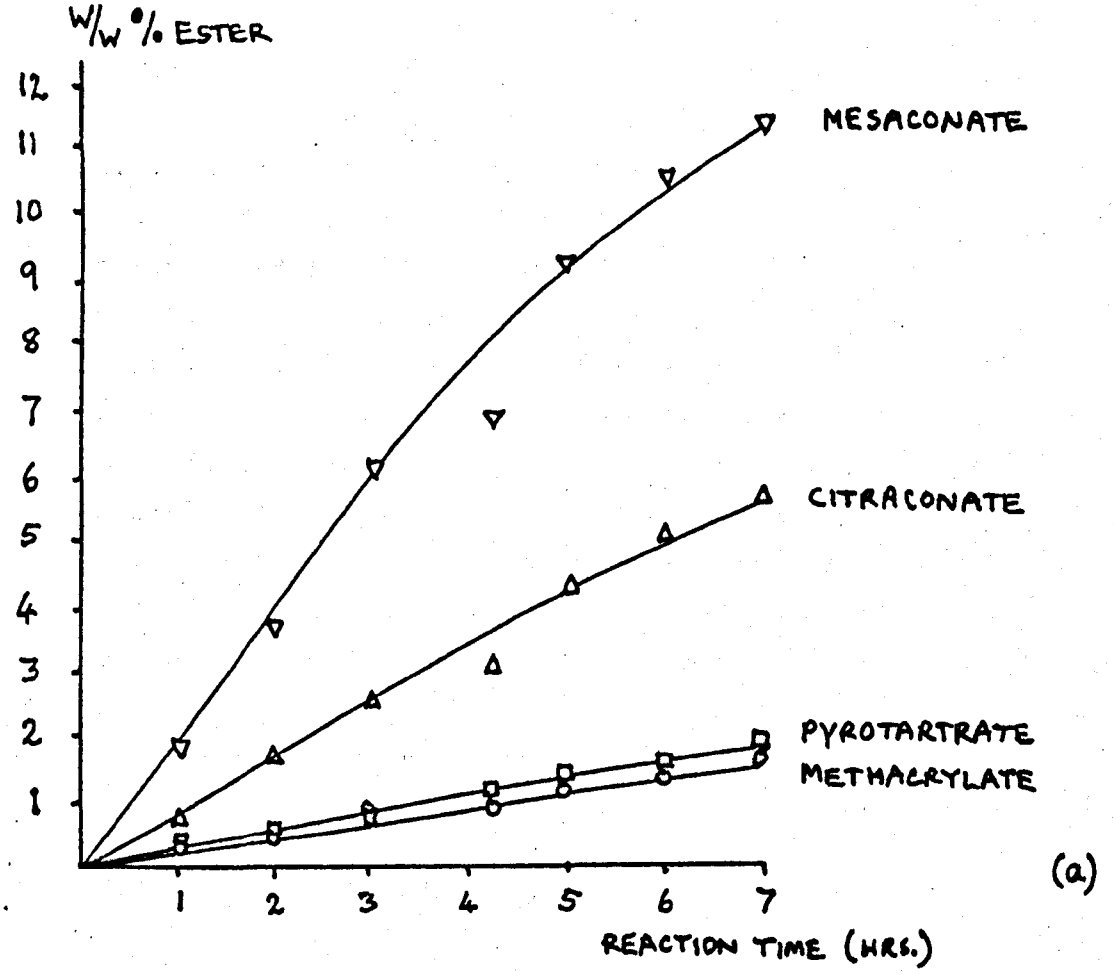


Fig. 3.6

AMOUNTS OF ESTER PRODUCTS OBTAINED BY CARBONYLATING METHYLACETYLENE AT VARIOUS TEMPERATURES



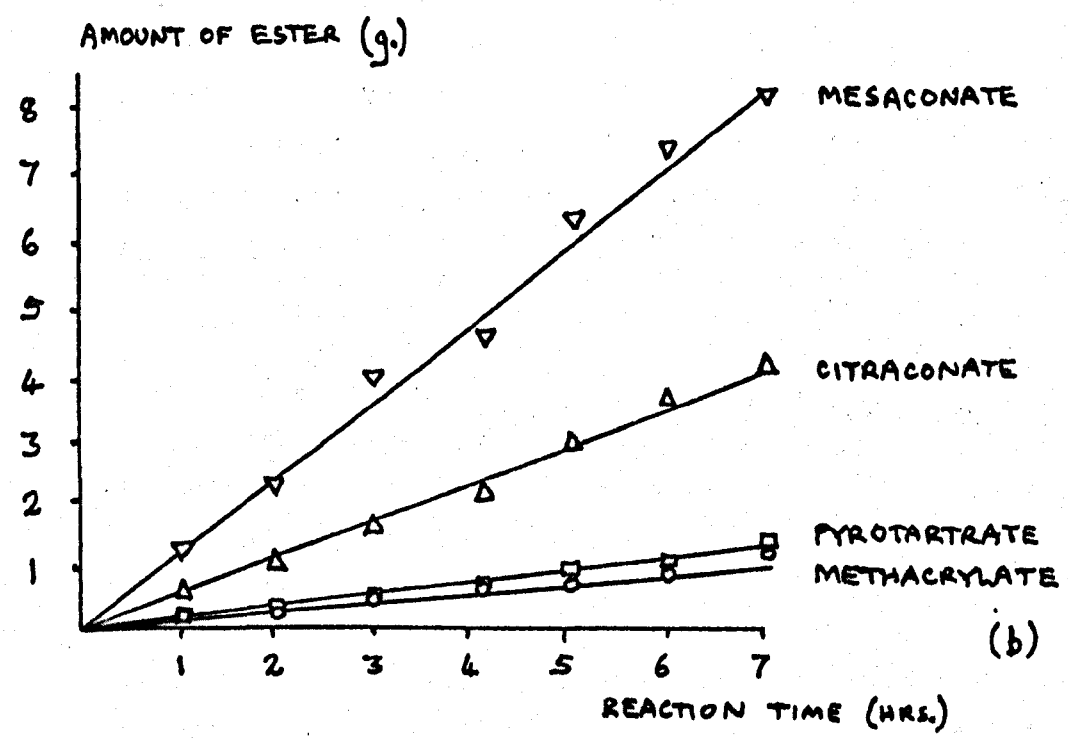


Fig. 3.7

Rm. 3.11

CARBONYLATION OF METHYLACETYLENE IN THE PRESENCE OF AIR (AIR FLOW RATE = 1–1.5 l/h)

continued to be formed at constant rate for 7 hours, in marked contrast with the result observed when air was not present. Slight curvature was imposed on the graphs by the method of analysis, i.e. the W/W% value represented a percentage of an increasing total. Since almost linear production was observed, it was valid to assume a linear weight increase, and interpolate intermediate overall weights and thence calculate the amount of each ester formed, in grams. Such a procedure yielded graphs which were straight lines to within the limits of experimental error (cf. fig. 3.7 (b)).

It is noteworthy that the passage of air at 1-1.5 l/h had only a small effect on the amounts of saturated species present, in contrast with the observations of Chiusoli et al.[9,10] but the relative amount of monoester was markedly reduced, as shown by comparison of the final analyses with those of reaction 3.5 (table 3.5).

Reaction No	3.5	3.11	3.12
Air (l/h)	0.0	1-1.5	2.0
Weight increase (g)	6.8	15.0	11.0
butyl methacrylate	4.0	1.8	0.6
dibutyl citraconate	6.0	5.8	5.6
dibutyl mesaconate	7.1	11.3	7.2
dibutyl pyrotartrate	2.8	2.0	0.0
total diesters	15.9	19.1	12.8
butyl methacrylate/diesters	0.25	0.09	0.05

Table 3.5 The Effect of Air on the Concentrations of Esters Formed on the Carbonylation of Methylacetylene Compared with the 'Standard' Reaction. (Concentrations expressed as a W/W% of the Reaction Mixture, initially 60 g).

In reaction 3.11, the highest conversion of methylacetylene to products in the present work was realised. The % yields of products based on the methylacetylene are artificially low inasmuch as the quantity of methylacetylene in the vent gases was not determined. Nevertheless they provide the best available comparison with the results obtained from other acetylenes, and will be quoted in this one case. The percentage yields based on methylacetylene (by gas chromatographic assay) are as follows: butyl methacrylate, 1.5; dibutyl citraconate, 2.9; dibutyl mesaconate, 5.6; dibutyl pyrotartrate. 1.0%, the overall total of recognised products being 11.0%. The 'productivity' of the palladium catalyst = 16.0 (i.e. a 1600% yield of recognised products, based on the catalyst). Thus the

reaction is seen to be truly catalytic.

A second reaction (Rn. 3.12) was carried out as above, but using a rather higher air flow-rate. The overall conversion was somewhat reduced, saturated esters were not detected by gas chromatography and the monoester to diester ratio was reduced even more than in 3.11, cf. table 3.5 and fig. 3.8.

In all the reactions during which 1.0 l/h or more of air was passed, the wine-red colour of the catalyst solution was maintained throughout the 7 hour period.

(v) The Effect of Iodine: In view of the beneficial effect of air on the carbonylation reactions, it was of interest to test other oxidising agents for their ability to promote carbonylation. Since the catalyst was an iodide salt, iodine was examined. A reaction (Rn. 3.21) was carried out under standard conditions, but with iodine (17% W/W) present. No ester products were detected. A small amount of acetone and butyl iodide were shown to be present, along with about 5% W/W of a substance which was separated by preparative gas chromatography and shown by n.m.r. spectroscopy and mass spectrometry to be trans-1,2-diiodopropene, MeIC=CIH:
n.m.r.: 3.27τ, quartet, 1H; 7.56τ, doublet, 3H; J = 8.5 Hz.
Mass spectrometry: $\frac{m}{e}$ = 294 (2.5%) $C_3H_4I_2^{\bullet\oplus}$; 167 (6.5%) $C_3H_4I^{\oplus}$; 40 (22%) $C_3H_4^{\bullet\oplus}$; 39 (100%) $C_3H_3^{\oplus}$; 28 (33.5%). Direct iodination of acetylenes is known to proceed, though good yields are not usually obtained[2].

Using the diiodopropene so obtained, it was shown by gas chromatography that traces of the substance were produced in reactions to which no iodine had been added (cf. Chapter 3.2 (ii) (d)).

A second reaction (Rn. 3.22) was carried out using only 3% W/W of iodine. No products at all were detectable by gas chromatography.

In a third reaction (Rn. 3.49), iodine (3% W/W) was present and air was passed at 1-1.5 l/h. The only significant products were dibutyl citraconate (0.3% W/W) and dibutyl mesaconate (0.6% W/W). It was concluded that iodine had an inhibiting effect on the reaction which was offset to some extent by the presence of air. Iodine is known to quantitatively displace carbonyl ligands from cobalt complexes[11]; similar behaviour towards any palladium complex which acted as an essential intermediate in the carbonylation reaction, could well account for the inhibition.

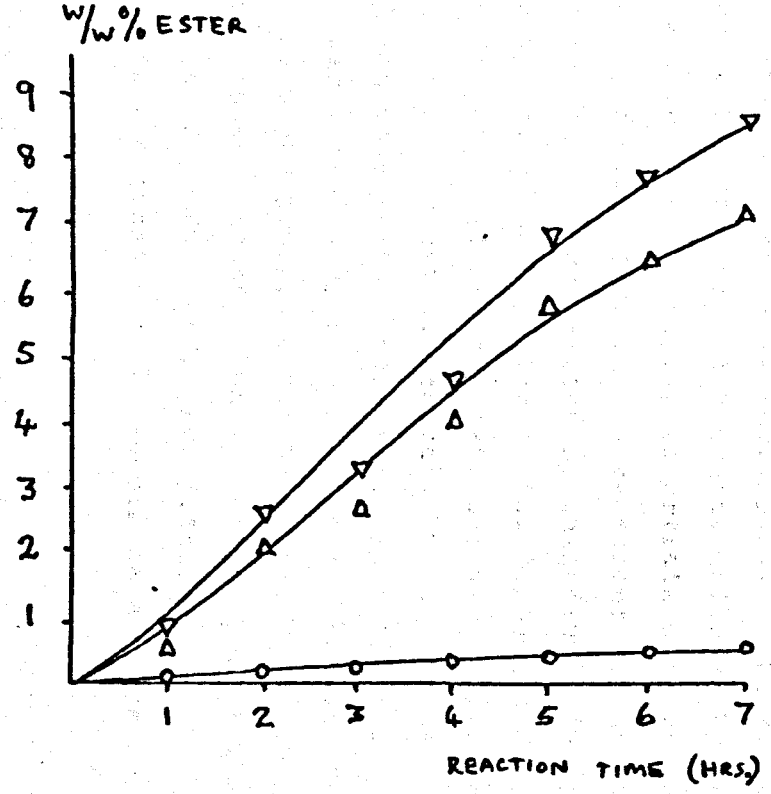


Fig. 3.8

Rm. 3.12

CARBONYLATION OF METHYLACETYLENE IN THE PRESENCE OF AIR (AIR FLOW RATE = 2 l/h)

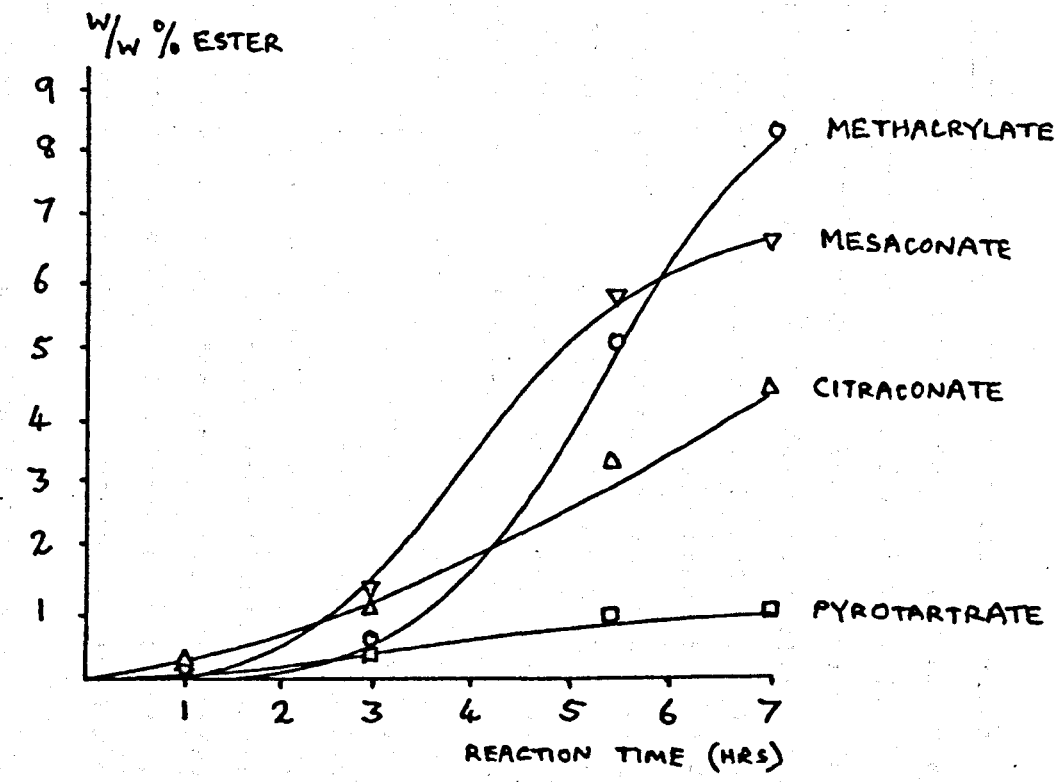


Fig 3.12

Rm 3.24

CARBONYLATION OF METHYLACETYLENE IN THE PRESENCE OF BENZOQUINONE

(vi) The Effect of Benzoquinone: The use of benzoquinone as a reoxidant for palladium was reported by I.I.Moiseev et al.[12] and is more fully discussed in Chapter 2.2 (iii) (c).

(a) The 'standard' methylacetylene reaction was studied in the presence of p-benzoquinone (17% W/W) (Rn. 3.23): methacrylate & pyrotartrate esters were not detected in the resulting mixture. Citraconate and mesaconate esters were present to 2.6% W/W and 0.6% W/W respectively. It is surprising that the trans-diester, usually predominant, was now present to a much smaller extent than the cis- isomer. Hydroquinone was present to about 1.0% W/W and was separated by preparative scale gas chromatography and identified by its infrared spectrum.

Another product, present to about 2.0% W/W, was separated by preparative scale gas chromatography and shown by its infrared and n.m.r. spectra (fig. 3.9) and mass spectrum (figs. 3.10, 3.11) to be butyl β-butoxycrotonate. An authentic sample was then prepared and shown to have identical n.m.r. and infrared spectra and gas chromatographic retention times on 4 columns.

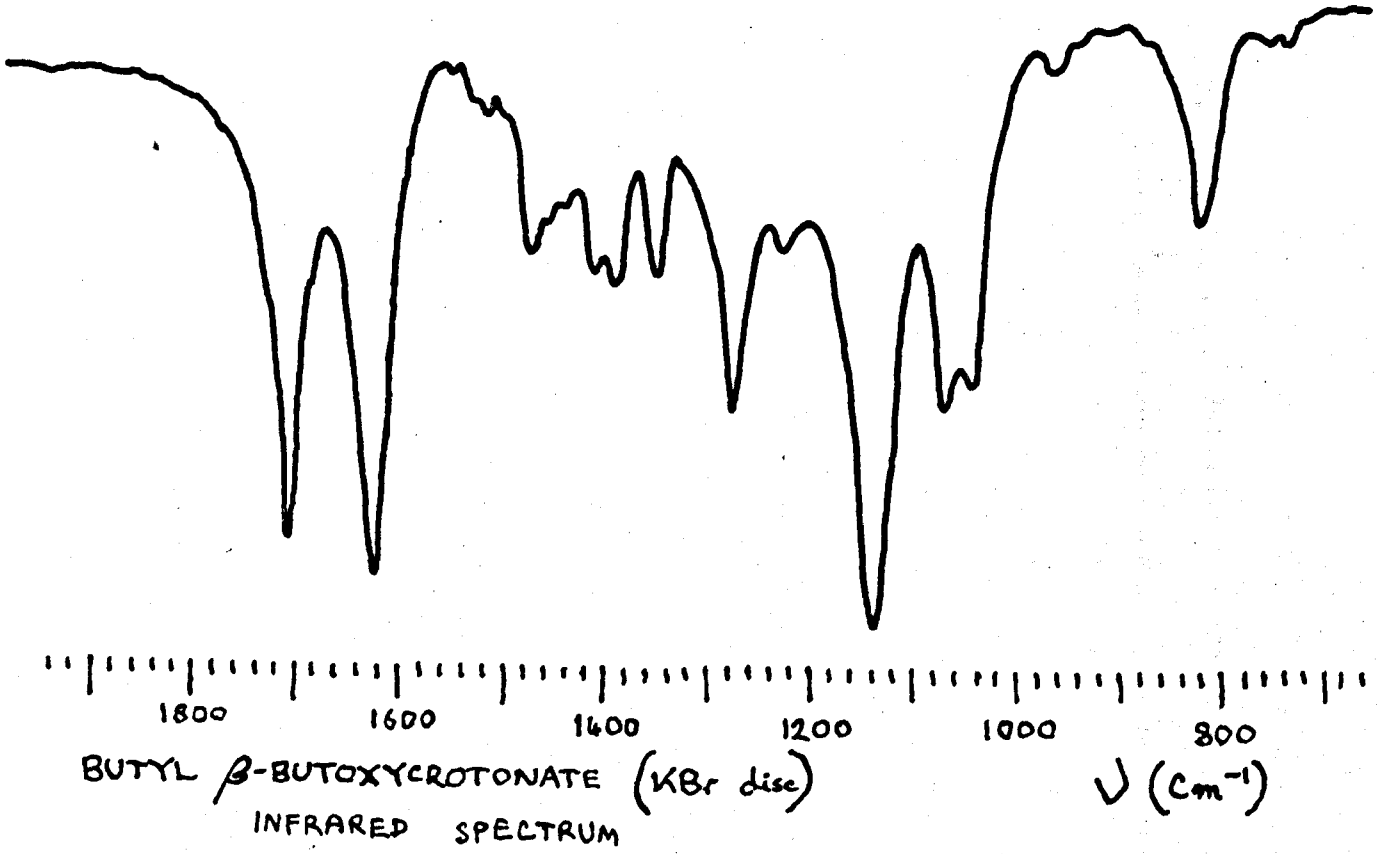
The colour of the catalyst solution remained wine-red throughout the reaction.

A carbonylation reaction (Rn. 3.24) was then carried out with the quantity of benzoquinone reduced to 1.7% W/W.

(b) Rather less butyl β-butoxycrotonate was formed, along with the other expected esters (cf. table 3.6). Butyl methacrylate had now become the predominant product, followed by mesaconate and citraconate esters. Dibutyl pyrotartrate was present in rather small amount (cf. fig. 3.12). The colour of the catalyst solution changed to yellow with deposition of palladium after about 3 hours.

(c) In the previous experiment (Rn. 3.24), it was observed that the production of butyl methacrylate was very rapid towards the latter part of the reaction, accordingly an extended reaction (Rn. 3.25) was undertaken under similar conditions. Butyl methacrylate production was inhibited for about 3 hours, but was then rapid until it became the major product after 14 hours. At its maximum, the methacrylate ester concentration was almost double that of mesaconate ester, the second product (cf. fig. 3.13).

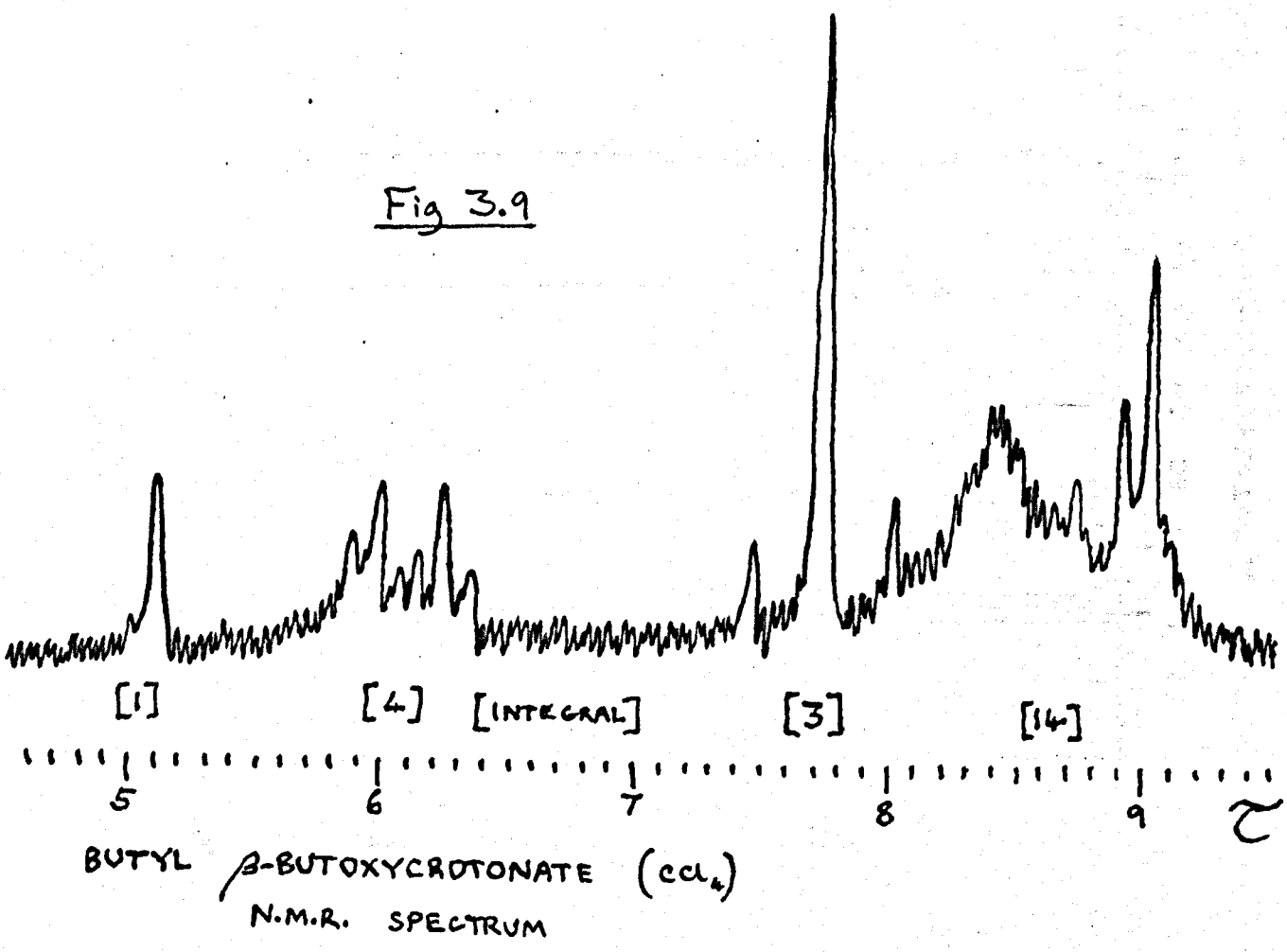
The three reactions with benzoquinone are summarised in table 3.6.



BUTYL β-BUTOXYCROTONATE (KBr disc)

INFRARED SPECTRUM

Fig 3.9



BUTYL β-BUTOXYCROTONATE (CCl_4)

N.M.R. SPECTRUM

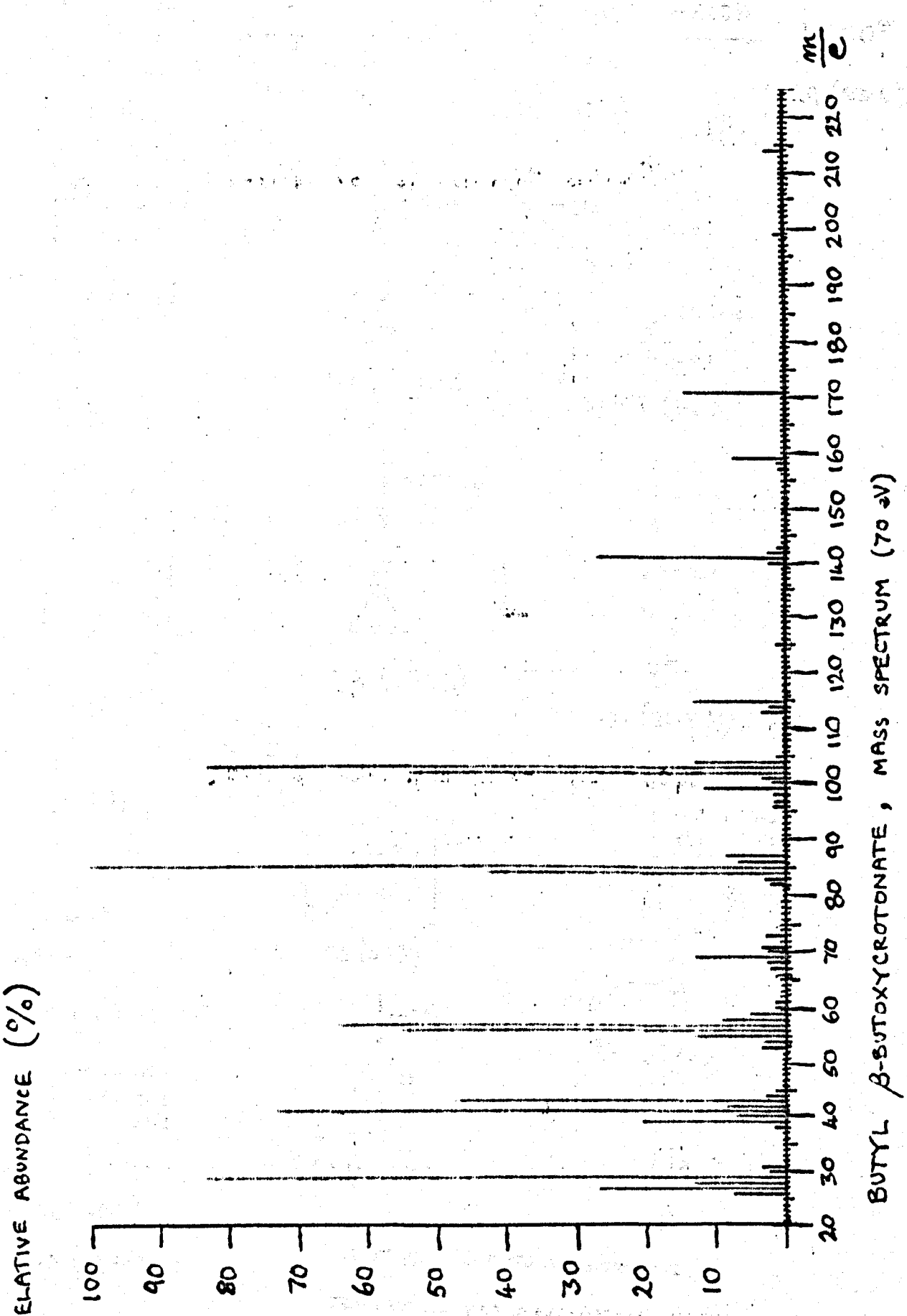

RELATIVE ABUNDANCE (%)
100
90
80
70
60
50
40
30
20
10
20 30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220
m/e
BUTYL β-BUTOXYCROTONATE, MASS SPECTRUM (70 eV)

Fig. 3.10

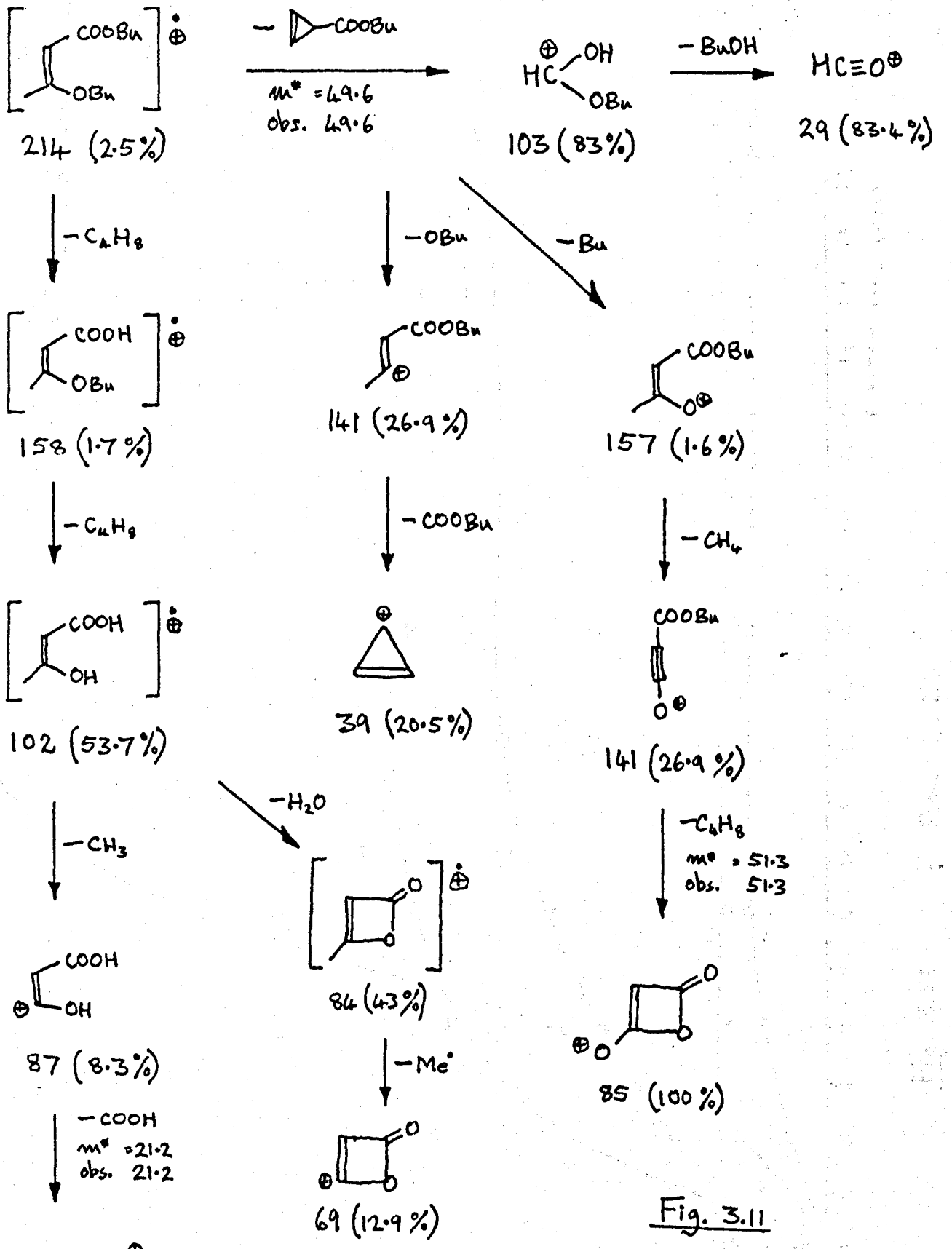


Fig. 3.11

BUTYL β-BUTOXYCROTONATE ; TENTATIVE FRAGMENTATION SCHEME

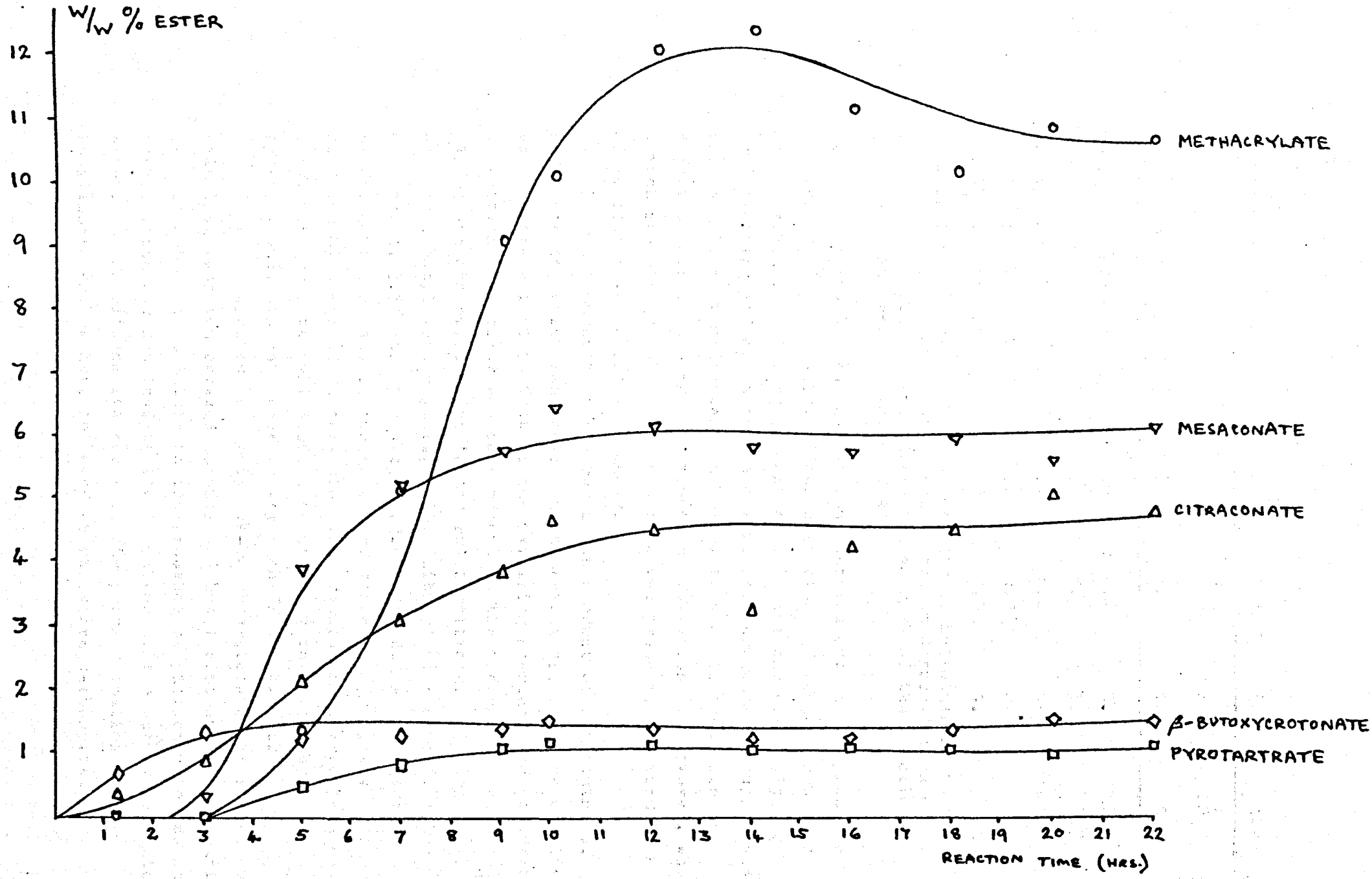


Fig. 3.13 ; Rn. 3.25

CARBONYLATION OF METHYLACETYLENE IN THE PRESENCE OF BENZOQUINONE OVER AN EXTENDED PERIOD

Reaction No	3.23	3.24	3.25	3.25
Reaction time (hours)	7	7	7	22
Benzoquinone (g.)	10.0	1.0	1.2	1.2
Butyl methacrylate	0.0	8.2	5.2	10.8
Dibutyl citraconate	2.6	4.4	3.1	4.7
Dibutyl mesaconate	0.6	6.6	5.2	6.1
Dibutyl pyrotartrate	0.0	1.1	0.9	1.2
Butyl β-butoxycrutonate	2.0	1.5	1.3	1.5

Table 3.6 The Effect of Varying Amounts of Benzoquinone on the Concentration of Esters Formed on Carbonylation of Methylacetylene (Expressed as W/W% of the Reaction Mixture, initially 60 g)

The contrast between reactions carried out in the presence of high (17%) and low (1.7%) concentrations of benzoquinone was most striking. A large amount of benzoquinone obviously had an inhibiting effect on the reaction, and particularly suppressed the formation of monoester, an observation consistent with the effect of air in suppressing monoester formation. However, when a much smaller amount of benzoquinone was present, the formation of monoester was greatly enhanced.

It was thought that the reduction product of benzoquinone, hydroquinone, which was formed in the reactions, might be exerting an opposite effect to that of the oxidising species, and accordingly a reaction (Rn. 3.45) was carried out in the presence of hydroquinone (1.7%) and otherwise under 'standard' conditions. The final analyses, butyl methacrylate, 4.3%; dibutyl citraconate, 3.5%; mesaconate, 5.5% and pyrotartrate, 1.6% W/W, did not indicate a significant increase in the amount of monoester produced. The reaction also served to show that free radical polymerisation of butyl methacrylate (which would be strongly inhibited by hydroquinone) did not occur to any significant extent.

It was suspected that butyl β-butoxycrotonate was formed by an oxidative reaction between butanol and butyl crotonate, but heating the two materials together in the presence of palladium iodide and benzoquinone did not lead to the formation of the butoxycrotonate ester. An alternative route is the prior formation of butylisopropenyl ether, followed by oxidative carbonylation.

3.4 CARBONYLATION IN THE PRESENCE OF ACID:

The effect of added acids, especially anhydrous hydrogen chloride, in increasing the amount of monoester produced in the carbonylation of acetylene, was recorded by C.B.Lines[7] and is discussed in Chapter 2.1 (ii); 2 (ii). It was therefore of interest to observe the effect of hydrogen chloride on the carbonylation of methylacetylene.

(i) 'Standard' Reactions in the Presence of Acid: Two carbonylation reactions of methylacetylene (Rns. 2.37, 2.38), were carried out under 'standard' conditions, but with hydrogen chloride present in each case. The results are compared in table 3.7 with those of the typical 'standard' reaction 3.5, and 3.28 is displayed in fig. 3.14. The presence of hydrogen chloride did not significantly change the relative amounts of mono- and diesters. The contrast with C.B.Lines' results using acetylene[7] when acrylate ester formation was favoured by acidity, and with the finding of Tsuji and Nogi[13] who, working with diphenylacetylene, showed that dicarbonylation was encouraged by the presence of hydrogen chloride, is noteworthy.

Reaction No	3.5	3.27	3.28
HCl (m mols)	0.0	10.0	10.0
Wt. increase (g)	6.8	7.6	6.8
butyl methacrylate	4.0	3.9	2.9
dibutyl citraconate	6.0	2.9	2.7
dibutyl mesaconate	7.1	7.9	7.9
dibutyl pyrotartrate	2.8	1.9	1.8
total diesters	15.9	12.7	12.4
butyl methacrylate/diesters	0.25	0.30	0.23

Table 3.7 The Effect of Hydrogen Chloride on the Concentrations of Esters Formed on Carbonylation of Methylacetylene (Concentration Expressed as W/W% of the Reaction Mixture, initially 60 g)

The ratio of *cis*- to *trans*- diester however was approximately halved, a result consistent with the fact that halogen acids are known to promote *cis*-/*trans*- isomerisation[14, 7]. However, the observation is again in contrast with the corresponding work of C.B.Lines, where it was found that the presence of acid increased the formation of dibutyl maleate.

(ii) The Effect of Acid in the Presence of Air: It was of interest to investigate the combined effect of air and acid on the carbonylation of methylacetylene. Accordingly a reaction (Rn. 3.29) was carried out in the presence of air (1-1.5 l/h) and hydrogen chloride (10 m mols), with the conditions otherwise 'standard'. Only very small amounts of esters were detected, butyl methacrylate, 0.1%; dibutyl citraconate, 0.6% and mesaconate 2.4% W/W, but a sticky black precipitate was obtained, as in the analogous acetylene experiment (Chapter 2.2 (iii) (b)). The residue was treated in the same way as that from the acetylene reaction: extraction with water yielded an infusible white solid, analysis of which showed it to be sodium chloride; extraction with chloroform yielded a sticky substance shown by comparison of its infrared spectrum (ν (cm^{-1}) = 1170 (m), 1265 (w), 1380 (m), 1470 (m), 1610 (w), 1715 (s), 2088 (s)) with that given by Haslam & Willis[15], to be poly(butyl methacrylate) and the remaining black material after thorough washing proved on analysis to be metallic palladium.

3.5 MISCELLANEOUS EXPERIMENTS DESIGNED TO ELUCIDATE ASPECTS OF THE MECHANISM OF CARBONYLATION

(i) Attempts to Isolate a Complex from Carbonylation Mixtures: A colour change, from wine red to yellow, accompanied by the deposition of palladium metal, has been observed in methylacetylene carbonylation reactions in the absence of air or other oxidising agent. A yellow substance, which rapidly decomposed with the deposition of palladium, could be obtained from such reaction mixtures by column chromatography. However, it was always heavily contaminated with esters and was not identified. Attempts to obtain a stabilised complex from the reaction mixtures were made by adding triphenylphosphine, but only bis(triphenylphosphine)palladium(II) iodide was obtained, and identified by its melting point and infrared spectrum (cf. Chapter 2.4 (i)). Attempts to precipitate either a cationic or anionic complex as its respective salt were made by adding potassium fluoroborate and tetraphenylarsonium chloride, but only the starting materials were recovered.

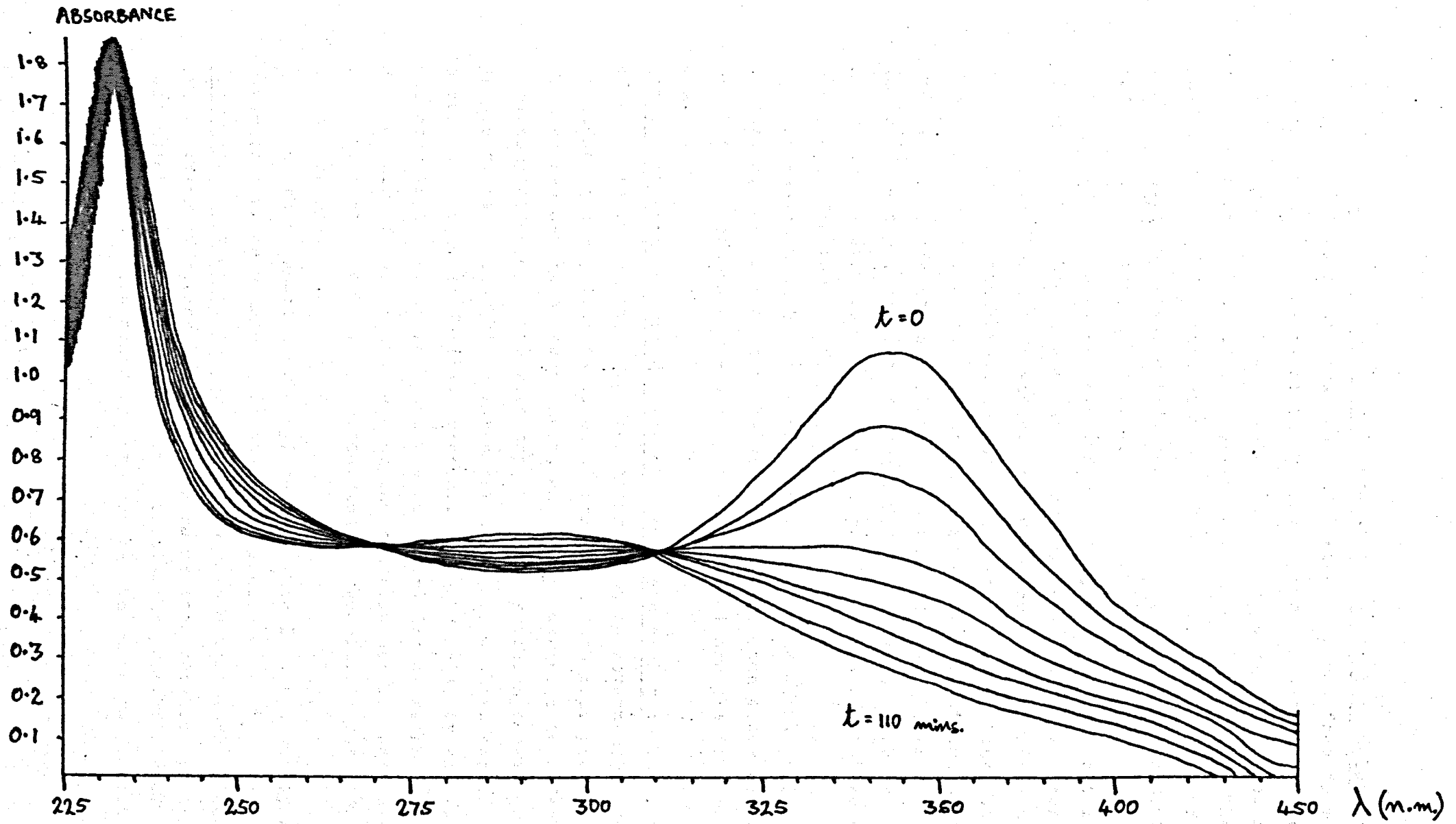


Fig. 3.15 SODIUM TETRAIODOPALLADATE(II) IN BUTANOL SATURATED WITH METHYLACETYLENE; ULTRAVIOLET SPECTRA AFTER 0, 5, 10, 15, 20, 30, 45, 80 & 110 MINS. REACTION

(ii) The Reaction of Methylacetylene with the Catalyst Solution: In an attempt to obtain the above palladium compound free from contaminants, a quantity of the catalyst solution was exposed to methylacetylene dissolved in butanol. The ultraviolet spectrum of the mixture (fig. 3.15) steadily changed over 2 hours: The Pd-I charge-transfer band at λ_{max} = 344 n.m. characteristic of Na_2PdI_4 solutions disappeared, consistent with the displacement of iodide ligands from the complex.

A more concentrated solution of catalyst and methylacetylene did not change colour, even after several weeks, or on exposure to methylacetylene at 20 atmos., but a yellow oil, homogeneous by thin layer chromatography, could be isolated by column chromatography. The identity of the oil was not established, but ignition showed that it did not contain palladium and the infrared spectrum (ν (cm^{-1}) = 1090, 1380, 1455, 1735, 2930) pointed to carbonyl groups in its structure. A similar result had been obtained with acetylene (Chapter 2.4 (ii)).

It was concluded that methylacetylene formed a π-complex with palladium, possibly able to be stabilised by carbon monoxide ligands, which then decomposed yielding palladium metal and the intractable oil.

(iii) Attempted Decarbonylation of Butyl Methacrylate: The ratios of products in carbonylation reactions might be governed by conditions influencing the positions of equilibria of a number of processes. To test one aspect of such theory an attempt was made to effect the decarbonylation of butyl methacrylate under reaction conditions. An acetylene carbonylation was carried out for a short period with an excess of butyl methacrylate present. No methylacetylene was detected in the cold trap, and the concentration of methacrylate ester did not significantly change over the reaction period, nor were any other product esters of methylacetylene carbonylation detected by gas chromatography.

Thus the formation of butyl methacrylate is not a significantly reversible process under the conditions used.

(iv) Carbonylation in Butanol-O-d: To obtain information concerning the position of attachment of the extra protons required in the carbonylation products, and to investigate the possibility of an isotope effect influencing the product ratios, a carbonylation reaction

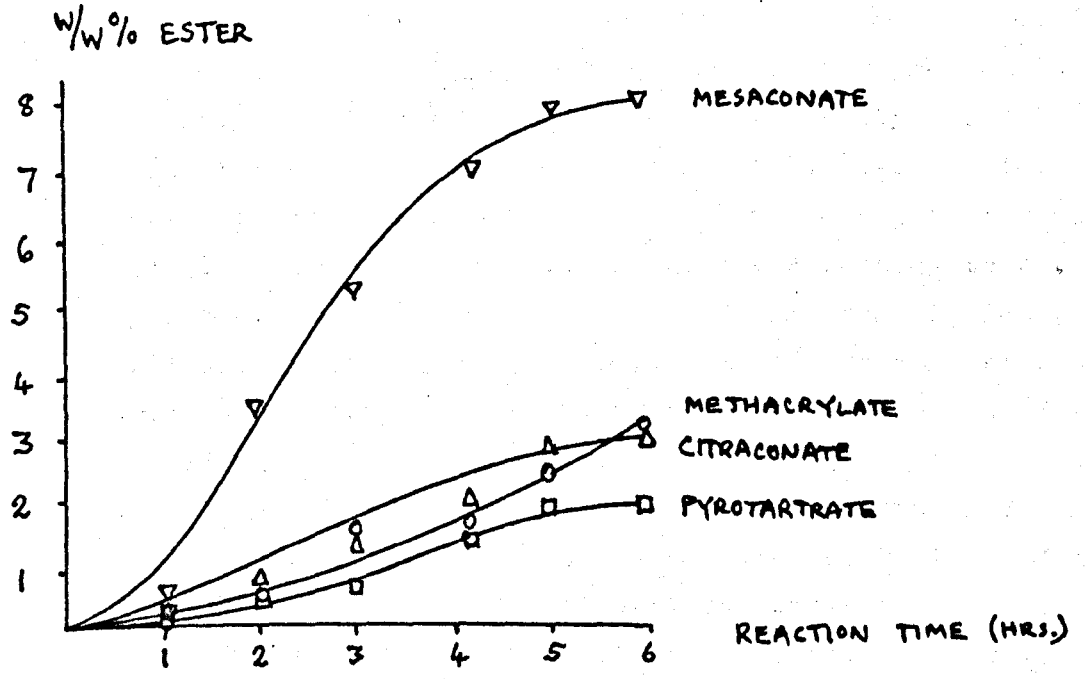


Fig. 3.14 ; Rm. 3.28

CARBONYLATION OF METHYLACETYLENE IN THE PRESENCE OF HYDROGEN CHLORIDE

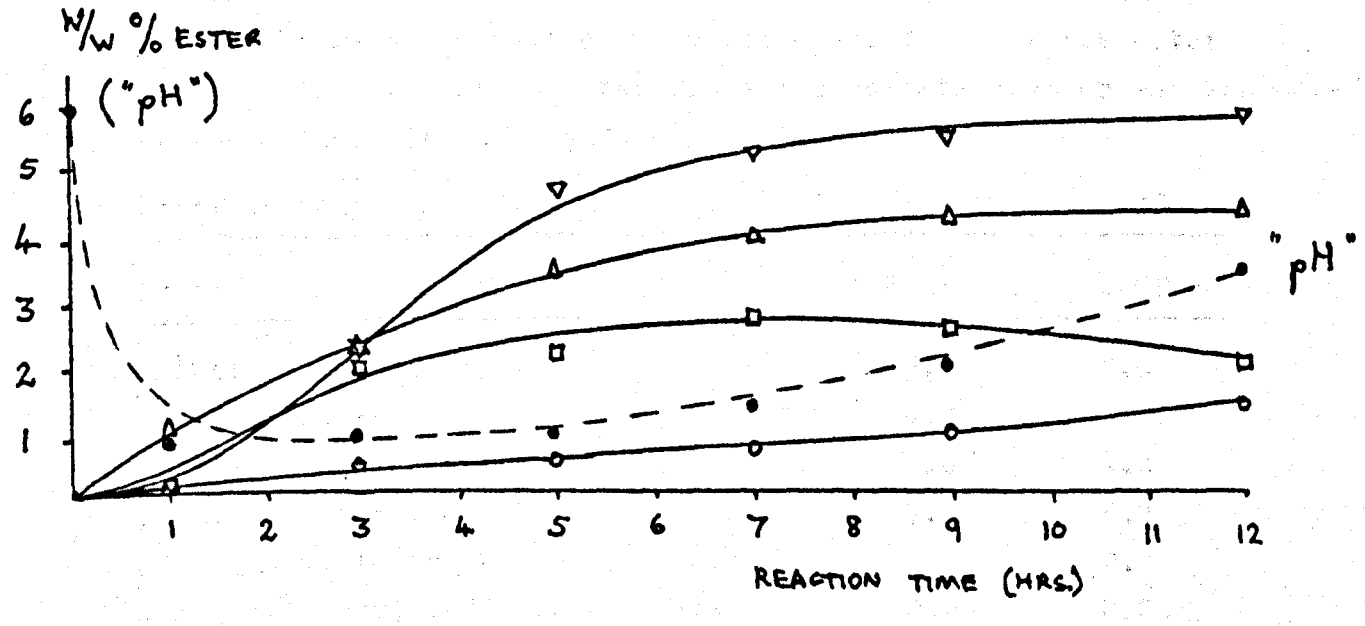


Fig. 3.16 ; Rm 3.32

CARBONYLATION OF METHYLACETYLENE IN BUTANOL-O-d

was carried out in butanol-O-d. To ensure a good yield of products and facilitate their separation the reaction was allowed to proceed for an extended period. The changing acidity was also followed with universal indicator paper as previously described (Chapter 2.2 (i)). The change in acidity was much more marked than had been observed in reaction 3.5, (cf. Chapter 3.2 (iii)) falling from an initial value of 5 to 1 in 3 hours and slowly rising to 3.5 after 12 hours and ultimately returning to ca. 5 (cf. fig.3.16). Since the acid dissociation constant is normally lower for deuterated acids than their proton counterparts[16], it must be assumed that the greater acidity was due to a higher concentration of the acidic species.

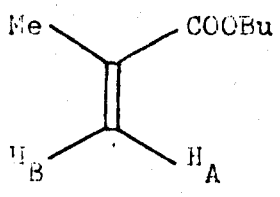
The rate of formation of esters is shown in fig. 3.16 and their proportions after 7 hours are compared with those of the products in the typical 'standard' reaction 3.5 in table 3.8.

The amount of methacrylate ester produced in the reaction was greatly reduced, and the formation of dibutyl pyrotartrate was somewhat increased, whilst the overall uptake of methylacetylene was slightly reduced by comparison with reaction 3.5. Comparable observations were made by C.B.Lines[7] when carrying out the carbonylation of acetylene in butanol-O-d, for acrylate ester concentration was greatly reduced and succinate diester was increased by comparison with a 'standard' reaction.

Reaction No	3.5	3.32
Solvent	BuOH	BuOD
'pH' after 3 hours	3.5	1.0
Butyl methacrylate	4.0	1.0
Dibutyl citraconate	6.0	4.0
Dibutyl mesaconate	7.1	5.2
Dibutyl pyrotartrate	2.8	2.8
Butyl methacrylate/Total diesters	0.25	0.08
Dibutyl pyrotartrate/Unsat. diesters	0.21	0.33

Table 3.8 A comparison of the Amounts of Products Obtained on Carbonylation of Methylacetylene in Butanol and Butanol-O-d. (Amounts Expressed as W/W% of the Reaction Mixture, initially 60 g).

Butyl methacrylate was isolated from the mixture by preparative scale gas chromatography and the n.m.r. spectrum was compared with that of the authentic ester (fig. 3.17). The two signals at τ = 4.00 and 4.54, corresponding to the methylene protons H_A and H_B respectively in I , integrated as a total of 0.75 protons in the ratio $H_A : H_B$ = 0.35 : 0.4, indicating that 1 deuterium atom was



I

incorporated in the molecule in the positions A & B with the A-deuterated form predominating. The methyl signal at 8.10 τ was changed from a doublet of doublets to a doublet with a singlet superimposed which, in conjunction with the integral (0.75 olefinic protons) suggested that in about 25% of the product, both olefinic positions were occupied by deuterium atoms.

The observation that cis- addition of the D-, -COOBu moieties is somewhat favoured, is qualitatively and quantitatively consistent with similar work on the acetylene system (cf. Chapter 2.4 (ix) (x)).

Dibutyl citraconate and mesaconate (BuOOC-CMe=CH-COOBu, cis- & trans-) were isolated as a mixture by preparative scale gas chromatography. N.m.r. spectroscopy and mass spectrometry showed that about 25% of the compounds had incorporated a deuterium atom in the olefinic position.

In the n.m.r. spectrum (fig. 3.18) the olefinic signals at 3.37 τ (mesaconate) and 4.29 τ (citraconate) integrated as a total of 0.73 protons, 0.40 mesaconate protons and 0.33 due to citraconate ester. The two isomers were themselves present in the ratio 0.4 : 0.33 as shown by the n.m.r. spectrum, and by gas chromatography, showing that deuterium was present to an equal extent in both esters. The side chain methyl signals at 7.76 (mesaconate) and 8.00 (citraconate) integrated as a total of 3 protons. They showed the expected splitting to doublets (J = 1.6 & 1.7 H_2 respectively), but an unsplit signal was superimposed on each doublet, confirming the presence of some deuterium in the olefinic position.

The mass spectrum of the mixture of mesaconate and citraconate

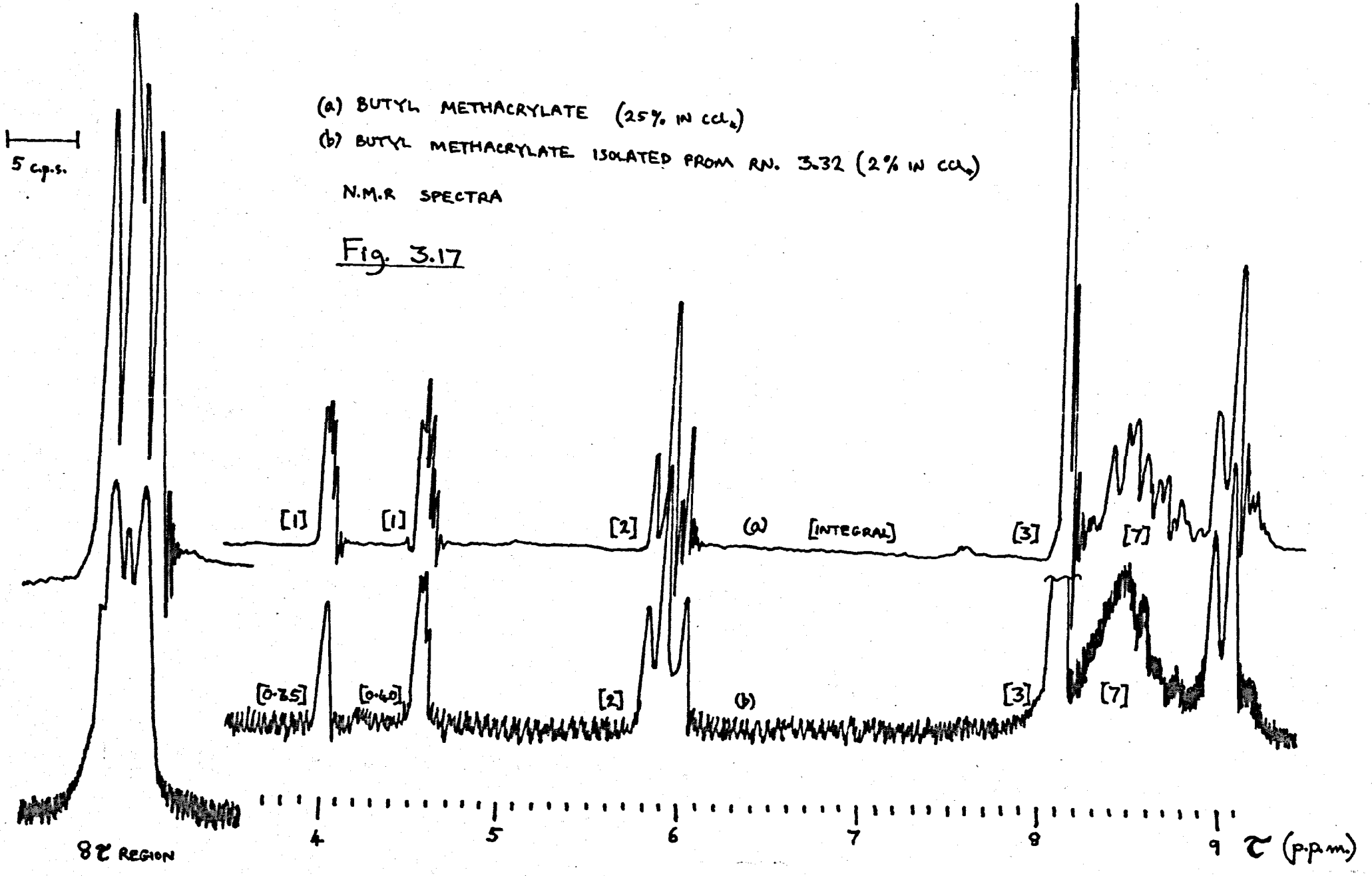

(a) BUTYL METHACRYLATE (25% IN CCl_4)
(b) BUTYL METHACRYLATE ISOLATED FROM RN. 3.32 (2% IN CCl_4)
N.M.R SPECTRA
5 c.p.s.
[1]
[1]
[2]
(a) [INTEGRAL]
[3]
[7]
[0·25]
[0·60]
[2]
(b)
[3]
[7]
8τ REGION
4
5
6
7
8
9
τ (p.p.m.)

Fig. 3.17

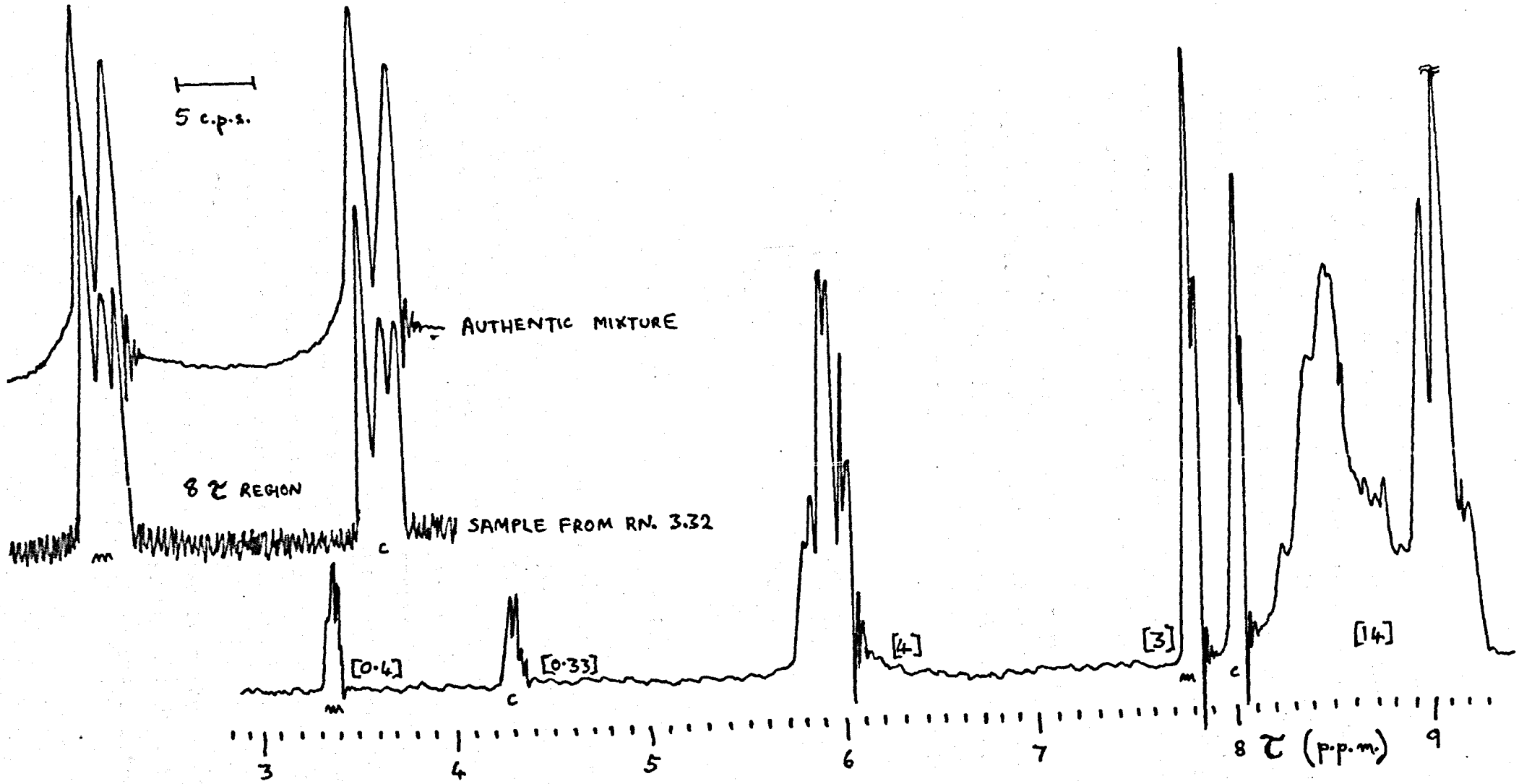
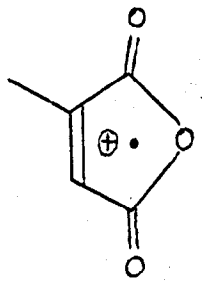


Fig. 3.18 MIXTURE OF DIBUTYL CITRACONATE (c) & MESACONATE (m) FROM REACTION 3.32

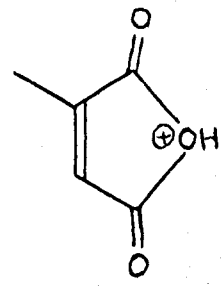
N.M.R. SPECTRUM (10% IN CCl_4)

esters (figs. 3.19, 3.20) showed evidence of partial deuteration. The parent peak was weak, but the peak of $\frac{m}{e}$ = 169 had a relative abundance of 24.0%. The relative abundance of the corresponding isotopic peak ($\frac{m}{e}$ = 170) was about 9.0% (i.e. 37% of the 169 peak), though in authentic mesaconate it amounted to only 2% and in citraconate 4.5% relative abundance (7% & 18% of the $\frac{m}{e}$ = 169 peak respectively). The peak at $\frac{m}{e}$ = 131 (due only to the trans- ester and apparently caused by loss of C_4H_7 followed by C_4H_8) was accompanied by 28% of a peak of $\frac{m}{e}$ = 132, not detectable in the authentic esters.

The base peak in the authentic trans- ester occurred at $\frac{m}{e}$ = 112, assigned as II, (III being present to about 25%) whilst in the authentic cis- ester, III had a relative abundance of 100% and II was scarcely detectable.



II ; $\frac{m}{e}$ = 112



III ; $\frac{m}{e}$ = 113

(The assignments were supported by a metastable ion for III, and accurate mass measurement for II, similar structures are well known as fragments due to maleate & fumarate esters[17].) The difference in the spectra of the two isomers was presumed to be due to the greater ease of H-transfer in the cis- ester. Hence it is difficult to interpret the anhydride-like fragments in terms of deuterated products. The other main fragments at $\frac{m}{e}$ = 39, 41, 55, 56, 57 were caused by cleavage of the butyl group with charge retention, and its subsequent breakdown, and were not materially different in the spectrum of the deuterated mixture and that of the two authentic isomers.

Dibutyl pyrotartrate was isolated from the reaction mixture by preparative scale gas chromatography, but unfortunately was not obtained quite free from traces of mesaconate & citraconate esters.

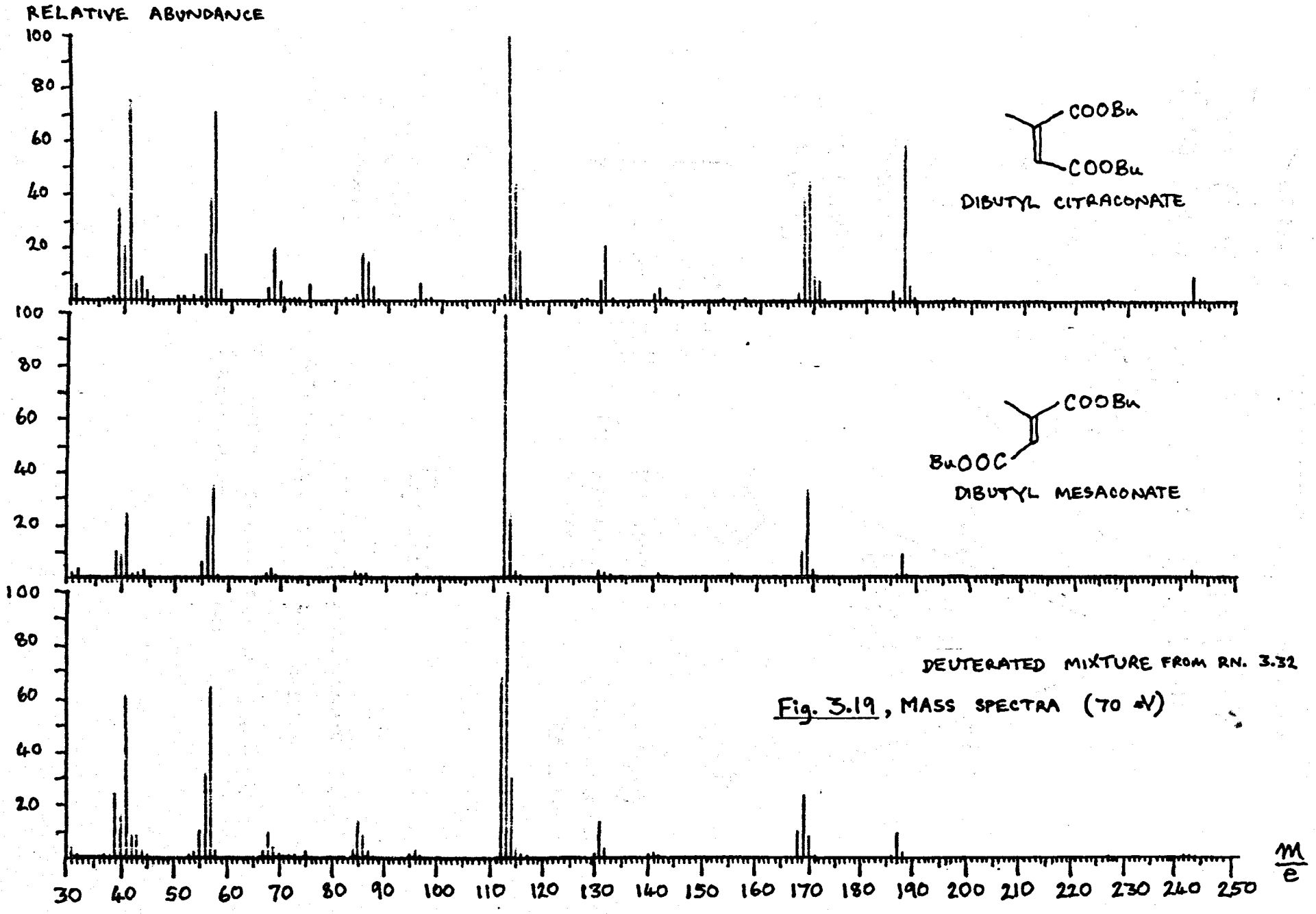


Fig. 3.19, MASS SPECTRA (70 eV)

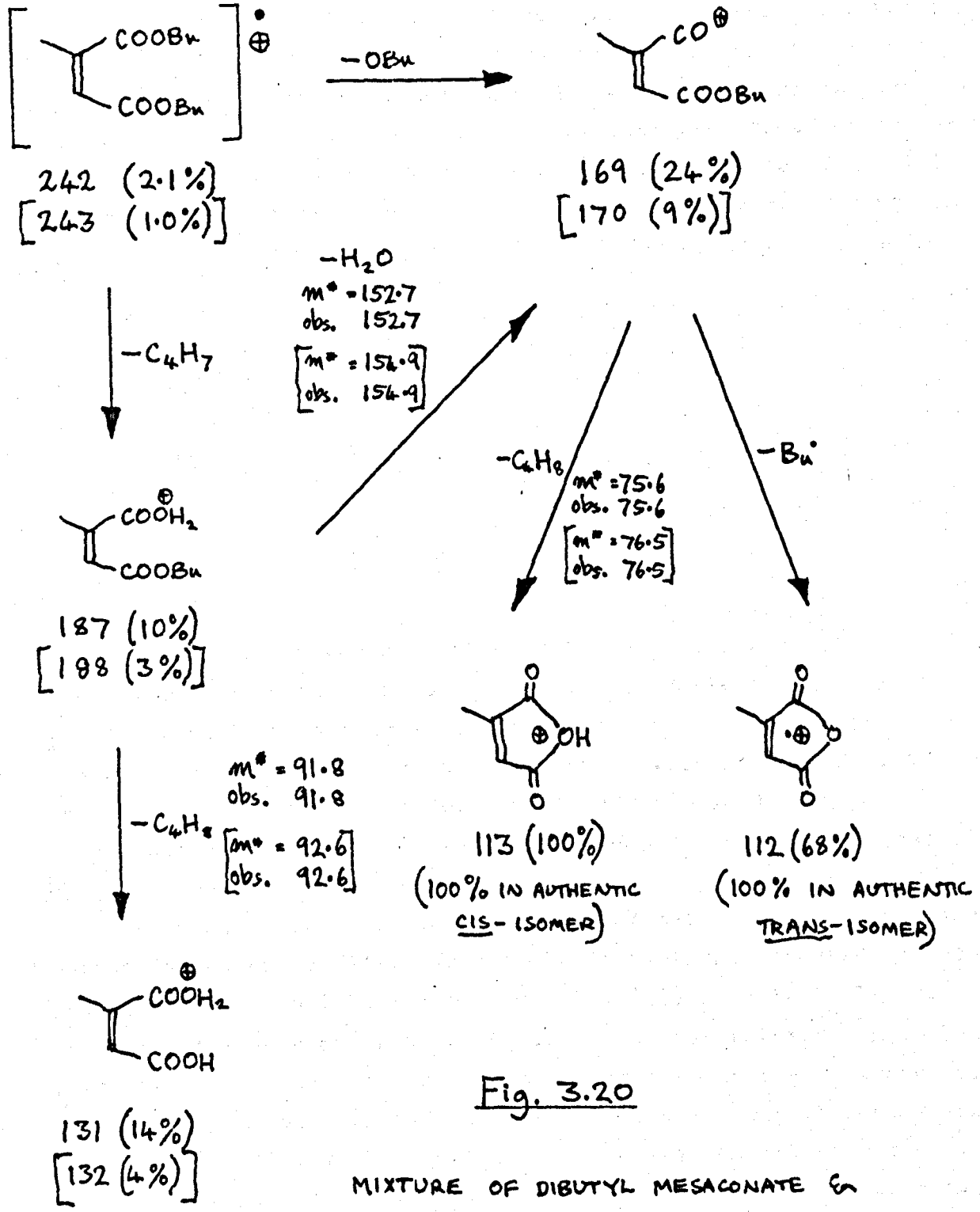
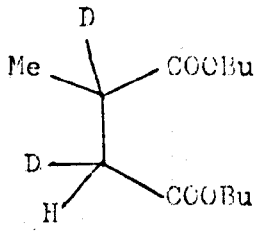


Fig. 3.20

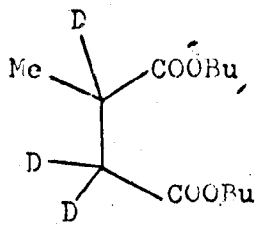
MIXTURE OF DIBUTYL MESACONATE & CITRACONATE FROM RN. 3.32

TENTATIVE FRAGMENTATION SCHEME (REPRESENTED AS THE CIS-ISOMER)

Its n.m.r. spectrum (fig. 3.21) showed that the multiplet between 6.9 and 7.9 τ , corresponding to three protons in the 'backbone' of the ester, was missing, and instead a singlet integrating as 0.75 protons was visible at 7.53 τ . It was concluded that two deuterium atoms were incorporated in the molecule as in the case of dibutyl succinate (cf. Chapter 2.4 (x)) as shown in structure IV, but that in about 25% of the sample, an additional deuterium was present as in V:



IV



V

The conclusion was supported by the mass spectrum (figs. 3.22,3.23) which showed a parent peak of $\frac{m}{e}$ = 246, accompanied by a peak at $\frac{m}{e}$ = 247 with about a quarter of its intensity. Fragments of the two peaks having a similar intensity ratio were at $\frac{m}{e}$ = 173 (20%) and 174 (4%) caused by loss of OBu and 117 (65%), 118 (16%) corresponding to the protonated anhydride structure due to loss of C_4H_8 followed by OBu.

The results from the carbonylation of methylacetylene in heavy butanol appeared to differ from those of similarly treated acetylene and butylacetylene (Chapter 2.4 (x), 4.4 (ii)) in that although the main products were consistent in each case one deuterium atom being incorporated in the unsaturated monoester, two in the saturated diester and none in the unsaturated diester, there was a significant amount of product (i.e. ca. 25%) formed in the methyl acetylene carbonylation, in which one more deuterium in each case had become incorporated. It seemed likely that the longer time involved in the methylacetylene reaction (i.e. 18 hours as opposed to 7) allowed some exchange to take place between the acetylenic hydrogen and the labile deuterium atom of the heavy butanol. Such exchange has not been observed in previous work[7], nor in experiments involving acetylene (Chapter 2.4 (ix) & (x)) or butylacetylene (Chapter 4.4 (ii)) under 'standard' conditions.

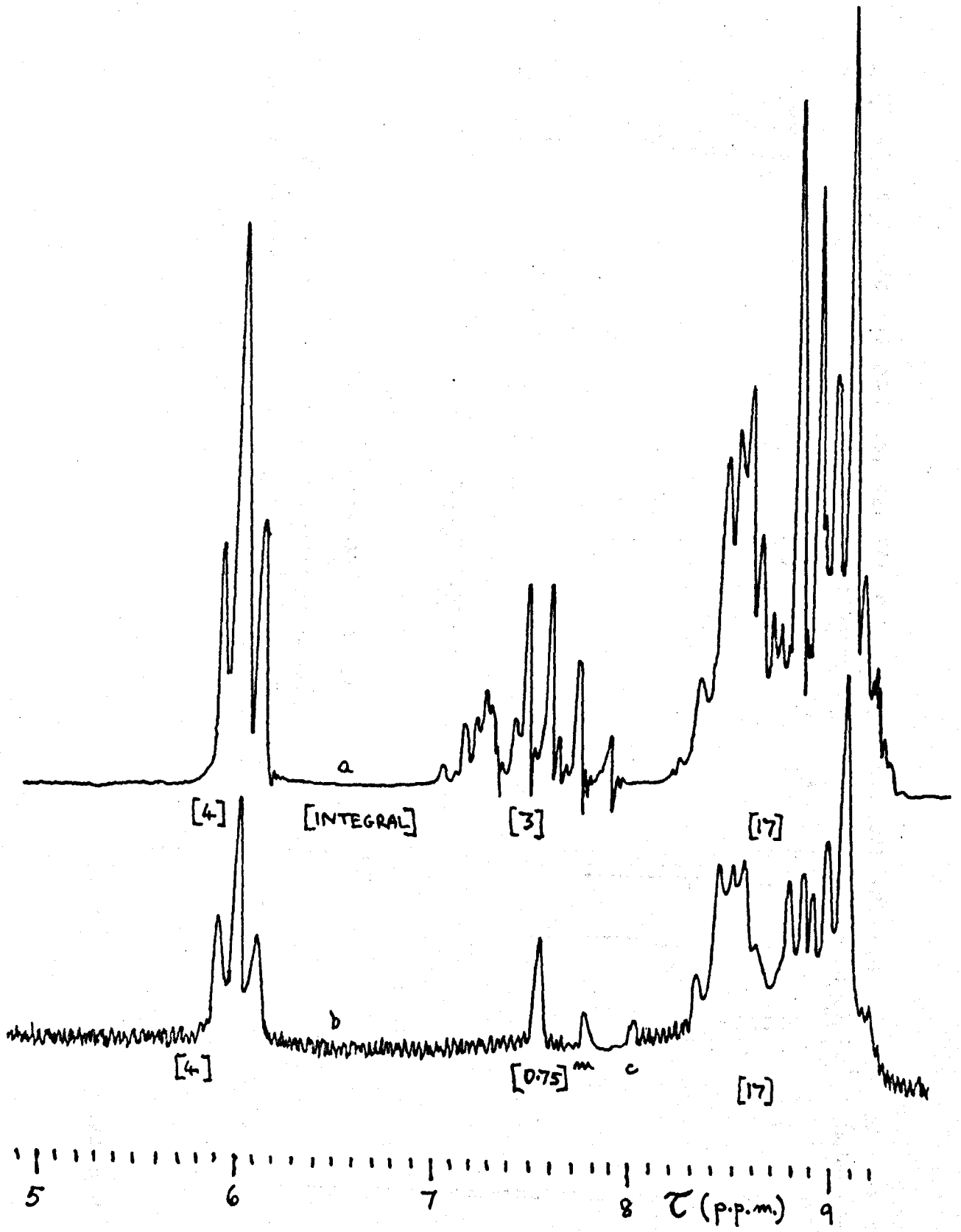
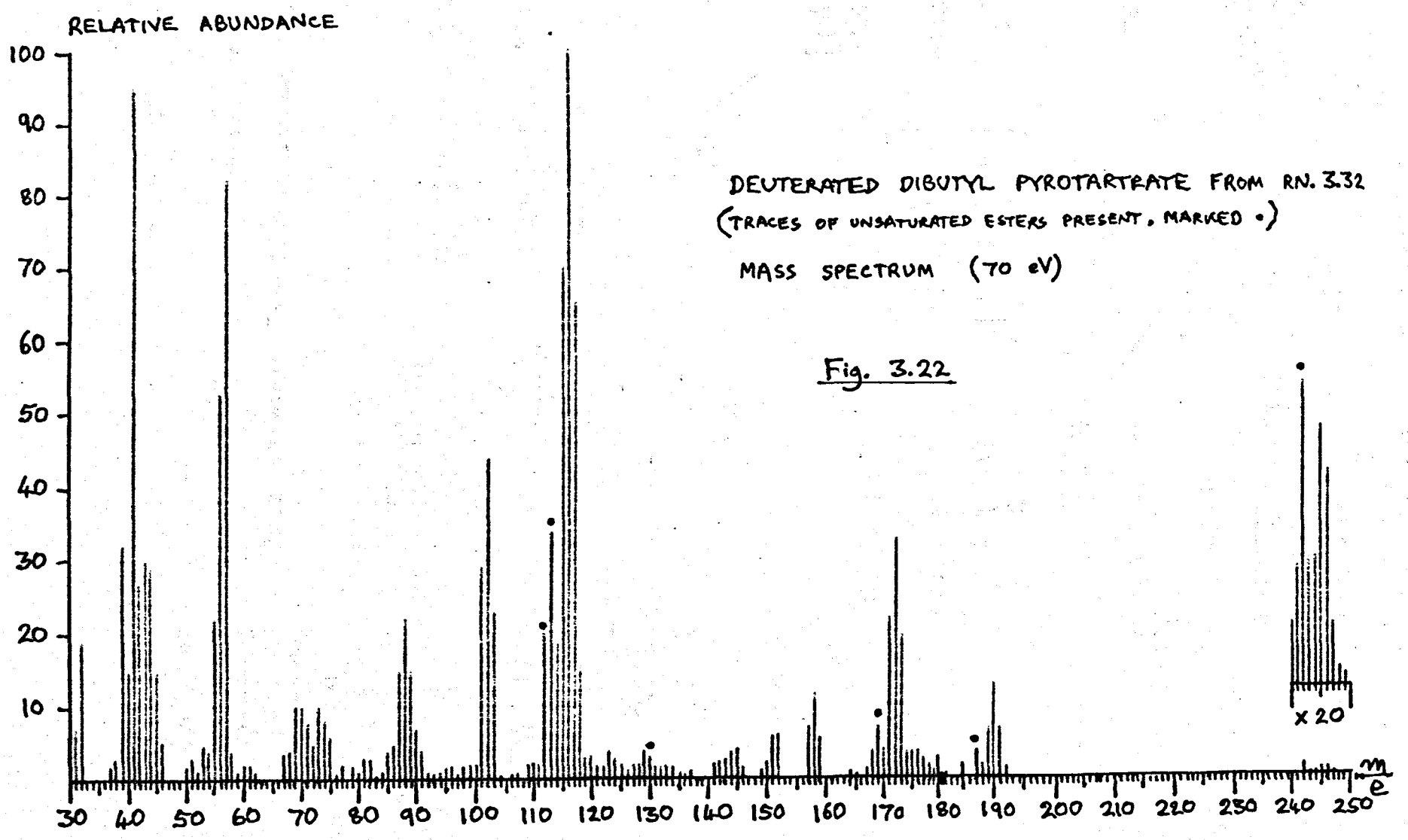


Fig 3.21

a - AUTHENTIC DIBUTYL PYROTARTRATE (25 % CCl_4)

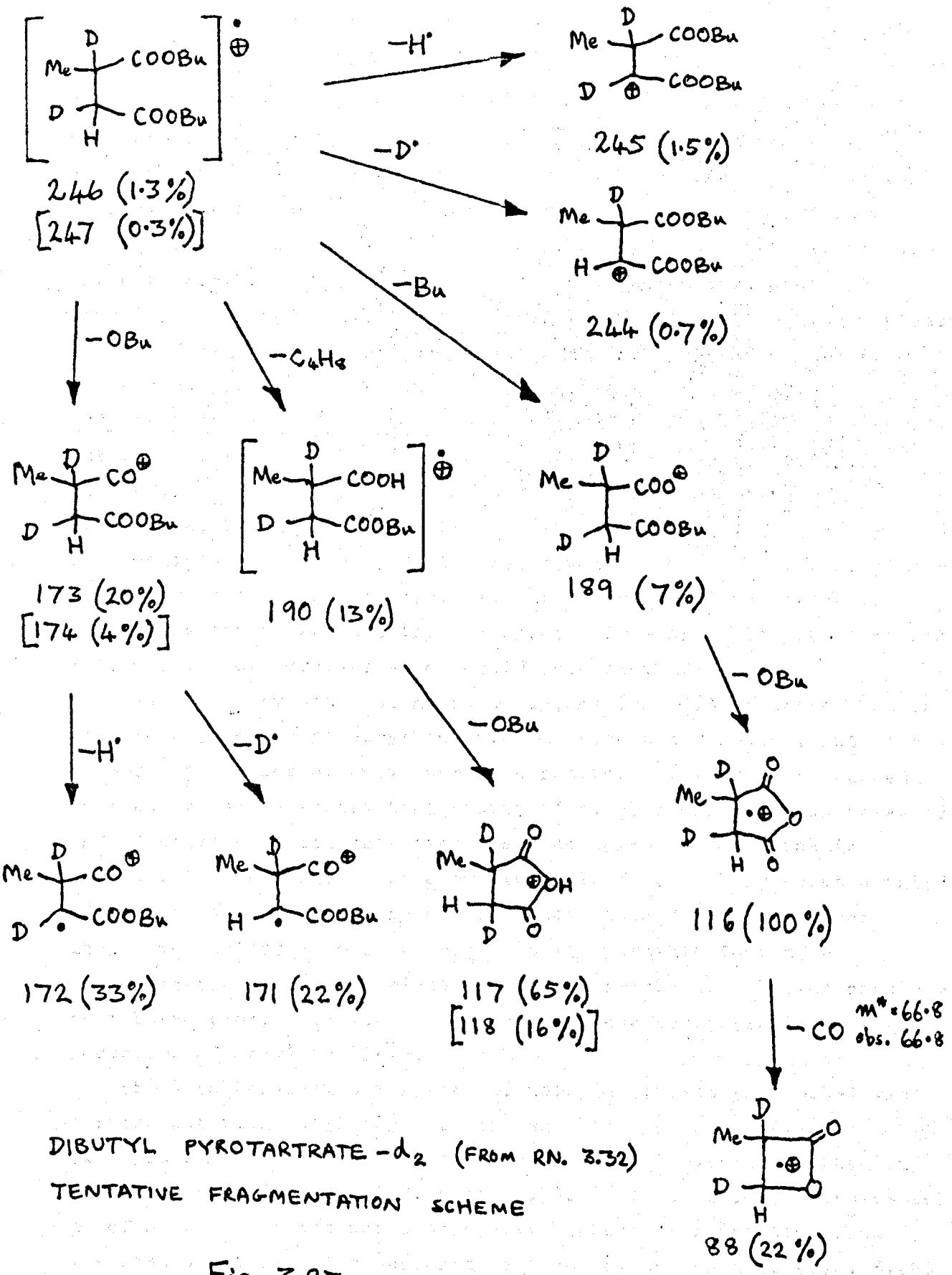
b - SAMPLE FROM RN. 3.32 (0.2 % CCl_4 ; C.A.T. 20 RUNS ACCUMULATED)

N.M.R. SPECTRA



DEUTERATED DIBUTYL PYROTARTRATE FROM RN. 3.32
(TRACES OF UNSATURATED ESTERS PRESENT, MARKED •)
MASS SPECTRUM (70 eV)

Fig. 3.22



DIBUTYL PYROTARTRATE-d_2 (FROM RN. 3.32)
TENTATIVE FRAGMENTATION SCHEME

Fig 3.23

An experiment with butylacetylene showed that no exchange took place with deuterium oxide even over several days in the presence of acid (cf. Chapter 4.4 (ii)). However, when methylacetylene was passed for 20 hours through a catalyst solution in heavy butanol held at 75°C, about 20% of the labile deuterium atoms were exchanged, presumably with the acetylenic proton, as shown by n.m.r. spectroscopy. It was concluded that over the time span involved and under the reaction conditions, methylacetylene could undergo proton exchange, thus giving an explanation for the above results.

(v) Reactions Involving Butyl Acrylate: Work with acetylene carried out by C.B.Lines[7] and in the present study (Chapter 2.4 (iii)) has indicated that butyl acrylate was the precursor of butyl propionate, but not of the other esters, although definite proof was lacking. By carrying out the carbonylation of methylacetylene in the presence of butyl acrylate, the formation of any products other than those expected from methylacetylene and which involved the intervention of acrylate ester could be observed.

(a) A carbonylation of methylacetylene (Rn. 3.33) carried out in the presence of butyl acrylate gave the expected products, but after 6 hours the amount of butyl acrylate remaining was greatly reduced in quantity and a substantial amount of butyl propionate was detected and identified by its retention times on three chromatographic columns. The results are shown in table 3.9. Only about a third of the added butyl acrylate could be accounted for and no other unexpected esters were detected; it was possible that some polymerisation had taken place during the reaction. It was concluded that butyl propionate was formed in acetylene carbonylations by reduction of acrylate ester.

(b) A carbonylation reaction of methylacetylene (Rn. 3.34) was carried out with butyl acrylate present and air passing. The expected products and a smaller amount of propionate ester than in (a) above were detected (cf. table 3.9). In addition, approximately 3% of a new substance was observed at higher retention time than mesaconate ester. The infrared spectrum of the product (fig. 3.24) showed that it was an unsaturated, unsymmetrical ester: ν (cm^{-1}) = 1170 (c-o stretch), 1650 (c=c stretch), 1710 (sh.), 1730 (c=o stretches in conjugated and unconjugated esters). The

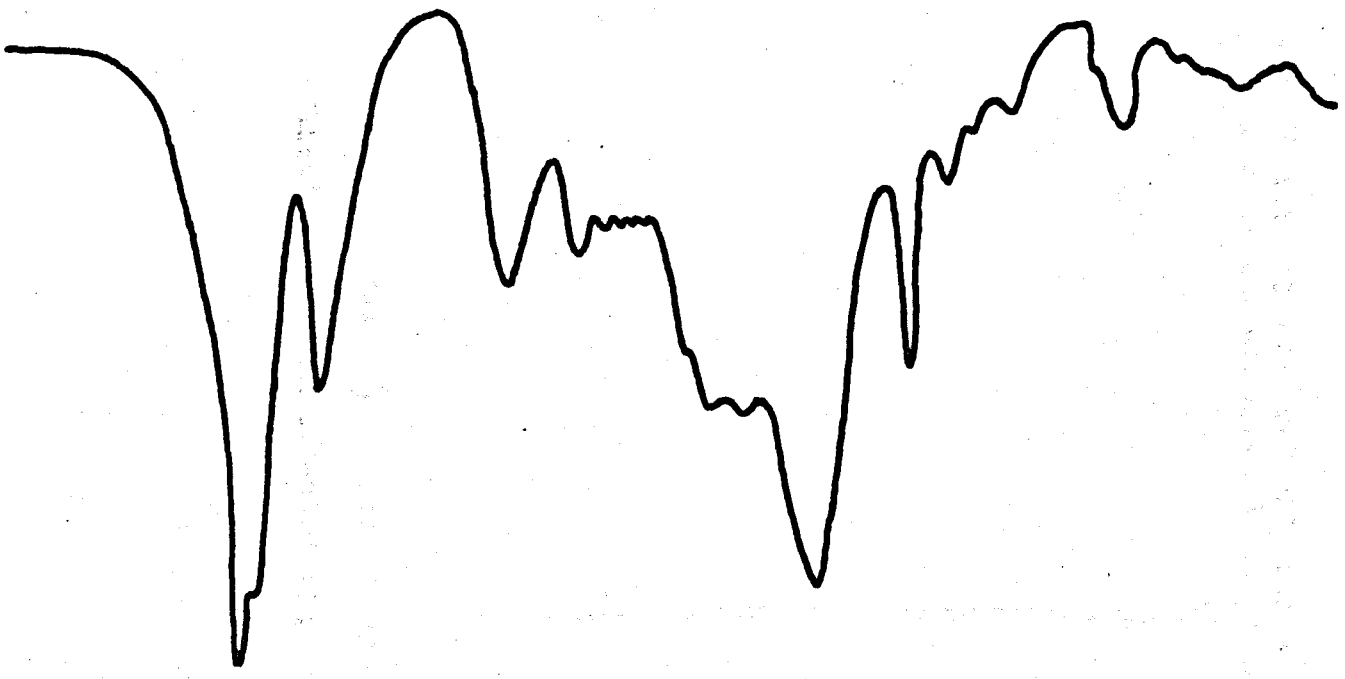
ultraviolet spectrum (fig. 3.24) suggested conjugation, with an intense absorption at λ_{max} 218 n.m., typical of a c===c—c===o K-band. The mass spectrum (fig. 3.25) showed a weak parent peak at $\frac{m}{e}$ = 270, for which a fragmentation pattern (fig. 3.26), consistent with the compound being the dibutyl ester of a 7-carbon acid, could be tentatively assigned. The n.m.r. spectrum (fig. 3.27) showed that the compound was dibutyl 3-methylhex-2-enedioate. An olefinic singlet at 4.30 τ , integrating as 1 proton, showed that the methyl group (doublet, 8.1 τ) was substituted on the double bond, which was known, from the infrared and ultraviolet spectra, to be conjugated with one of the carbonyl groups. The two remaining methylene groups occurred as distorted triplets at 7.08τ and 7.47τ . When the olefinic proton was irradiated, the 7.0 - 7.7τ region was not greatly changed (though the methyl doublet collapsed to a singlet, (cf. fig. 3.28)) and it was concluded that the methyl group was substituted on the 3-position rather than the 2-position, and thus the olefinic proton did not couple strongly with the methylene groups.

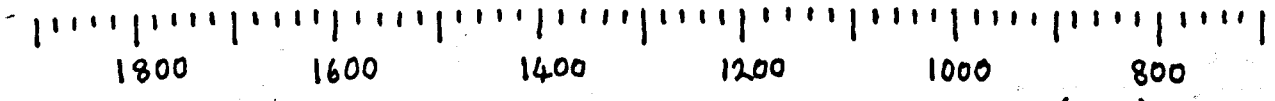
The shift value obtained for the methyl side chain compared closely with that given by Weedon and his co-workers[18] for dimethyl 3-methyl-cis-hex-2-enedioate (i.e. 8.09τ as opposed to 7.85τ in the trans-compound) and it was concluded that the ester was dibutyl 3-methyl-cis-hex-2-enedioate.

(c) In an attempt to obtain a high yield of the new ester, a methylacetylene reaction (Rn. 3.35) was carried out under the same conditions as above, but using a solvent consisting of ca. 60% butyl acrylate, 40% butanol. However, no products were detected by gas chromatography. The wine red colour of the catalyst solution was unchanged at the end of the reaction.

(d) Since a large excess of butyl acrylate apparently had the effect of suppressing the carbonylation, it was decided to slowly add a large amount of the ester whilst the reaction was under way. The results in fig. 3.29 and table 3.9, interpolated at six hours, showed that formation of the mono- and vic-diesters was greatly suppressed, whilst the yield of coupled product was enhanced. The yield so obtained was 3.3% based on the acetylene or 5.0% based on butyl acrylate.

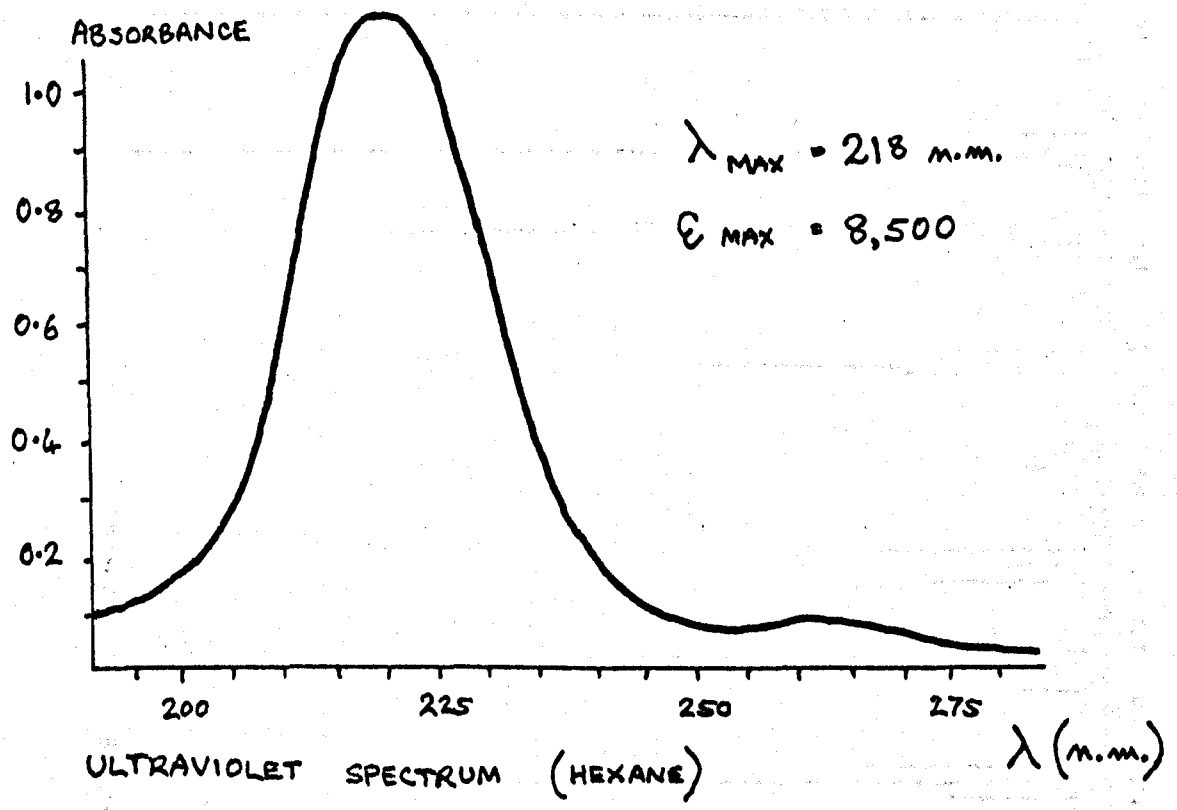
A trace of butyl propionate was formed in the reaction, but it could not be analysed quantitatively since it was largely masked by the acrylate peak in the gas chromatogram.





DIBUTYL 3-METHYL-CIS-HEX-2-ENEDIOATE

INFRARED SPECTRUM (KBr DISC)



ULTRAVIOLET SPECTRUM (HEXANE)

Fig. 3.24

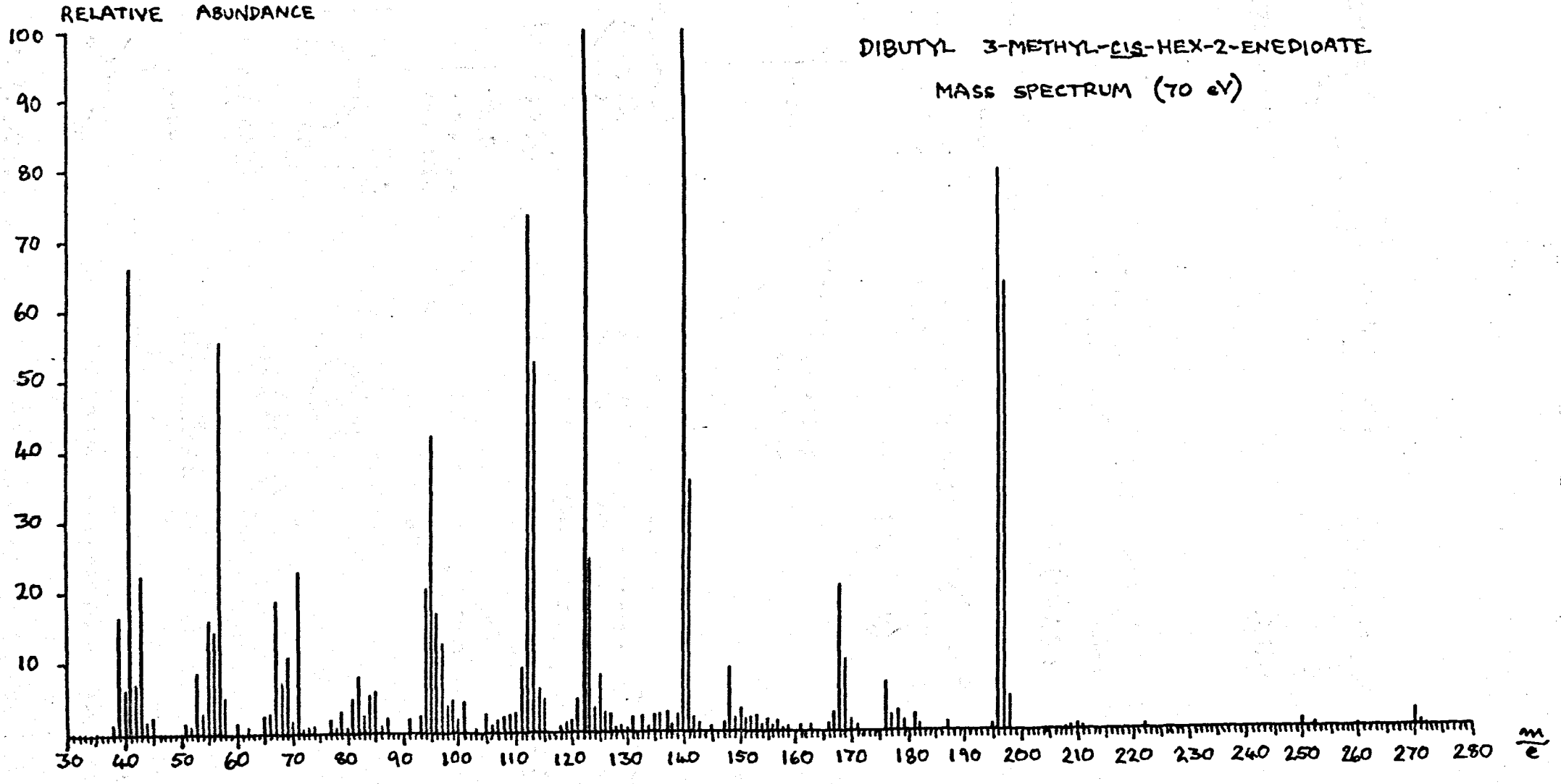

RELATIVE ABUNDANCE
DIBUTYL 3-METHYL-CIS-HEX-2-ENEDIOATE
MASS SPECTRUM (70 eV)
100
90
80
70
60
50
40
30
20
10
30 40 50 60 70 80 90 100 110 120 130 140 150 160 170 180 190 200 210 220 230 240 250 260 270 280
m/e

Fig. 3.25

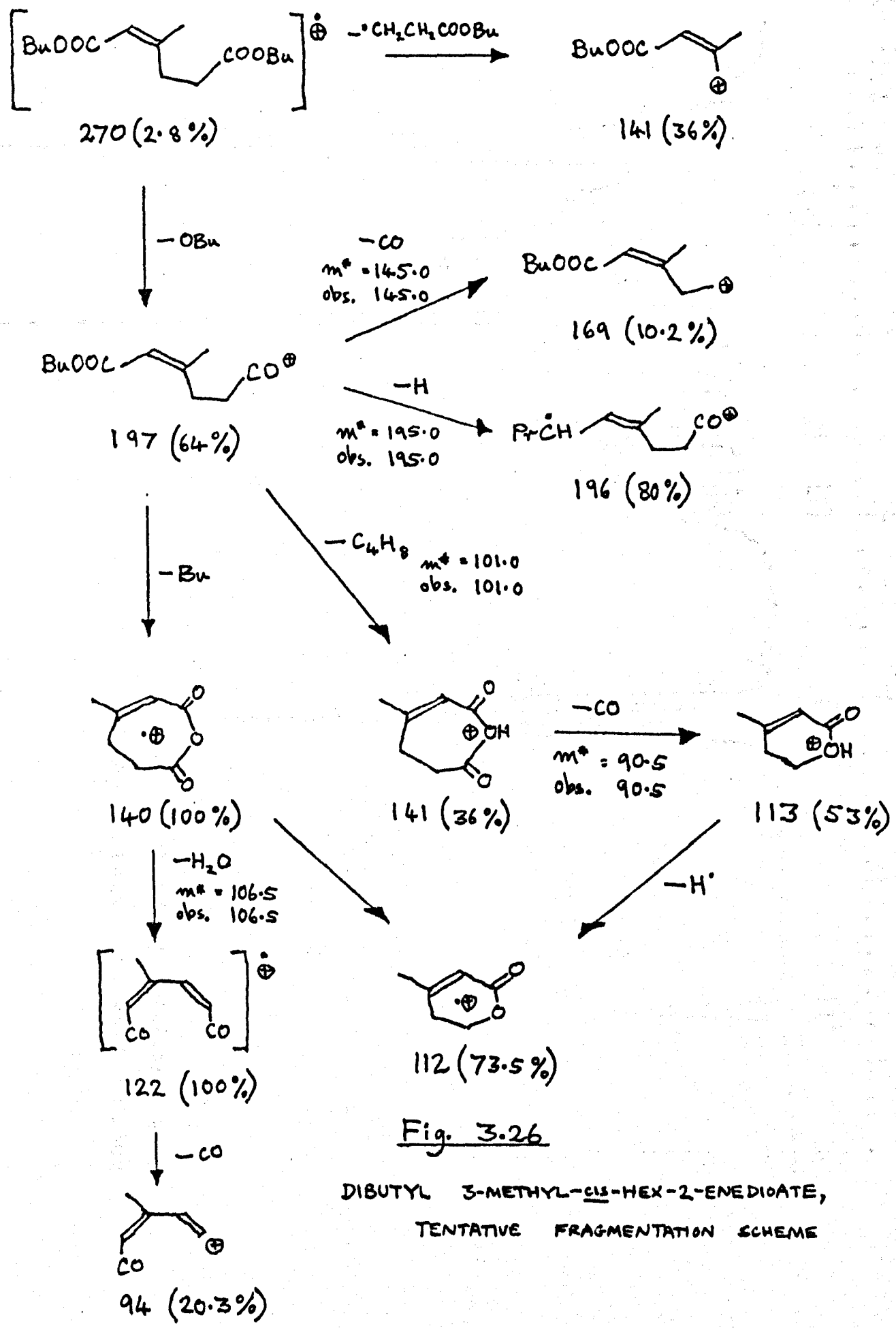


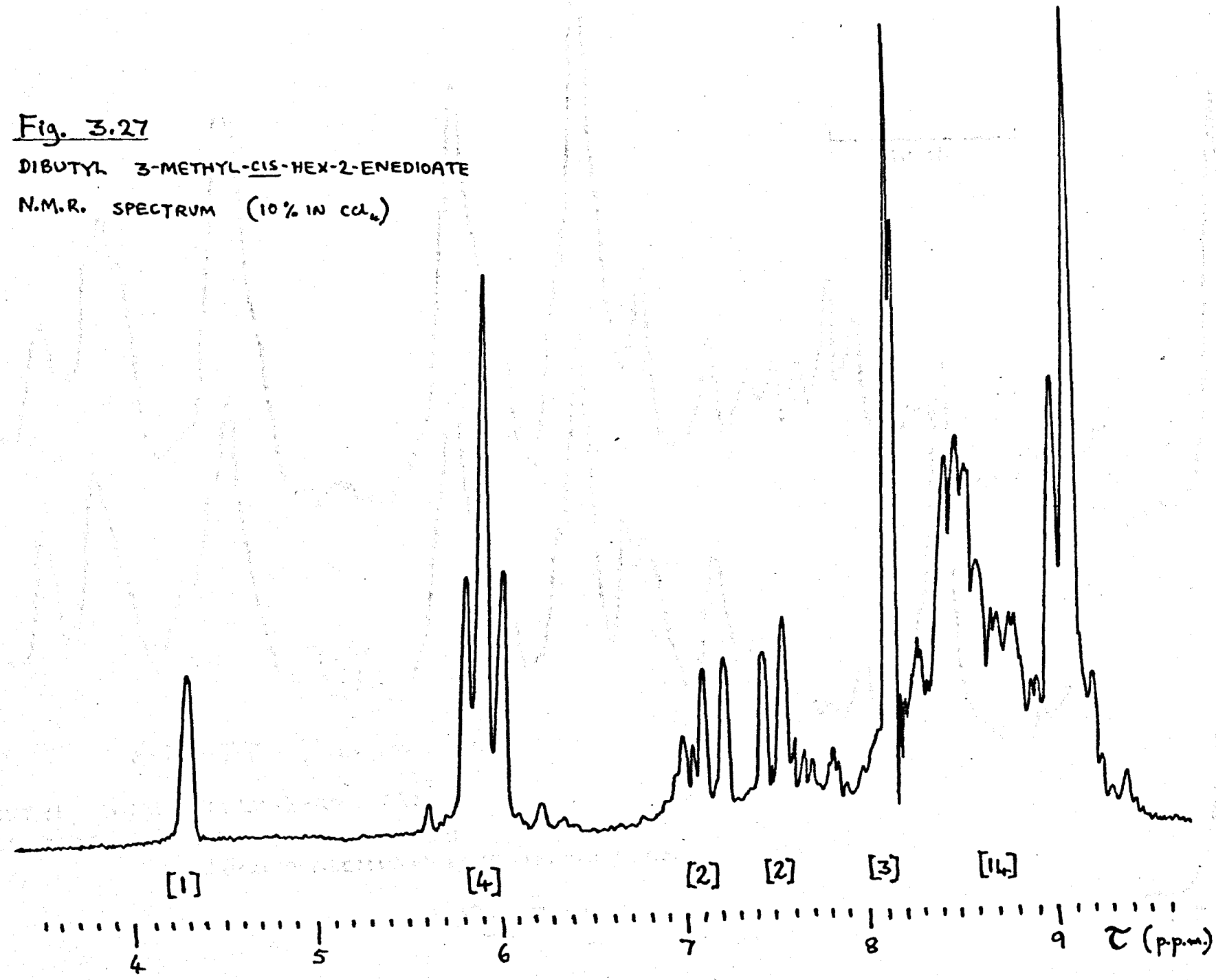
Fig. 3.26

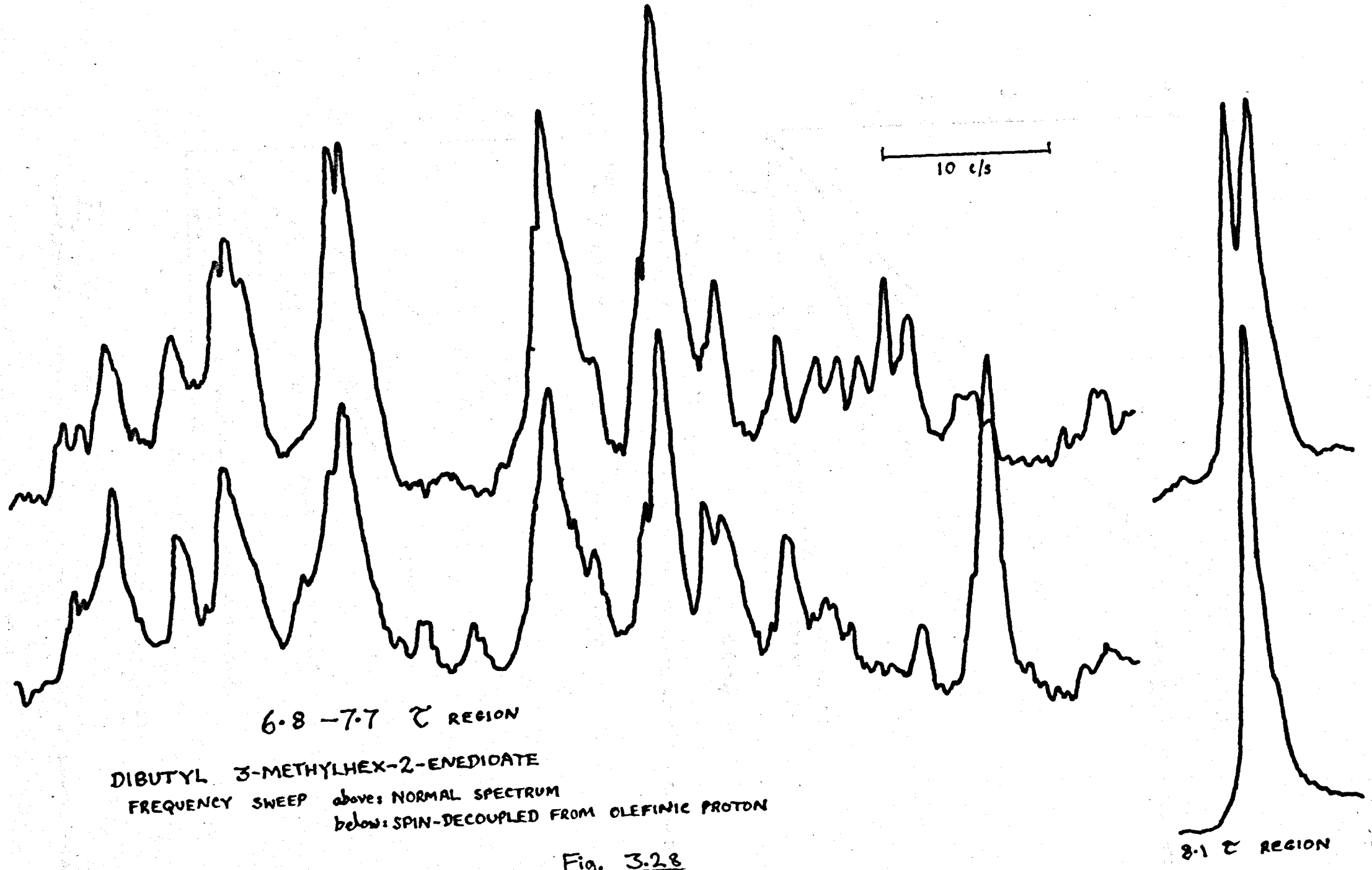
DIBUTYL 3-METHYL-cis-HEX-2-ENEDIOATE, TENTATIVE FRAGMENTATION SCHEME

Fig. 3.27

DIBUTYL 3-METHYL-CIS-HEX-2-ENEDIOATE

N.M.R. SPECTRUM (10% IN CCl_4)





DIBUTYL 3-METHYLHEX-2-ENEDIOATE

FREQUENCY SWEEP above: NORMAL SPECTRUM
below: SPIN-DECOUPLED FROM OLEFINIC PROTON

Fig. 3.28

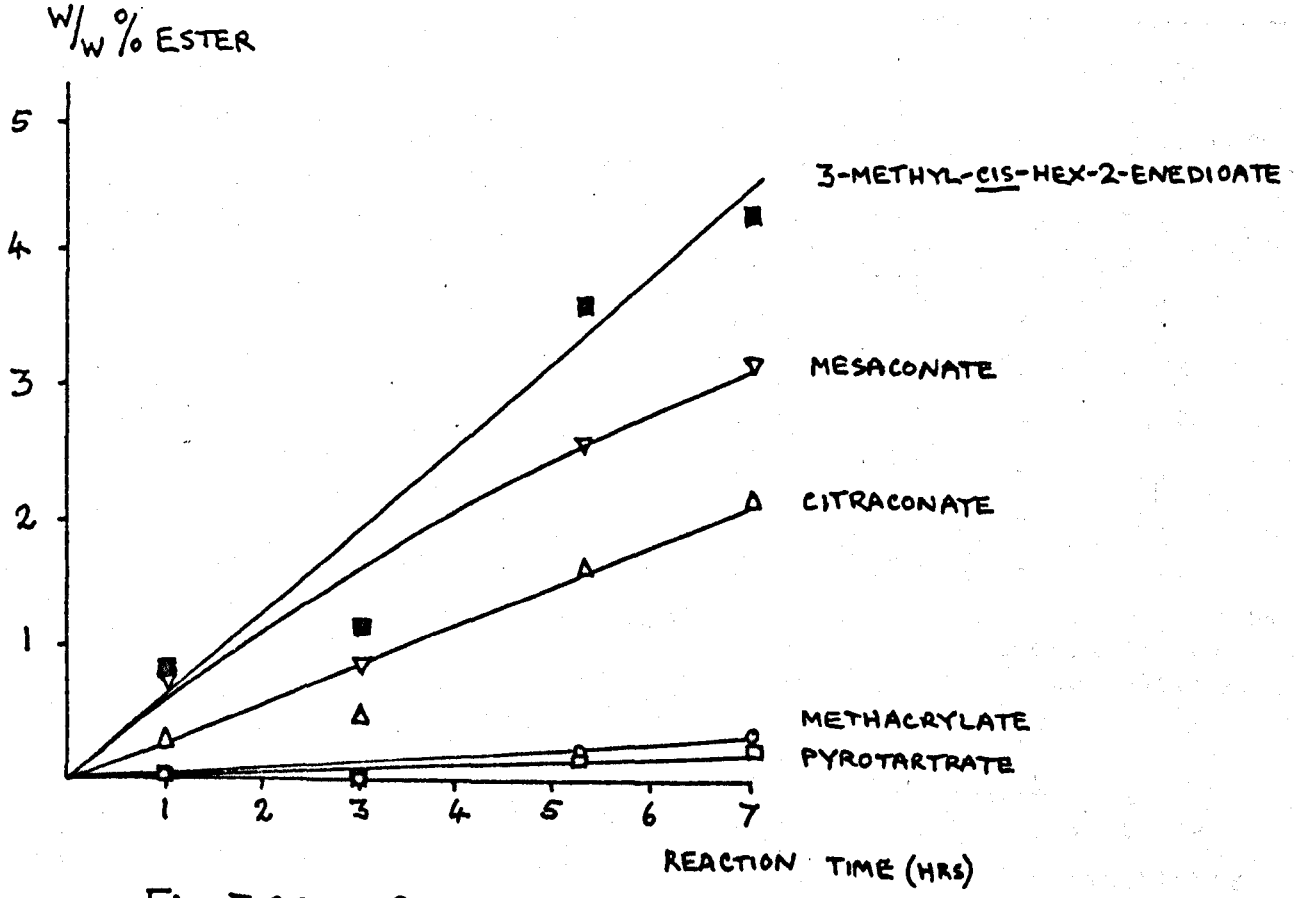


Fig. 3.29, Rm. 3.36

CARBONYLATION OF METHYLACETYLENE IN THE PRESENCE OF BUTYL ACRYLATE

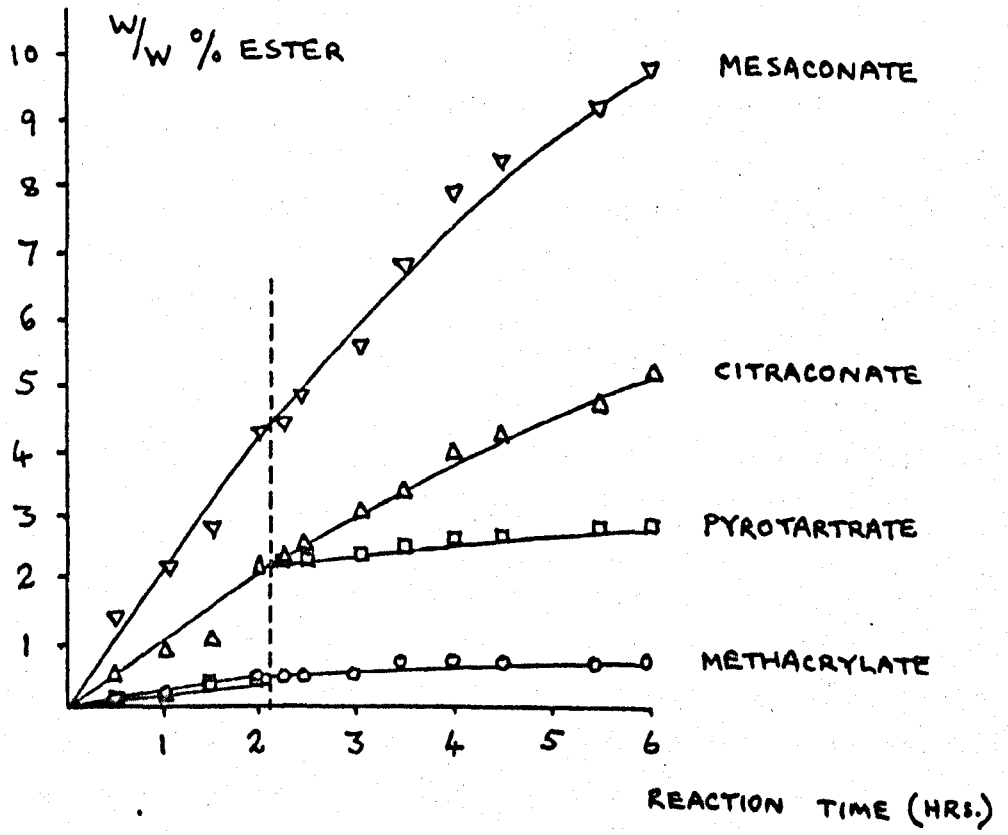


Fig. 3.34, Rm. 3.42

CARBONYLATION OF METHYLACETYLENE IN THE PRESENCE OF DIBUTYL PYROTARTRATE

Reaction No	3.33	3.34	3.35	3.36
Air flow (l/h)	0.0	1-1.5	1-1.5	1-1.5
Added butyl acrylate (g)	4.5	4.7	40.0	40.0 (progr.)
Wt. increase (g)	10.6	10.4	0.0	10.9
Butyl acrylate	[0.5]	[1.6]	high	high
Butyl propionate	1.8	1.4	-	-
Butyl methacrylate	3.0	0.9	-	0.3
Dibutyl citraconate	4.0	4.2	-	1.7
Dibutyl mesaconate	8.4	8.6	-	2.9
Dibutyl pyrotartrate	0.6	-	-	0.2
Dibutyl 3-methyl-cis-hex-2-enedioate	-	2.9	-	3.7

Table 3.9 The Concentrations of Products Obtained When Varying Amounts of Butyl Acrylate were Present During the Carbonylation of Methylacetylene (Amounts Expressed as W/W% of the Reaction Mixture, initially 60 g),

(vi) Reactions Involving the Homologues of Acrylate Ester:

(a) Butyl methacrylate: Since butyl acrylate was shown to be reactive under the conditions used for carbonylation, the reactivity of butyl methacrylate under similar conditions seemed relevant to the study of the differences between the carbonylation reactions of acetylene and methylacetylene. It had already been shown (Chapter 2.4 (iii)) that addition of butyl methacrylate to acetylene carbonylations with or without the passage of air, did not give rise to reduction products such as isobutyrate ester, or products of coupling of the substituted hexenedioate ester type.

Again, when a methylacetylene carbonylation reaction was carried out in the presence of air and a quantity of butyl methacrylate, no new product was observed, and the amount of isobutyrate ester obtained remained at its normal trace level. There was, however, a small decrease in the W/W% of methacrylate present, suggesting that some form of side-reaction such as polymerisation was taking place (cf. fig. 3.30).

(b) Butyl crotonate: The non-reactivity of butyl methacrylate towards either reduction or coupling might be due to steric hindrance and the isomeric crotonate ester might therefore exhibit greater reactivity. A reaction was carried out under the same conditions as in (a) above, but with a quantity of butyl trans—crotonate

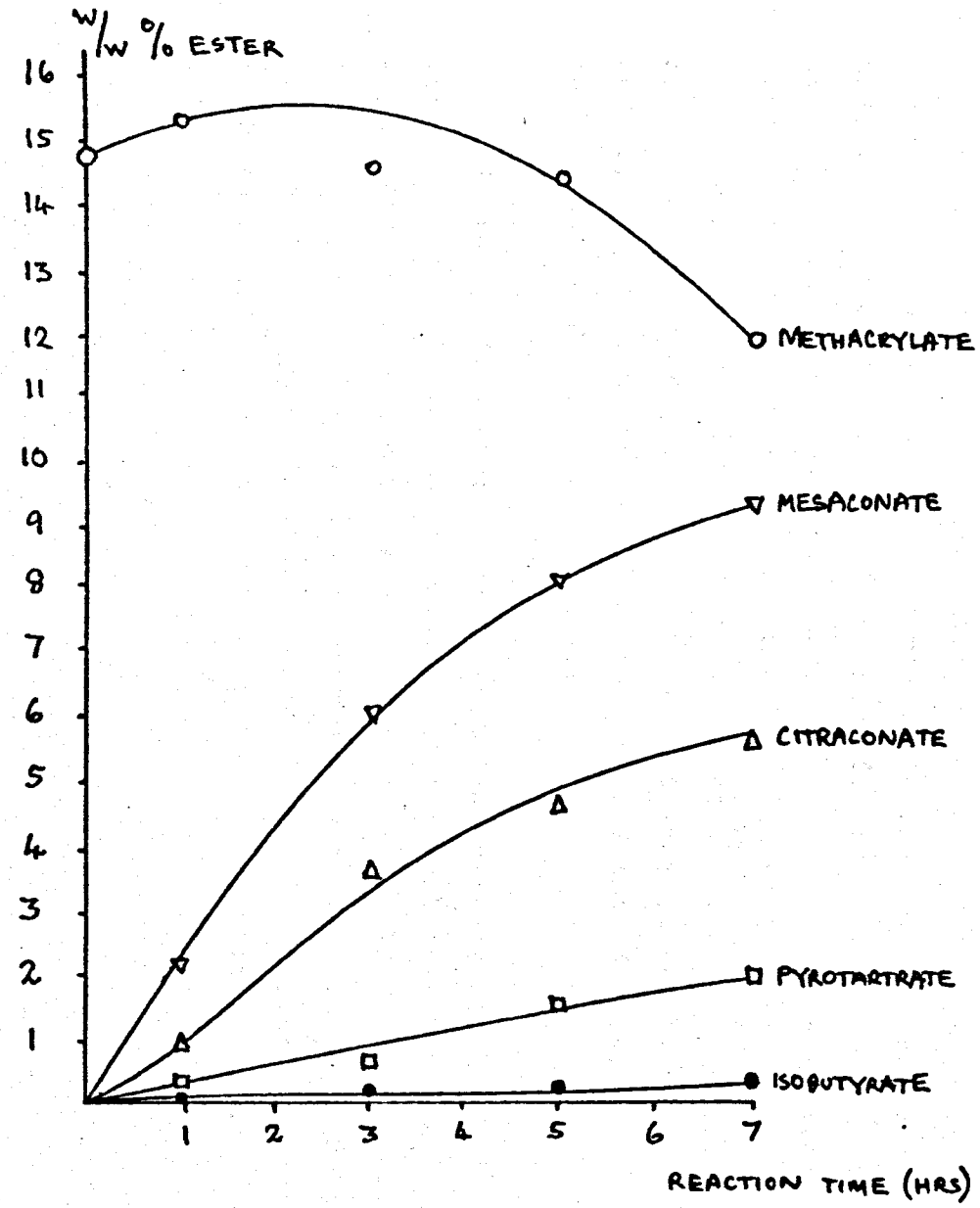


Fig. 3.30, Rm. 3.37

CARBONYLATION OF METHYLACETYLENE IN THE PRESENCE OF BUTYL METHACRYLATE

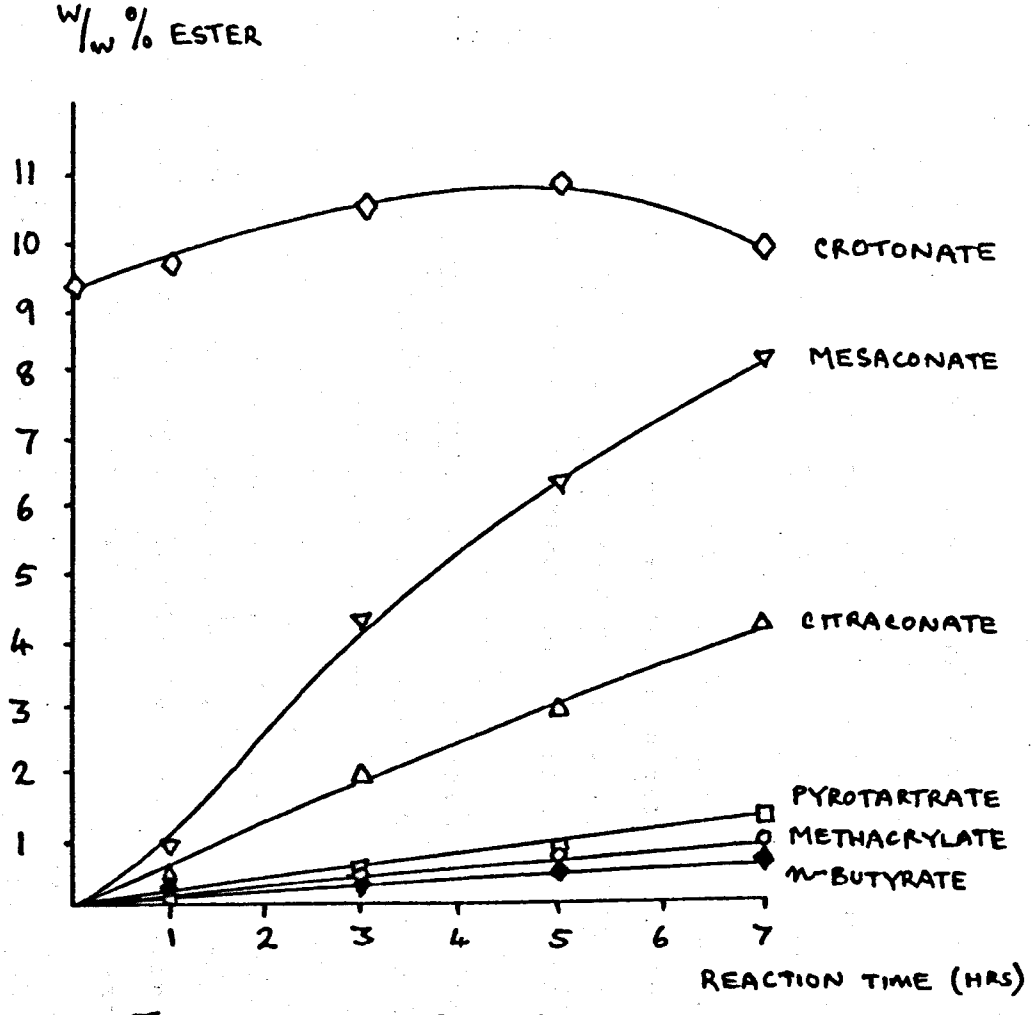


Fig. 3.31, Rm. 3.38

CARBONYLATION OF METHYLACETYLENE IN THE PRESENCE OF BUTYL CROTONATE

substituted for the methacrylate. Similar yields of esters were observed (fig. 3.31) along with a small amount of butyl n-butyrate which was not normally detected in the carbonylation mixtures and was therefore assumed to have been formed by reduction of the crotonate ester.

No new higher products were detectable by gas chromatography. It was clear that the presence of a methyl group in either the 2- or 3- position almost completely deprived acrylate ester of its reactivity in the system, whether by virtue of steric or electronic effects is not clear.

(vii) Reactions Involving Diesters: Since the saturated monoester was derived from the unsaturated compound, attempts were made to investigate whether the saturated diesters were produced by reduction of the corresponding unsaturated esters.

(a) Dibutyl maleate: A methylacetylene carbonylation reaction (Rn. 3.39) was carried out in the presence of 14.5 W/W% of added dibutyl maleate, and a striking conversion to the succinate ester was observed over the seven hour period. 50% of the maleate was converted to succinate ester, 35% being unchanged. 15% was unaccounted for, since no isomerisation to the fumarate ester was observed. It was also interesting to note that the expected colour change of the catalyst from wine red to yellow was not observed and that the rate of production of esters (cf. fig. 3.32) was constant, suggesting that the unsaturated ester is as effective in removing some inhibiting species as air had been found to be.

The succinate ester observed in mixtures obtained from the carbonylation of acetylene was almost certainly formed by reduction and, by implication, the smaller amounts of diesters observed in the carbonylation of substituted acetylenes were formed in an analogous way.

(b) Dibutyl fumarate: A methylacetylene carbonylation reaction (Rn. 3.40) was carried out in the presence of dibutyl fumarate. A 30% conversion to succinate ester was observed, 70% of the fumarate being unchanged. However, the conversion was much smaller than in the case of the cis-ester, and the normal reaction products were only produced in limited amounts and after a long induction period (cf. fig. 3.33).

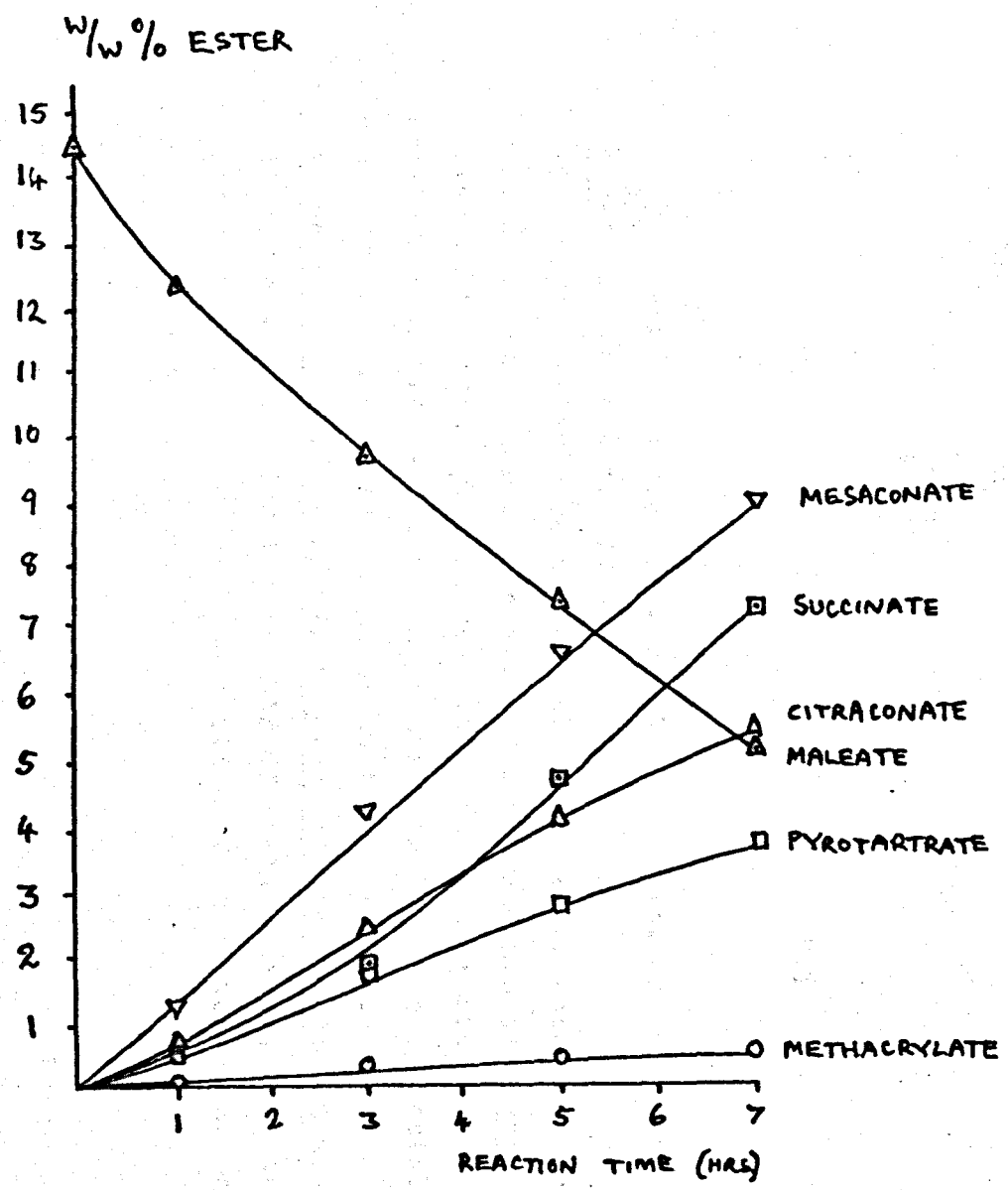


Fig. 3.32, Rm. 3.39
CARBONYLATION OF METHYLACETYLENE IN THE PRESENCE OF DIBUTYL MALEATE

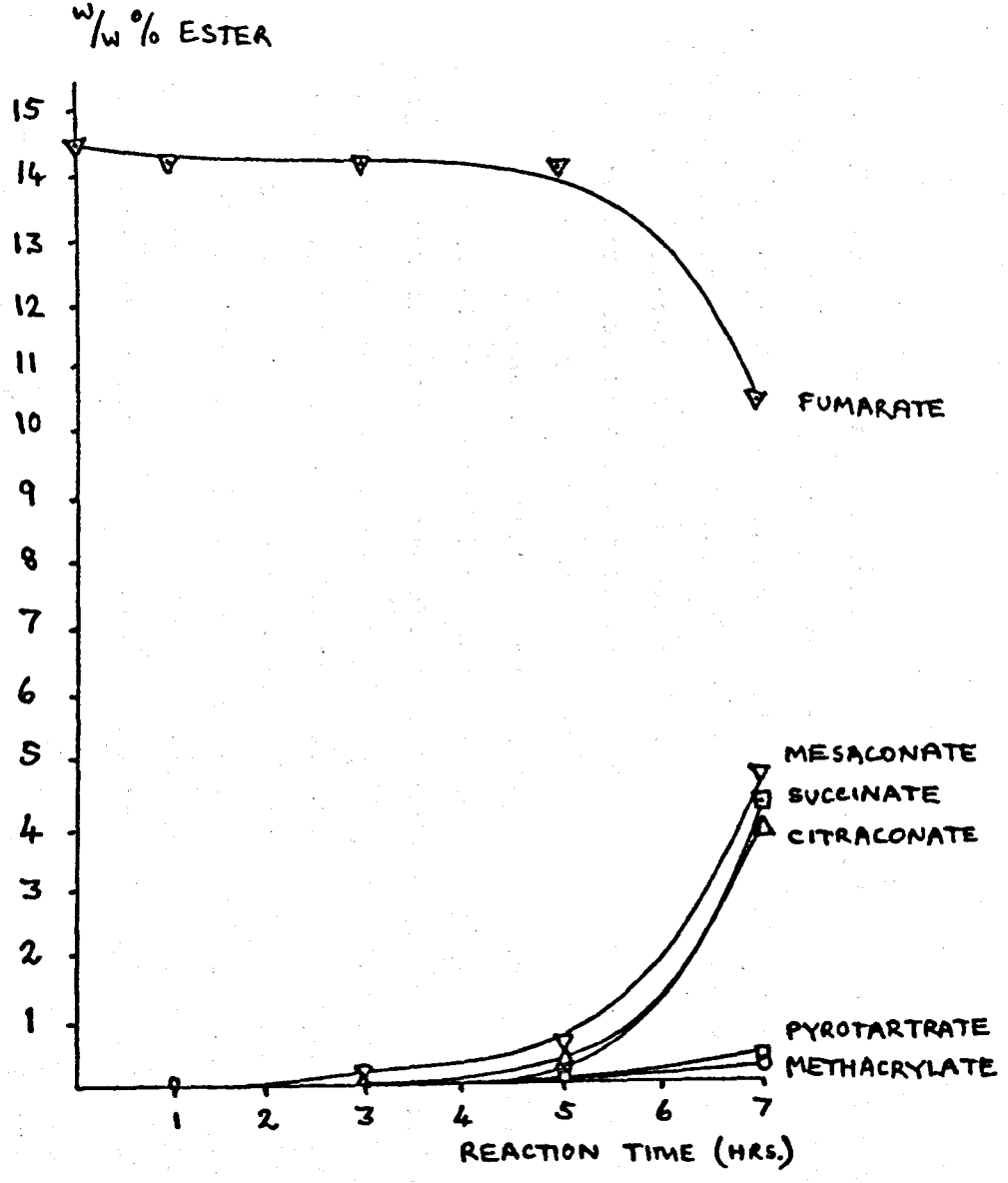
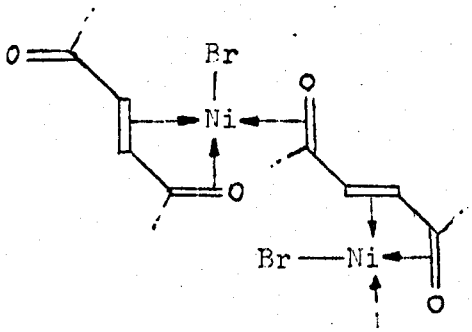


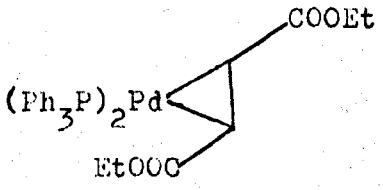
Fig. 3.33, Rm. 3.40
CARBONYLATION OF METHYLACETYLENE IN THE PRESENCE OF DIBUTYL FUMARATE

The greater ease of reduction of the cis-ester was consistent with a mechanism involving heterogeneous hydrogenation. Markman[19] has shown that when mixtures of maleic and fumaric acids were hydrogenated over palladium, maleic acid was reduced before fumaric acid. However, a homogeneous mechanism cannot be ruled out, since the greater chelating power of maleate ester would be expected to play an important part in such a reaction.

The observed reduction in the conversion of methylacetylene has a parallel in the previous work on acetylene[7] when fumarate ester was present in amounts approaching 40 m mols (cf. Chapter 2.2 (iii). The phenomenon was attributed[7] to formation of a complex analogous to the polymeric dimethyl fumarate - nickel bromide complex (VI) described by Dubini & Montino[20], although a similar complex of greater stability was formed from dimethyl maleate. Since that date, a palladium complex of formula (fumarate)$Pd(PPh_3)_2$,(VII) has been reported by Fitton & McKeon[21] as formed from the zero-valent



VI



VII

$Pd(PPh_3)_4$ species and diethyl fumarate. A similar reaction with the cis-ester was not reported.

The much greater ease of reduction of maleate ester may be a partial explanation for the relatively large amounts of trans- ester observed in the carbonylation reactions, especially since the predominance of trans- ester was greatest in the case of acetylene, where large amounts of saturated product were formed.

(viii) Reactions in the Presence of Pyrotartrate Ester: It was possible, notwithstanding the results of section (vii), that the saturated diester was active, and could undergo dehydrogenation to yield the unsaturated compounds.

Two reactions, 3.41 and 3.42 were carried out under 'standard' conditions, but with air passing and a quantity of dibutyl pyrotartrate added to each after the reaction had been under way for some time.

The formation of unsaturated diesters was unaffected except for a small downward inflection in the W/W% value caused by the increased mass of the solution.

Analyses at the end of the reaction period are given in table 3.10 and compared with the typical reaction in the presence of air, Rn. 3.11 and the results of Rn. 3.42 are given in fig. 3.34. They show that dehydrogenation of dibutyl pyrotartrate did not take place under the reaction conditions.

Reaction No	3.11	3.41	3.42
Reaction time (hours)	7.0	6.5	6.0
Dibutyl pyrotartrate added (g)	0.0	1.0	0.8
Time when added (hours)	-	4.0	2.0
Wt. increase (g)	15.0	14.7	10.8
Butyl methacrylate	1.8	1.4	0.8
Dibutyl citraconate	5.8	4.9	5.2
Dibutyl mesaconate	11.3	11.4	9.8
Dibutyl pyrotartrate	2.0	[2.8]	[2.9]

Table 3.10 The Amounts of Product Esters Obtained in Methylacetylene Carbonylation Reactions Carried out in the Presence of Dibutyl Pyrotartrate (Expressed as W/W% of the Reaction Mixture, initially 60 g).

3.6 CARBONYLATION IN THE PRESENCE OF VARIOUS ADDITIVES

(i) Gases Other than Air:

(a) Hydrogen: It was noted in Chapter 2.2 (iv) that the passage of hydrogen during the carbonylation of acetylene had very little effect on the relative amounts of products, but suppressed the overall reaction to some extent. A reaction (Rn. 3.44) was carried out to investigate the role of hydrogen in methylacetylene carbonylation reactions. The reaction was carried out under 'standard' conditions but with hydrogen passing at 2.2 l/h. The results, shown in table 3.11 alongside the typical 'standard' reaction (Rn. 3.4) do not show any marked deviation from the 'standard' results, except a small decrease in overall yield, and a small relative increase in the trans- diester.

Thus as in acetylene carbonylations, hydrogen did not increase the yield of saturated products.

(b) Nitrogen: A high concentration of methylacetylene was believed to cause undesirable side effects which led to a low overall conversion (Chapter 3.2 (iii), and to observe whether dilution of the reactant gases would have a beneficial effect, a reaction (Rn. 3.43) was carried out under 'standard' conditions but with nitrogen passing at 1-1.5 l/h.

The relative proportions of the products were not greatly changed though again the trans- diester was somewhat favoured, the actual amounts of esters were lowered to an extent comparable with that observed with hydrogen ((a) above), cf. table 3.11.

It was concluded that hydrogen was unreactive under the reaction conditions, and that both it and nitrogen had a slightly adverse effect.

Reaction No	3.4	3.44	3.43
Gas passed (l/h)	-	H_2(2.2)	N_2(1-1.5)
Wt. increase (g)	7.5	6.1	6.0
Butyl methacrylate	5.6	2.2	2.6
Dibutyl citraconate	4.2	2.9	2.7
Dibutyl mesaconate	6.3	6.5	6.8
Dibutyl pyrotartrate	2.2	1.9	1.5

Table 3.11 The Concentrations of Products Obtained from Methylacetylene Carbonylation Reactions Carried Out in the Presence of Hydrogen and Nitrogen (Expressed as W/W% of the Reaction Mixture, initially 60 g).

(ii) Unsaturated Additives: The coupling reaction exhibited by butyl acrylate but not by its homologues was of considerable interest, and a number of other olefins, activated and otherwise, were examined in the hope of observing analogous behaviour. However, none of them reacted to any significant extent; neither coupled nor reduced products were detected. The results are summarised in table 3.12:

Reaction No	3.46	3.47	3.48
Additive (amount)	C_2H_4 (1.5 l/h)	PhC_2H_3 (9.5g)	C_2H_3CN (9.7g)
Air (l/h)	0.0	1-1.5 l/h	1-1.5 l/h
Wt. increase (g)	7.5	7.0	2.5 *
Butyl methacrylate	3.8	0.8	0.2
Dibutyl citraconate	3.3	3.4	7.7
Dibutyl mesaconate	5.3	8.4	6.8
Dibutyl pyrotartrate	1.0	-	-

* low value due to evaporation.

Table 3.12 The Concentrations of Products Obtained from Methylacetylene Carbonylation Reactions Carried Out in the Presence of Various Unsaturated Compounds (Expressed as W/W% of the Reaction Mixture, initially 60 g).

3.7 SUMMARY AND CONCLUSIONS

It has been shown that although acetylene and methylacetylene gave rise to parallel series of products, they differed markedly in their behaviour towards carbonylation. Methylacetylene apparently reacted with the catalyst solution much more readily than acetylene, giving rise to an unidentified oil and palladium metal. Addition of air or benzoquinone had a beneficial effect on the overall conversion of the substituted acetylene, whereas it had a slightly adverse effect in the case of acetylene itself. (The difference may, of course, be attributed to the differing solubilities of the two gases in butanol).

Methylacetylene also differed from the other monosubstituted acetylenes studied, in that the presence of hydrogen chloride during carbonylation reactions did not exert any great effect on the ratio of mono- to diesters.

The most striking difference between methylacetylene and the parent compound, was the ratio of saturated to unsaturated esters. The ratio was quite high in the case of acetylene (though falling short of a 'mass balance'), but the reactions with methylacetylene produced only trivial amounts of saturated products. When methylacetylene product esters were present during the carbonylation of acetylene, significant amounts of saturated products were not formed, but when acetylene product esters were present during the

carbonylation of methylacetylene, they were reduced to a significant extent. Hence it was concluded that a species capable of effecting reduction was generated in the reaction mixtures, but it was relatively ineffective for reducing the branched chain products.

A reaction common to all the monosubstituted acetylenes studied, was the formation of a 3-substituted hex-2-enedioate ester when butyl acrylate was present during carbonylation in the presence of air. The major difference between acetylene and methylacetylene in this context was that methylacetylene produced specifically the 3-methyl-cis-hex-2-enedioate ester, whereas acetylene produced predominantly the trans-hex-2-enedioate ester along with the cis-isomer and trans-hex-3-enedioate and some muconate. Moreover, the acetylene reaction did not require the passage of air.

It is clear from the above that a methyl substituent exerted a considerable effect on the chemistry of the triple bond in the field under consideration.

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CHAPTER FOUR

Studies on the Carbonylation of Butylacetylene

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4.1. INTRODUCTION

A number of marked differences had been observed between the behaviour of acetylene and that of methylacetylene towards carbonylation in the presence of a palladium iodide catalyst (cf. Chapters 2 & 3). The most notable difference was the relatively low yield of saturated products obtained in the case of the substituted acetylene. It was thus of great interest to compare the properties of another alkyl-substituted acetylene with those of methylacetylene. n-Butylacetylene (hex-1-yne), available as a volatile liquid, was chosen as a suitable higher alkyl-substituted acetylene.

4.2. EXPLORATORY WORK

As with acetylene and methylacetylene, it was considered desirable to designate a set of conditions as 'standard' for the purposes of comparing the results obtained by subsequent variation of the experimental conditions. It was not possible to use the same method for the carbonylation of butylacetylene as had been used for the gaseous acetylenes. Moreover, since high concentrations of methylacetylene had been shown to be undesirable in carbonylation reactions (Chapter 3.2 (iii)), it was proposed to introduce butylacetylene slowly during the reaction, rather than to include all the liquid reactant in the initial reaction mixture.

The conditions chosen as 'standard' were as follows: The catalyst solution was made up, as before, with palladium iodide and sodium iodide dissolved in n-butanol, and carbon monoxide was passed at 3 litres/hour, whilst the reactor was held at 65°C and vigorously stirred. Butylacetylene (10 g) was run in progressively from a dropping funnel over the 7 hour period of the reaction. The yields of products obtained were recorded as percentage yields based on butylacetylene rather than the W/W% of the reaction mixture usually used for the gaseous acetylenes.

When butylacetylene was carbonylated under 'standard' conditions (Rn. 4.1) the colour of the catalyst solution was unchanged. Several products were formed, and they were identified as follows, figures referring to labelled peaks in the chromatogram of the reaction mixture, fig. 4.1.

(a) 'A' was shown by gas chromatography to be unreacted butylacetylene.

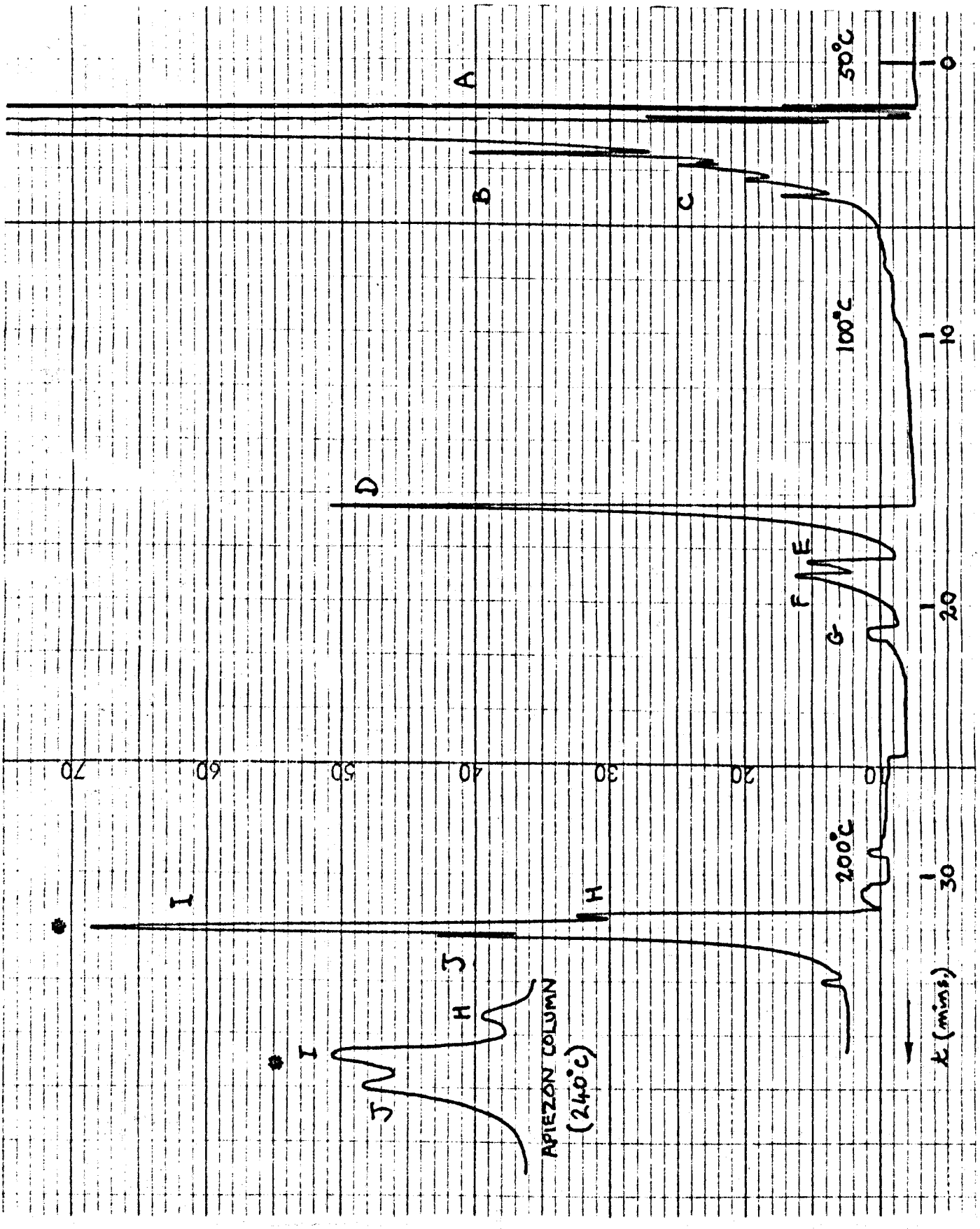
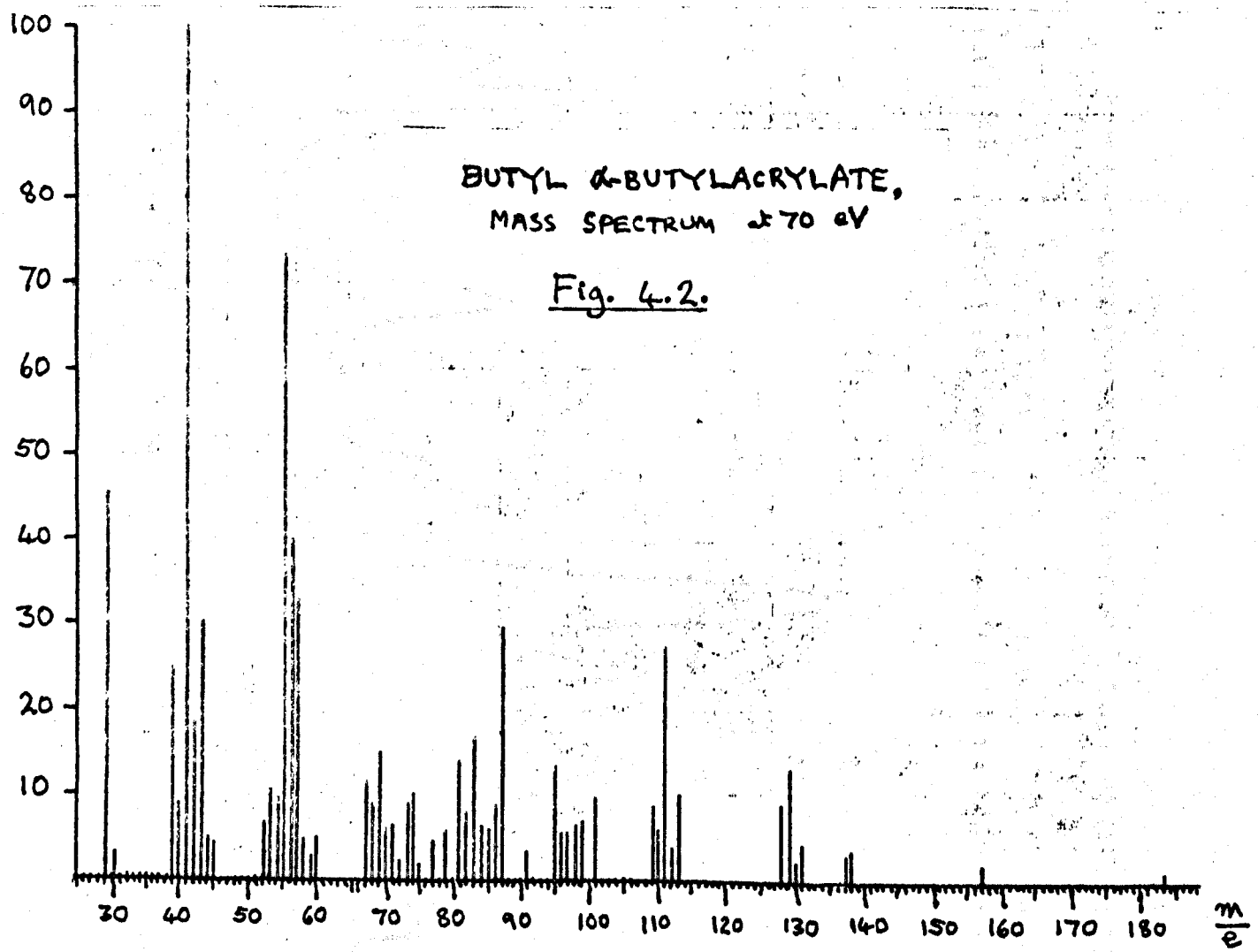


Fig. 4.1. PRODUCTS FROM THE CARBONYLATION OF BUTYLACETYLENE, GAS CHROMATOGRAM ON SILICONE COLUMN



BUTYL α-BUTYLACRYLATE,
MASS SPECTRUM at 70 eV

Fig. 4.2.

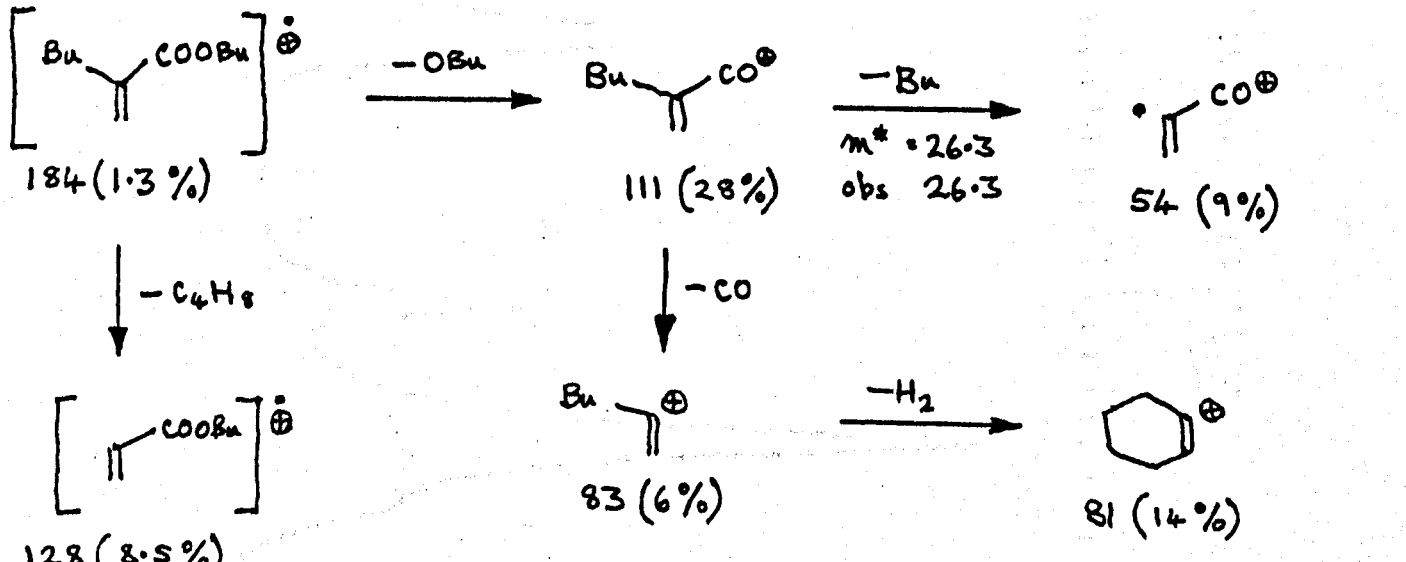


Fig. 4.3. TENTATIVE FRAGMENTATION SCHEME FOR BUTYL α-BUTYLACRYLATE

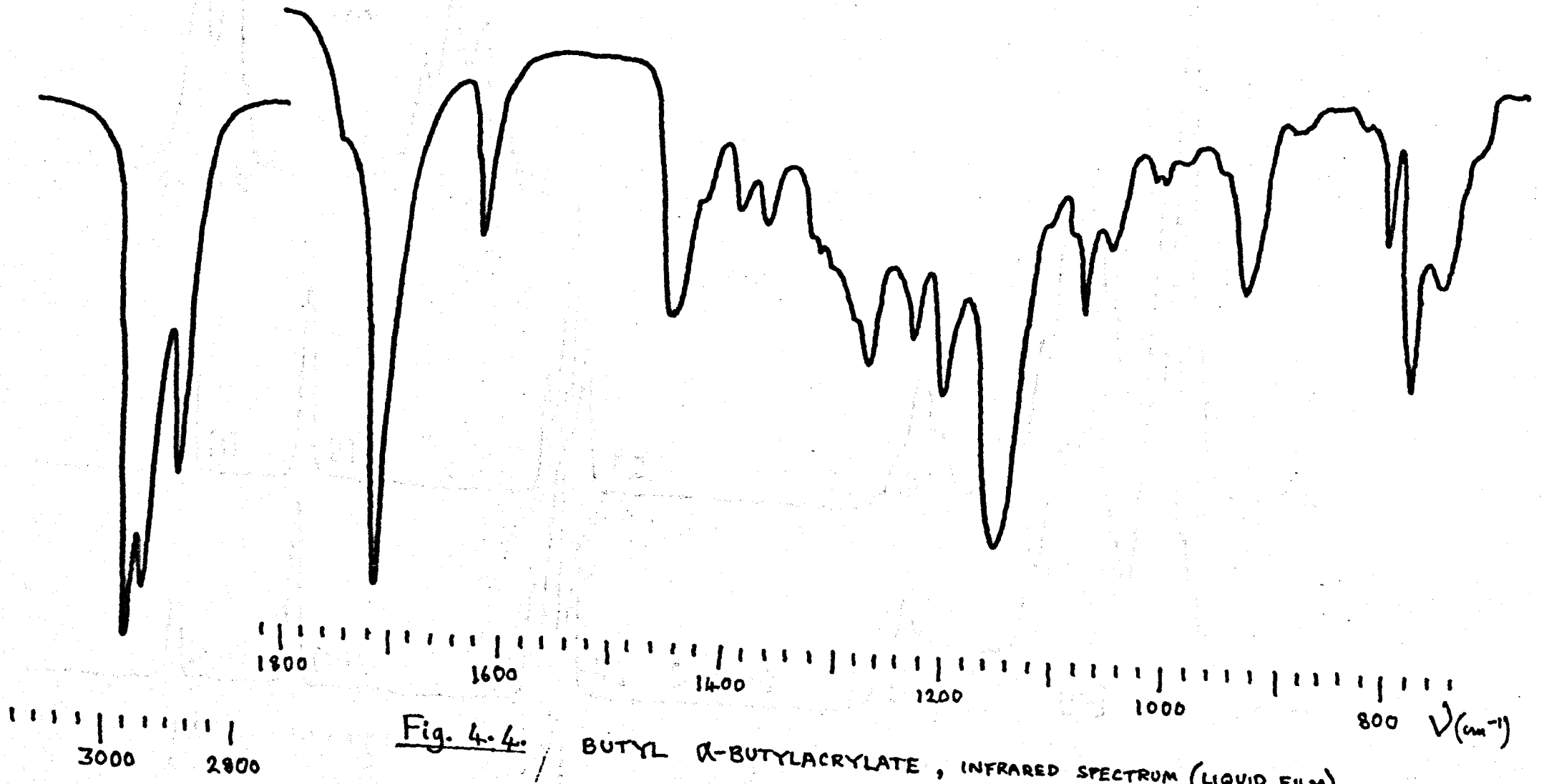


Fig. 4.4. / BUTYL α-BUTYLACRYLATE, INFRARED SPECTRUM (LIQUID FILM)

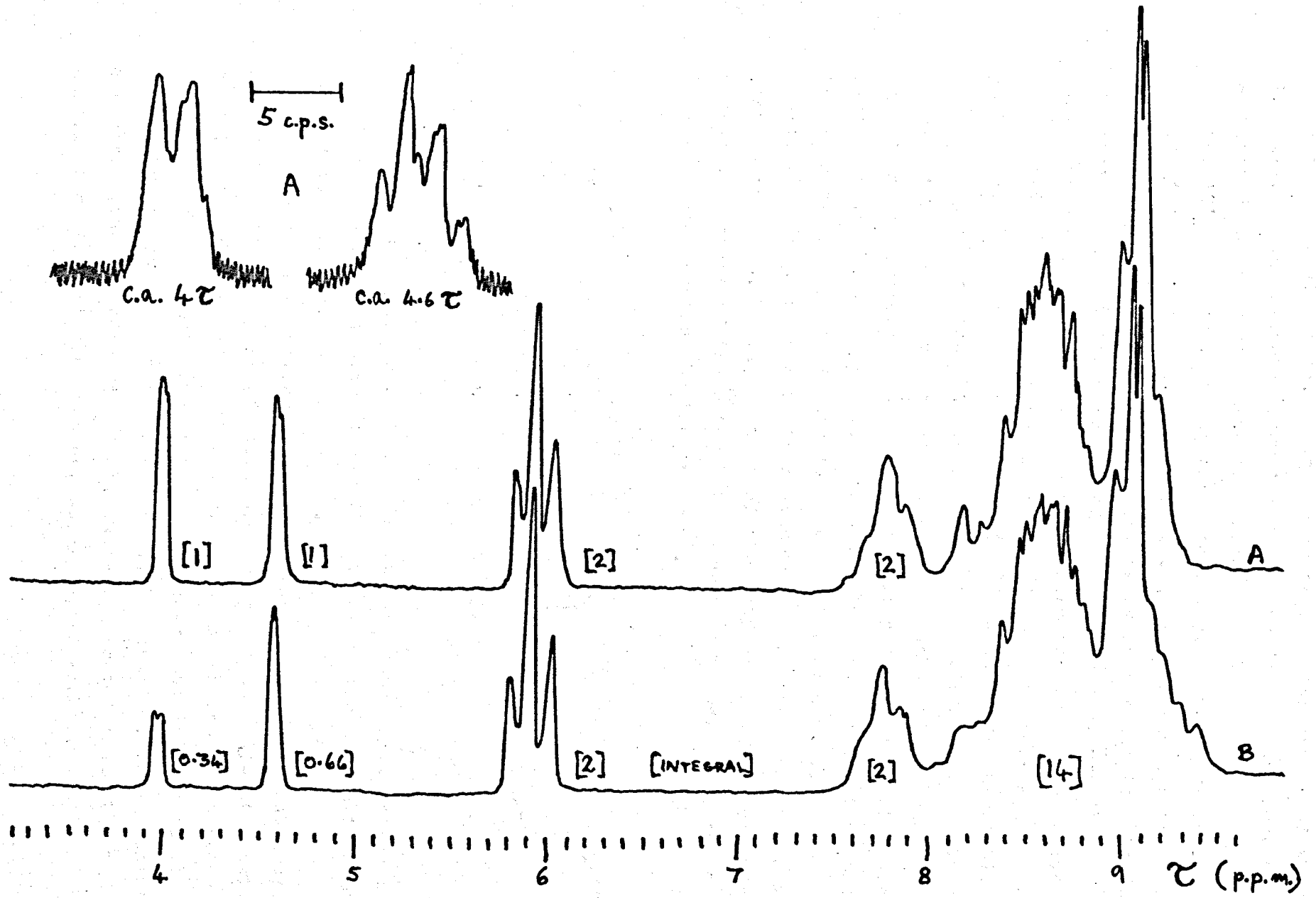
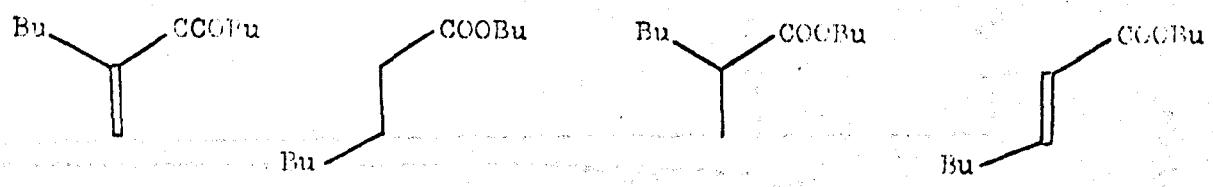


Fig. 4.5. BUTYL α-BUTYLACRYLATE, A – FROM RN. 4.1, B – FROM RN. 4.7 (d, COMPOUND)
N.M.R. SPECTRA, 10 % IN CCl_4

(b) 'B' was shown, by comparison of gas chromatographic retention times, on 3 columns, with those of the authentic compound to be butylmethyl ketone. It was present to the extent of about 1.5% W/W. The ketonic product was not unexpected since acetone was formed in methylacetylene reactions.

(c) 'C' was shown, by gas chromatography, to be butyl iodide.

(d) 'D' was isolated by preparative scale gas chromatography and identified as butyl α-butylacrylate by spectroscopic methods. Its mass spectrum (fig. 4.2) showed a parent peak at $\frac{m}{e}$ = 184 and fragments consistent with the assigned structure. A tentative fragmentation scheme is given in fig. 4.3. The infrared spectrum (fig. 4.4) showed strong bands at ν (cm^{-1}) = 1160 (C-O stretch), 1635 (C=C stretch) and 1710 (C=O stretch). The n.m.r. spectrum showed very strong similarities to that of methacrylate ester, the two methylene protons occurring at virtually the same shift positions, 3.95 and 4.55 τ, with splitting to a doublet and a doublet of doublets respectively. The small coupling constant (1.7 c.p.s.) between the two olefinic protons was further evidence that they constituted a vinylidene group. The protons of the butyl side-chain were partly obscured by those of the ester butyl group, but their presence and identity were revealed by the integral.



'D' 'E' 'F' 'G'

(e) 'E' was shown to be butyl oenanthate (butyl heptanoate) by comparison of its retention times with those of the authentic compound on four gas chromatographic columns.

(f) The reaction mixture was hydrogenated over palladium/charcoal, when gas chromatography (cf. fig. 4.6) revealed that α-butylacrylate ester, 'D', was reduced in quantity, and a corresponding increase in peak 'F' was observed; thus it was concluded that 'F' was butyl α-methylcaproate. A slight increase in peak 'E', butyl oenanthate, and corresponding decrease in 'G', suggested that 'G' was the unsaturated straight chain ester, butyl hept-2-enoate.

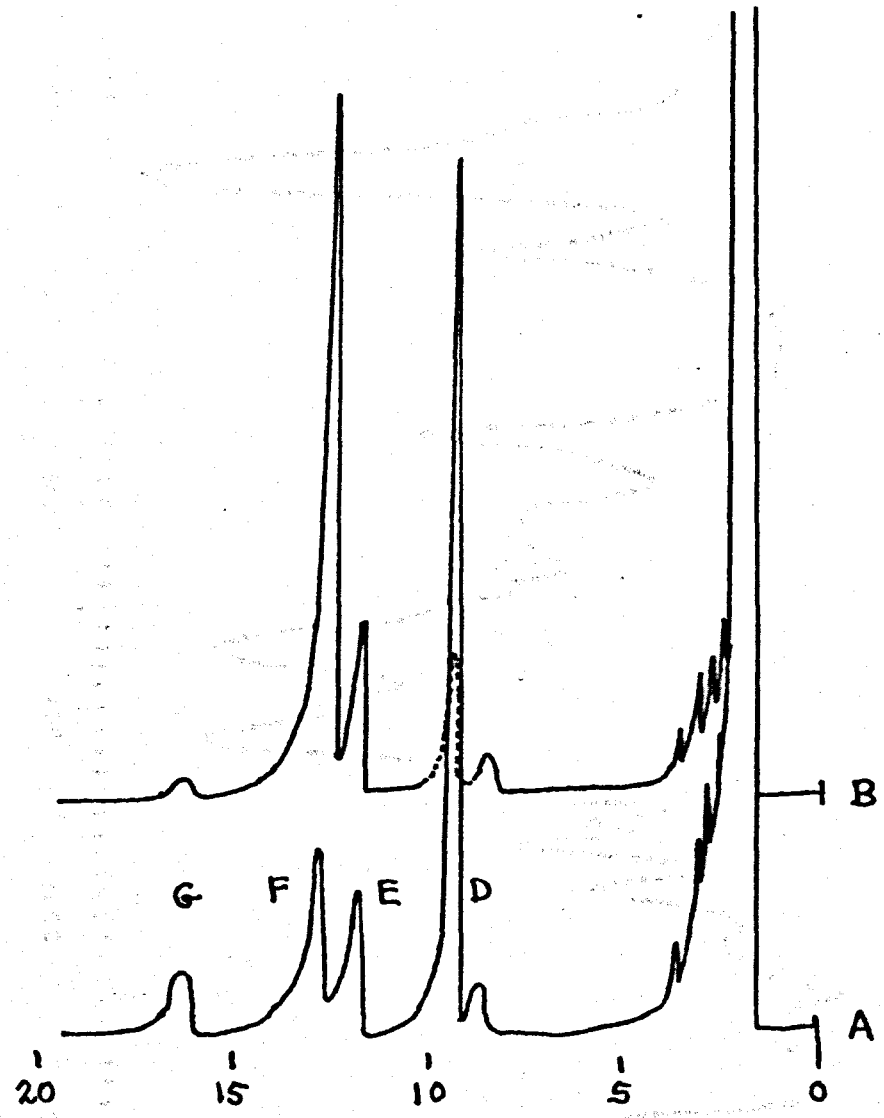


Fig. 4.6. MONOESTERS FROM Rm. 4.1
A – BEFORE, B – AFTER HYDROGENATION
SILICONE COLUMN AT 105°C

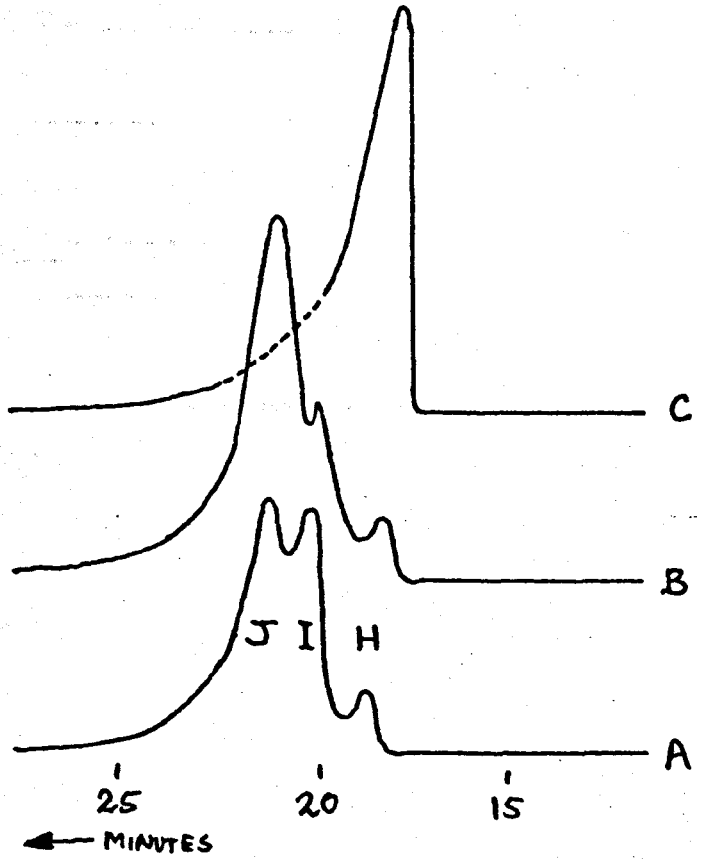
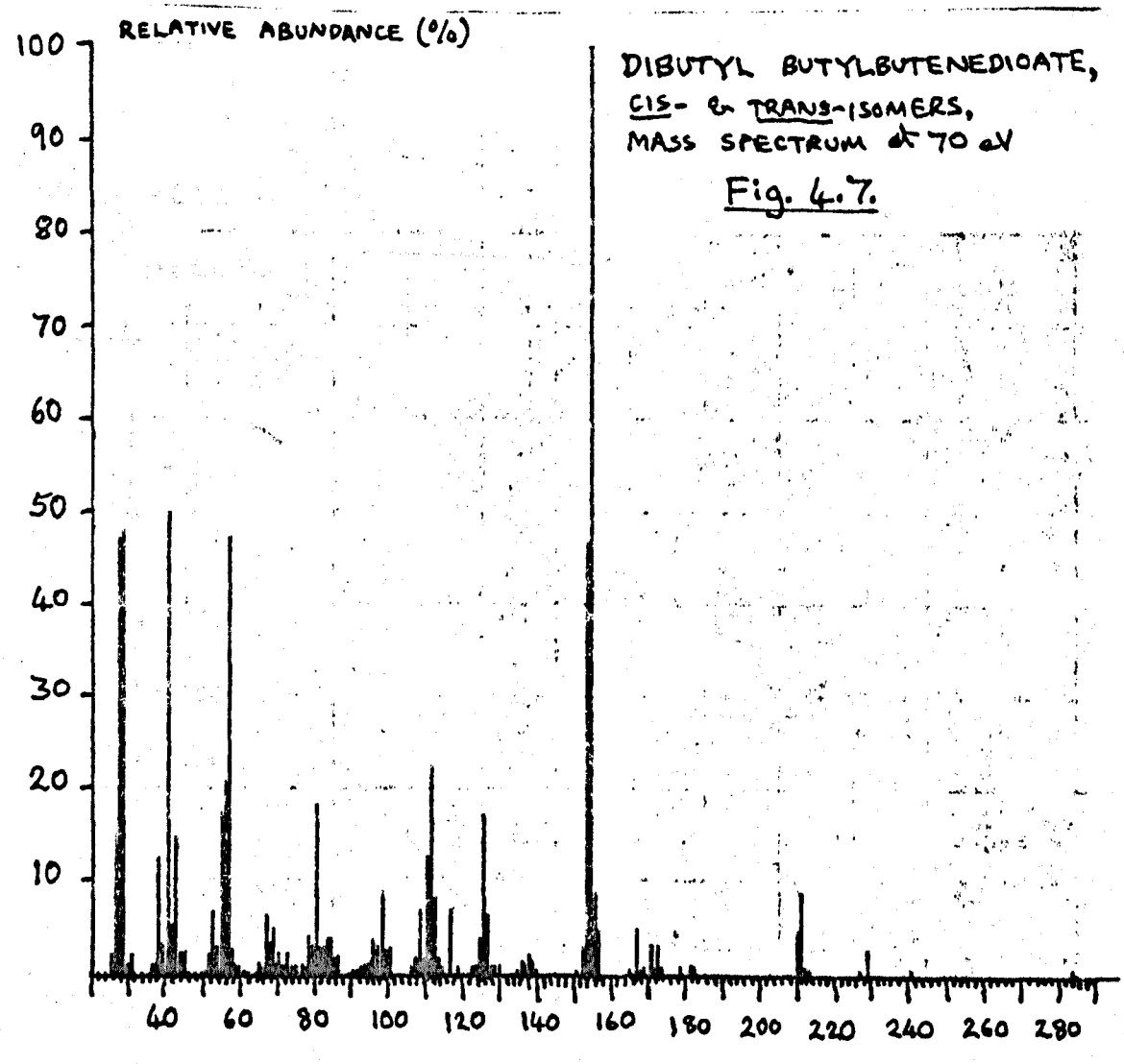


Fig. 4.11. DIESTERS FROM Rm. 4.1
A – AS ISOLATED
B – AFTER EXPOSURE TO NO
C – AFTER HYDROGENATION
APIEZON COLUMN AT 230°C



DIBUTYL BUTYLBUTENEDIOATE,
CIS- & TRANS-ISOMERS,
MASS SPECTRUM at 70 eV

Fig. 4.7.

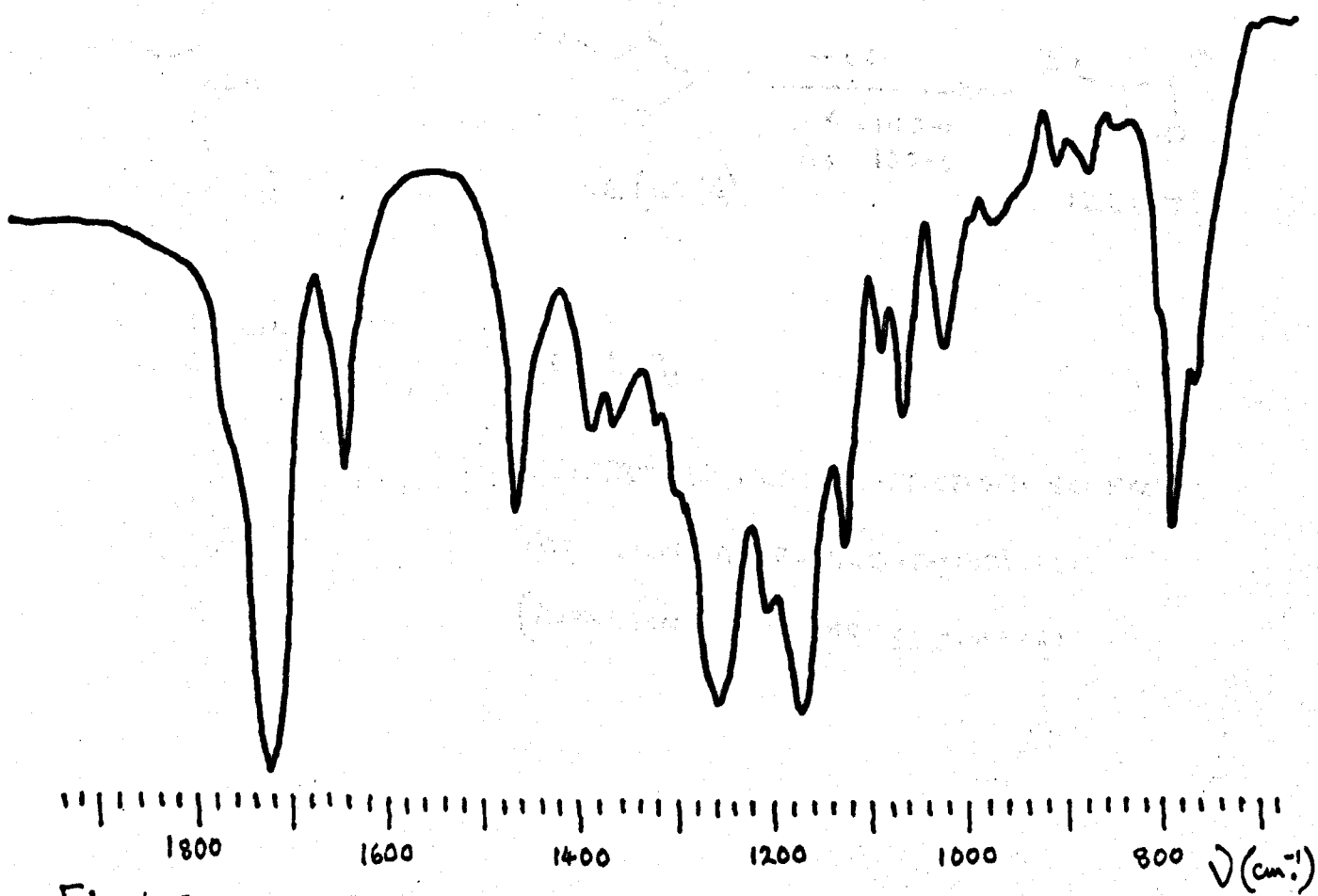


Fig. 4.9. DIBUTYL BUTYLBUTENEDIOATE, CIS- & TRANS- ISOMERS, INFRARED SPECTRUM, KBr Disc.

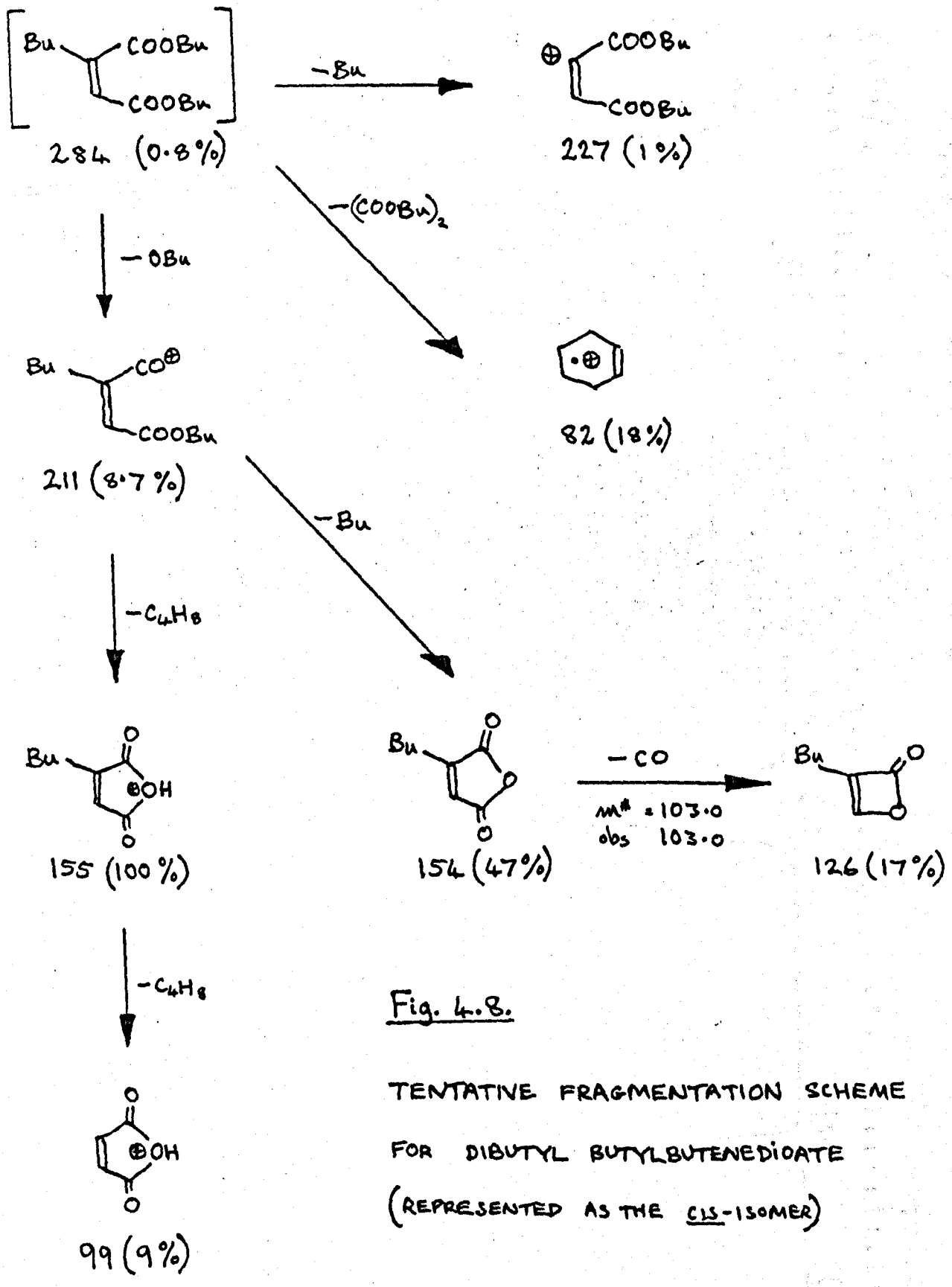


Fig. 4.8.

TENTATIVE FRAGMENTATION SCHEME FOR DIBUTYL BUTYLBUTENEDIOATE (REPRESENTED AS THE cis-ISOMER)

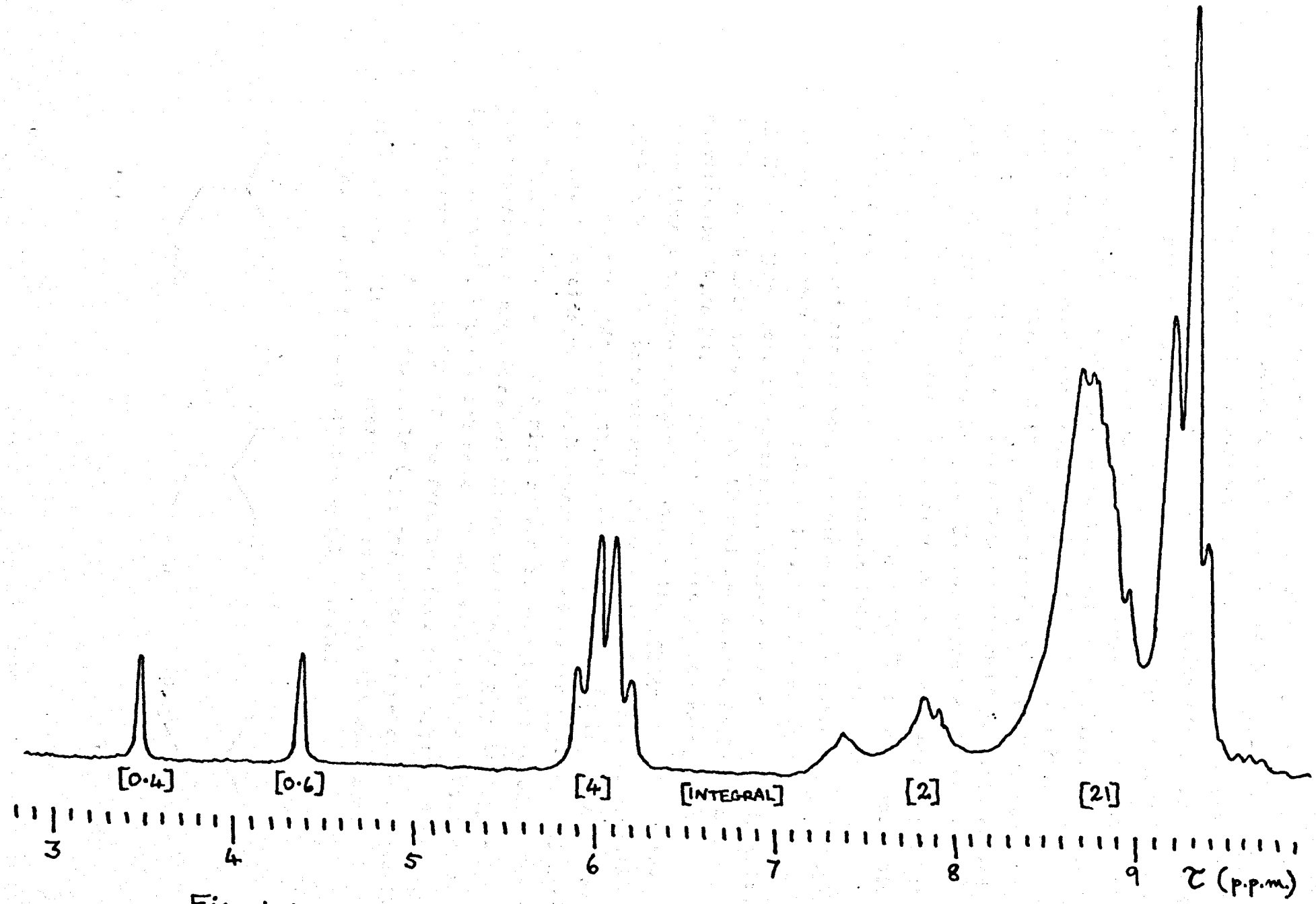
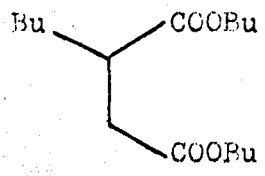


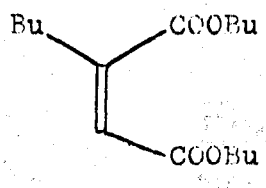
Fig. 4.10. DIBUTYL BUTYLBUTENEDIOATE, N.M.R. SPECTRUM (10 % IN CCl_4)

(g) A fraction was obtained by preparative scale gas chromatography, containing the substances corresponding to peaks 'I' and 'J' and a trace of 'H'. Spectroscopic work showed that the fraction was substantially a mixture of the cis- and trans- isomers of dibutyl butylbutenedioate, i.e. dibutyl butylmaleate and dibutyl butylfumarate. The mass spectrum (fig. 4.7) showed a weak parent ion at $\frac{m}{e} = 284$, and important fragments corresponding to the loss of OBu followed by C_4H_8 and C_4H_9. A tentative fragmentation scheme is given in fig. 4.8. The infrared spectrum (fig. 4.9) showed strong bands at ν (cm^{-1}) = 790, 1175, 1260 (C-O stretch), 1470 (CH_2 scissoring), 1642 (C=C stretch) and 1720 (C=O stretch). The n.m.r. spectrum (fig. 4.10) showed two overlapping triplets at 6.0 τ, corresponding to the four protons of the methylene groups nearest to the oxygens in the butyl ester groups and 23 protons in the 7.2 - 9.4 τ region, assignable as protons of the ester and side-chain butyl groups.

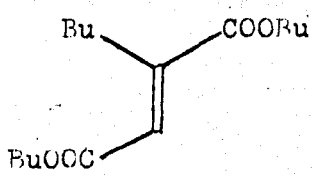
In the olefinic region, two signals, integrating as a total of one proton were visible at 3.45 and 4.35 τ, obviously due to the trans- and cis-esters respectively, being closely similar in shift values to signals observed in dibutyl mesaconate (3.37 τ) and citraconate (4.28 τ). The signals were in the ratio 7:10, suggesting a mixture containing 41% of the trans- and 59% of the cis-ester. Gas chromatography showed the fraction to contain 47% of component 'J' and 51% of component 'I', and it was not therefore possible to decide which peak corresponded to the cis- and which to the trans- isomer. The mixture was exposed to nitric oxide for a short period, a procedure well known to promote cis- to trans- isomerisation[2], after which peak 'J' was very much intensified, to correspond to about 80% of the fraction (cf. fig. 4.11) and the n.m.r. spectrum showed the downfield (trans-) signal to be correspondingly intensified. It was therefore concluded that 'I' was dibutyl butylmaleate and 'J' was dibutyl butylfumarate.



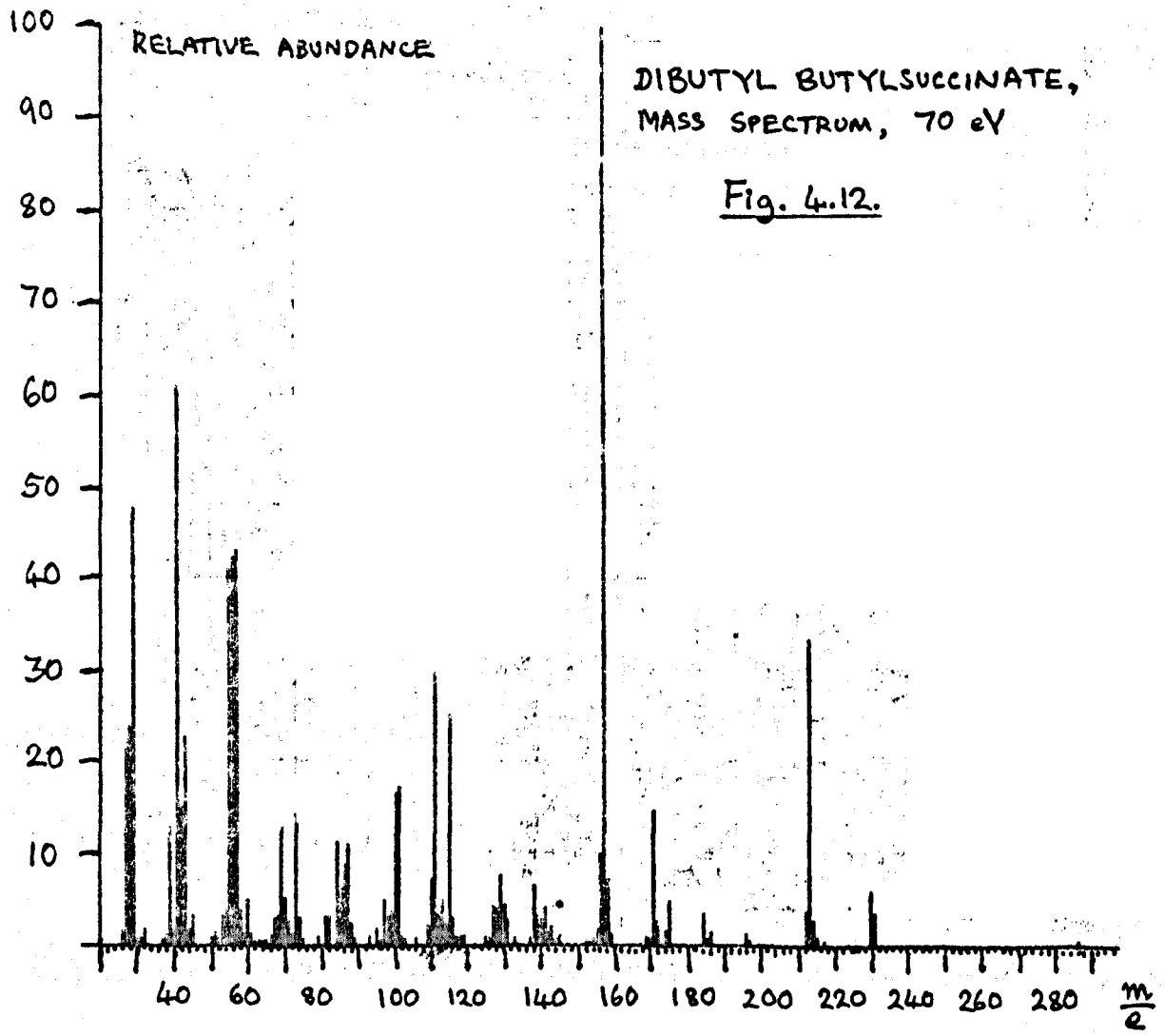
'H'



'I'



'J'



DIBUTYL BUTYLSUCCINATE, MASS SPECTRUM, 70 eV

Fig. 4.12.

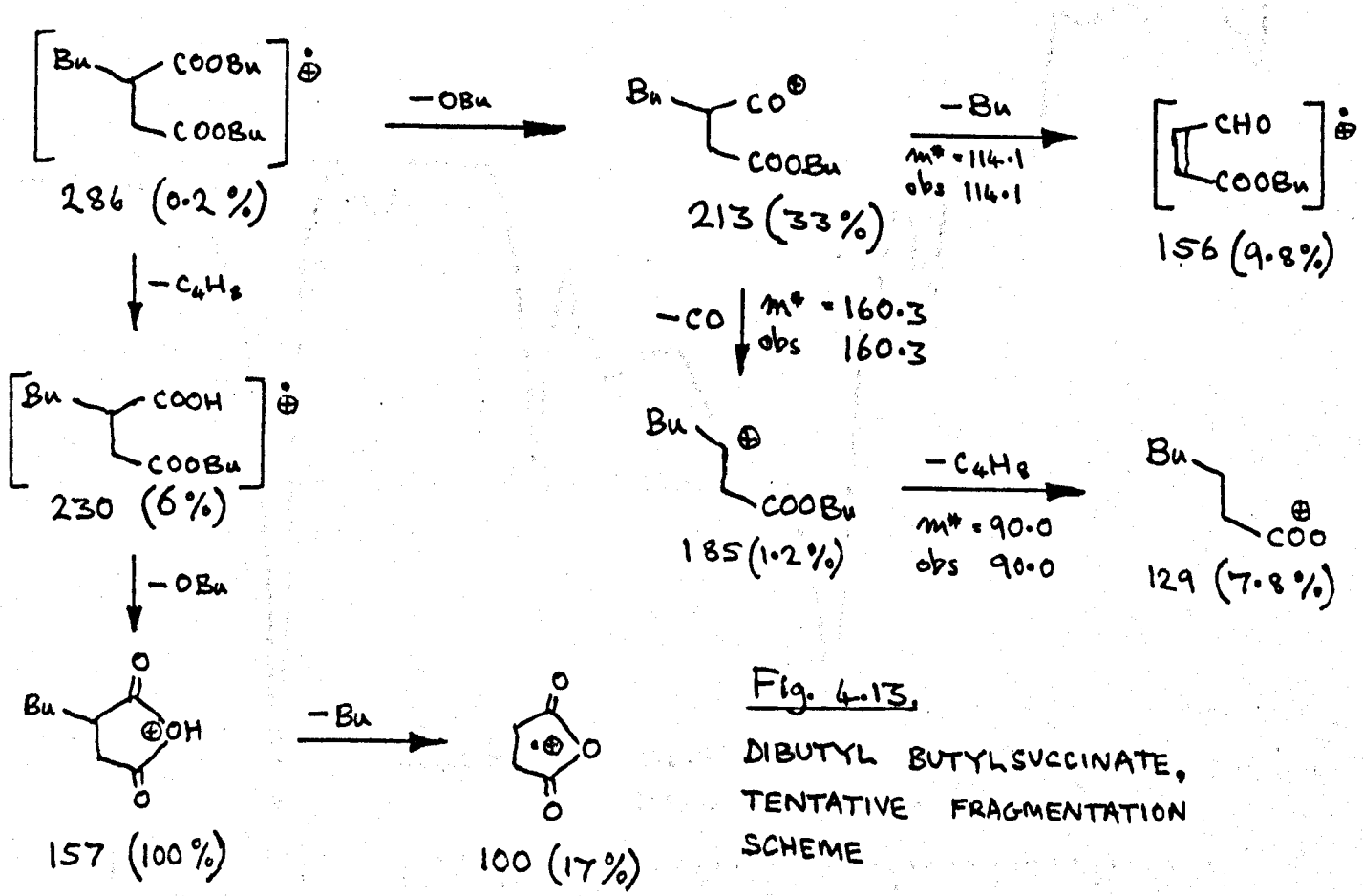


Fig. 4.13.

DIBUTYL BUTYLSUCCINATE, TENTATIVE FRAGMENTATION SCHEME

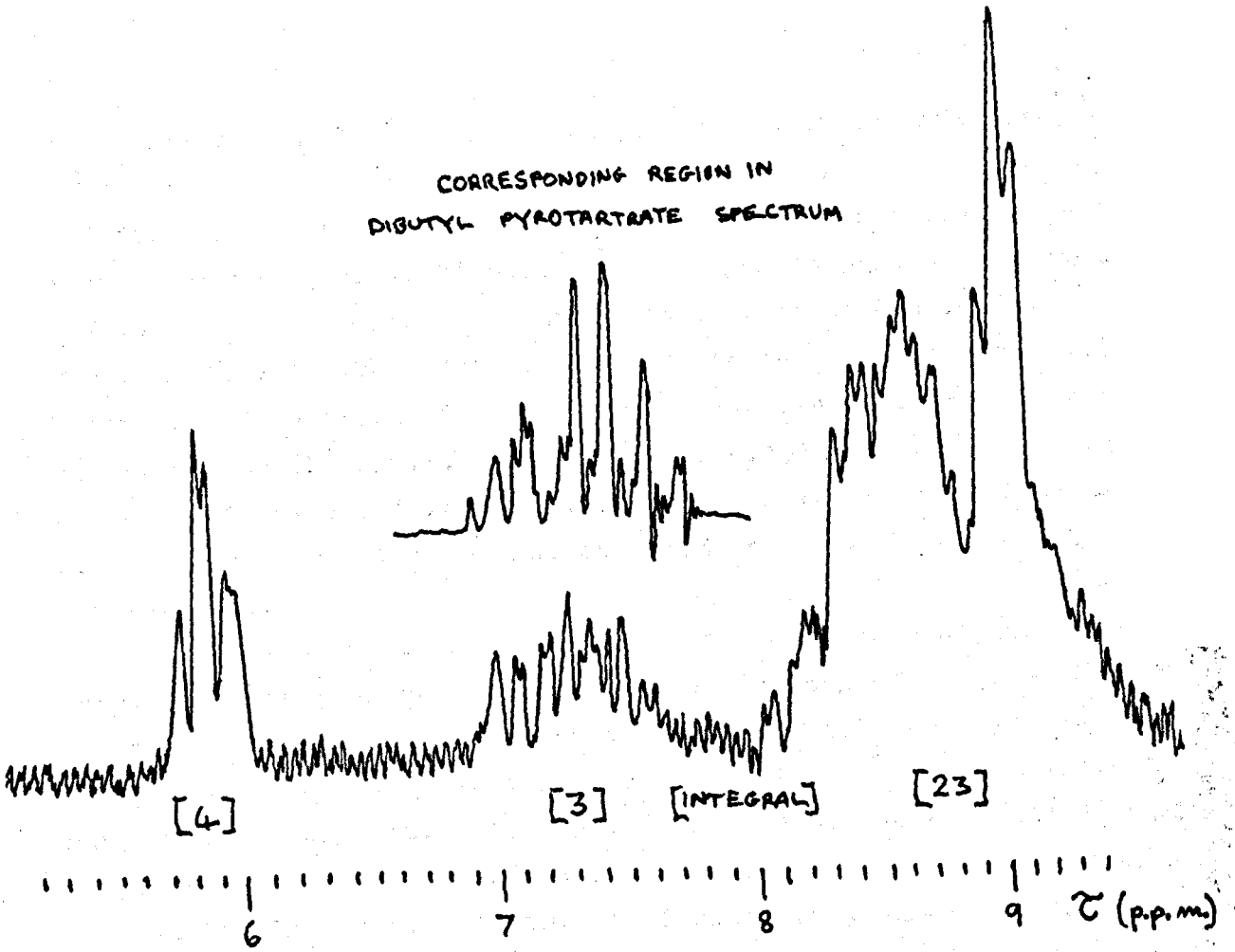


Fig. 4.15. DIBUTYL BUTYLSUCCINATE, N.M.R. SPECTRUM (2% IN $CDCl_3$)

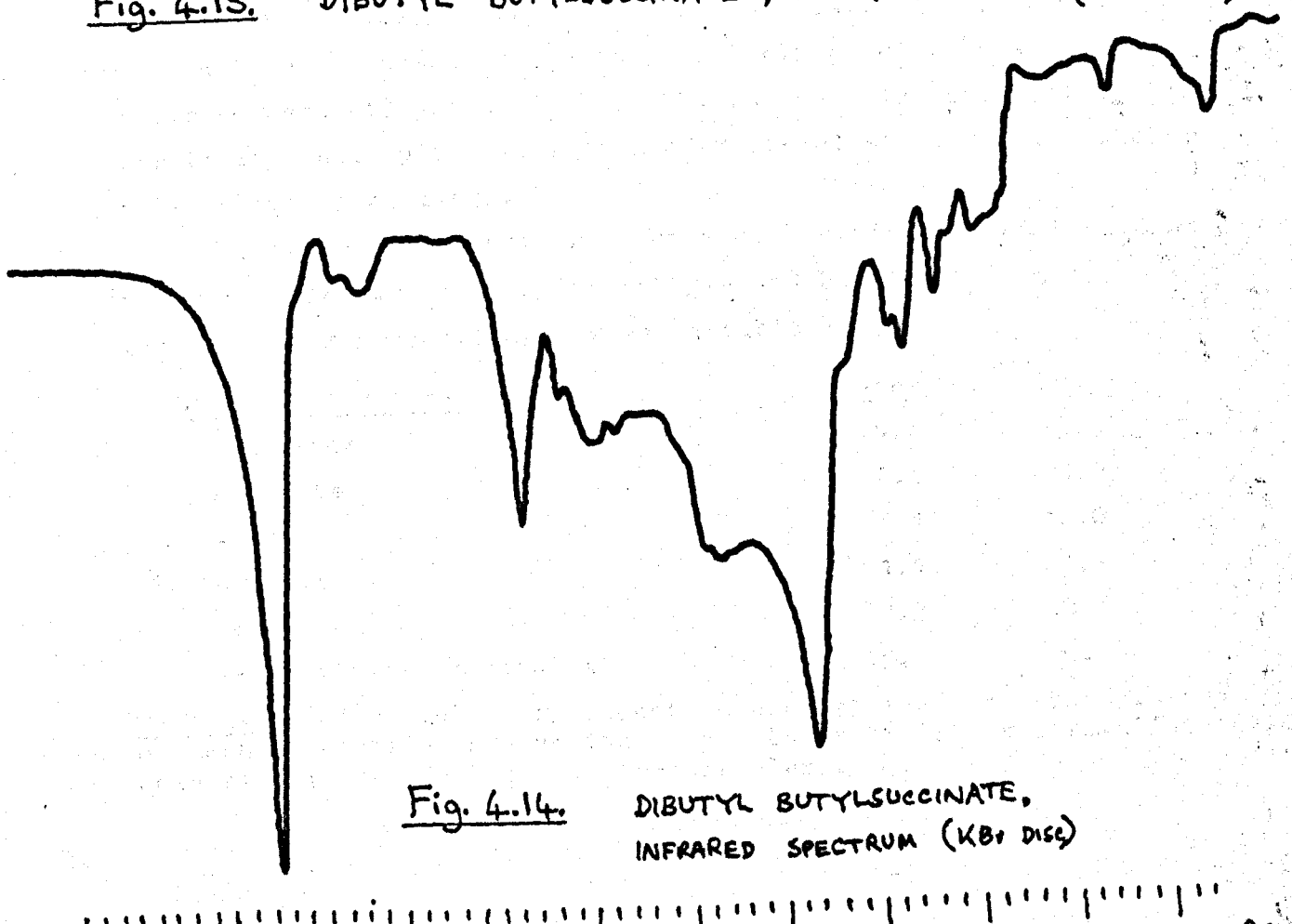


Fig. 4.14. DIBUTYL BUTYLSUCCINATE, INFRARED SPECTRUM (KBr DISC)

Final evidence was obtained by hydrogenation of the mixture over platinum to yield a substance with spectroscopic properties (as follows) which showed it to be dibutyl butylsuccinate. The mass spectrum (fig. 4.12) showed a weak parent peak at $\frac{m}{e} = 286$, and important fragments corresponding to loss of OBu followed by C_4H_8. A tentative fragmentation scheme is given in fig. 4.13. The infrared spectrum (fig. 4.14) was characteristic of a saturated ester, whilst the n.m.r. spectrum (fig. 4.15) did not reveal the presence of any olefinic protons, but a complex multiplet between 6.8 and 7.9 τ similar to that observed in the spectrum of dibutyl pyrotartrate.

(h) 'H' was shown to be identical to the sample of dibutyl butylsuccinate prepared as above, by comparison of the gas chromatograms of the two substances on three columns (cf. fig. 4.11). The yields of products obtained from reaction 4.1 were as follows: butyl α-butylacrylate, 'D', 5.3%; butyl hept-2-eneoate, 'G', 0.5%; butyl α-methylcaproate, 'F', 1.0%; butyl oenanthate, 'E', 0.7%; dibutyl butylmaleate, 'I', 10.9%; dibutyl butylfumarate, 'J', 10.0%; dibutyl butylsuccinate, 'H', 1.1%.

In the following discussion the mono-esters 'G', 'F' and 'E' will not be discussed, since they are only present to a total (fairly constant) yield of about 2%, but an allowance will be made for their contribution to ratios of mono-/diesters and in other relevant considerations.

The range of products was comparable with that obtained from methylacetylene. Yields for methyl- and butylacetylene 'standard' carbonylation products are given in table 4.1:

α-Substituted Ester	Methyl	Butyl
-acrylate	4.8	5.3
-maleate	2.1	10.9
-fumarate	3.1	10.0
-succinate	1.1	1.1
Total	12.2	30.8
Productivity of catalyst	15.3	9.3

Table 4.1: The Yields of Product Esters Obtained by Carbonylation of Methylacetylene and Butylacetylene Under their Respective 'Standard' Conditions; Yields Based on the Acetylene.

It is apparent that the formation of diesters from butylacetylene was favoured, possibly due to the low acetylene concentration.

4.3 THE CARBONYLATION OF BUTYLACETYLENE UNDER VARIOUS CONDITIONS:

(i) Carbonylation in the Presence of Air: The presence of air had been observed to considerably influence the amount of monoester formed in methylacetylene carbonylation reactions (cf. Chapter 3.3 (i)). The effect of air on the carbonylation of butylacetylene was therefore investigated.

A reaction was carried out under the 'standard' conditions, but with air passing at 1 - 1.5 l/h (Rn. 4.2). The overall uptake of butylacetylene was the same as had been observed for the 'standard' reaction, but the amount of monoester was reduced relative to the diester (cf. table 4.2).

(ii) Carbonylation in the Presence of Benzoquinone: The effect on the carbonylation of methylacetylene of large amounts of benzoquinone was to reduce the amount of monoester formed, but small amounts caused an increase in the yield of monoester. It also caused the formation of a new product; butyl β-butoxycrotonate. It was thus of interest to study the behaviour of butylacetylene towards carbonylation in the presence of benzoquinone. A reaction was carried out under the 'standard' conditions, but with benzoquinone present at a level of 5% W/W (Rn. 4.3). A considerable increase in the overall conversion of butylacetylene was observed, but the production of butyl α-butylacrylate was particularly promoted, the yield being more than doubled by comparison with the 'standard' reaction (cf. table 4.2).

The ratio of cis- to trans- diester was also much greater in the presence of benzoquinone than in the 'standard' reaction. A similar observation was made in the case of methylacetylene (cf. Chapter 3.3 (vi)).

A new substance, $I^{SE.30}_{230^\circ} = 1686$, was detected in small amounts in the chromatogram, and was believed to be butyl β-butoxyhept-2-enoate since the analogous β-butoxycrotonate ester was formed in methylacetylene reactions in the presence of benzoquinone (cf. Chapter 3.3 (vi)) and its retention index was consistent with the structure. Attempts to isolate the substance by gas chromatography were not successful.

(iii) Carbonylation in the Presence of Hydrogen Chloride: The presence of hydrogen chloride in acetylene carbonylations greatly influenced the product distribution[1], whereas it had very little effect on the methylacetylene reactions (cf. Chapter 3.4 (ii). The effect of hydrogen chloride on butylacetylene carbonylation reactions was studied by carrying out a reaction (Rn. 4.4) in the presence of hydrogen chloride (10 m mol), but otherwise under 'standard' conditions.

The overall yield of products was similar to that obtained in the 'standard' reaction but the product distribution was different, the yield of monoester being increased, and that of the diester being correspondingly decreased. The result forms a close parallel with the behaviour observed with the corresponding studies on acetylene.

Reaction No	4.1	4.2	4.3	4.4
Additive (amount)	-	Air (1-1.5 l/h)	Quinone (3.1 g)	HCl (10 m mol)
Butyl α-butylacrylate	5.3	3.4	13.5	7.9
Dibutyl butylmaleate	10.9	12.2	16.8	6.9
Dibutyl butylfumarate	10.0	10.0	8.1	8.3
Dibutyl butylsuccinate	1.1	1.3	2.7	1.9
Total	29.3	28.9	43.1	28.0
Monoester/Diester	0.33	0.23	0.56	0.64

Table 4.2: The Yields of Product Esters Obtained by Carrying Out the Carbonylation of Butylacetylene in the Presence of Various Additives. % Yields Based on Butylacetylene

(iv) Carbonylation in the Presence of a High Concentration of Butylacetylene:

Since a rather low concentration of butylacetylene had been used in the above reactions, it was of interest to investigate a situation where the acetylene was present in high concentration. Accordingly reaction 4.5 was carried out.

A catalyst solution containing about 25% W/W of butylacetylene was vigorously stirred under an atmosphere of carbon monoxide for 7 hours, whilst held at a temperature of 40°C, some 25% lower than usual, dictated by the boiling point of butylacetylene. The colour of the solution changed after about two hours to olive green,

reminiscent of the greenish yellow colour observed in methylacetylene reactions. Column chromatography of the reaction mixture yielded a yellow substance, which left a residue of palladium on ignition. However, gas chromatography and infrared spectroscopy of the yellow material showed large amounts of esters and no useful information could be obtained about the complex. The colour reverted to wine red after about 48 hours. The yield of α-butylacrylate ester showed about a sevenfold increase by comparison with the 'standard' reaction (cf. table 4.3), but the diesters and the other monoesters were produced in about the same yields as in the 'standard' reaction.

The increase in the relative amount of monoester was expected on two counts. Firstly, a lower temperature was observed to increase the yield of methacrylate ester from methylacetylene carbonylations (cf. Chapter 3.2 (v)), and secondly a high concentration of butylacetylene relative to carbon monoxide would be expected to favour rapid formation of monoester rather than the diester, notwithstanding the previous observation[1] that the availability of carbon monoxide for reaction exercised a controlling role in acetylene carbonylations.

(v) Carbonylation Under an Elevated Carbon Monoxide Pressure: Work on the carbonylation of disubstituted acetylenes showed marked differences from the behaviour of the monosubstituted acetylenes. Thus it proved necessary to employ elevated pressures to achieve any reaction, and the products obtained included lactones as well as esters (cf. Chapters 6.3 (i) and 7.3 (ii)). It was therefore of interest to observe the effect of elevated pressures and temperatures on the carbonylation of butylacetylene, in particular, evidence of the formation of lactones was sought.

A reaction (Rn. 4.6) was carried out under a carbon monoxide pressure of 100 atmospheres and a temperature of 90°C, but otherwise in the same way as reaction 4.5 above.

At the end of the reaction, the colour of the solution was almost completely discharged, and a precipitate of palladium was present. Gas chromatographic analysis showed the usual products in good yield (totalling about 90%), and no new substances. No solid organic material could be recovered from the residue in the way that tetramethylbifurandione had been obtained from the dimethylacetylene

reaction mixture (cf. Chapter 6.3 (i)). It was concluded that no significant amounts of lactones were formed in the reaction. By comparison with reaction 4.5, the yields of diesters were greatly increased (cf. table 4.3) as would be expected in view of the much greater concentration of carbon monoxide in the solution. The higher temperature used may also have influenced the product spectrum.

Reaction No	4.1	4.5	4.6
Butylacetylene (W/W%)	-	25	25
Carbon Monoxide (atmos.)	1	1	100
Butyl α-butylacrylate	5.3	36.0	23.0
Dibutyl butylmaleate	10.9	11.5	30.0
Dibutyl butylfumarate	10.0	11.5	32.0
Dibutyl butylsuccinate	1.1	2.0	1.7
Total	29.3	63.0	88.7

Table 4.3: The Yields of Product Esters Obtained by the Carbonylation of Butylacetylene at Various Concentrations and Carbon Monoxide Pressures. % Yields Based on Butylacetylene

4.4 MISCELLANEOUS REACTIONS DESIGNED TO ELUCIDATE ASPECTS OF THE MECHANISM OF CARBONYLATION

(i) The Reaction of Butylacetylene with the Catalyst Solution:

Since an unstable complex was apparently formed between the acetylene and catalyst during carbonylation reactions (Chapter 4.3 (iv)) attempts were made to reproduce such behaviour with butylacetylene under controlled conditions.

An aliquot of catalyst solution was added to a solution of butylacetylene in butanol such as to produce a solution 8×10^{-5} molar with respect to sodium tetraiodopalladate(II). Ultraviolet spectra of the mixture were run at intervals. Over a period of several hours, the characteristic Na_2PdI_4 band at λ_{MAX} = 344 n.m. disappeared, whilst a very broad absorption at lower wavelength developed (cf. fig. 4.16). The development of the latter band occurred during the later part of the reaction, whilst the band at 344 n.m. disappeared in the first few hours, suggesting a two step process, such as complex formation and subsequent breakdown.

In a second experiment, a concentrated catalyst solution was shaken

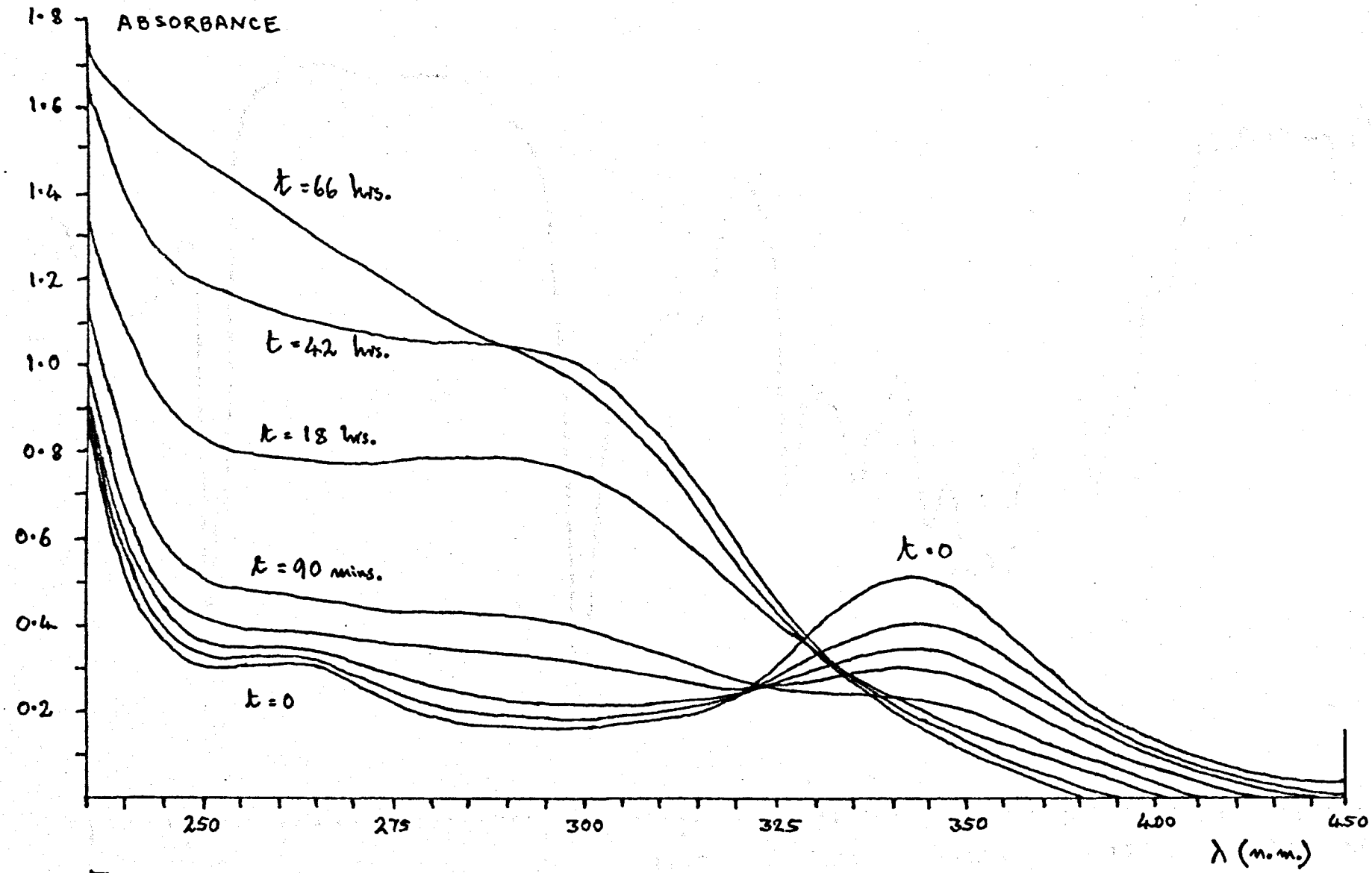


Fig 4.16. MIXTURE OF BUTYLACETYLENE AND SODIUM TETRAIODOPALLADATE (II) IN BUTANOL AFTER 0, 20, 40, 70 & 90 mins, 18, 42 & 66 hrs., ULTRAVIOLET SPECTRUM

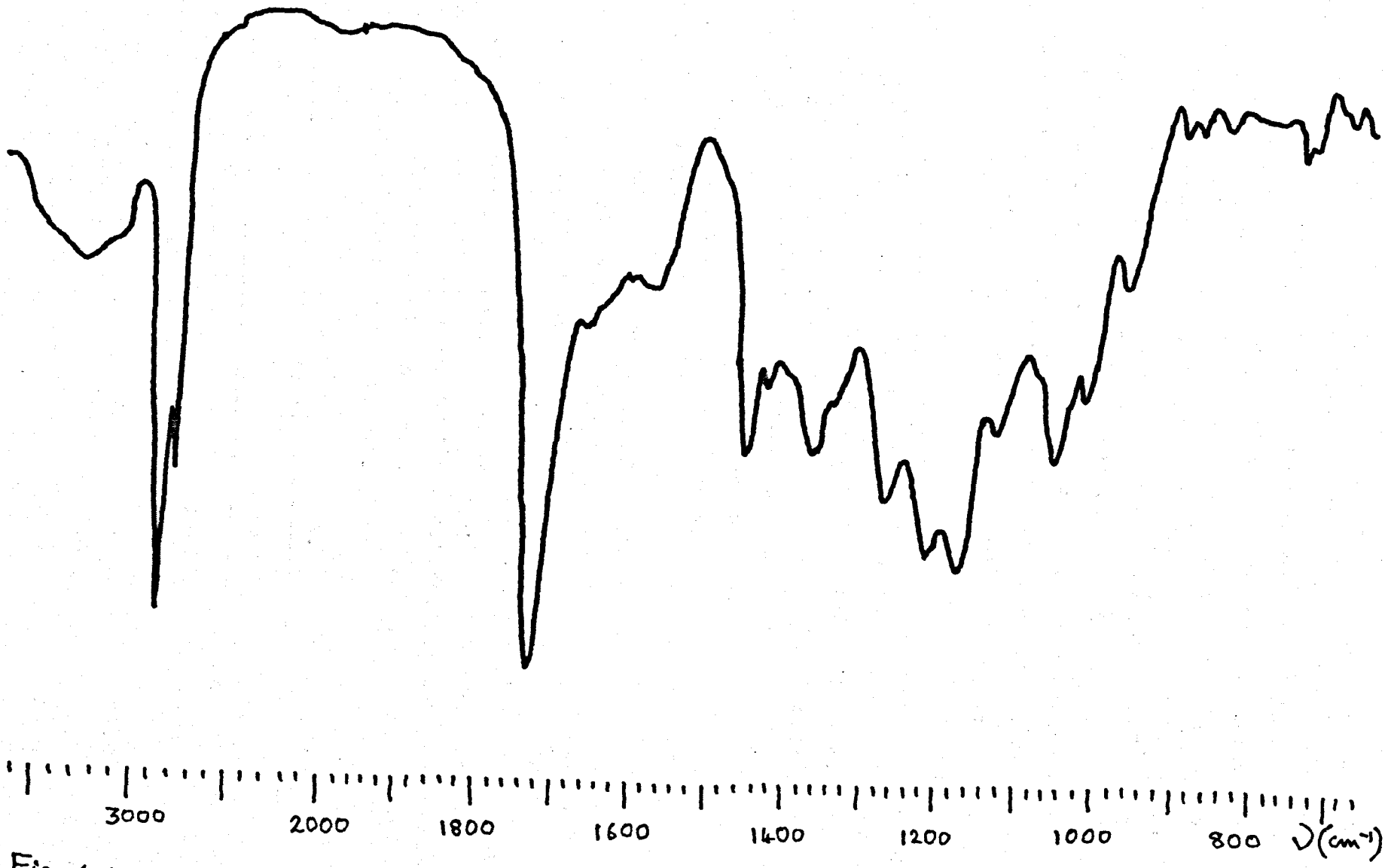


Fig. 4.17. PRODUCT FROM THE INTERACTION OF BUTYLACETYLENE AND SODIUM TETRAIODOPALLADATE(II), INFRARED SPECTRUM, (KBr DISC)

with butylacetylene for a few hours. The wine red colour of the solution was discharged and an intense yellow colour was formed whilst palladium was deposited. The 'pH' of the solution was found to have decreased from 6 to 4 as measured with universal indicator paper. A yellow oil not containing palladium was observed by thin layer chromatography and isolated by column chromatography. The infrared spectrum of the product (fig. 4.17) showed the presence of aliphatic protons (ν = 2900 cm^{-1}) and a carbonyl group (1730 cm^{-1}). The n.m.r. spectrum showed only a complex multiplet in the aliphatic region. The spectroscopic information was insufficient to permit an identification of the oil which may possibly have been the decomposition product of an unstable complex.

(ii) Carbonylation in Butanol-O-d: Experiments with both acetylene (C.B.Lines[1] and Chapter 2.4 (x)) and methylacetylene (Chapter 3.5 (iv)) in butanol-O-d have shown a number of features in common. Thus monoester formation was inhibited relative to 'standard' reactions, whilst saturated diester formation was somewhat enhanced. Also the deuterium label was incorporated in corresponding positions in the product esters. The carbonylation of butylacetylene was accordingly investigated.

Having established by means of an n.m.r. experiment, that significant exchange of the acetylene proton would not occur, the carbonylation reaction was carried out under exactly the same conditions as had been used for reaction 4.5, except that the deutero-solvent was used. As with reaction 4.5, the wine-red colour changed to an olive green during the reaction, but was restored within two days. The yields of each product are given in table 4.4 and compared with those of reaction 4.5.

Reaction No	4.5	4.7
Solvent	BuOH	BuOD
Butyl α-butylacrylate	36.0	27.0
Dibutyl butylmaleate	11.5	7.8
Dibutyl butylfumarate	11.5	10.9
Dibutyl butylsuccinate	2.0	0.8
Total	63.0	48.5
Monoester/Diester	1.52	1.43

Table 4.4: The Yields of Products Obtained by the Carbonylation of Butylacetylene in Butanol-O-d, Compared with Those Obtained in Butanol. % Yields Based on Butylacetylene

The relative yield of monoester was reduced, and the yield of saturated diester was considerably reduced relative to reaction 4.5.

Butyl α-butylacrylate was isolated from the reaction mixture by preparative scale gas chromatography. The n.m.r. spectrum (fig. 4.5) showed a total of one proton in the vinylidene positions, 0.34 H cis- to the ester grouping and 0.66 H trans-. The finding was in qualitative agreement with those from acetylene and methylacetylene, the BuOOC- and D moieties showing a 2:1 preference for cis- addition to the acetylene. The unsaturated diesters were isolated as a single fraction by preparative scale gas chromatography, and shown to have n.m.r. and mass spectra identical to those of the sample isolated from 4.1, i.e. no deuterium had been incorporated, again in agreement with the results obtained from acetylene and methylacetylene.

(iii) Carbonylation in the Presence of Butyl Acrylate: Since a coupled product, dibutyl 3-methyl-cis-hex-2-enedioate had been obtained from methylacetylene and butyl acrylate during carbonylation (Chapter 3.5 (v)), and hexenedioates were detected in acetylene reaction mixtures, presumably arising in a similar way (Chapter 2.3 (v)), it was of interest to observe whether the generality of the reaction extended to butylacetylene.

Reaction 4.8 was carried out under 'standard' conditions, but with air passing at 1-1.5 l/h, and butyl acrylate (10.0 g) added progressively throughout the reaction together with the butylacetylene. Rather better yields of the expected products were obtained than from a 'standard' reaction with air passing. The yields are given in table 4.5.

Reaction No	4.2	4.8
Butyl α-butylacrylate	3.4	5.5
Dibutyl butylmaleate	12.2	15.2
Dibutyl butylfumarate	10.0	15.1
Dibutyl butylsuccinate	1.3	2.3
Dibutyl 3-butylhex-2-enedioate	-	8.2
Total	28.9	48.3

Table 4.5: The Yields of Product Esters Obtained by the Carbonylation of Butylacetylene in the Presence of Air & Butyl Acrylate Compared with a Reaction with No Butyl Acrylate Present. % Yields Based on Butylacetylene

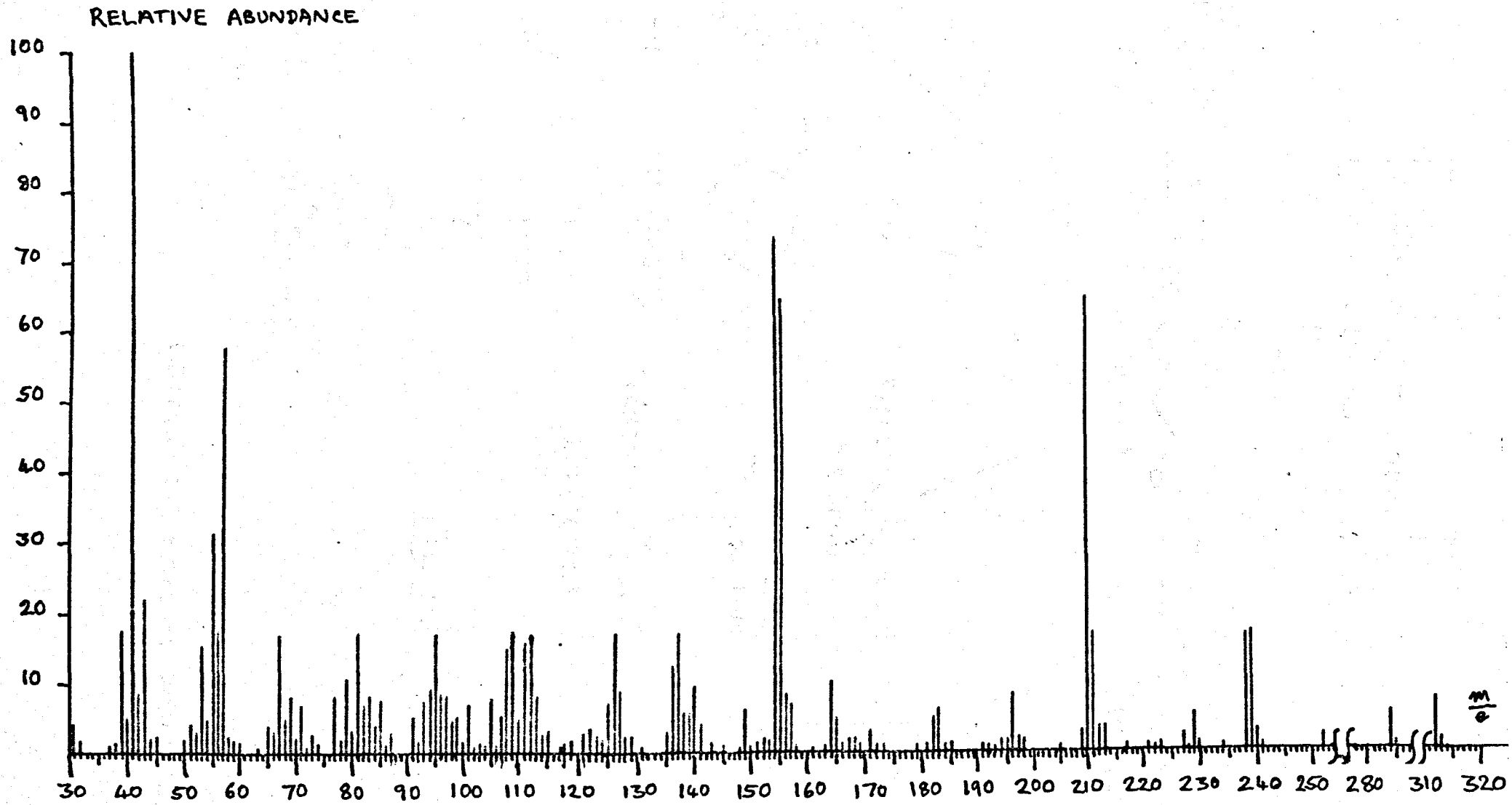


Fig. 4.18. DIBUTYL 3-BUTYLHEX-2-ENEDIOATE, MASS SPECTRUM at 70 eV

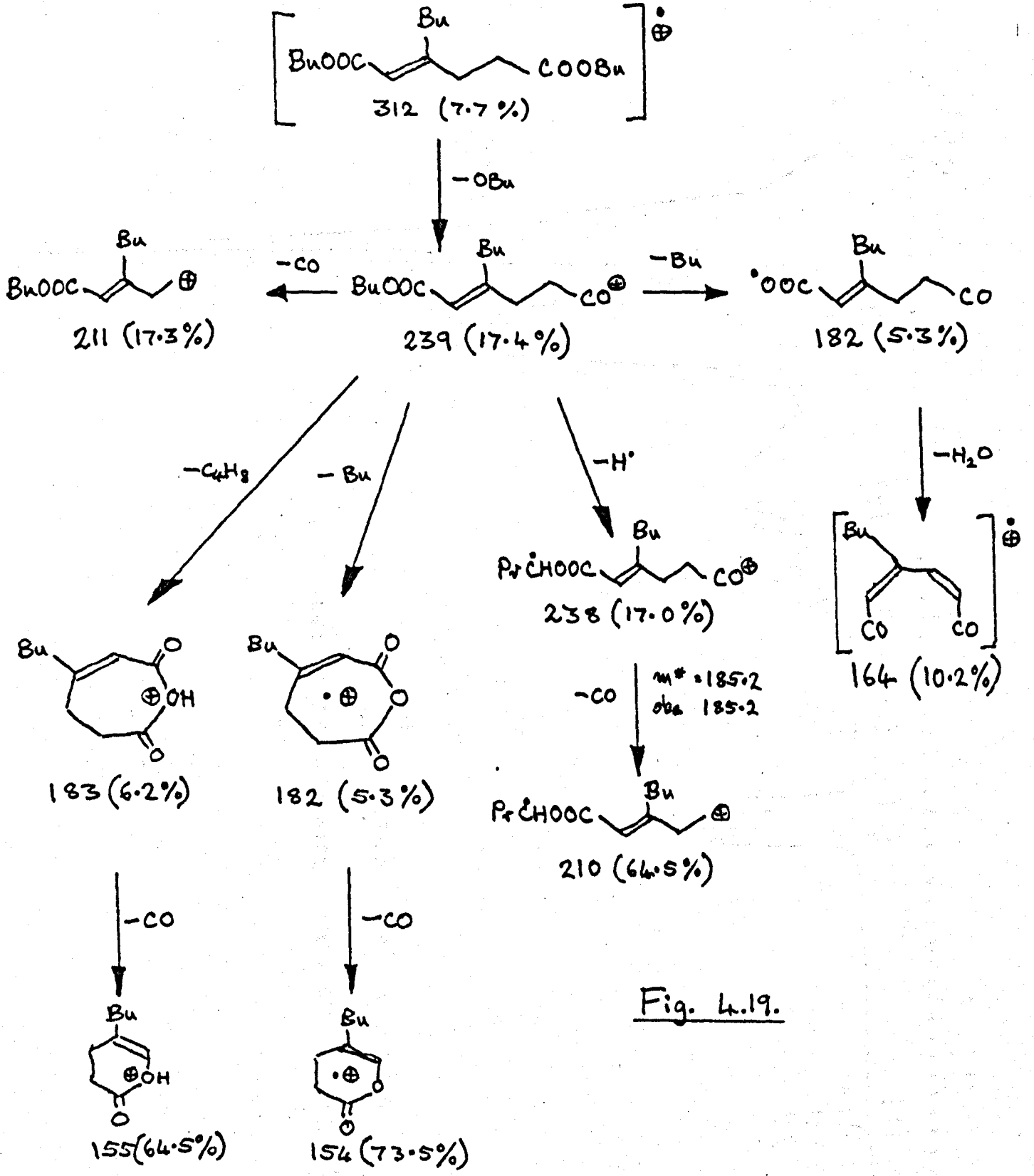
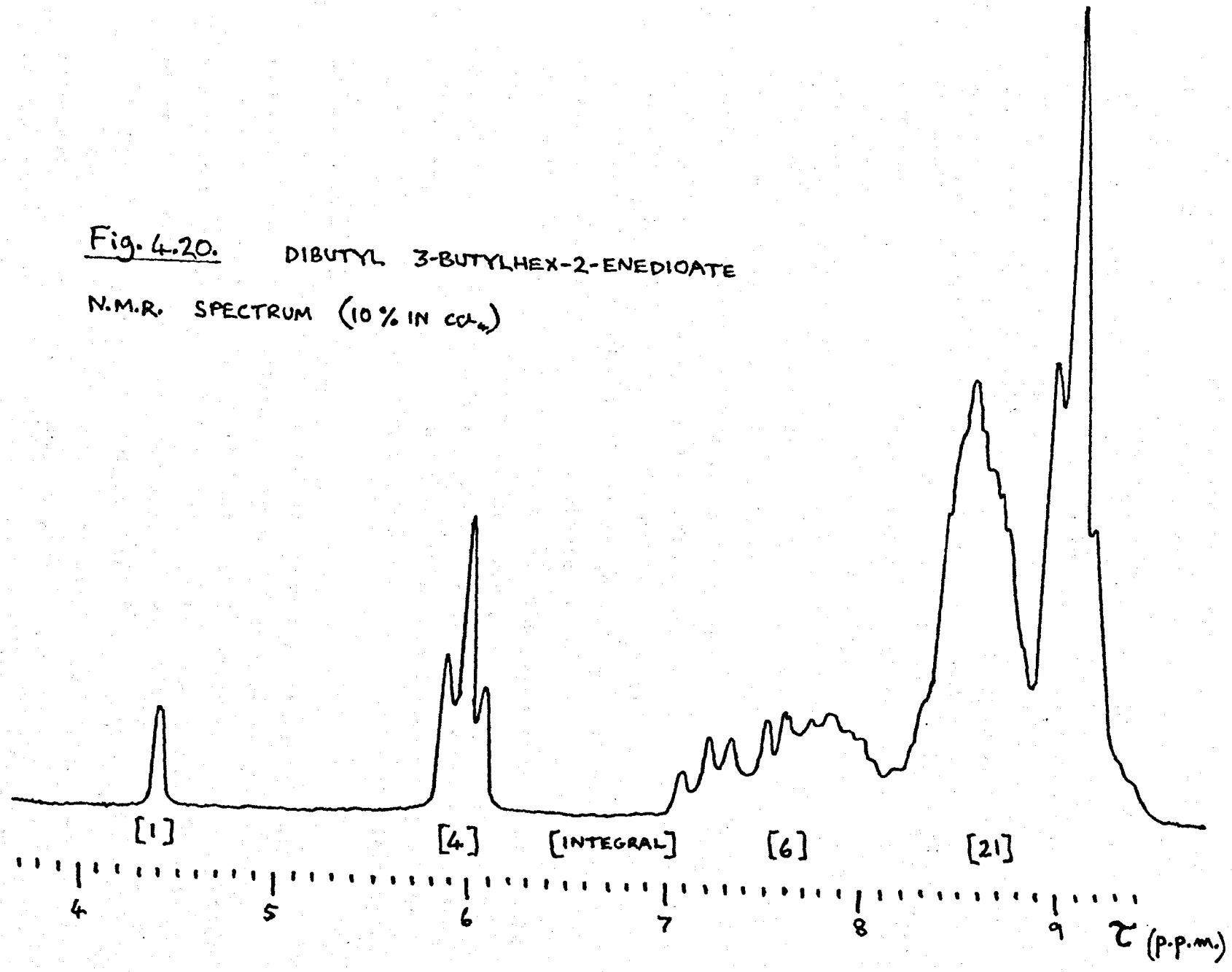


Fig. 4.19.

DIBUTYL 3-BUTYLHEX-2-ENEDIOATE, TENTATIVE FRAGMENTATION SCHEME

Fig. 4.20. DIBUTYL 3-BUTYLHEX-2-ENEDIOATE

N.M.R. SPECTRUM (10 % IN CCl_4)



In addition, two new peaks were observed, one representing about 0.5 g, and the other representing about 2.8 g. The latter was isolated by preparative scale gas chromatography and shown to be dibutyl 3-butylhex-2-enedioate by spectroscopic methods. The yield based on butylacetylene was 8.2%.

The mass spectrum, fig. 4.18, showed a parent ion of $\frac{m}{e}$ = 312.2292, $C_{18}H_{32}O_4$ requires 312.2300. The most important fragments could be attributed to the sequential loss of OBu, CO, C_4H_8 &c. from the diester, and loss of a butyl group with charge retention by the butyl group, and its subsequent breakdown. A tentative fragmentation scheme is given in fig. 4.19. The n.m.r. spectrum of the substance (fig. 4.5) showed it to be dibutyl 3-butylhex-2-enedioate. The methylene groups appeared as two distorted triplets, at 7.18 and 7.59 τ, indicating the marked asymmetry of the molecule, the upfield signal being partly overlain by the α-methylene group of the butyl side-chain, the rest of which augmented the integral of the ester butyl groups to a total of 21 protons (in addition to the downfield triplet of 4 protons). The olefinic signal appeared as a singlet at 4.39 τ , integrating as one proton and revealing the presence of a substituent on the double bond, whereas its singlet character showed that the substituent was in the 3-position, since a proton in the 3-position would couple strongly with the adjacent methylene group. The spectrum showed marked similarities to that of dibutyl 3-methyl-cis-hex-2-enedioate (fig. 3.27), but it was not possible to assign the geometry of the butyl-substituted compound on the basis of the available information.

4.5 SUMMARY AND CONCLUSIONS

Subject to differences resulting from the manner in which it was introduced into reactions, butylacetylene appeared to behave towards carbonylation very much like methylacetylene. Thus parallel series of products were obtained from the two acetylenes, and both showed a tendency (in which they differed from acetylene) to produce only small amounts of saturated products.

The presence of air caused a decrease in the relative amount of monoester formed from butylacetylene, whereas a small amount of benzoquinone increased it, as had been the case in methylacetylene reactions. The presence of hydrogen chloride increased the amount

of monoester formed, in which respect butylacetylene bore more resemblance to acetylene than methylacetylene.

In common with the other acetylenes, butylacetylene apparently formed an unstable complex with the palladium catalyst, which decomposed to yield an intractable oily material as in the case of methylacetylene. The reaction proceeded at a sufficient rate to destroy the catalyst during a carbonylation reaction (provided that a high enough concentration of the acetylene was available).

Deuterium labelling experiments showed that, as with other acetylenes, butylacetylene reacted without incorporating any external hydrogen atoms into its unsaturated diester products, but incorporated hydrogen from the hydroxyl group of the solvent into the β-position of its monoester product, preferentially in the position cis- to the ester group.

Butylacetylene was also able to couple with butyl acrylate during carbonylation to yield the 3-substituted hex-2-enedioate ester, as had acetylene and methylacetylene.

In general terms, it is clear that a normal butyl substituent effects the acetylenic bond in much the same way as does a methyl group.

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CHAPTER FIVE

Studies on the Carbonylation of Phenylacetylene

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5.1. INTRODUCTION

Having observed the rather similar effects of methyl- and butyl- groups on the reactivity of acetylene towards carbonylation, it was of interest to examine the influence of an aromatic substituent.

Thus phenylacetylene, which is readily available as a liquid, was chosen for the following work.

The properties of the phenyl- group which were expected to influence the behaviour of the acetylene were its relatively bulky nature, and its ability to act as an electron donor or acceptor as required[1], whereas alkyl groups are always electron releasing.

5.2. EXPLORATORY REACTIONS

(i) The Attempted Carbonylation of Phenylacetylene Using a High Initial Concentration:

Reaction 5.1 was carried out by placing phenylacetylene in the reactor with the usual catalyst solution, and passing carbon monoxide for 7 hours at 65°C. Only traces of products were detected by gas chromatography. Evaporation of solvent followed by trituration with methanol yielded a yellow solid. The solid melted over a very wide range, and attempts to re-crystallise it from a variety of solvents led to the formation of intractable oils, as did attempts to purify it by column chromatography. Thin layer chromatography showed that the substance was a complex mixture. Cryoscopic data suggested an average molecular weight of 390 whilst combustion analysis showed that the mixture did not consist exclusively of oligomers of phenylacetylene:

Found C, 89.0; H, 6.6 $(PhCCH)_n$ requires C, 94.1; H, 5.9%.

Since sodium fusion tests showed iodine to be absent from the mixture, and ignition had demonstrated the absence of palladium, it was concluded that some components contained oxygen functions. The infrared spectrum of the mixture showed a strong similarity to that of 1,2,4-triphenylbenzene, suggesting the presence of a high proportion of the trimer.

(ii) The Reaction of Phenylacetylene with the Catalyst Solution:

Since reactions had been observed to take place between the three acetylenes used previously and the catalyst solution (cf. Chapter 2.4 (ii), 3.5 (i) and 4.4 (i)) it was considered likely that a similar reaction

would occur with phenylacetylene and might explain the formation of the mixture in (i) above.

Several attempts were made to monitor the reaction between phenylacetylene and the catalyst solution using ultraviolet spectroscopy, and evidence was obtained to show that the P—I charge-transfer band of λ_{MAX} = 344 m.m. diminished with time. However, the charge-transfer band was largely overlain by the aromatic bands of the phenylacetylene (which were apparently intensified as the reaction proceeded). However, when phenylacetylene was added to a concentrated catalyst solution, an immediate colour change to a reddish yellow was evident and the 'pH' of the solution fell from 6.0 to 4.0. Thin layer chromatography, using benzene as the mobile phase, revealed a single yellow spot, R_F = 0.75. A sticky yellow substance, which hardened to a glassy solid, was isolated by column chromatography. The n.m.r. spectrum of the substance showed only a broad multiplet due to aromatic protons (in the region of 2.8τ) whilst the infrared spectrum (ν (cm^{-1}) = 692,755, 1445, 1492, 1592) was similar to that given by Doss and Solomon[2] for 1,2,4-triphenylbenzene. The mass spectrum showed a strong peak at $\frac{m}{e}$ = 102, suggesting the presence of either unreacted phenylacetylene (which seems unlikely in view of the separation process) or an oligomer which readily decomposed to its constituent phenylacetylene units (i.e. not triphenylbenzene).

It was concluded that reaction of phenylacetylene with the palladium iodide catalyst led primarily to an oligomer of phenylacetylene whether or not carbon monoxide was present. The reaction was essentially different from that shown by alkylacetylenes, since the latter gave rise to substances containing carbonyl functions.

Oligomerisation of phenylacetylene has been reported by Odaira and his co-workers[3], who refluxed phenylacetylene with palladium chloride and obtained a mixture containing 1,2,4-triphenylbenzene, 1,3,5-triphenylhexa-3,5-diene-1-yne, and a yellowish brown solid deduced to be a polyenyne compound. The Japanese workers also studied the behaviour of acetylene and methylacetylene in the presence of palladium chloride, but the aliphatic hydrocarbons proved to be much less reactive than phenylacetylene.

(iii) The Reaction of Phenylacetylene with an Excess of Carbon Monoxide:

In view of the observations reported above (ii) it was concluded

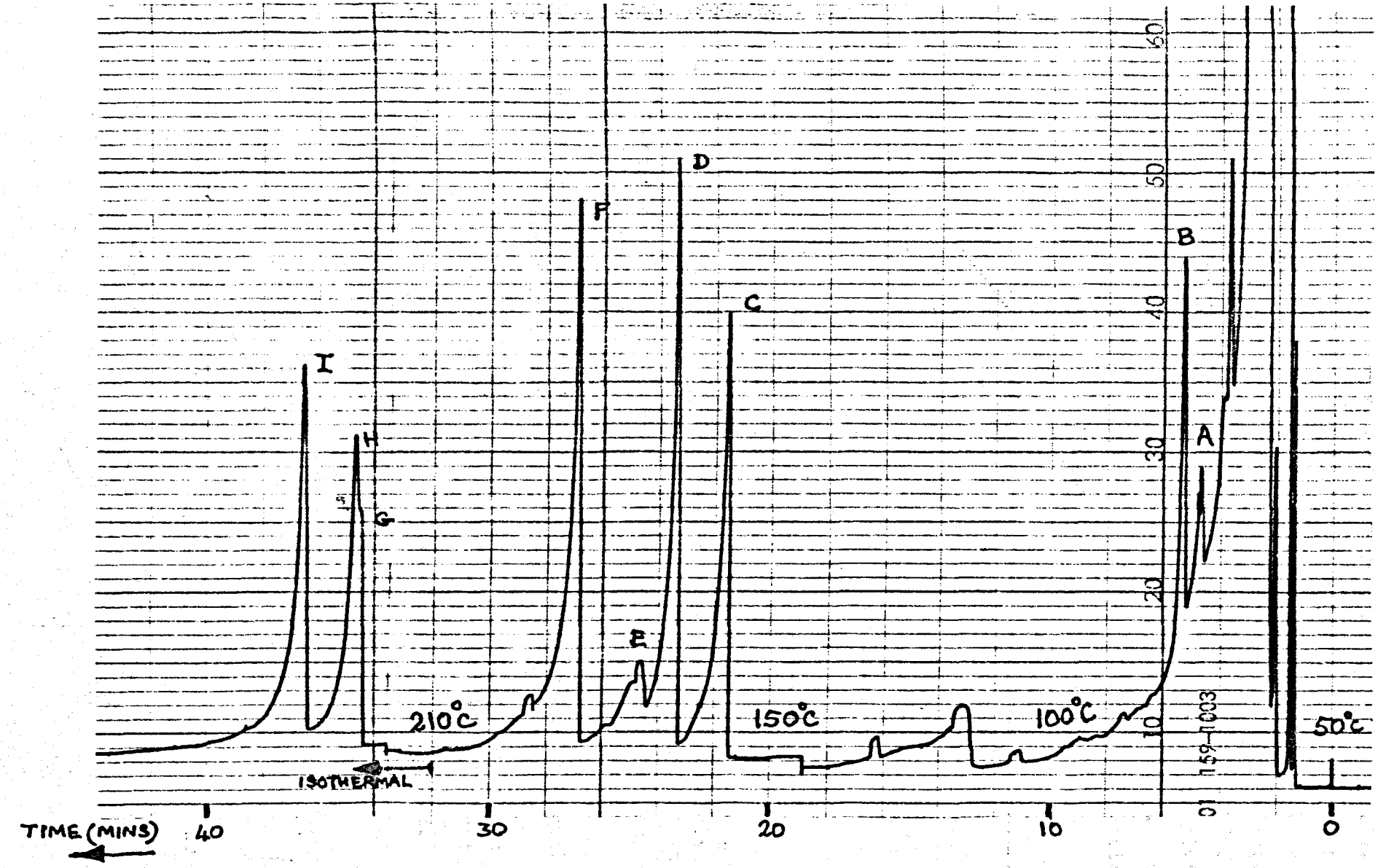


Fig. 5.1. PRODUCTS FROM THE CARBONYLATION OF PHENYLACETYLENE, PROGRAMMED TEMPERATURE GAS CHROMATOGRAM, SILICONE COLUMN

that carbonylation might be achieved by introducing the hydrocarbon progressively in the presence of an excess of carbon monoxide. Accordingly, a high flow rate of carbon monoxide was used in reaction 5.2 and allowed to entrain phenylacetylene held in a warmed bubbler thereby carrying it into the reaction mixture. 12 hours were required to introduce 0.1 mols of phenylacetylene, and most of the butanol was swept out of the system leaving a concentrated mixture of products identified as described in table 5.1 below. A small amount of brown residue, having similar spectroscopic properties to that obtained in reaction 5.1, was also observed.

Peak	Identity	Means of Identification
'A'	butyl iodide	C (1)
'B'	acetophenone	C (4)
'C'	butyl hydratropate	C (4), i(n.m.r.,i.r.)
'D'	butyl atropate	C (4), i(n.m.r.,i.r.)
'E'	butyl hydrocinnamate	C (4)
'F'	butyl cinnamate	C (4), i(n.m.r.,i.r.)
'G'	dibutyl phenylsuccinate	C (3)
'H'	dibutyl phenylmaleate	Isolated as mixture, identified by n.m.r., m.s., i.r. and combustion analysis. Hydrogenated to 'G', C (3), i.r.,n.m.r.
'I'	dibutyl phenylfumarate	

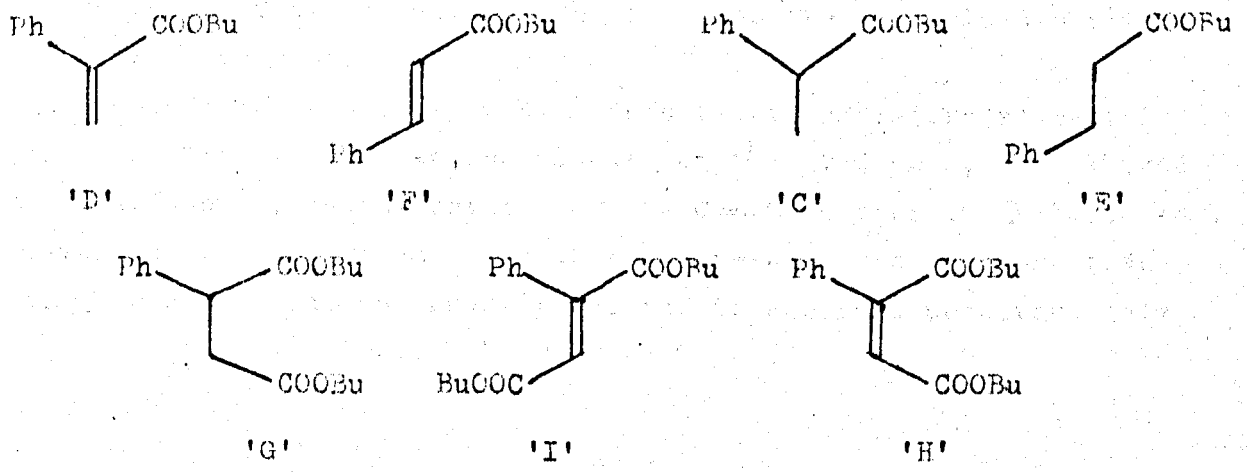
The letter corresponds to the appropriate peak in the gas chromatogram (fig. 5.1.).

C (n) = Comparison of the retention time with that of the authentic compound on n gas chromatographic columns.

i = Isolation by preparative scale gas chromatography and spectroscopic comparison with the authentic compound.

Table 5.1 Identification of the Products from Reaction 5.2.

The structures of the products are as follows:

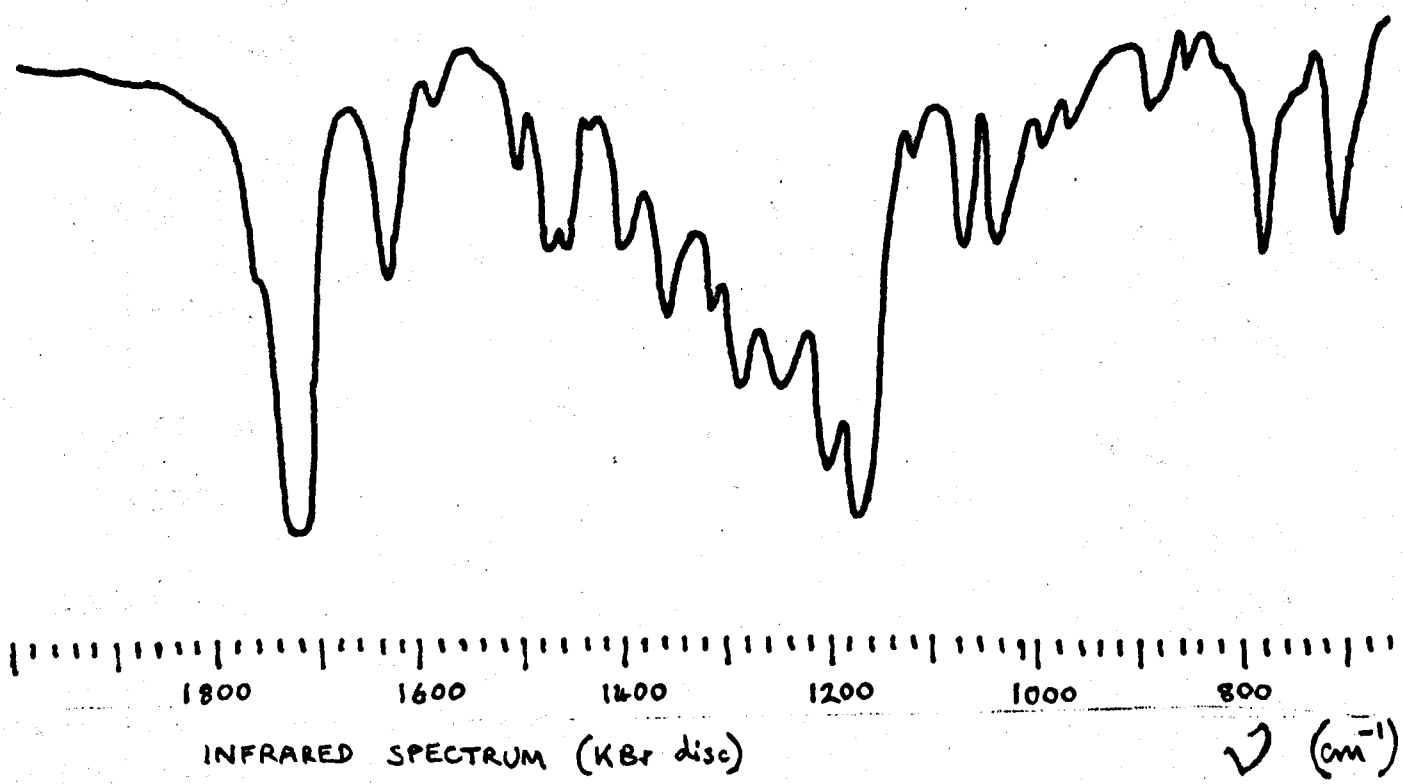


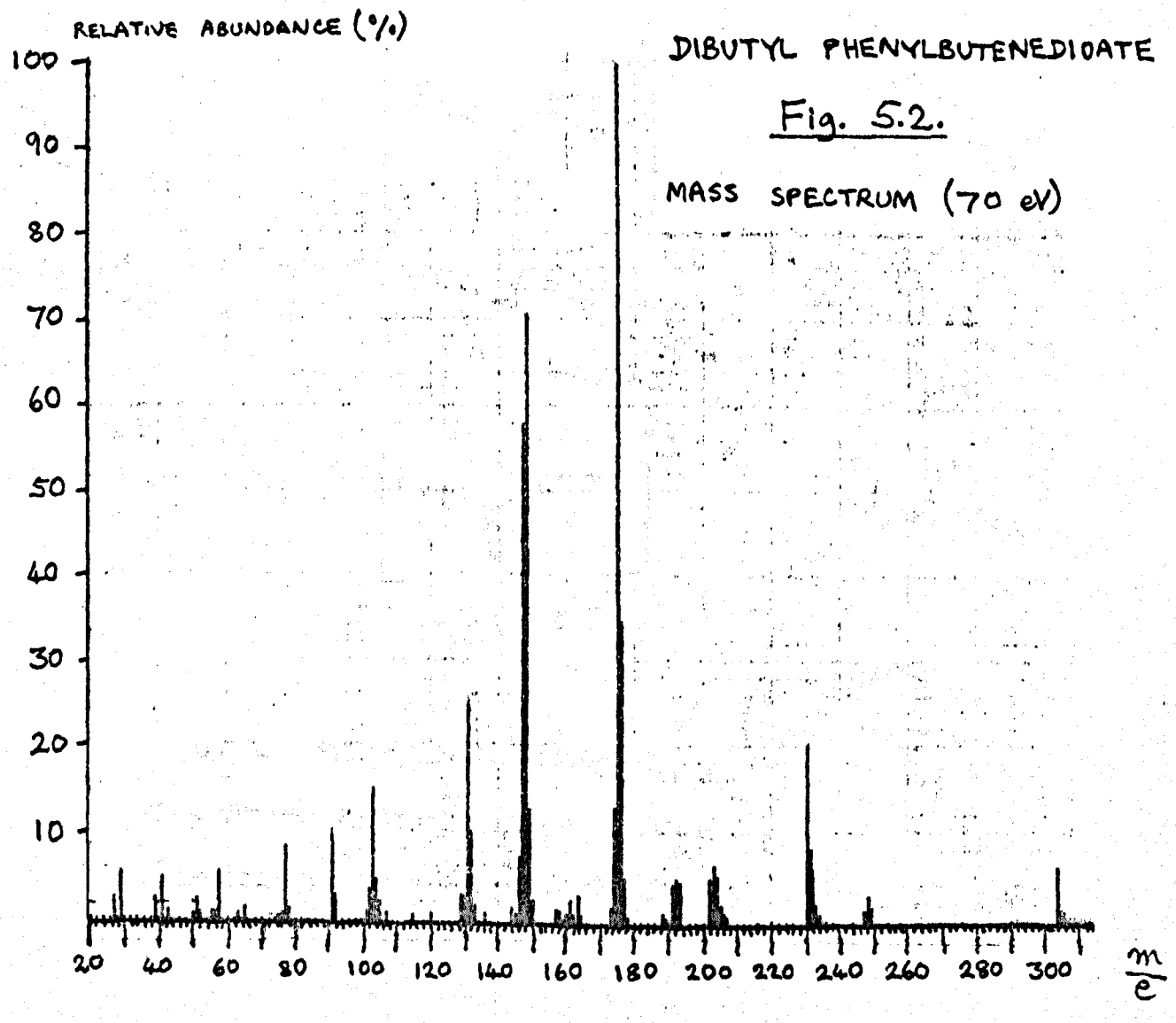
The fraction containing 'H' and 'I' together with traces of dibutyl phenylsuccinate ('G') was isolated by preparative scale gas chromatography. The mixture was hydrogenated over platinum to a substance, the infrared and n.m.r. spectra and 3 gas chromatograms of which were identical to those of dibutyl phenylsuccinate. The mass spectrum (fig. 5.2), for which a fragmentation scheme is tentatively proposed (fig. 5.3), the infrared spectrum (fig. 5.2), which shows an unsaturated aromatic ester (ν (cm^{-1}) = 1625, C=C stretch; 700, 790 aromatic C-H; 1170, C-O stretch; 1720, C=O stretch) and particularly the n.m.r. spectrum, afforded additional evidence for the structures of the unsaturated diesters. The n.m.r. spectrum of the mixture (fig. 5.4) showed two peaks, h and i in the olefinic region at τ = 3.06 and 3.78 respectively. The ratio of the integrals $\frac{h}{i}$ (=0.3), was sufficiently close to the ratio $\frac{'H'}{I}$ (=0.29) of the two components as measured by gas chromatography, to establish that signal h was due to 'H' and i to 'I'. Signals h and i together integrated as one proton and the spectrum was otherwise consistent with the assignment, i.e. 5 phenyl protons and 18 butyl protons.

Prolonged treatment of the mixture with nitric oxide failed to cause any appreciable change in the ratio of the two products, suggesting that the major component was the trans- isomer. Exposure for 30 minutes to ultraviolet light, a procedure well known to lead to the formation of cis- isomers[4], caused an inversion in the product ratio to $\frac{H}{I}$ = 3.4 by gas chromatography and $\frac{h}{i}$ = 3.6 from the n.m.r. integral. It was thus concluded that H was the cis- and I was the trans- isomer.

It was noteworthy that the olefinic proton of the substituted maleate ester occurred at lower field than that of the substituted fumarate, the reverse of the position noted when the substituent was an alkyl group. However, the phenomenon may be explained by the proximity of the phenylmaleate proton to the deshielded perimeter of the aromatic ring.

The infrared spectrum of the crude reaction mixture showed, besides an intense ester-carbonyl band at ν = 1730 cm^{-1}, a weak band at ν = 1770 cm^{-1}, characteristic of the C=O stretch in γ-lactones[5], however no peak in the gas chromatogram corresponding to more than C.a. 0.2 g of product was unassigned, and it was concluded that only a





DIBUTYL PHENYLBUTENEDIOATE

Fig. 5.2.

MASS SPECTRUM (70 eV)

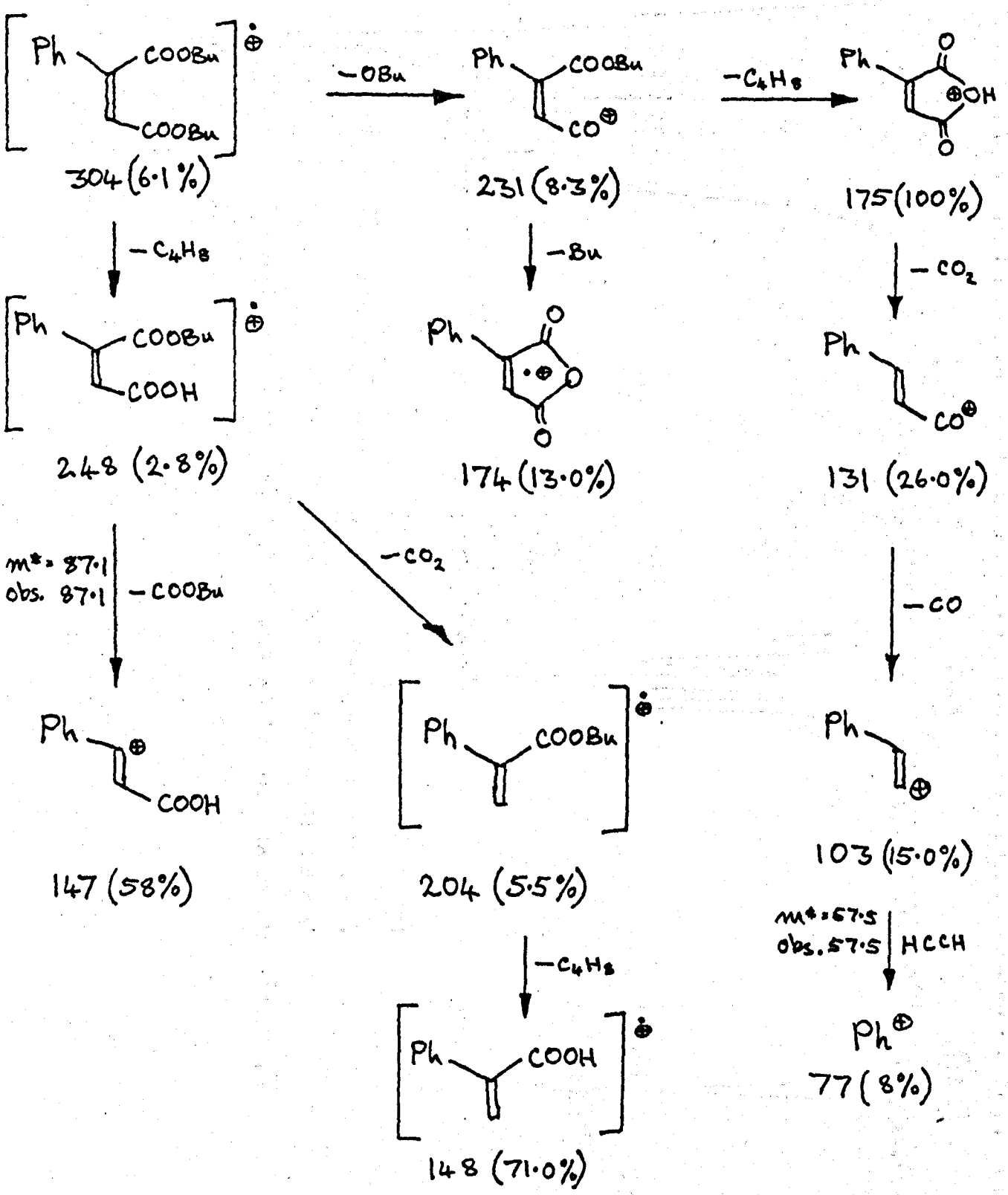


Fig. 5.3.

DIBUTYL PHENYLBUTENEDIOATE,
TENTATIVE FRAGMENTATION SCHEME
(REPRESENTED AS THE cis- ISOMER)

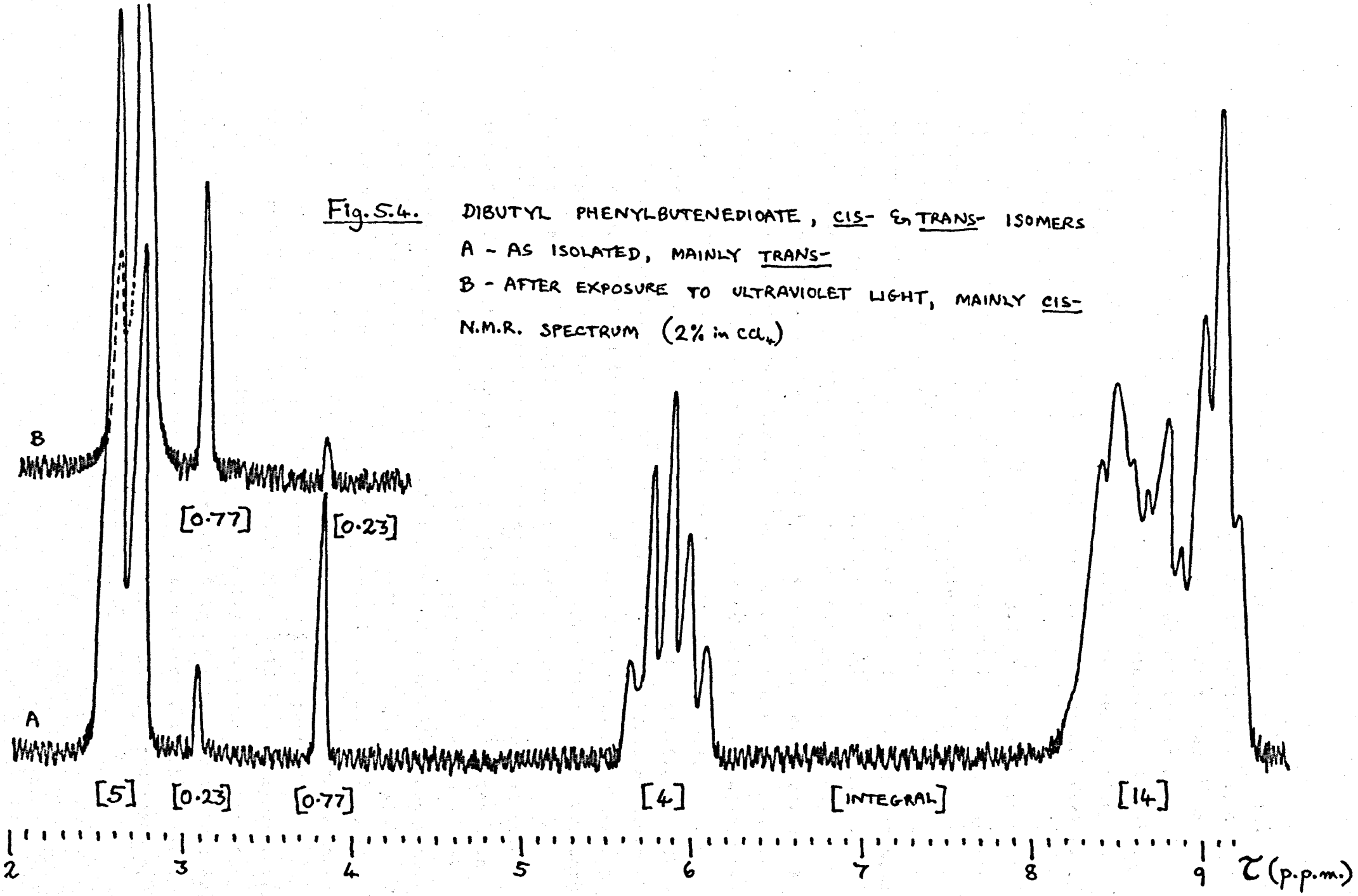


Fig. S.4. DIBUTYL PHENYLBUTENEDIOATE, CIS- & TRANS- ISOMERS
A - AS ISOLATED, MAINLY TRANS-
B - AFTER EXPOSURE TO ULTRAVIOLET LIGHT, MAINLY CIS-
N.M.R. SPECTRUM (2% in CCl_4)

very small amount of lactone, if any, was present in the mixture.

It was also interesting to note that butyl allocinnamate, the cis-isomer, was not present in the reaction mixture to any significant concentration, indicating that linear monoester was formed by exclusively cis- addition of the H- and -COOBu moieties. A similar conclusion was suggested by deuterium labelling studies on acetylene and the mono-alkyl substituted acetylenes (cf. Chapters 2.4 (ix),(x); 3.5 (iv); 4.4 (ii).

(iv) The 'Standard' Reaction: In reaction 5.1, too high an initial concentration of phenylacetylene was present, and in 5.2, the flow-rate of carbon monoxide was too great. An intermediate set of conditions was chosen as 'standard' and was as follows: Phenylacetylene (0.1 mols) was introduced progressively to the reactor in which the usual catalyst solution was vigorously stirred at 65°C over a period of 7 hours. The procedure was, in essence, the same as that used to carbonylate butylacetylene (cf. Chapter 4.2 (i)). Reaction 5.3 was carried out under the 'standard' conditions. The yields of the products so obtained expressed as mol % (based on phenylacetylene) were as follows: butyl atropate, 12.3; cinnamate, 14.7; hydratropate, 8.4; hydrocinnamate, 2.1; dibutyl phenylmaleate, 13.2; phenylfumarate, 44.6 and phenylsuccinate, 8.1%. The total yield of identified products was thus 94.6% (neglecting acetophenone which, here and in subsequent reactions was present to about 4%). The high conversion of products was in marked contrast with the findings using acetylene and methyl- & butylacetylene, but it may be due in part to the relative involatility of the substrate. Acetylene and methylacetylene being gases, and butylacetylene (b.p. 71.5°C[6]) being almost gaseous at the reaction temperature of 65°C, would only have a short residence time. Phenylacetylene, however, has a boiling point of 143°C[6], and would not be swept from the reaction vessel to any significant extent.

Another difference between the behaviour of phenylacetylene and and the monoalkylacetylenes carbonylated under their respective 'standard' conditions was the relatively high yield of linear monoester. Thus the yield of butyl cinnamate was slightly greater than that of butyl atropate. The difference may possibly be ascribed to the steric effect of the bulky phenyl group. Alternatively, the high yield of butyl hydratropate may have arisen from the selective reduction of initially produced unsaturated branched ester.

5.3 CARBONYLATION OF PHENYLACETYLENE IN THE PRESENCE OF HYDROGEN CHLORIDE

The presence of hydrogen chloride had increased the yield of monoesters produced in the carbonylation of acetylene[7] (cf. also Chapter 2.2 (i)) and butylacetylene (Chapter 4.3 (iii) and it was thus of interest to examine the effect of acid on the carbonylation of phenylacetylene. Reaction 5.4 was carried out under 'standard' conditions, but with hydrogen chloride (10 m mol) present. The results are summarised in table 5.2.

Reaction No.	5.3	5.4
HCl added (m mols)	0.0	10.0
Butyl atropate	11.3	19.0
Butyl cinnamate	13.7	5.8
Butyl hydratropate	7.6	9.7
Butyl hydrocinnamate	2.0	2.7
Total monoesters	34.6	37.4
Dibutyl phenylmaleate	12.2	6.9
Dibutyl phenylfumarate	40.3	20.2
Dibutyl phenylsuccinate	7.5	3.6
Total diesters	60.0	30.7
Monoesters/Diesters	0.58	1.22

Table 5.2. The Yields of Esters Obtained by Carbonylation of Phenylacetylene in the Presence of Hydrogen Chloride, Compared with Those from a 'Standard' Reaction. % Yields Based on Phenylacetylene

The yield of diesters was considerably reduced by the presence of hydrogen chloride, but in addition the overall conversion of phenylacetylene was reduced (from 95% to 68%). The amount of non-linear monoester was increased , whilst the amount of linear monoester was diminished by comparison with the 'standard' reaction. Such behaviour was quite different from that observed for acetylene and butylacetylene where the overall yield of monoesters was enhanced, though it led to a similar observation that the ratio of monoester to diester was increased by the presence of the acid.

5.4 CARBONYLATION OF PHENYLACETYLENE IN THE PRESENCE OF OXIDISING AGENTS

(i) Carbonylation in the Presence of Air: Reaction 5.5 was carried out

under the 'standard' conditions, but with air passing at 1 - 1.5 l/h. The final analyses, shown in table 5.3, were not consistent with the general pattern, observed with the carbonylation of acetylene and the alkyl substituted acetylenes, of enhanced diester formation and reduced monoester formation (cf. Chapters 2.2 (iii) (a), 3.3 (i) and 4.3 (i)), the ratio of mono- to diesters being slightly increased by the presence of air. Surprisingly the yields of saturated esters appeared to be slightly increased. No explanation has been found for such inconsistent behaviour.

(ii) Carbonylation in the Presence of Benzoquinone: Reaction 5.6 was carried out under 'standard' conditions, but in the presence of benzoquinone (3 g). The analyses, given in table 5.3 showed very marked differences from the 'standard' reaction.

The overall uptake of phenylacetylene was greatly reduced and saturated products were not detected. The cis- diester was produced in higher yield than the trans- isomer, a reversal of the situation observed in 'standard' reactions. The same effect was noted for methyl- and butylacetylene, but not for acetylene itself (cf. tables 2.1, 3.5 and 4.2).

No new peak which could correspond with butyl β-butoxycinnamate (the phenyl- analogue of the β-butoxycrotonate ester found amongst the products of the corresponding methylacetylene reaction (Chapter 3.3 (iv)) was observed, but hydroquinone (c.a. 0.5 g) was detected by gas chromatography.

Reaction No.	5.3	5.5	5.6
Oxidising Agent	-	Air (1-1.5 l/h)	Benzoquinone (3 g)
Butyl atropate	11.3	14.8	1.5
Butyl cinnamate	13.7	11.2	2.0
Butyl hydratropate	7.6	9.6	-
Butyl hydrocinnamate	2.0	3.0	-
Total monoesters	34.6	38.6	3.5
Dibutyl phenylmaleate	12.2	12.7	3.5
Dibutyl phenylfumarate	40.3	35.0	2.4
Dibutyl phenylsuccinate	7.5	8.5	-
Total diesters	60.0	56.2	5.9
Monoesters/Diesters	0.58	0.69	0.59

Table 5.3 The Yields of Products Obtained by the Carbonylation of Phenylacetylene in the Presence of Oxidising Agents. % Yields Based on Phenylacetylene

5.5 CARBONYLATION OF PHENYLACETYLENE IN THE PRESENCE OF BUTYL ACRYLATE

The formation of esters of the 3-substituted hex-2-enedioate type had been observed when acetylene and alkyl substituted acetylenes were carbonylated in the presence of butyl acrylate (cf. Chapters 2.3; 3.5 (v) and 4.4 (iii)). Hence it was of interest to examine the carbonylation of phenylacetylene in the presence of butyl acrylate. Reaction 5.7 was carried out under the 'standard' conditions, but with butyl acrylate added progressively throughout the reaction and with air passing at 1 - 1.5 l/h. The usual products were present in low yields, i.e. butyl atropate, 3.2; cinnamate, 1.1; hydratropate, 0.6; hydrocinnamate, 0.3; dibutyl phenylmaleate, 3.2; phenylfumarate, 4.4 and phenylsuccinate, 1.1%. In addition, two new peaks were visible in the gas chromatogram, having retention indecies, $I^{SE\ 30}_{230^\circ} = 2336$ and 2387, equivalent to amounts of 1.3 g. and 0.4 g. respectively. The substance corresponding to the first peak was isolated by preparative scale gas chromatography (though not entirely free from traces of the second, which was probably a condensed aromatic hydrocarbon) and was identified by the following spectroscopic evidence as dibutyl 3-phenylhex-2-enedioate.

The infrared spectrum (ν (cm^{-1})(KBr disc) = 700 (s), 761 (m) (phenyl group) 1030 (w), 1065 (w), 1165 (s), 1250 (m,b), 1400 (m), 1455 (m), 1500 (w), 1600 (w) (aromatic C=C stretch), 1631 (m) (olefinic C = C stretch), 1720 (vs) (ester C=O stretch), 2902 (s) showed that the substance was an unsaturated aromatic ester. The mass spectrum (fig. 5.5) gave a parent ion of $\frac{m}{e}$ =332.1984; $C_{20}H_{28}O_4$ requires 332.1987. Subtraction of two -COOBu groups from the molecular formula, a reasonable procedure in view of the mode of formation, left a residue which could be interpreted as $-C_4H_5Ph-$.

The n.m.r. spectrum (fig. 5.7) showed two ester-butyl groups in markedly different environments (as shown by the partial superimposition of the α-methylene triplets in the 6τ region). A sharp singlet, integrating as one proton, was evident at 3.97 τ, presumably an olefinic proton having no adjacent protons with which to couple. It was therefore concluded that a double bond was adjacent to one of the -COOBu groups, and that a phenyl- group was present in the 3-position. The remaining $-C_2H_4-$ was concluded to be two methylene groups between the BuOOC-CH=CPh- group and the second -COOBu. They were evident as a triplet (J = 10.5 c.p.s.) at 7.64τ and a multiplet at 6.63τ,

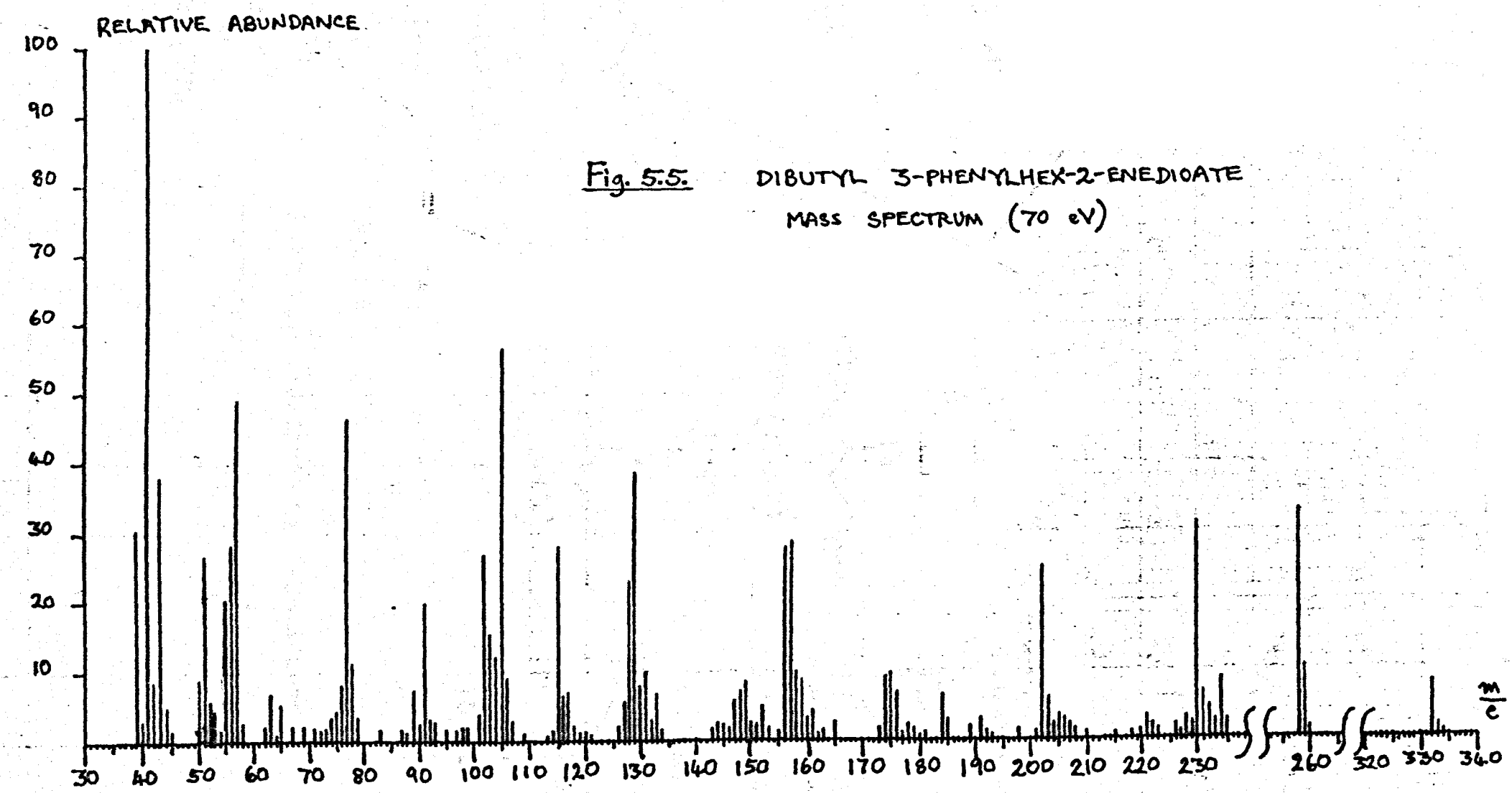


Fig. 5.5. DIBUTYL 3-PHENYLHEX-2-ENEDIOATE MASS SPECTRUM (70 eV)

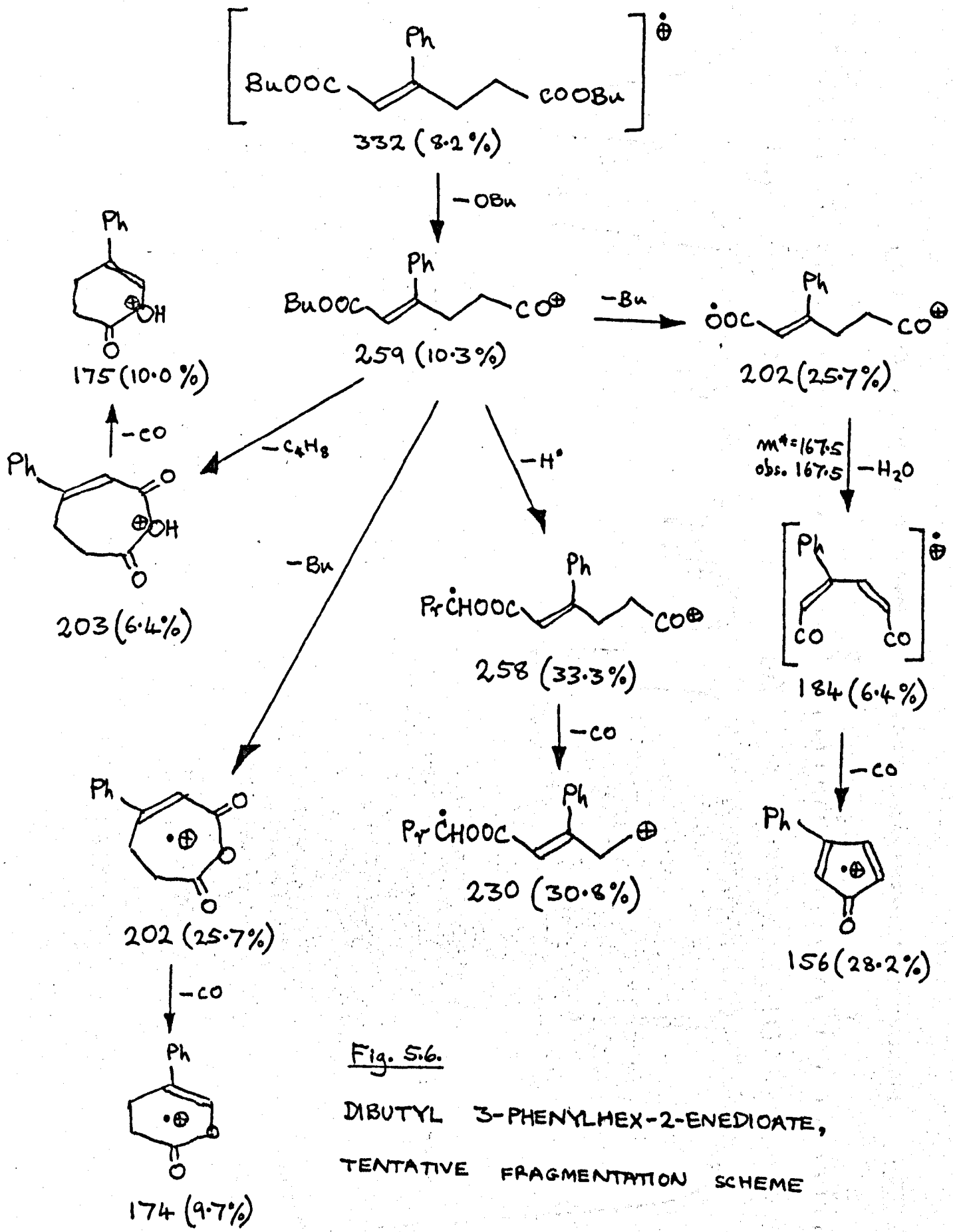


Fig. 5.6.

DIBUTYL 3-PHENYLHEX-2-ENEDIOATE,

TENTATIVE FRAGMENTATION SCHEME

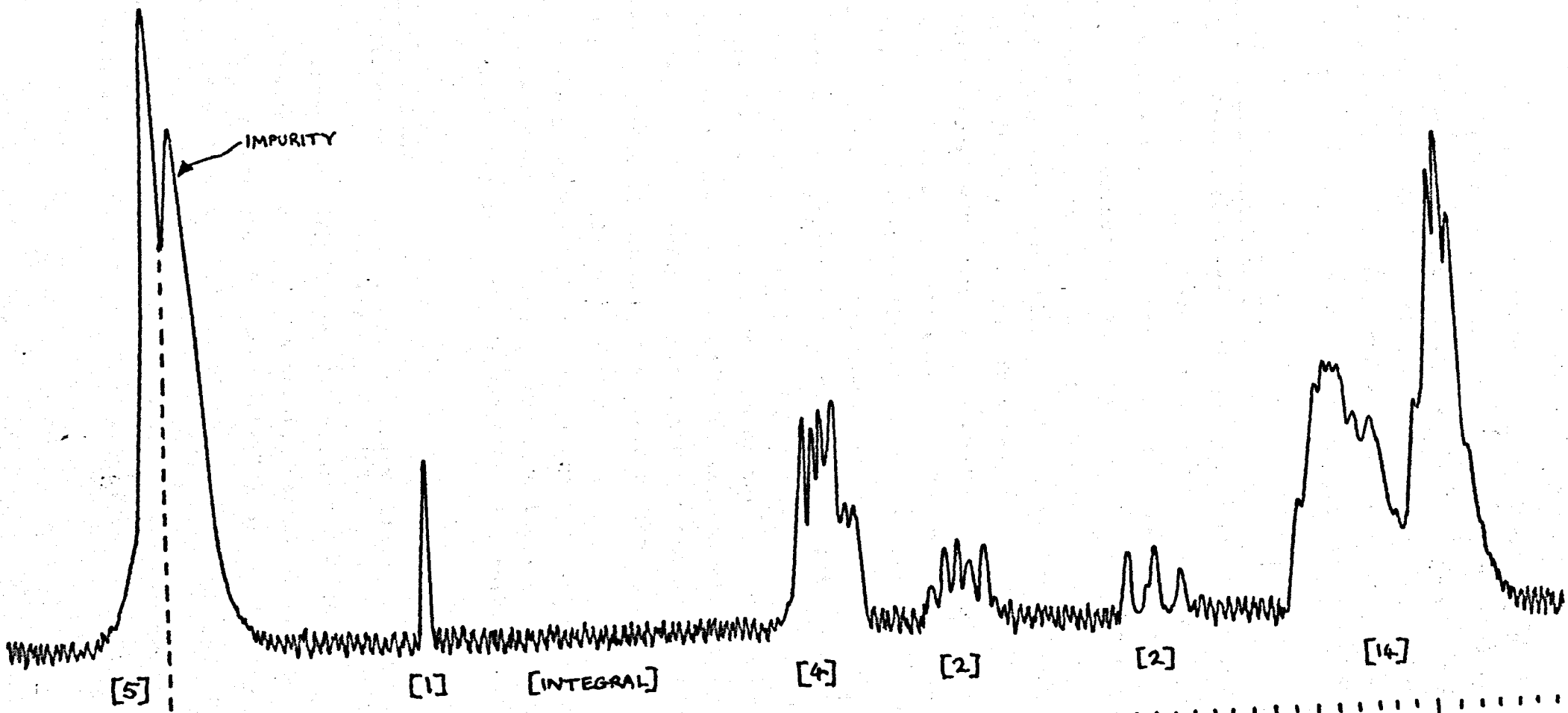


Fig. 5.7. DIBUTYL 3-PHENYLHEX-2-ENEDIOATE, N.M.R. SPECTRUM (10% IN CCl_4)

both integrating as two protons. The phenyl group was present at 2.63τ, integrating as 5 protons, but unfortunately an impurity was present as a rather broad band at 2.75τ, presumed to be a condensed aromatic hydrocarbon. With the structure of the compound established as 3-phenylhex-2-enedioate, it was possible to interpret the mass spectrum in terms of a fragmentation scheme, which is given in fig. 5.6.

5.6 SUMMARY AND CONCLUSIONS

The behaviour of phenylacetylene towards carbonylation, followed some broad trends which have been observed with the alkylacetylenes, thus the expected range of product esters was produced in very high yield. The presence of hydrogen chloride caused the ratio of mono- to diester to increase, though by depressing diester rather than enhancing monoester formation. Phenylacetylene also underwent a coupling reaction with butyl acrylate during carbonylation, similar to that observed with methylacetylene and butylacetylene to yield the 3-phenylhex-2-enedioate ester. However, in some important respects phenylacetylene differed from the alkylacetylenes, thus the linear monoester, butyl cinnamate, was produced in higher yield than the branched isomer, butyl atropate, though its analogues had only been produced in trace amounts by the carbonylation of methyl- and butylacetylene. The formation of butyl cinnamate was, moreover, discouraged by the presence of hydrogen chloride, though butyl atropate formation was favoured. Also, the passage of air did not have the expected effect of reducing the yield of monoesters (or saturated esters) produced from phenylacetylene.

The main effects of the phenyl group on the carbonylation chemistry of the acetylenic linkage were thus, to increase its reactivity, and to significantly alter the orientation of attack.

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CHAPTER SIX

Studies on the Carbonylation of Dimethylacetylene

C O N T E N T S

6.1. INTRODUCTION

6.2. ATTEMPTS TO CARBONYLATE METHYLACETYLENE AT ATMOSPHERIC PRESSURE

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6.1. INTRODUCTION

The carbonylation of a number of monosubstituted acetylenes having been investigated, attention was given to examining the behaviour of disubstituted acetylenes.

Dimethylacetylene (But-2-yne), a volatile liquid (b.p. = 27°C[1]), was chosen as representative of the aliphatic non-terminal acetylene series, being the simplest member.

6.2. ATTEMPTS TO CARBONYLATE DIMETHYLACETYLENE AT ATMOSPHERIC PRESSURE

(i) Attempted Carbonylation in a Flow System: Initially, a system resembling that used for the 'standard' reaction with other acetylenes was used, (e.g. Chapter 4.2 (i)). A quantity of dimethylacetylene was introduced progressively, as a butanol solution, into a vigorously stirred solution of palladium iodide/sodium iodide in butanol whilst passing carbon monoxide. The procedure was tried at 20°C (Rn. 6.1) and repeated at 65°C (Rn. 6.2). In the latter case, as a precaution against excessively rapid vaporisation, the dimethylacetylene solution was introduced through the hollow shafted stirrer with the gas stream. However, in neither case was any product detected by gas chromatography, and the colour of the solution remained wine-red.

(ii) Attempted Carbonylation in a Closed System: The negative results obtained in (i) above suggested that dimethylacetylene was unreactive towards carbonylation, but it was also considered possible that its high volatility had prevented adequate contact with the reaction medium. A further reaction (Rn. 6.3) was therefore carried out at low temperature in a closed system. A butanol solution of the palladium iodide catalyst (8 m molar) containing some 12% by weight of dimethylacetylene was vigorously stirred whilst exposed to an atmosphere of carbon monoxide at 16°C for 22 hours. Again no reaction products were detected, and it was concluded that methylacetylene was unreactive towards carbon monoxide in the presence of palladium iodide at atmospheric pressure.

6.3 CARBONYLATION OF DIMETHYLACETYLENE ABOVE ATMOSPHERIC PRESSURE

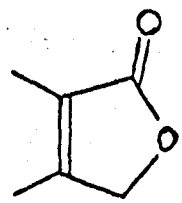
Since carbonylation had not been accomplished using atmospheric pressure, the effect of employing an increased pressure of carbon

monoxide was studied.

(i) Carbonylation Under Moderate Pressure: Two reactions (Rns. 6.4 & 6.5) were carried out at a pressure of 17 atmospheres and a temperature of 65°C. Three main products, 'A', 'B' and 'C' were detected by gas chromatography (having retention indecies, $I^{SE\ 30}$, of 1153, 1611 and 1676 respectively), whilst a fourth product 'D' was precipitated and could be recovered by filtration. Surprisingly, no ethylmethyl ketone was detected in the reaction mixtures, although the carbonylation of monosubstituted acetylenes had yielded small quantities of the corresponding ketones (cf. Chapters 3.2 (ii), 4.2 (ii) and 5.2 (iii)). No evidence for the presence of the expected ester product, butyl tiglate (MeCH=CMe-COOBu) and dibutyl 2,3-dimethylsuccinate (BuOOC-CHMe-CHMe-COOBu) could be obtained.

Samples of 'A', 'B' and 'C' were obtained by preparative scale gas chromatography, whilst 'D' was collected and purified by recrystallisation.

(a) 'A' was identified by spectroscopic methods as 2,3-dimethylcrotonolactone. The infrared spectrum (fig. 6.1)



'A'

showed a strong absorption at ν (cm^{-1}) = 1752, characteristic of a C = O stretching frequency in an α,β-unsaturated γ-lactone (Ames, Bowman and Grey[2] give ν = 1761 for 2,3-dimethylcrotonolactone), and at 1680 (C = C), 1080 and 1030. The ultraviolet spectrum gave a band at λ_{MAX}^{MeOH} = 214 n.m., ε_{MAX} = 16,500 which compared closely with λ_{MAX} = 213 n.m., ε_{MAX} = 13,400 quoted by Ames et al.[2]. The n.m.r. spectrum (fig. 6.2) showed two multiplets, both integrating as 3 protons at τ = 8.00 & 8.24, characteristic of methyl groups substituted on an olefinic bond, and a multiplet integrating as 2 protons at τ = 5.49. The latter signal was attributed to a methylene group adjacent to oxygen in the γ-lactone. Finally, the mass spectrum (fig. 6.3) showed a strong parent peak at $\frac{m}{e}$ = 112, with important fragments corresponding to loss of CHO followed by CO, and by loss of CO_2 with charge retention by the CO_2. A tentative

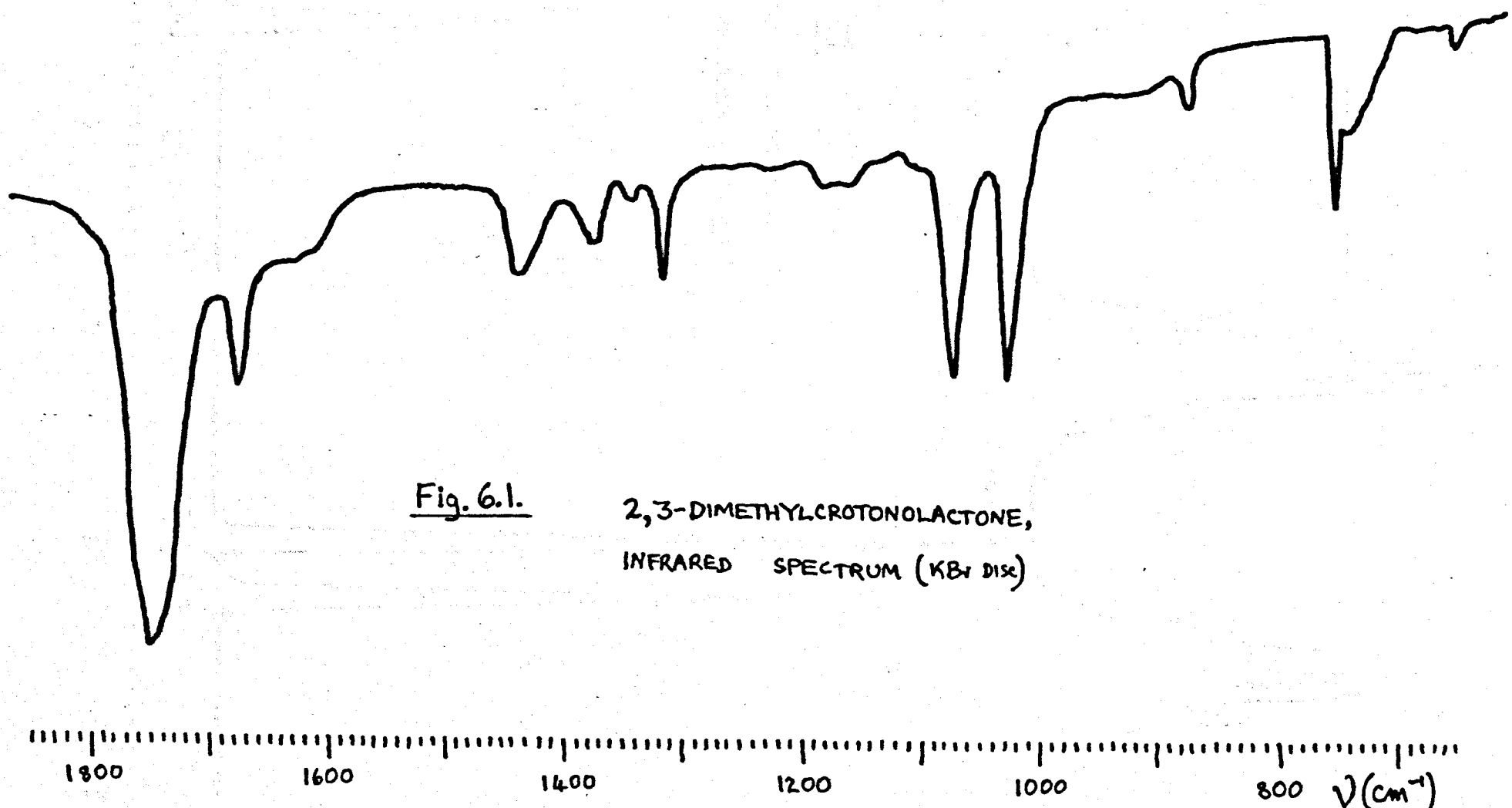


Fig. 6.1. 2,3-DIMETHYLCROTONOLACTONE, INFRARED SPECTRUM (KBr DISC)

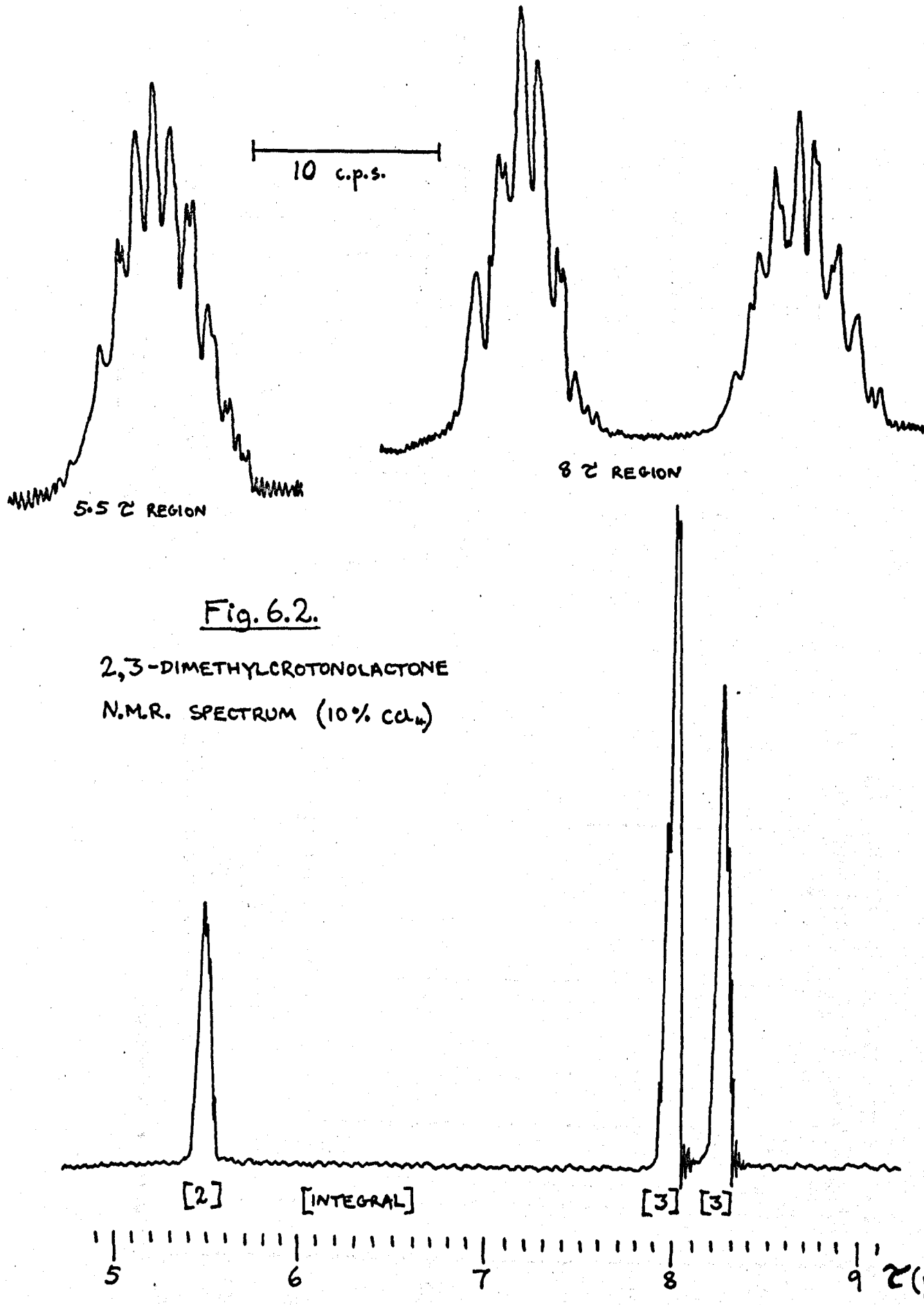
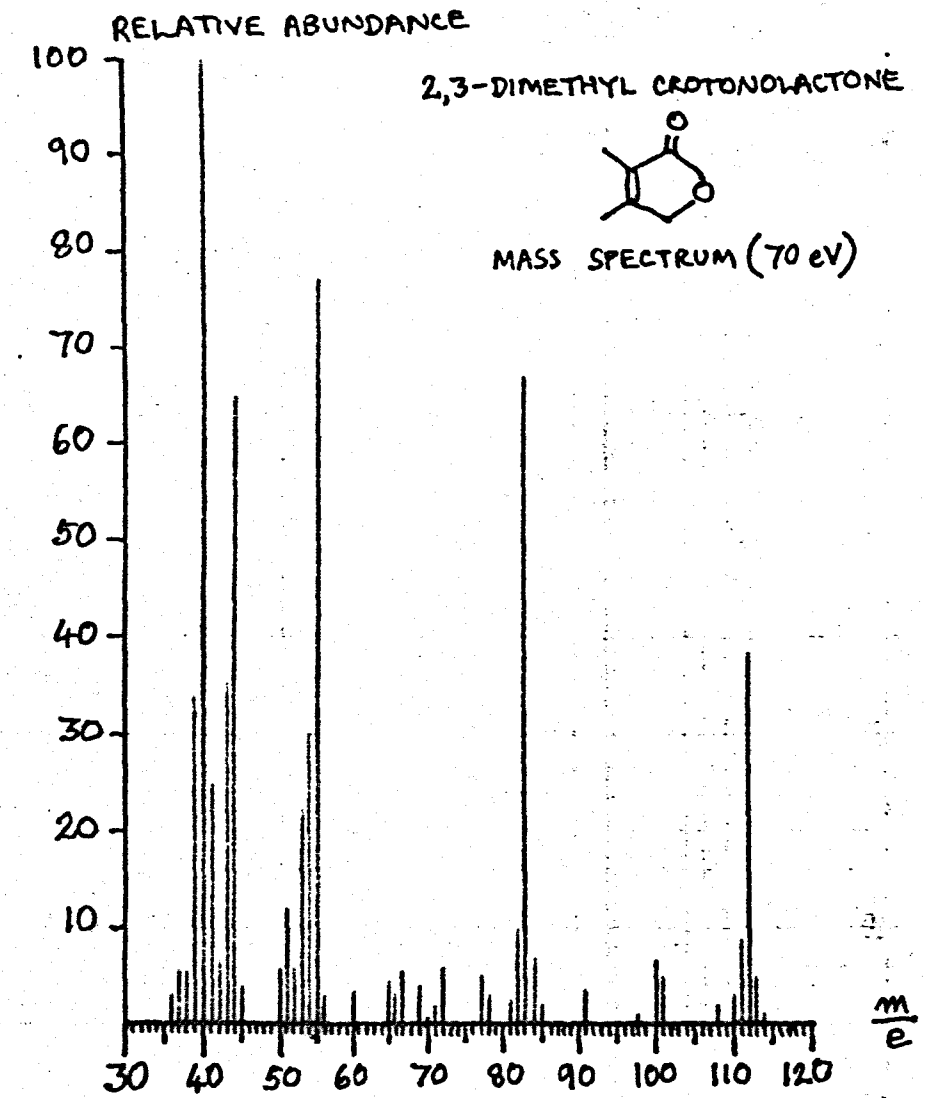
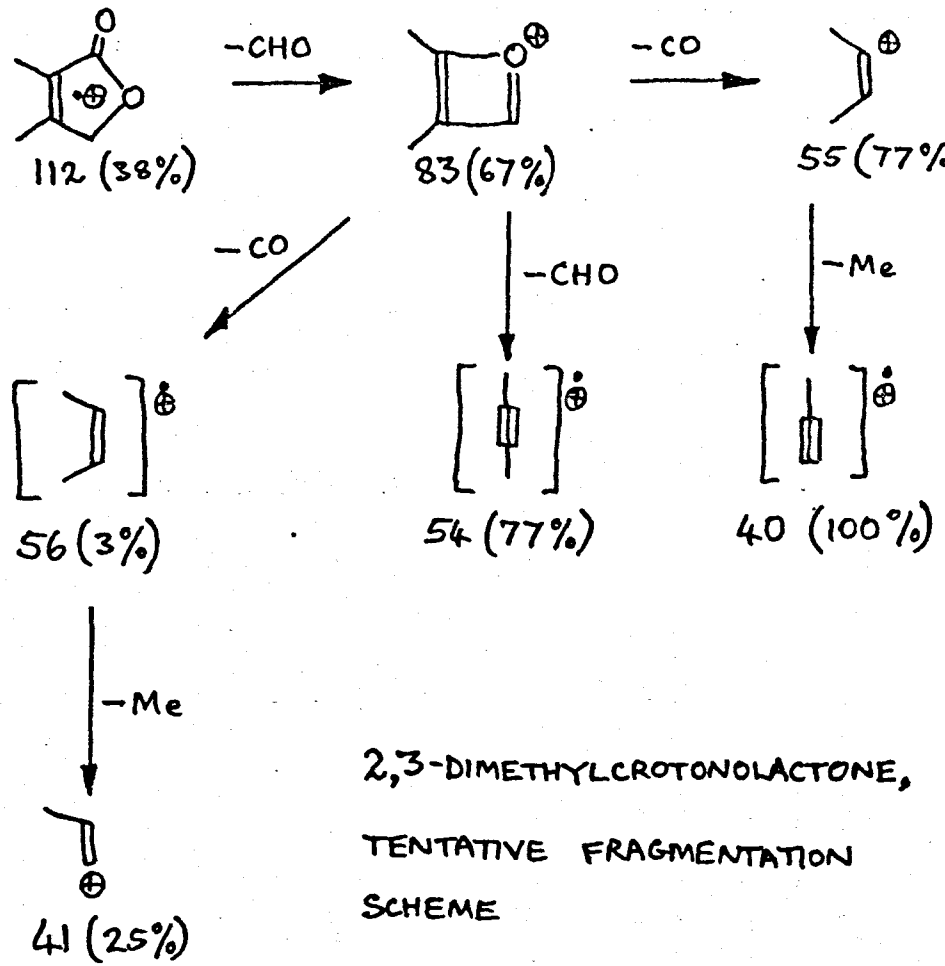


Fig. 6.2.

2,3-DIMETHYLCROTONOLACTONE

N.M.R. SPECTRUM (10% CCl_4)



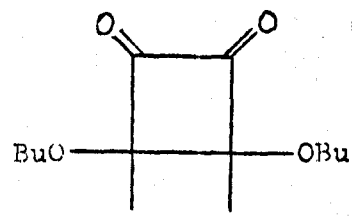


2,3-DIMETHYLCROTONOLACTONE, TENTATIVE FRAGMENTATION SCHEME

Fig. 6.3.

fragmentation scheme is included in fig. 6.3.

(b) 'B' showed a weak parent ion in the mass spectrum, of $\frac{m}{e}$ = 256.1710, which corresponds to the molecular formula $C_{14}H_{24}O_4$ which requires $\frac{m}{e}$ = 256.1675. The main fragments in the mass spectrum (fig. 6.4) could be attributed to loss of OBu (183, 11%) followed by C_4H_8 (127, 100%) followed by CO_2 (83, 20%) and to loss of a butyl group, with charge retention by the butyl group and its fragments. Assuming the presence of 2 butoxy- groups, the remainder of the molecule would be $C_6H_6O_2$ which would correspond to a molecule of methylacetylene and two molecules of carbon monoxide. The n.m.r. spectrum (fig. 6.5) showed a multiplet, integrating as 4 protons at τ = 6.5. The chemical shift was characteristic of CH_2 adjacent to O in an ether (cf. diethylether[3]). A sharp singlet was visible at 8.2 τ , integrating as 6 protons, assigned as 2 methyl groups. A broad multiplet, characteristic of the β, γ, δ protons of a butyl group, and integrating as 14 protons was visible between 8.3 - 9.3 τ . It was concluded from the n.m.r. spectrum, in conjunction with the mass spectrum, that the only protons present were due to two butoxy-groups and two methyl groups in a symmetrical molecule. The infrared spectrum of the substance (fig. 6.6) showed a strong bond at ν = 1775 cm^{-1}, characteristic of a C=O stretch in a strained ring[4], a C - O stretch (1120 cm) and aliphatic C - H stretching modes (2875, 2960 cm^{-1}). No absorption was observed in the 1600 - 1700 cm^{-1} region, indicating the absence of doubly bonded carbon atoms. The only structure consistent with the above data was I, 1,2-dibutoxy-1,2-dimethylcyclobutan-3,4-dione.



'B'

The n.m.r. spectral data was in agreement with structure I except that the 6.5 τ region was not a simple triplet, but had the appearance of two overlapping triplets. The infrared spectrum was also consistent with I if it were assumed that the expected doublet in the

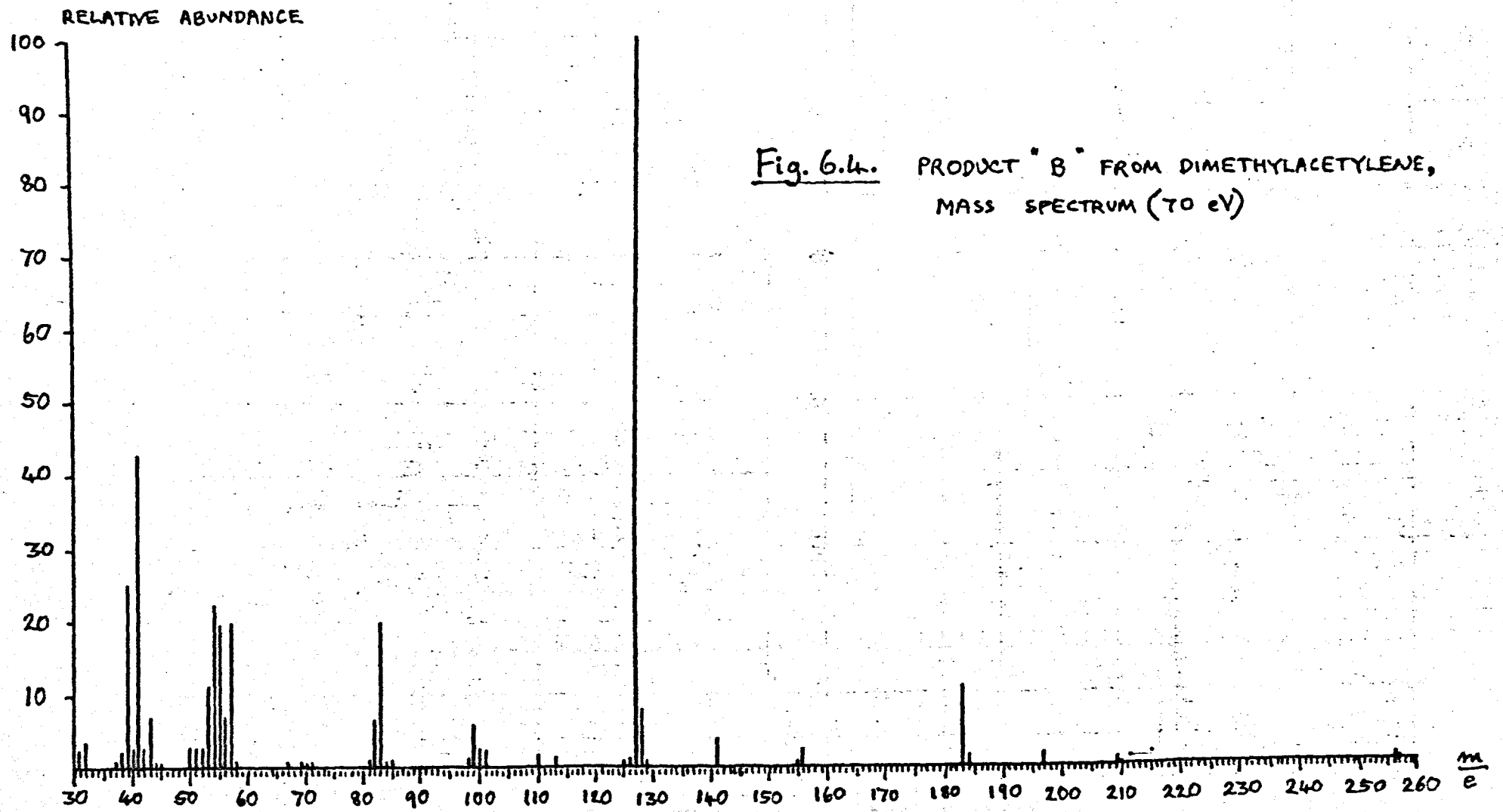


Fig. 6.4. PRODUCT "B" FROM DIMETHYLACETYLENE, MASS SPECTRUM (70 eV)

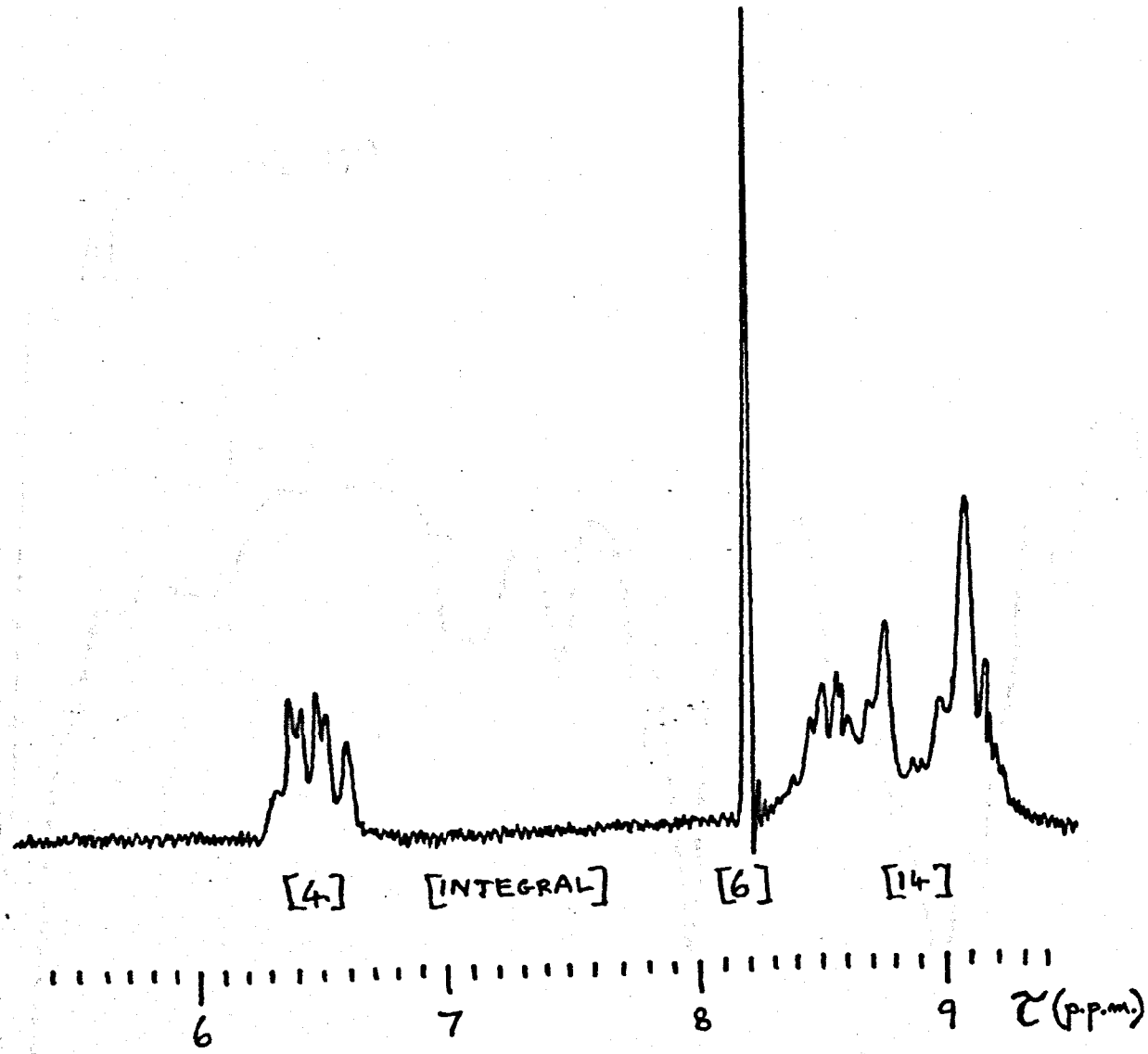


Fig. 6.5. PRODUCT 'B' FROM DIMETHYLACETYLENE, N.M.R. SPECTRUM (C.A.T., 70 RUNS ACCUMULATED)

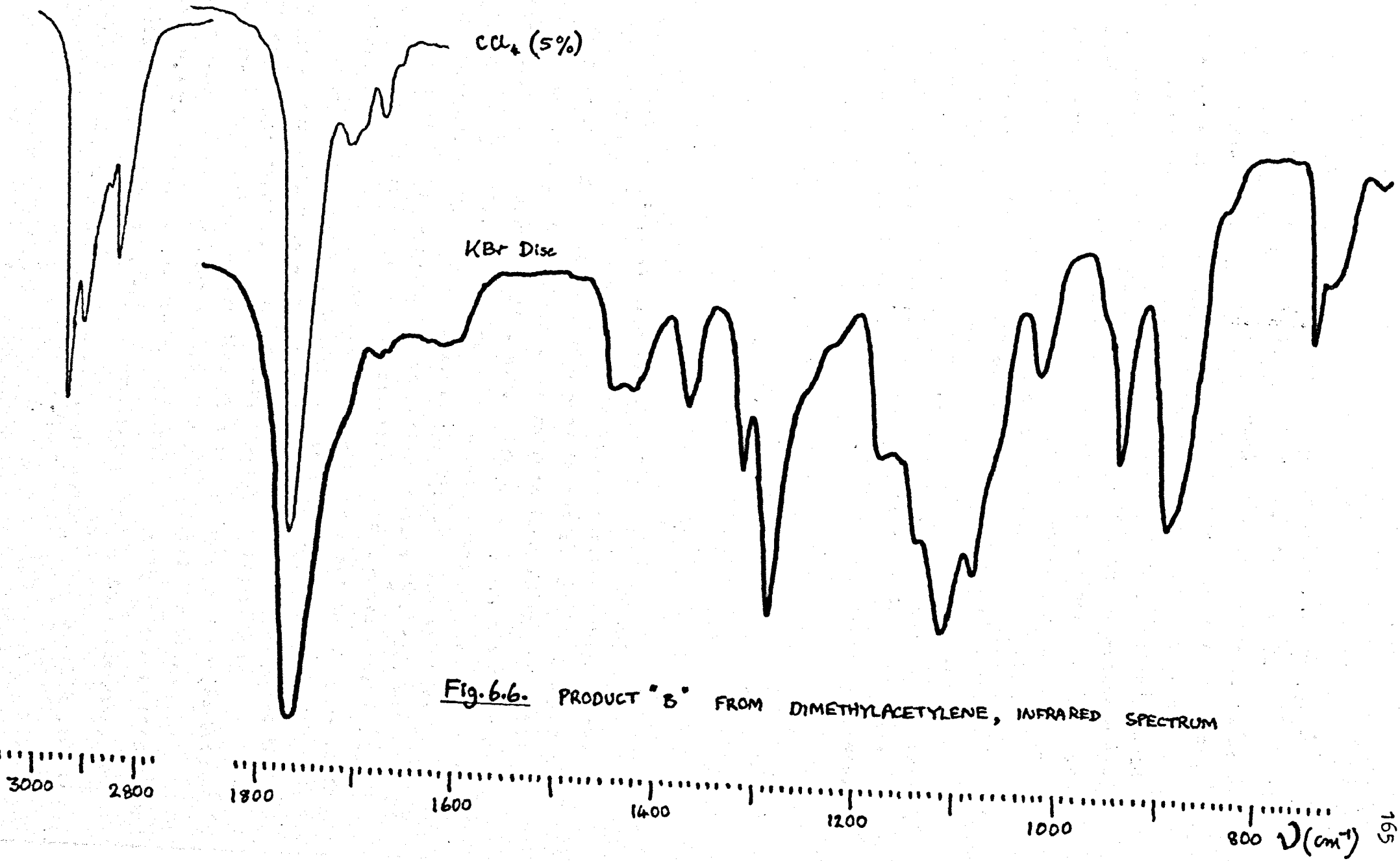
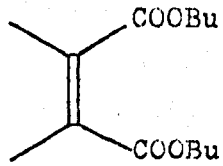


Fig. 6.6. PRODUCT "B" FROM DIMETHYLACETYLENE, INFRARED SPECTRUM

carbonyl region was not resolved, cf. cyclopentane-1,2-dione[5] (ν =1760, 1776 cm^{-1}) and cyclobutanone[4] (ν =1775 cm^{-1}).

Attempts to confirm the proposed structure by the preparation of suitable derivatives were not successful. When a reaction mixture containing 'B' was heated at 90°C for two hours with (a) an excess of 2,4-dinitrophenylhydrazine and hydrochloric acid or (b) phenylenediamine, in the hope of producing respectively the bis(2,4-dinitrophenylhydrazone) or the quinoxaline derivatives of the α-diketone[6], precipitates were not obtained and the peak in the gas chromatogram corresponding to 'B' was not reduced in intensity. The assignment of 'B' as I remains tentative; 4-membered α-diketones are known to be unstable and have only been prepared as butenediones[7,8,9] or heavily halogenated compounds[10].*

(c) 'C' was isolated by preparative scale gas chromatography and identified by spectroscopic methods as dibutyl dimethylmaleate.



'C'

The infrared spectrum (fig. 6.7) (ν (cm^{-1}) = 1640 (W) (C=C), 1715 (S)(C = O))was consistent with an unsaturated ester. The mass spectrum (fig. 6.8) showed a weak parent ion of $\frac{m}{e}$ = 256 and a set of daughter ions which could be rationalised according to the tentative scheme given in fig. 6.9. In particular, the major peak occurred at $\frac{m}{e}$ = 127, corresponding to a protonated anhydride structure due to loss of OBu followed by C_4H_8. The relative abundance of the non-protonated anhydride species ($\frac{m}{e}$ = 126) was only 12%. In the mass spectra of citraconate and mesaconate esters, the protonated anhydride was the major ion from the cis- ester and the non-protonated form was the major ion derived from the trans- isomer (cf. Chapter 3.5 (iv)). Hence it was concluded that 'C' was a cis- diester. The n.m.r. spectrum (fig. 6.7) was consistent with the structure dibutyl dimethylmaleate, thus the butyl group appeared as a triplet at 5.95 τ and a multiplet between 8.3 - 9.3 τ. The methyl groups occurred as a sharp singlet integrating as six protons at 8.11 τ, being identical to the shift value given by

* Cyclobutane-1,2-dione has recently been prepared[17] as a solid, stable for several weeks in a sealed tube. Infrared: ν =1778, 1810 cm^{-1}.

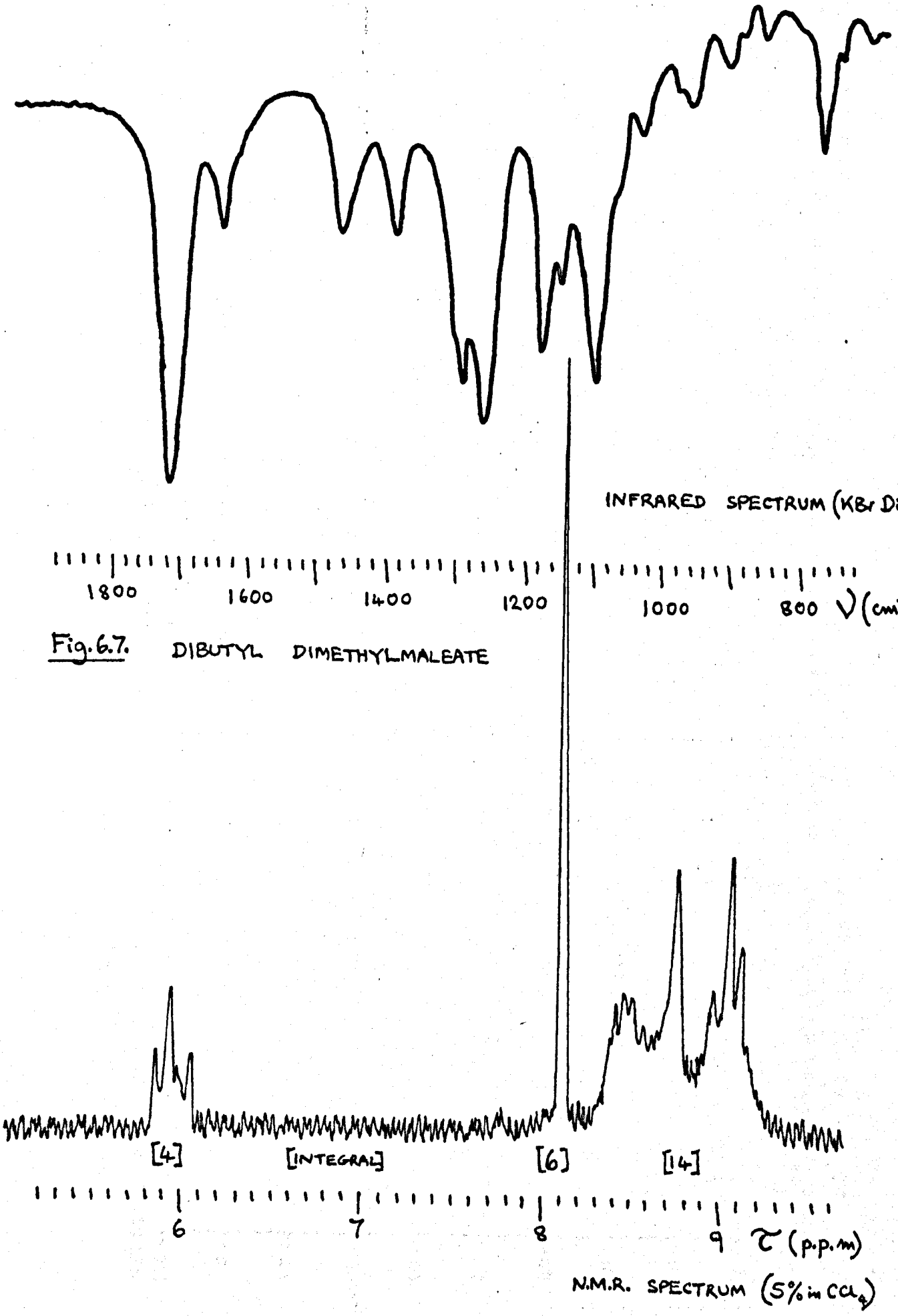


Fig. 6.7. DIBUTYL DIMETHYLMALEATE

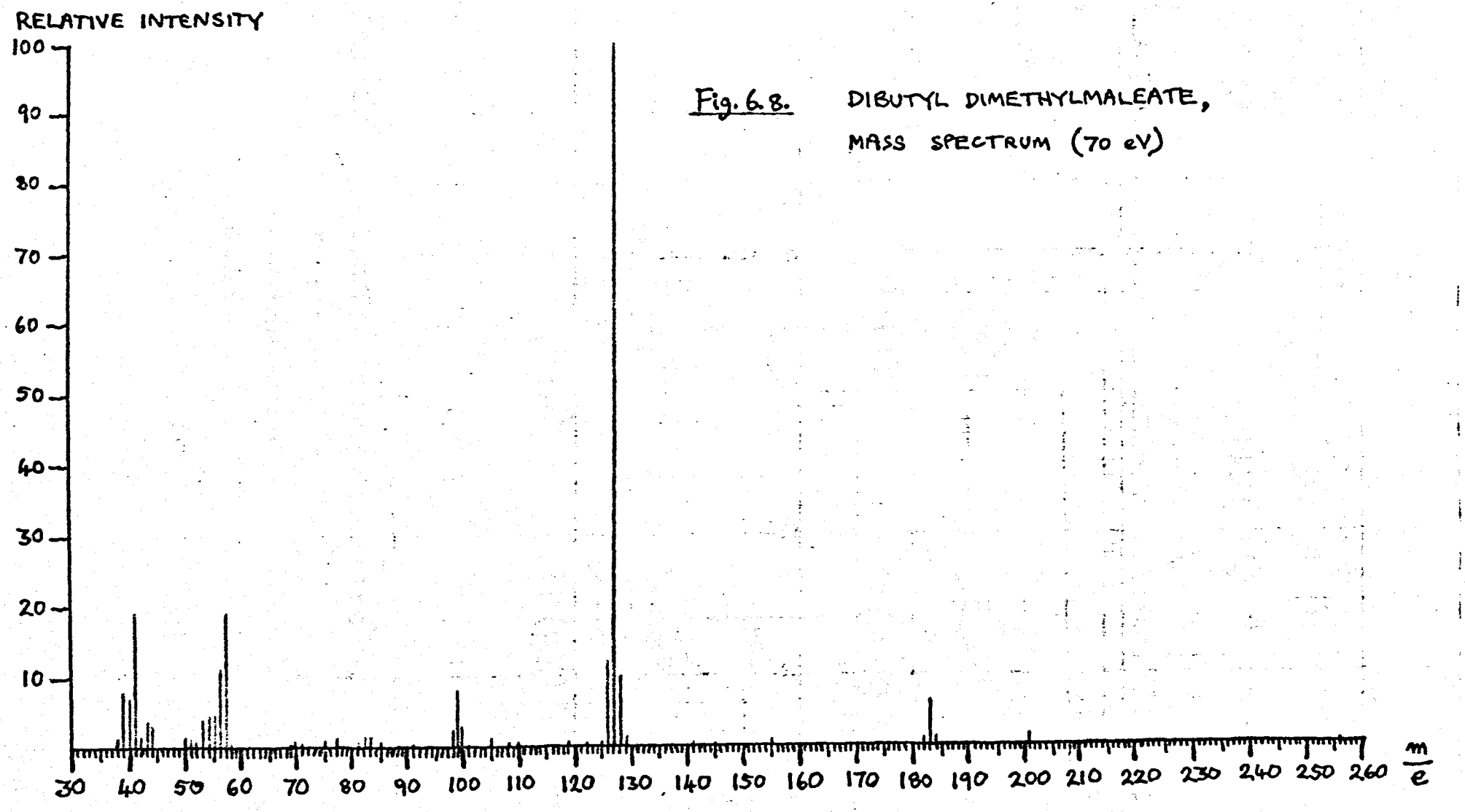


Fig. 6.8. DIBUTYL DIMETHYLMALEATE, MASS SPECTRUM (70 eV)

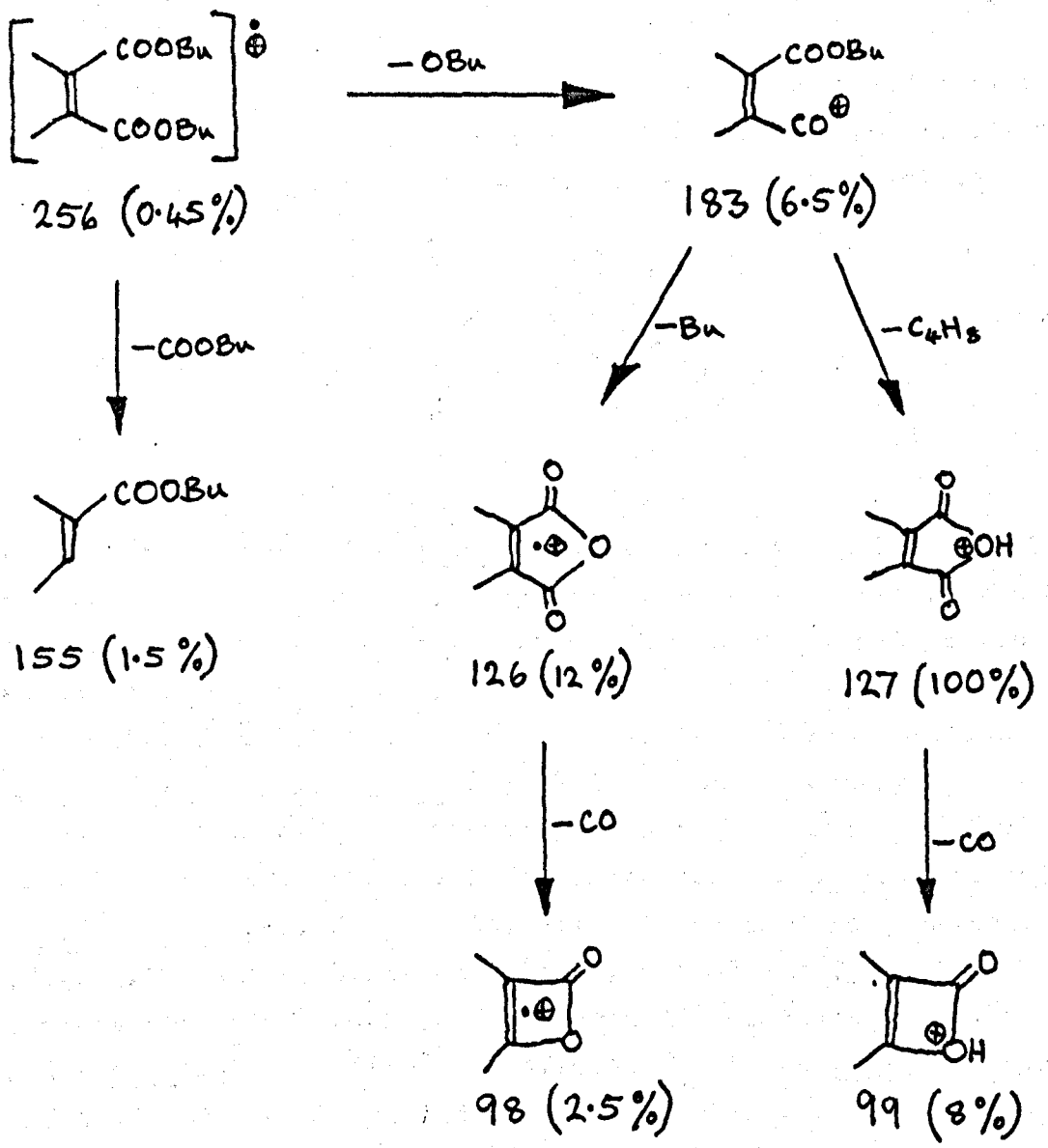
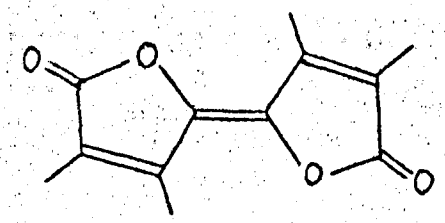


Fig. 6.9. DIBUTYL DIMETHYLMALEATE TENTATIVE FRAGMENTATION SCHEME

Jackman & Wiley[11] for the olefinic methyl groups in dimethyl dimethylmaleate.

(d) 'D' was filtered from the reaction mixture and purified by crystallisation. It was shown by spectroscopic methods to be trans-2,3:6,7-tetramethylocta-2,4,6-triene-1,4:5,8-diolide



'D'

(hereafter referred to as trans-tetramethylbifurandione). The n.m.r. spectrum showed two singlets of equal integral at 7.6 and 8.0 τ in carbon tetrachloride (typical values for methyl groups attached to a double bond) whilst in benzene solution, the signals were shifted to 8.7 and 9.0 τ. The ultraviolet spectrum, λ_{MAX}^{HEXANE} = 338 n.m., ε_{MAX} = 31,000, suggested considerable conjugation (as did the intense yellow colour) and was very similar to a literature spectrum for the unsubstituted trans-bifurandione[12] (λ_{MAX}^{MeCN} = 340 n.m., ε_{MAX} = 33,058). The infrared spectrum (fig. 6.10) showed bonds at ν (cm^{-1}) = 1762 and 1775 (sh), characteristic of C=O in a conjugated γ-lactone, and 1618 (C=C). Sauer et al.[12] give ν(cm^{-1}) = 1770,1538 for the trans-bifurandione and 1780,1538 (doublet) and 1688 (very intense) for the cis- isomer. The presence of only one olefinic stretching band argued for the trans- isomer. Two olefinic bands were visible in the Raman spectrum, at ν = 1655 & 1618 cm^{-1}. The 1655 band was attributed to the linkage between the two furanone rings. The stretching of the exocyclic double bond would be a symmetrical mode in the trans- and antisymmetric in the cis- isomer. Thus the appearance of a band in the Raman spectrum, and its absence in the infrared established 'D' as the trans- isomer. Finally the mass spectrum (fig. 6.11) was consistent with the proposed structure, with the parent peak (being also the major peak) at $\frac{m}{e}$ = 220. A fragmentation scheme consistent with the data is given in fig. 6.12.

The formation of lactones in carbonylation reactions has been reported by a number of workers. Lactones were produced as might be expected when acetylenic alcohols were carbonylated by Jones and his co-workers[13] using nickel tetracarbonyl as a catalyst, and

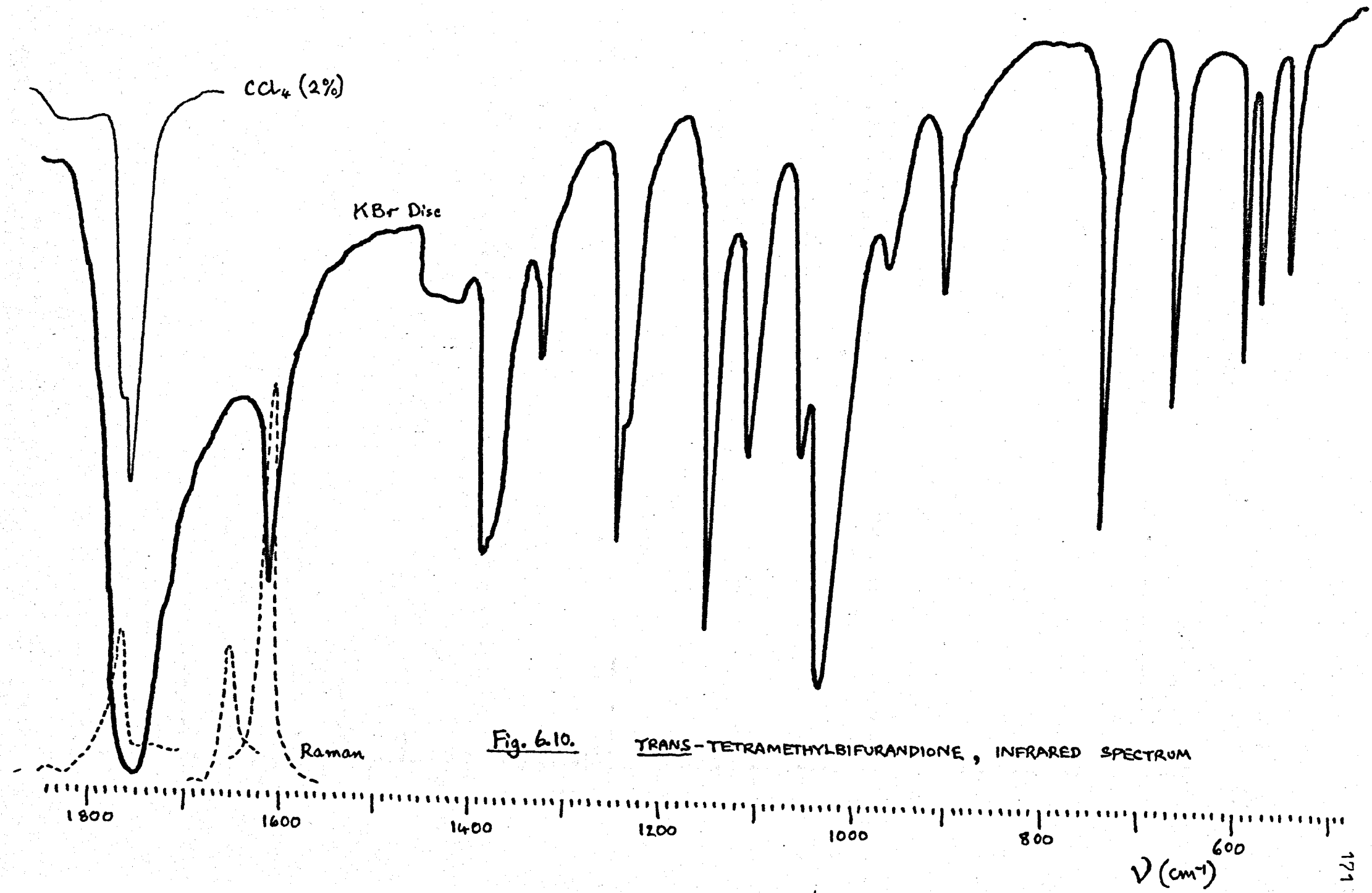


Fig. 6.10. TRANS-TETRAMETHYLBIFURANDIONE, INFRARED SPECTRUM

Fig. 6.11.

TRANS-TETRAMETHYL-BIFURANDIONE,
MASS SPECTRUM (70 eV)

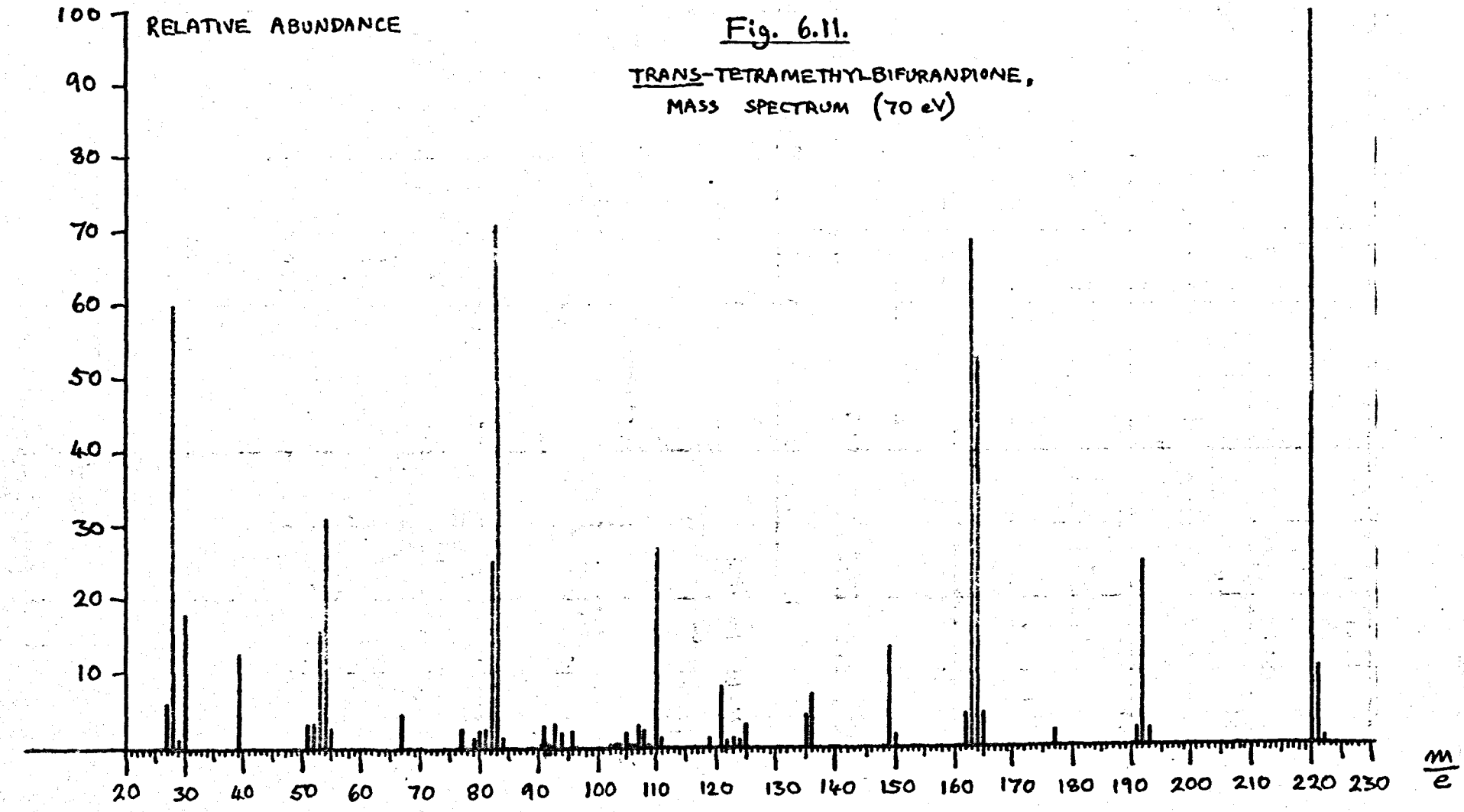
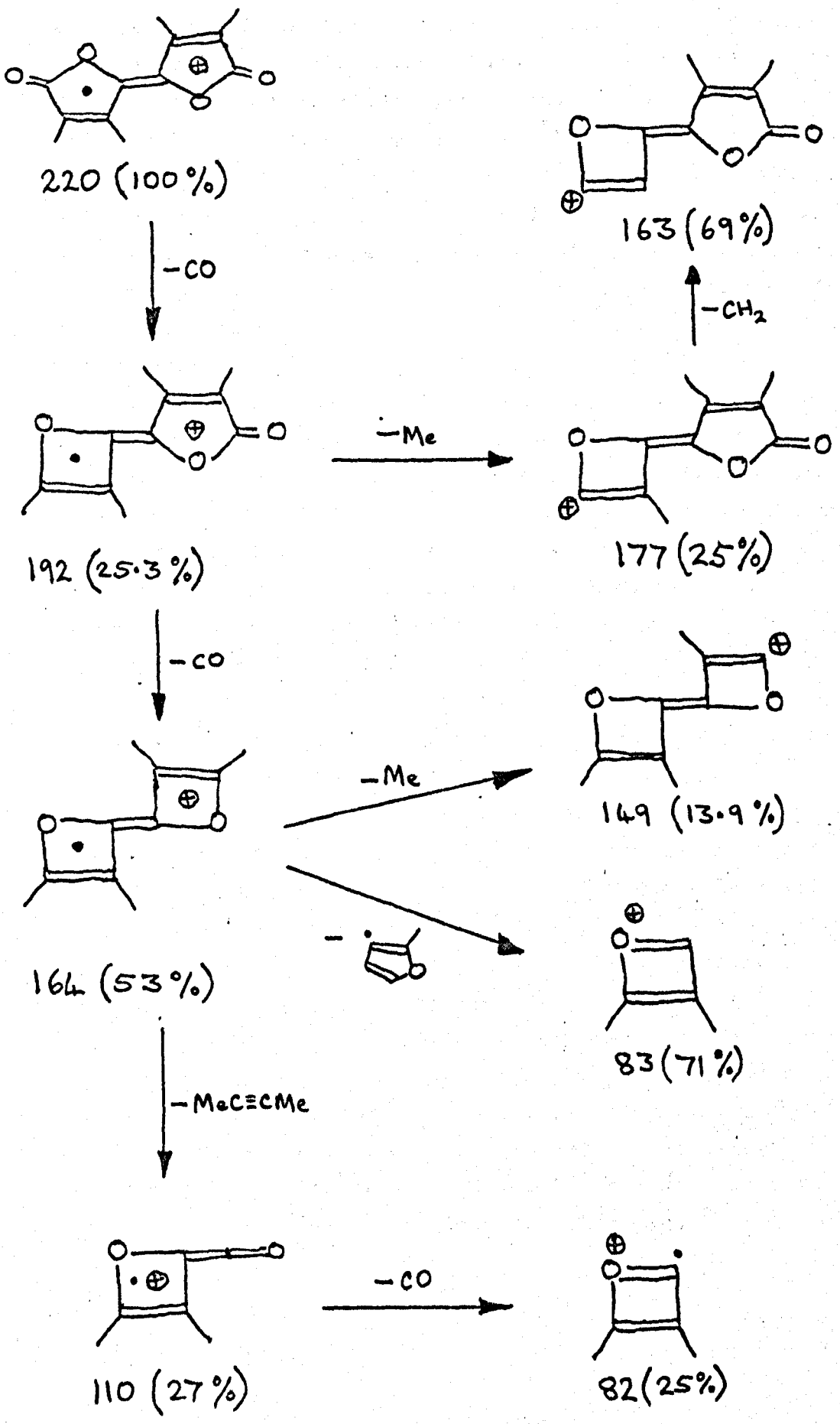


Fig. 6.12. TRANS-TETRAMETHYL BIFURANDIONE, TENTATIVE FRAGMENTATION SCHEME



by Tsuji and Nogi[14] using palladium chloride. However Tsuji and Nogi[15] have also obtained a substituted crotonolactone analogous to 'A' by the palladium catalysed carbonylation of diphenylacetylene (cf. Chapter 7.3). The formation of bifurandiones from the interaction of acetylenes and carbon monoxide under high pressure in the presence of a cobalt catalyst has been observed by Sauer et al.[12]. Acetylene, methylacetylene and diethylacetylene all gave mixtures of the isomeric bifurandiones. Sternberg and his co-workers[16] produced a complex containing a lactone skeleton by carbonylation of a dicobalt octacarbonyl/acetylene adduct, and such a complex may well be an intermediate in the formation of the bifurandiones.

Whilst lactones were the principal products obtained by palladium iodide catalysed carbonylation of dimethylacetylene, none was detected amongst the products of carbonylation of monosubstituted acetylenes, even when the carbonylation was carried out at elevated pressure (cf. Chapter 4.3 (v)). A possible exception was the evidence for a trace of lactone in the infrared spectrum of a concentrated phenylacetylene reaction mixture (cf. Chapter 5.2 (iii)).

Having established the identities of the products from the carbonylation of dimethylacetylene as far as possible, the reaction mixtures were analysed quantitatively. 'A', 'B' and 'C' were determined by gas chromatography, whilst the yield of 'D' was based on the amount recovered after recrystallisation. The yields obtained in reactions 6.4 and 6.5 are given in table 6.1 (the yields of 'B' being based on the assumption that the mass-spectral parent ion corresponded to the correct molecular weight, and that only one dimethylacetylene unit was involved in its structure). It was apparent that the 2,3-dimethylcrotonolactone was by far the most important product under a moderate carbon monoxide pressure.

(ii) Carbonylation Under a Higher Pressure: Having obtained small amounts of various products by carbonylating dimethylacetylene under a moderate pressure, it was of interest to use higher pressures. Three reactions (Rn. 6.6, 6.7 and 6.8) were carried out under various conditions and results are given in table 6.1.

Reaction No	6.4	6.5	6.6	6.7	6.8
Temperature (°C)	65	65	80	75	90
CO Pressure (atmos.)	17	17	100	90	90
Reaction Time (hours)	65	28	18	7	17
Catalyst (m.mols)	0.28	0.28	1.0	1.4	0.9
Butanol (g)	4.5	4.3	23.0	21.1	16.2
Dimethylacetylene (g)	0.42	0.44	2.5	3.0	3.2
2,3-Dimethylcrotonolactone	19.0	12.0	12.0	1.8	5.7
'B' ($C_{14}H_{24}O_4$)	0.9	0.8	11.5	0.6	1.9
Dibutyl dimethylmaleate	1.0	1.6	2.0	1.4	5.4
Trans-tetramethylbifurandione	0.4	0.4	2.5	0.1	1.8
Total Uptake	21.3	14.8	27.0	3.9	14.8

Table 6.1 The Yields of Products Obtained by the Carbonylation of Dimethylacetylene Under Various Conditions, % Yield Based on Dimethylacetylene

Under the most favourable conditions, a 27% conversion of dimethylacetylene was achieved, the catalyst exhibiting a productivity of 12.5. Considerable variation in the products was obtained when pressure and temperature were altered: low pressure and temperature favouring formation of dimethylcrotonolactone, high pressure favouring the tetramethylbifurandione and 'B', whilst higher temperature enhanced the ester formation.

6.4 THE ATTEMPTED INTERACTION OF DIMETHYLACETYLENE WITH THE CATALYST SOLUTION

Since acetylene and the monosubstituted acetylenes had undergone reactions when held in contact with the palladium iodide catalyst solution (cf. Chapters 2.4 (ii), 3.5 (i), 4.4 (i) and 5.2 (ii)) it was of interest to examine the behaviour of dimethylacetylene. A 0.5% solution of dimethylacetylene in butanol was prepared, and the catalyst solution added so as to produce a mixture of 8×10^{-5}m in sodium tetraiodopalladate(II) and its ultraviolet spectra were observed at intervals. As had been observed with the other acetylenes, the Pd-I charge transfer band at λ_{MAX} = 344 n,m. was reduced in intensity over a few days, whilst an intense absorption band appeared at short wavelength, its maximum possibly being beyond the range of the instrument. The spectra (fig. 6.13) constituted clear evidence of reaction, probably ligand displacement. However, no new

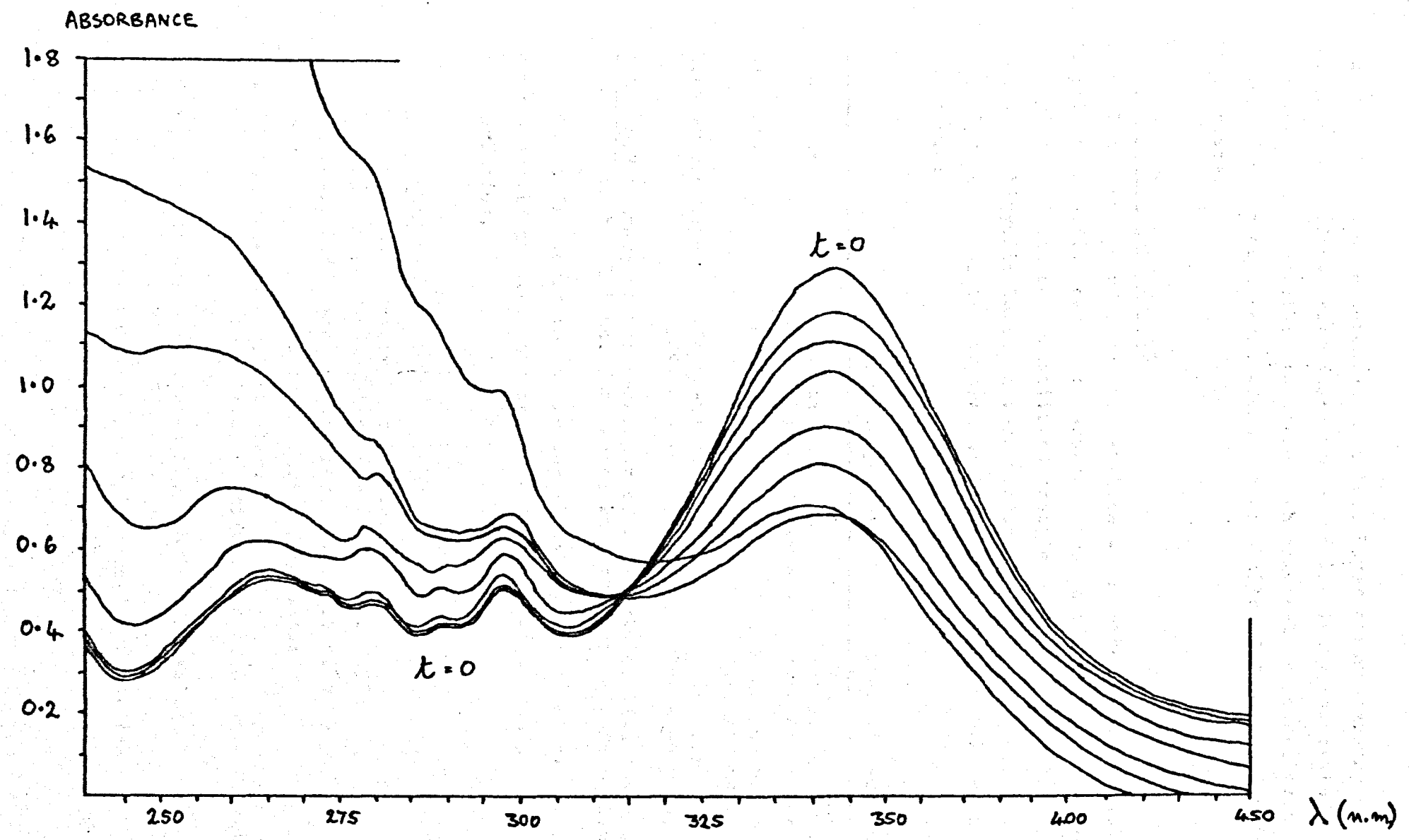


Fig 6.13 MIXTURE OF Me-C≡C-Me (0·5%) & Na_2PdI_4 (8×10^{-5}m) IN BUTANOL, ULTRAVIOLET SPECTRA AFTER 0, 5, 30 mins, 2, 5 hrs, 1, 2 and 5 days.

substances could be detected when thin layer chromatography was used as before (references above) to examine concentrated mixtures of the catalyst solution with dimethylacetylene, even after a period of several weeks had been allowed for reaction to take place.

6.5 SUMMARY & CONCLUSIONS

The reaction of dimethylacetylene with carbon monoxide using a palladium iodide catalyst, showed a most striking contrast with acetylene and the monosubstituted acetylenes, notably in that mono- and bicyclic lactones were produced.

Its behaviour is compared with that of methylacetylene in table 6.2:

	Methylacetylene	Dimethylacetylene
Reactivity	Reactive at atmospheric pressure	Unreactive at atmospheric pressure
Products	Mono- and Diesters	Mono- and Bicyclic Lactones and some Diester
Diester Products	Trans-isomer predominated	Cis-isomer predominated

Table 6.2 Summary of the Behaviour of Dimethylacetylene Towards Carbonylation, Contrasted with that of Methylacetylene

It is difficult to understand why the presence of two methyl groups should so alter the response of the triple bond to carbonylation.

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CHAPTER SEVEN

Studies on the Carbonylation of Diphenylacetylene

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7.1. INTRODUCTION

Having studied the effects of aliphatic and aromatic monosubstituents and aliphatic disubstituents on the carbonylation chemistry of the acetylenic bond, it was of interest to investigate an acetylene bearing two aromatic substituents. Diphenylacetylene being the simplest member of such a series, was chosen for the following work.

7.2. THE ATTEMPTED CARBONYLATION OF DIPHENYLACETYLENE AT ATMOSPHERIC PRESSURE

Initially, the carbonylation was attempted under conditions similar to those previously used for monosubstituted acetylenes, i.e. carbon monoxide was passed through a solution of the catalyst at atmospheric pressure, whilst a solution of diphenylacetylene in butanol was added progressively to the stirred solution. However no products were detected by gas chromatography, and it was concluded that diphenylacetylene was unreactive to carbonylation at atmospheric pressure.

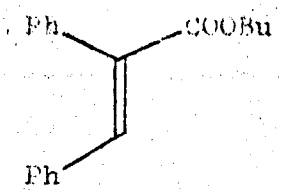
7.3. THE CARBONYLATION OF DIPHENYLACETYLENE ABOVE ATMOSPHERIC PRESSURE

(i) The Carbonylation Reaction: Carbonylation at atmospheric pressure having been unsuccessful, the reaction of diphenylacetylene with carbon monoxide at 100 atmos. and 80°C in the presence of palladium iodide was investigated. The gas chromatogram of the products (fig. 7.3) showed, besides butanol and diphenylacetylene, three peaks, 'A', 'B' and 'C'. The ketone desoxybenzoin was not present in detectable amounts, an observation which paralleled the finding that ethylmethyl ketone was not formed during the carbonylation of dimethylacetylene (cf. Chapter 6.3 (i)). Thin layer chromatography of the reaction mixture revealed three spots of the following R_F values: 0.64 (large), 0.26 and 0.18, which were presumed to correspond to the peaks 'A', 'B' and 'C' in the gas chromatogram. Unreacted diphenylacetylene was not detected.

(ii) Identification of the Products of Carbonylation:

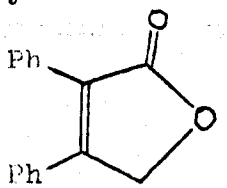
(a) A clear liquid corresponding to peak 'A' in the gas chromatogram and the large spot in the thin layer chromatogram was isolated from the reaction mixture by column chromatography. It proved to have

infrared and n.m.r. spectra and thin-layer and gas chromatograms identical with those of an authentic sample of butyl α-phenylcinnamate and was therefore concluded to be α-phenylcinnamate ester:



'A'

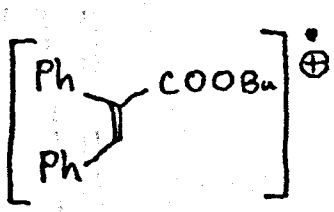
(b) A small amount of a substance corresponding to peak 'C' in the gas chromatogram and the spot of R_F = 0.18 in the thin-layer chromatogram was also obtained by column chromatography. The n.m.r. data (cf. fig. 7.2 (d) was identical with that quoted by Tsuji and Nogi[1] for 2,3-diphenylcrotonolactone vis. τ = 2.71, multiplet, 5H; τ = 4.98, singlet, 1H. The infrared bands at ν = 1751 (C=O stretch) and 1638 cm^{-1} (C=C stretch) were also close to those published by the Japanese workers (1750, 1640 cm^{-1}). It could thus be concluded that 'C' was 2,3-diphenylcrotonolactone:

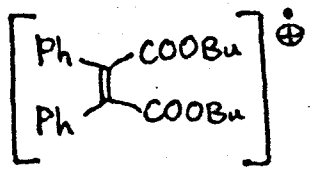


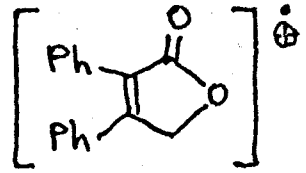
'C'

(c) A sample of 'B' was not isolated, but the mass spectrum of a crude mixture of products obtained from the reaction mixture (fig. 7.1) showed a peak of $\frac{m}{e}$ = 380.1917; $C_{24}H_{28}O_4$ requires 380.1987 (as well as those at $\frac{m}{e}$ = 280 and 236, corresponding to 'A' and 'C' respectively). $C_{24}H_{28}O_4$ was reasonably assigned as dibutyl diphenylbutenedioate. Gas chromatography revealed the presence of only traces of 'B' in the mixture.

Using a modified isolation procedure, it was possible to obtain a second mixture which contained about 7% of 'B' according to gas chromatographic analysis. The n.m.r. spectrum of the mixture (fig. 7.2 (a)) revealed ester- butyl and aromatic protons present to an extent of some 9% greater than could be accounted for by a mixture of 'A' and 'C' alone, supporting the presence of the diester. The mixture was subjected to vigorous hydrogenation, after which peak 'B' was no longer evident, and a new peak in the gas chromatogram and a new spot in the thin-layer chromatogram corresponded with dibutyl 2,3-diphenylsuccinate (cf. fig. 7.3).

A = 

B = 

C = 

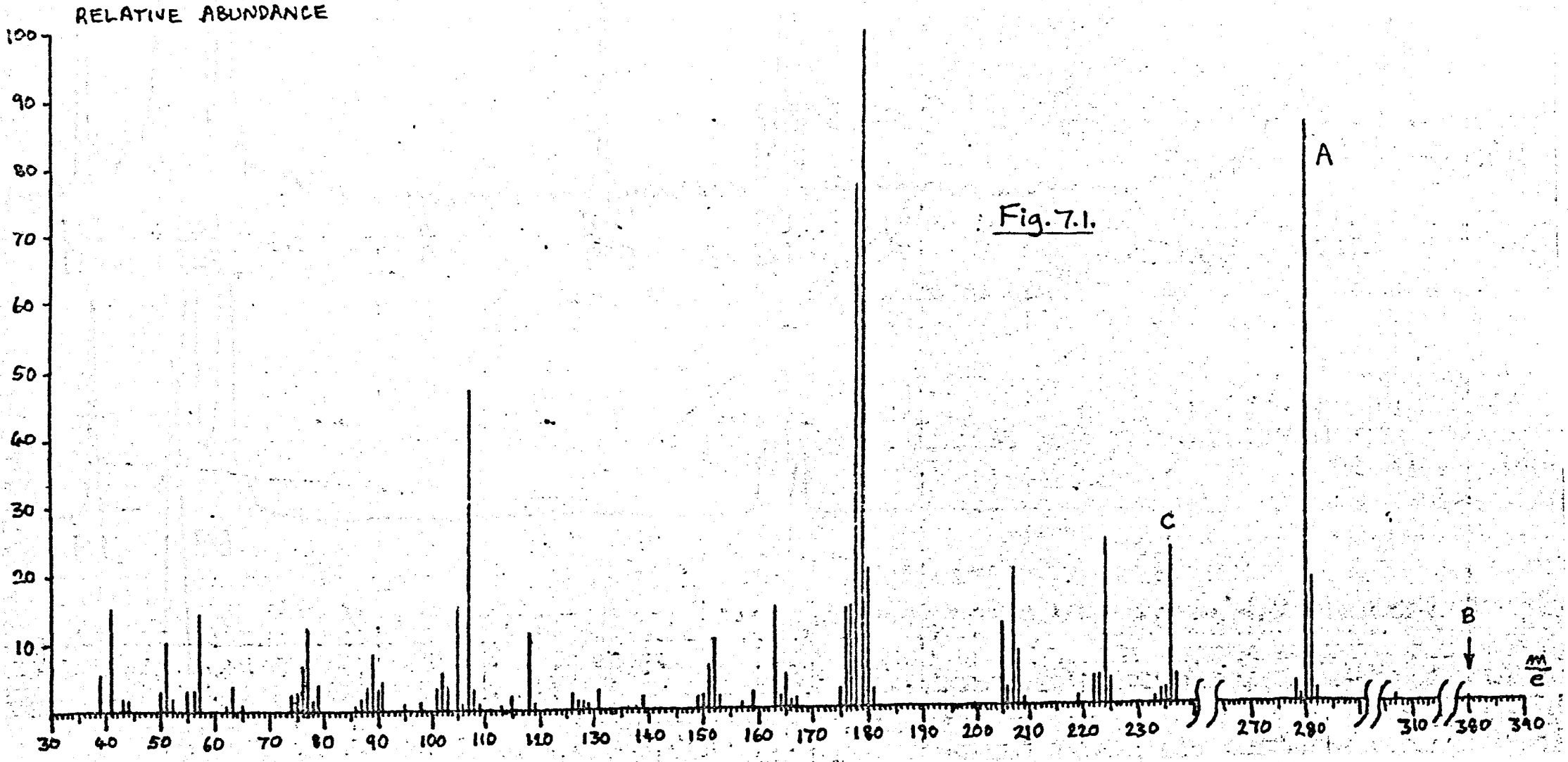


Fig. 7.1.

THE PRODUCT OF CARBONYLATION OF DIPHENYLACETYLENE, MASS SPECTRUM (M.S. 9, 70 eV)

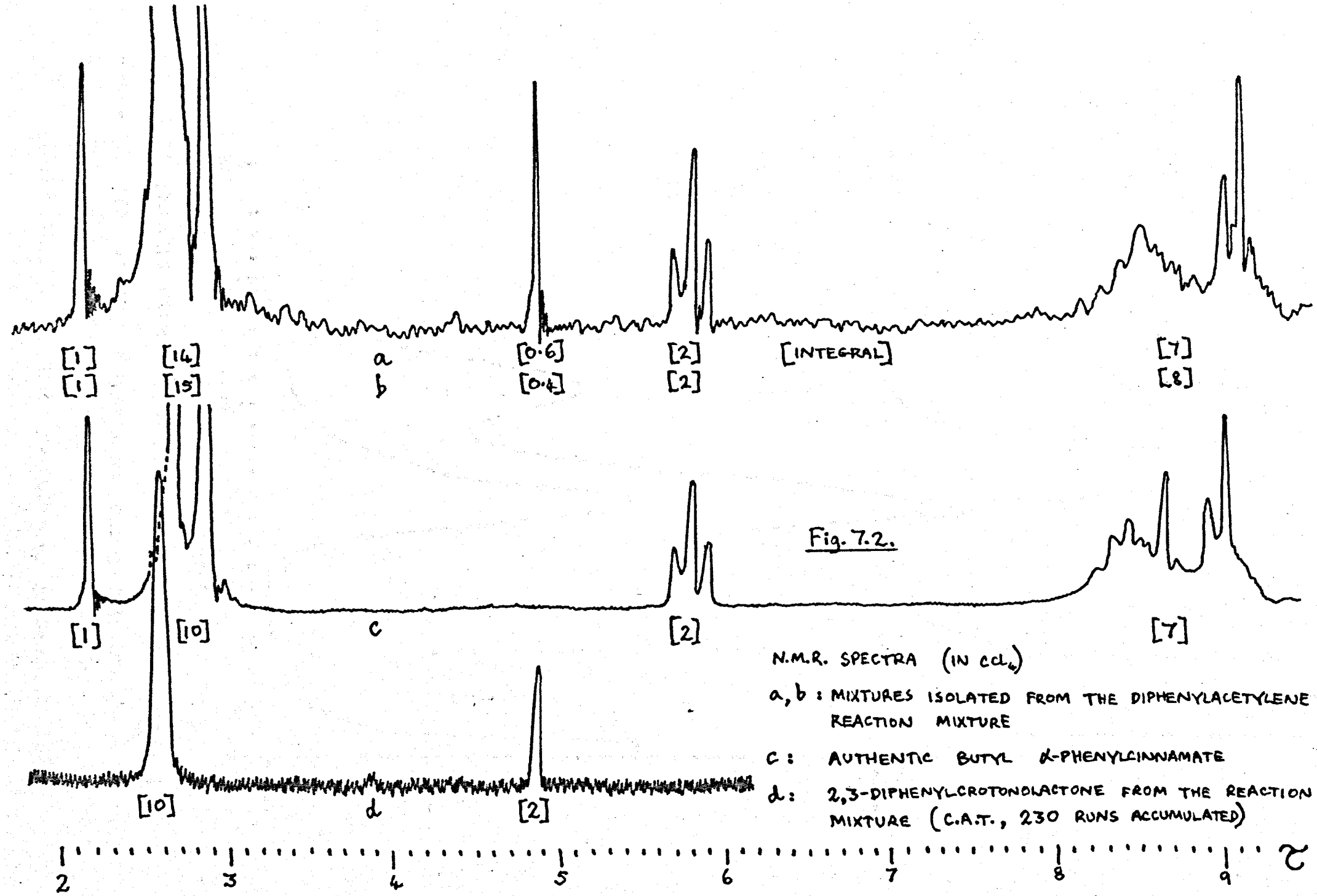


Fig. 7.2.

N.M.R. SPECTRA (IN CCl_4)

a, b : MIXTURES ISOLATED FROM THE DIPHENYLACETYLENE REACTION MIXTURE

c : AUTHENTIC BUTYL α-PHENYLCINNAMATE

d : 2,3-DIPHENYLCROTONOLACTONE FROM THE REACTION MIXTURE (C.A.T., 230 RUNS ACCUMULATED)

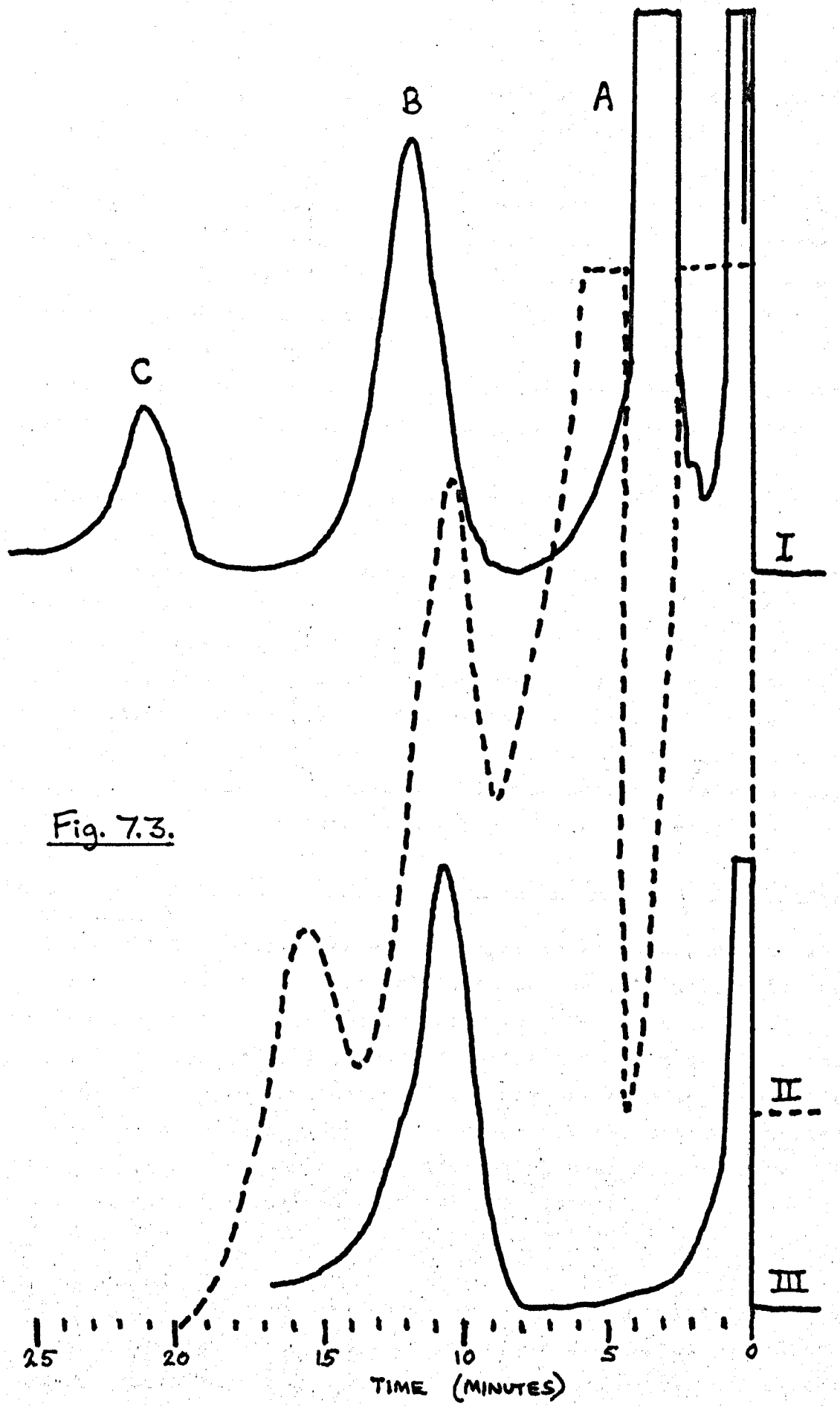


Fig. 7.3.

—— I PRODUCTS FROM THE CARBONYLATION OF DIPHENYLACETYLENE

- - - - II HYDROGENATED DIPHENYLACETYLENE PRODUCTS

—— III AUTHENTIC DIBUTYL 2,3-DIPHENYLSUCCINATE

GAS CHROMATOGRAMS ON N.P.G.S. COLUMN AT 160°C

From the above evidence, it was concluded that peak 'B' corresponded with dibutyl diphenylbutenedioate, PhC(COOBu)=CPh(COOBu). Although no assignment of stereochemistry was possible, a cis-configuration would appear to be consistent with previous work when dibutyl dimethylmaleate was formed in dimethylacetylene reactions, (cf. Chapter 6.3 (i) and Tsuji and Nogi[1] reported the formation of diphenylmaleate ester on carbonylating diphenylacetylene with a palladium chloride catalyst.

'A', 'B' and 'C' were analysed quantitatively by gas chromatography. They were present as follows, 'A' = butyl α-phenylcinnamate in 44% yield, 'B' = dibutyl diphenylbutenedioate in 3% yield, and 'C' = 2,3-diphenylcrotonolactone in 8% yield, based on the diphenylacetylene.

The conversion of diphenylacetylene was 55% and the productivity of the catalyst was 6.

These observations contrast with the results of Tsuji and Nogi[1], who obtained a 20% yield of the lactone and only traces of the monoester from a reaction using a palladium chloride catalyst in ethanol and carbon monoxide at 100 atmos. Yields of the diester were increased when hydrogen chloride was present. In the iodide catalysed reaction described above, the monoester was the predominant product.

7.4. THE ATTEMPTED INTERACTION OF DIPHENYLACETYLENE AND THE CATALYST SOLUTION

Since all the acetylenes examined previously had shown a tendency to undergo a reaction with the palladium iodide catalyst, which could be followed by ultraviolet spectroscopy (cf. Chapters 2.4 (ii), 3.5 (i), 5.2 (ii), and 6.4) it was of interest to examine the spectrum of a diphenylacetylene/palladium iodide mixture over a period of time. No changes were evident, neither could any new product be detected in the mixture by thin-layer chromatography, even after several weeks had been allowed for any reaction to take place.

7.5. SUMMARY AND CONCLUSIONS

It was apparent from the above work that diphenylacetylene to some extent shares the tendency of dimethylacetylene to form lactones on reaction with carbon monoxide in the presence of palladium iodide. However, the monoester α-phenylcinnamate was by far the most important product. Such predominance of monoester had not previously been

observed in the present study, and it may be attributed in part to the steric properties of the phenyl groups.

7.6. REFERENCE

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CHAPTER EIGHT

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T A B L E S

8.1. Electron Densities on the Atoms of Free and Complexed Methylacetylene

8.1. INTRODUCTION

Prior to a detailed discussion of mechanisms of relevance to the present work, it is desirable to review the chemistry of acetylene and carbon monoxide in relation to palladium. A similar review was given by C.B.Lines[1].

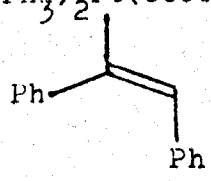
(i) The Interaction of Acetylene with Palladium Compounds: Complexes involving acetylenic moieties co-ordinated to platinum are well known[2, 3, 4, 5], and the π-bonding involved in them is well understood[6, 7]. Many other transition metals have also yielded acetylene complexes[8]. However, palladium complexes do not appear to be so stable[9] and are usually formed from acetylenes with electronegative substituents[10], although Hosokawa and his co-workers[11] have isolated the dimeric ditertiarybutylacetylenepalladium(II) chloride complex.

(ii) The Interaction of Carbon Monoxide with Palladium Compounds: Carbonyl compounds of many transition metals are well known and documented[12], but palladium only forms a few, poorly defined complexes[13]. $(Pd(CO)Cl_2)_2$ was described by Manchot[14] and the polymeric Pd(CO)Cl was prepared by Dent, Long and Whitfield[15]. The formation of $Pd_2(CO)_2Cl$ was claimed by Fischer and Vogler[16], but later discounted by Schnabel and Kober[17].

(iii) The Formation of Palladium Hydride Complexes: Palladium hydride complexes are apparently very unstable though $(Et_3P)_2PdHCl$ was obtained in an impure state by Chatt and his co-workers[18], and later isolated by Brooks and Glockling[19]. The transient formation of species such as PdHCl and PdH_2 has been postulated by Tsuji[20] to account for palladium catalysed carbonylation of olefins.

(iv) Palladium Vinyl Formation: The formation of platinum vinyls from acetylenes is known to occur, thus the reaction of bis(triphenylphosphine)platinum(II) trifluoracetate, I, with diphenyl acetylene gave II[21]

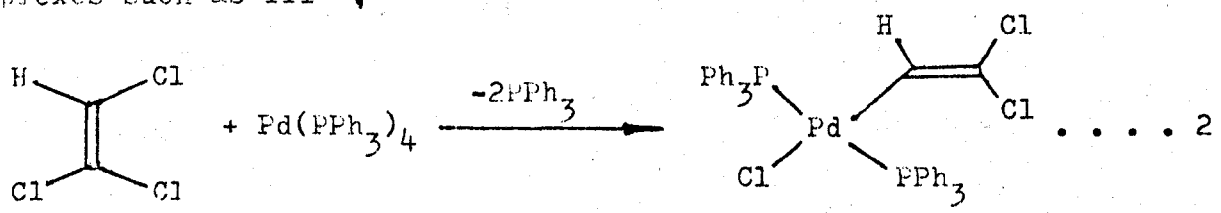
$$(Ph_3P)_2Pt(OCOCF_3)_2 + PhC{\equiv}CPh \xrightarrow{MeOH} (PPh_3)_2Pt(OCOCF_3) \quad \text{. . . . . 1}$$



I II

The nature of the anion was critical; thus with the corresponding acetate, only an acetylene co-ordination complex was obtained.

Palladium vinyls are also known, thus a number of chloroolefins reacted with tetrakis(triphenylphosphine)palladium(0) to yield complexes such as III[22],



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III

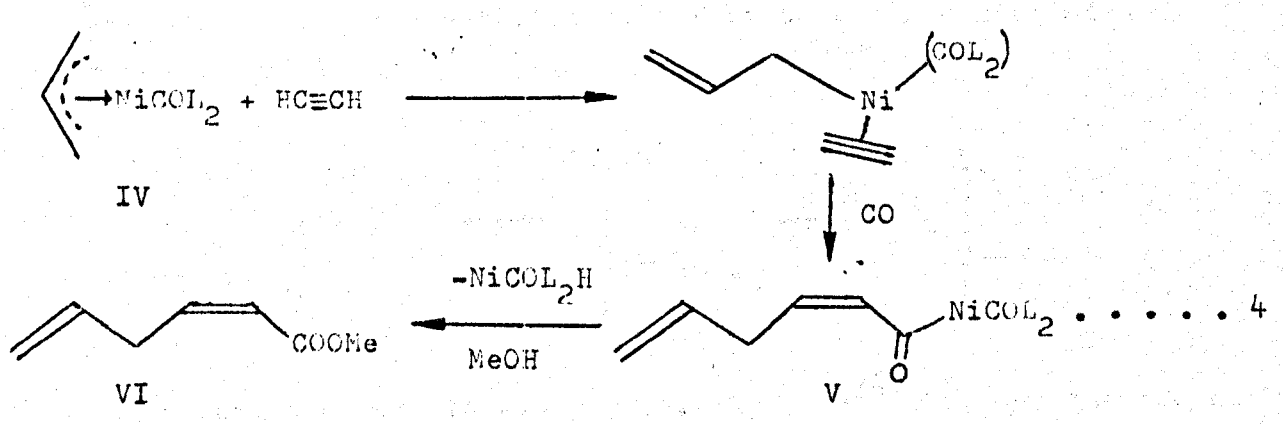
(v) The Insertion of Carbon Monoxide into Palladium - Carbon σ-Bonds:

The insertion of carbon monoxide between a metal and its σ-alkyl ligand has been observed by a number of workers[23, 24]. Booth and Chatt[24, 25] have prepared a number of acyl and aroyl complexes by treating the corresponding alkyl and aryl compounds with carbon monoxide at room temperature and pressure, e.g.

$$PdClMe(PEt_3)_2 + CO \longrightarrow PdCl(COMe)(PEt_3)_2 \quad \ldots\ldots\ldots 3$$

(vi) The Insertion of Unsaturated Moieties into Palladium - Carbon σ-Bonds:

This subject has been reviewed by Heck[23]. Clear examples of the insertion of olefins are rare, but reactions between cobalt acyls and olefins occur at high temperatures and pressures in the presence of hydrogen donors and carbon monoxide to yield ketones[26]. The reaction discovered by Chiusoli[27], in which an allyl compound was linked to an acetylene during carbonylation, was assumed[28] to proceed by insertion of an acetylene unit into a nickel-carbon bond:



. 4

Ryang and his co-workers[29] have postulated the insertion of olefins

into σ-vinyl complexes formed between nickel compounds and styrene, to yield coupled products.

(vii) Mechanisms Previously Postulated for the Carbonylation of Olefins and Acetylenes:

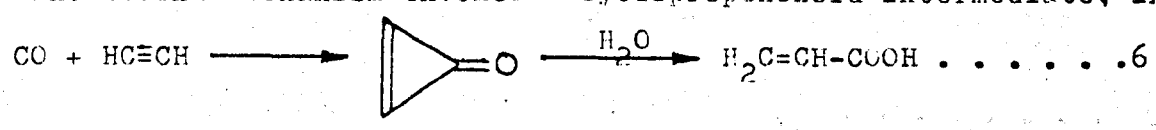
Reppe[30] originally proposed three formal mechanisms for the nickel catalysed reaction. The first involved a ketenoid intermediate, VII:

$$CO + HC\equiv CH \longrightarrow O{=}C{=}C{=}CH_2 \xrightarrow{H_2O} H_2C{=}CH{-}COOH \quad \ldots\ldots\ 5$$

VII

but dismissed such mechanism because it predicted the formation of only linear products from substituted acetylenes, whereas branched acids and esters predominated.

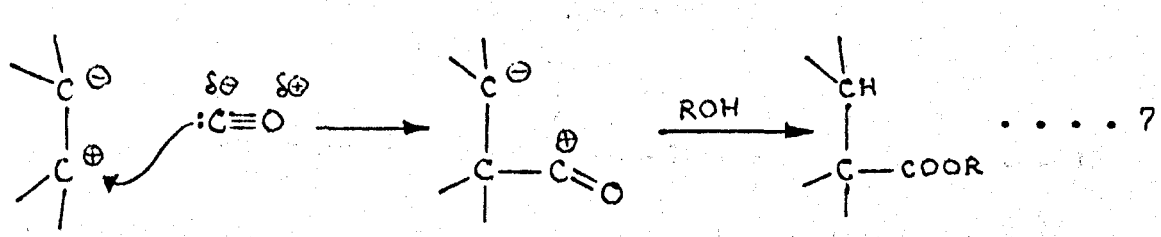
The second mechanism invoked a cyclopropenonoid intermediate, IX



IX

However, Bird and Hudec[31] have demonstrated that the route is untenable. They treated diphenylcyclopropenone with ethanolic benzene and hydrochloric acid; it decomposed to diphenylacetylene and carbon monoxide.

The last of Reppe's mechanisms invoked nucleophilic attack on acetylene by carbon monoxide. The same idea has been used by a number of authors, thus Jones and his co-workers[32] applied this concept to reactions between nickel tetracarbonyl and acetylenic alcohols. More recently, Bittler et al.[33] carbonylated olefins under mild conditions, using palladium phosphine complexes as catalysts. They proposed a mechanism involving nucleophilic attack by carbon monoxide on a polarised double bond:



An alternative scheme was proposed by Heck[34, 23], for the nickel

catalysed reaction. A nickel hydride species, X, combined with acetylene to give a σ-vinyl complex, XI, which could then insert a carbonyl moiety from its co-ordination sheath to yield XII. The acyl group would then be cleaved off as halide or ester:

$$\underset{X}{HNi(CO)_2X} + HC{\equiv}CH \longrightarrow \underset{XI}{CH_2{=}CHNi(CO)_2X}$$

$$\downarrow CO$$

$$H_2C{=}CH{-}COOR + HNi(CO)_2X \xleftarrow{ROH} \underset{XII}{CH_2{=}CH{-}CO{-}Ni(CO)_2X} \quad \ldots\ldots\ldots \quad 8$$

Cleavage of cobalt acyl complexes by alcohols to yield esters is known to occur[35], e.g.

$$Me{-}CO{-}Co(CO)_4 + MeOH \longrightarrow MeCOOR + HCo(CO)_4 \quad \ldots\ldots\ldots\ldots \quad 9$$

though a more normal course would be cleavage to yield aldehydes[36]. Wilkinson and his co-workers[37] cleaved a number of acyl rhodium complexes with hydrochloric acid to obtain the aldehyde, e.g.

$$L_2CORhCOEt + HCl \longrightarrow EtCHO + RhCOL_2Cl \quad \ldots\ldots\ldots\ldots \quad 10$$

Henry[38] has carbonylated phenylmercuric chloride in the presence of palladium and obtained benzoyl chloride:

$$PhHgCl + PdCl_2 + CO \longrightarrow PhCOCl + Pd + HgCl_2 \quad \ldots\ldots\ldots\ldots \quad 11$$

The reaction was presumed to proceed via PhPdCl and PhCOPdCl. When alcohols were used as solvents, ester products were obtained. The reaction thus affords a further example of carbon monoxide insertion with acyl cleavage.

A mechanism similar to that of Heck was advanced by Tsuji[20] to explain the palladium chloride catalysed carbonylation of olefins:

$$\underset{XIII}{HPdCl} + R{-}CH{=}CH_2 \longrightarrow \underset{XIV}{R{-}CH_2CH_2{-}PdCl}$$

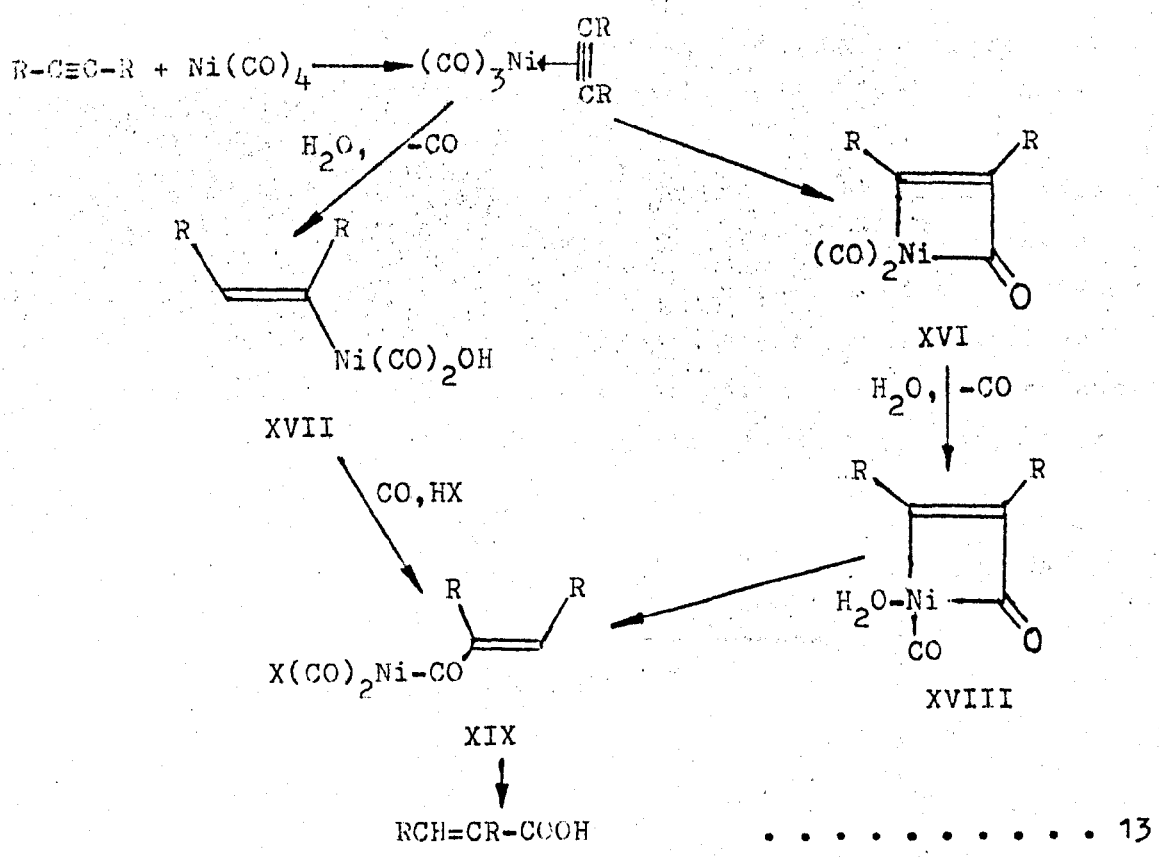
$$\downarrow CO$$

$$\underset{XV}{R{-}CH_2CH_2{-}CO{-}PdCl}$$

$$\downarrow$$

$$RCH_2CH_2COOR + HCl \xleftarrow{ROH} R{-}CH_2CH_2{-}CO{-}Cl + Pd^{o} \quad \ldots\ldots\ldots \quad 12$$

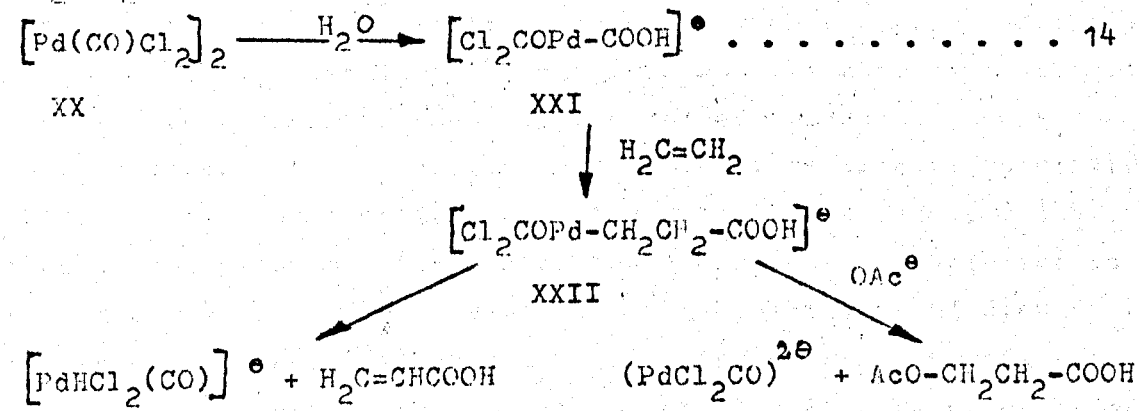
A variant of the mechanism was suggested by Bird and Briggs[39] for the stoicheiometric reaction between diarylacetylenes and nickel carbonyl.



. 13

The cyclic intermediates, XVI, XVIII, which they proposed are of some interest in relation to the present work.

The suggestion has been made by Olivier et al.[40] that the carbonylation of ethylene using a palladium chloride catalyst in the presence of acetate ion may proceed from a palladium carbonyl to a Pd-COOH species, thence by co-ordination and insertion of the olefin to a species XXII which can split off a palladium hydride to yield acrylic acid, or be cleaved by acetate ion to give $AcO-CH_2-CH_2-COOH$:

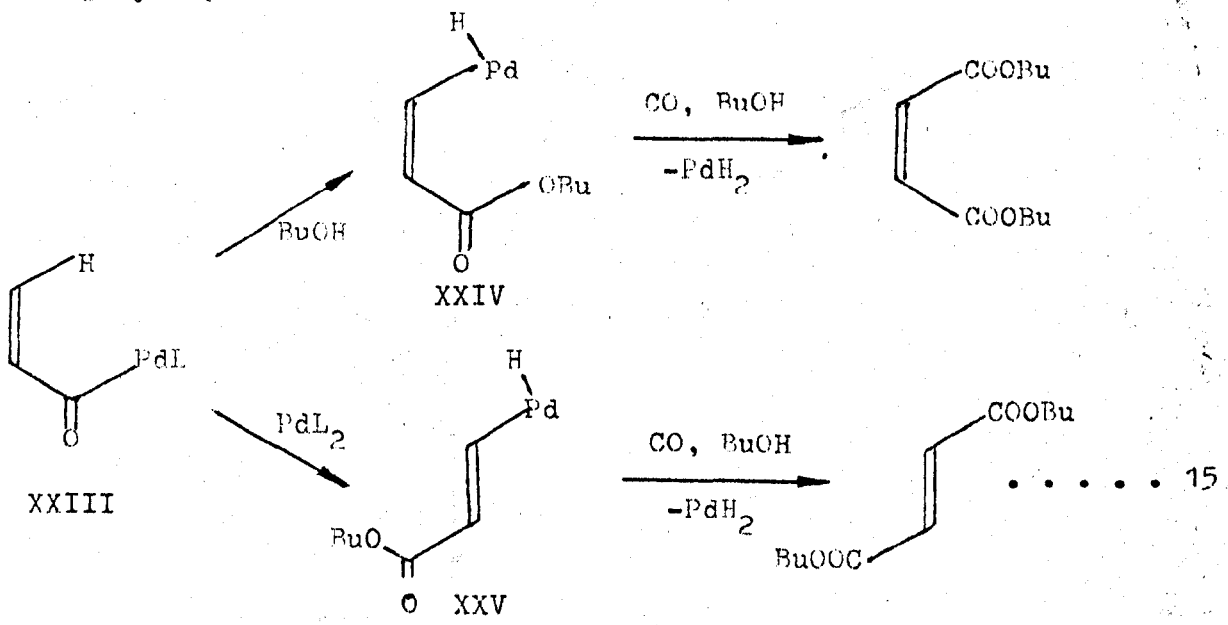


. 14

However, Bittler et al.[33] have discounted the possibility that carbon monoxide could be activated by palladium compounds below 150°C, on the grounds that they were unable to achieve the carbonylation

of non-olefinic substances such as alcohols and alkyl halides using palladium catalysts, though they could be carbonylated with other transition metal catalysts.

Very little has been written about possible mechanisms leading to products of dicarbonylation, though Tsuji and Nogi[44] suggest a 'concerted cis- attack on the triple bond' in the reaction of diethyl acetylenedicarboxylate. C.B.Lines[1] proposed a mechanism similar to those of Heck[34] and Tsuji[20] for the formation of monoesters, and extended it to include diesters by proposing further carbonylation following hydrogen transfer:



. 15

An intramolecular hydrogen transfer yielded the cis- diester whilst an intermolecular transfer yielded the trans- isomer.

8.2. SUGGESTED MECHANISMS OF REACTIONS IN THE PRESENT WORK

The results described in the previous six chapters showed certain trends and certain anomalies. Acetylene and the three monosubstituted acetylenes gave broadly the same type of ester products, though the presence of a substituent greatly reduced the formation of saturated products. The presence of an aromatic substituent favoured linear addition of the ester moiety; such behaviour was only observed to a minor extent with alkyl acetylenes. The reactivity of disubstituted acetylenes was markedly different, an elevated carbon monoxide pressure being required to achieve carbonylation, and lactones being observed amongst the products.

A number of additives had a noticeable effect on the reactions of

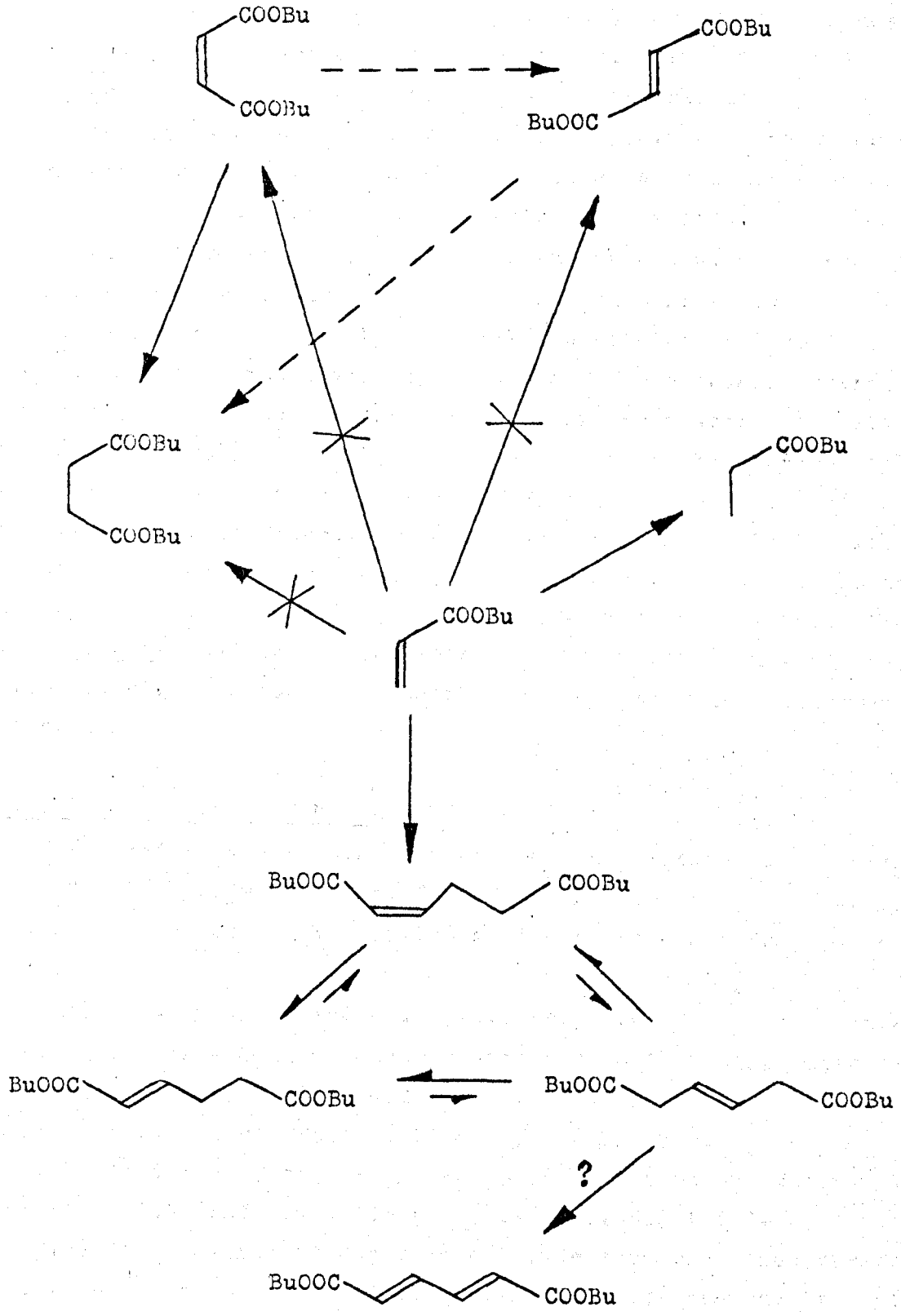


Fig. 8.1

Known Relationships Amongst the Acetylene Carbonylation Products

monosubstituted acetylenes and the parent hydrocarbon. Thus, in most cases, the presence of hydrogen chloride increased the yield of monoester, whilst the passage of air decreased it.

Ideally, a general mechanism would explain all the observed phenomena and anomalies, but in practice an account of possible modes of formation of the principal products must suffice.

The interrelationships of the ester products, which need to be considered in proposing a mechanism, are summarised in fig. 8.1. Acrylate ester (or its alkyl or aryl substituted analogue) was reduced to propionate, whilst maleate and, to a lesser extent, fumarate, were reduced to succinate under the reaction conditions. Maleate ester was partially isomerised, but in the absence of hydrogen chloride, it did not seem possible for such a route to yield all the observed fumarate ester. Carbonylation of acrylate to yield diesters did not occur, equally the diesters were not decarbonylated to monoesters. Reaction of acrylate with a further unit of acetylene yielded cis-hex-2-enedioate, which was in equilibrium with the other hexenedioate esters. Oxidation to muconate was an unproven possibility.

8.3. THE FORMATION OF MONOESTERS

The simplest products arising from the carbonylation reactions were unsaturated monoesters, formed by the addition of CO and BuOH to the triple bond. The following facts are known from the preceding studies:

(a) Non-linear addition was favoured, i.e. in a monosubstituted acetylene, the -COOBu moiety was attached to the substituted carbon atom (cf. Chapter 3.2(i), 4.2 (ii)). This trend was not entirely borne out by phenylacetylene (Chapter 5.2 (iii)).

(b) Addition of the H- and -COOBu moieties was predominantly cis- (Chapters 2.4 (ix), (x), 3.5 (i), 4.4 (ii), 5.2 (iii).

(c) The presence of hydrogen chloride favoured monoester formation cf. Lines[1] and (Chapter 2.2 (ii), 4.3 (iii)); however the effect was not observed in the cases of methylacetylene and phenylacetylene (Chapter 3.4, 5.3).

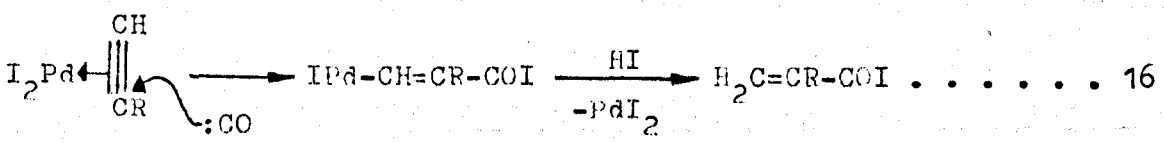
(d) The passage of air during the reaction had the effect of reducing the amount of monoester formed (Chapter 2.2 (iii) (a), 4.3 (i)), except in the case of phenylacetylene (Chapter 5.4 (i).

(e) Low concentrations of benzoquinone enhanced monoester formation, but high levels inhibited it (Chapter 3.3 (vi)).

(f) Carbonylation of acetylenes in butanol-O-d led to lower yields of monoesters than were obtained in butanol.

Inasmuch as no reaction occurred between carbon monoxide and the acetylene in the absence of catalyst, it is apparent that one or both reagents is activated by co-ordination prior to reaction. A number of routes may be considered:

(i) Carbon Monoxide as a Nucleophile: Following the suggestion of Bittler et al.[33], activation of the acetylene can be envisaged, with nucleophilic attack by carbon monoxide:



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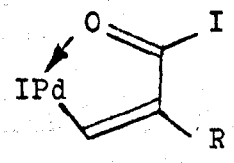
XXVI

Alcoholysis of -COI to -COOBu and HI could occur either before or after the organic moiety had been cleaved from the palladium.

The route would be expected to involve both cis- and trans- addition of -COOBu and H, with the latter predominating. In practice, predominantly cis- addition has been observed, and it is necessary to assume either prior co-ordination of the carbonyl entity or stabilisation of the intermediate complex such as XXVII



XXVII

It can be argued that cleavage of XXVI or XXVII would be greatly accelerated by the presence of added hydrogen chloride, and slowed by the removal of hydrogen iodide by benzoquinone or air, thus explaining the respective increases and decreases of monoester formed. However, there are serious objections to the pathway.

The carbonylation of acetylene could not be effected with a mercuric iodide catalyst (Chapter 2.4 (vi)) though the latter is well known to activate acetylenes to nucleophilic attack. Moreover, the

reaction of a model nucleophile (cyanide ion) with acetylene was not promoted by the palladium catalyst (cf. Chapter 2.4 (vii)).

Doubt is also cast on the nucleophilic role of carbon monoxide in the present reaction, by the calculations of Nelson et al.[7]. The population analyses based on either Löwdin or Mulliken (L or M) procedures for square planar or pseudotetrahedral complexes of methylacetylene with $(PH_3)_2Pt$ were in qualitative agreement (cf. fig.8.2). They showed that the co-ordinated acetylene (in contrast with the free molecule) had a negative charge on the substituted carbon atom, and therefore the terminal carbon atom would be more susceptible to nucleophilic attack, and in the present case, linear monoester should be formed preferentially from methylacetylene, assuming that a change of metal had no great effect.

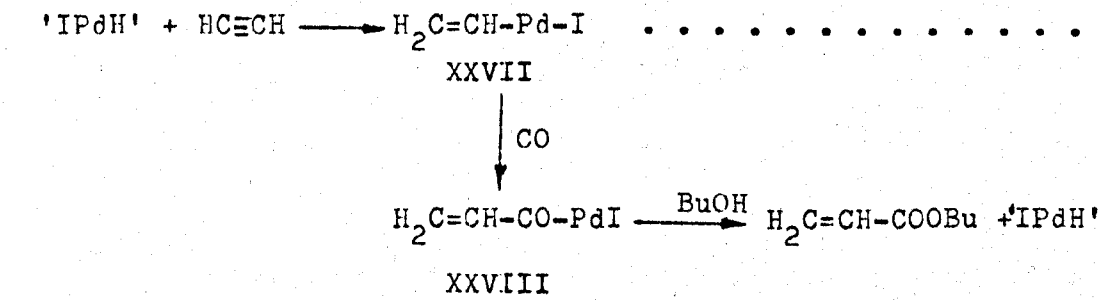
	UNCOMPLEXED MOLECULE		PSEUDOTETRAHEDRAL COMPLEX		SQUARE PLANAR COMPLEX	
	L	M	L	M	L	M
H	-0.046*	-0.052	-0.055	-0.076	-0.066	-0.087
C	+0.285	+0.317	+0.310	+0.303	+0.262	+0.256
C	+0.242	+0.239	-0.441	-0.713	-0.584	-0.839
C	-0.409	-0.442	+0.326	+0.077	-0.084	-0.356
H	+0.021	+0.041	+0.025	-0.006	-0.025	-0.057

* +0.046 in original paper, but -0.046 required to give overall electroneutrality

Table 8.1: Electron Densities on the Atoms of Free and Complexed Methylacetylene, According to Nelson et al.[7].

(ii) The Insertion of Carbon Monoxide into a Palladium-Vinyl Bond:

It is possible to envisage palladium compounds bringing about the carbonylation of acetylene by a route similar to that proposed by Heck[23, 34] for nickel, i.e.



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It is assumed that the palladium-vinyl is formed from co-ordinated acetylene and the regenerated palladium hydride species represented

'IPdH'. The formation of esters can be envisaged as the direct cleavage of the Pd-C bond by alcohol, or prior formation of the acid iodide, followed by alcoholysis. It would be surprising for such a route to operate in the presence of metal hydrides with no aldehyde formation:

$$\underset{\text{XXVIII}}{H_2C{=}CH{-}CO{-}PdI} + HPdI \longrightarrow H_2C{=}CH{-}CHO + PdI_2 + Pd^{\circ} \quad \ldots\ldots 18$$

But otherwise, the route provides a good explanation of the observed facts, e.g. added acid would promote more rapid cleavage of XXVIII, and thus increase the amount of monoester observed. However, it is difficult to envisage a consistent pathway giving both mono- and diesters (v.i.)

(iii) The Insertion of Acetylene into a Palladium-Carbonyl Bond:

A third possibility involves the insertion of acetylene into a palladium-carbon monoxide bond:

$$\underset{\text{XXIX}}{I_2Pd{-}C{\equiv}O} + RC{\equiv}CH \longrightarrow \underset{\text{XXX}}{IPd{-}CH{=}CR{-}COI} \xrightarrow{BuOH} H_2C{=}CR{-}COOBu + PdI_2 \quad \ldots 19$$

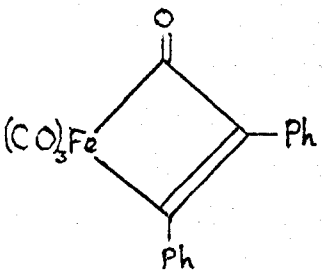
The mechanism resembles that proposed by Olivier et al.[40] for the carbonylation of ethylene. It would lead predominantly to cis- esters as observed, and cleavage of XXX by added acid would lead to an enhanced yield of monoester. Moreover, in the case of monosubstituted acetylenes, steric effects would lead to the predominant formation of the non-linear monoester as observed, and the low reactivity of disubstituted acetylenes could be explained on steric grounds. However, insertion of hydrocarbons into metal carbonyl bonds has never been substantiated[23].

(iv) The Formation of a Cyclic Intermediate: Finally, monoester formation via a cyclic intermediate XXXI can be postulated:

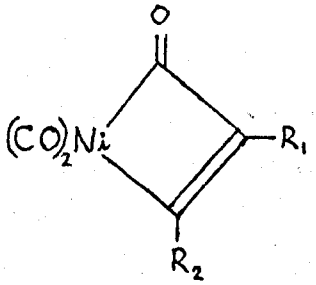
$$PdI_2 + CO + HC{\equiv}CR \longrightarrow \underset{\text{XXXI}}{I_2Pd\langle \overset{O}{\overset{\|}{C}}{=}CH{-}CHR\rangle} \xrightarrow{BuOH} PdI_2 + H_2C{=}CR{-}COOBu \quad \ldots\ldots 20$$

Though obviously a highly strained system, it is not unreasonable to postulate the transient formation of XXXI, as Schrauzer[42] has isolated a complex formulated as XXXII. Bird and Briggs[39] proposed the corresponding nickel compound, XXXIII as an intermediate in the

stoicheiometric carbonylation of a variety of diarylacetylenes with nickel tetracarbonyl:



XXXII



XXXIII

Again, steric effects must be invoked to explain the observed orientation of attack.

(v) Butyl β-Butoxycrotonate: The anomalous product, butyl β-butoxycrotonate was detected in small amounts when benzoquinone was present in carbonylation mixtures (cf. Chapter 3.3 (vi)). Addition of butanol across the triple bond of methylacetylene, followed by oxidative carbonylation of isopropenylbutyl ether is one possible route to the butoxy- ester:

$$Me\text{-}C{\equiv}CH \xrightarrow{BuOH} H_2C{=}CMeOBu \xrightarrow{CO,BuOH} BuOOC\text{-}CH{=}C(OBu)Me \quad \ldots\ldots 21$$

which might be favoured by the formation of butoxide ions from butanol by the action of benzoquinone.

A second route, formation of butyl crotonate, followed by attack by butoxide ion can be discounted since no butoxycrotonate was formed when butyl crotonate was warmed in the presence of butanol and benzoquinone

$$Me\text{-}C{\equiv}CH \xrightarrow{CO,BuOH} BuOOC\text{-}CH{=}CH\text{-}Me \xrightarrow[-H^{\oplus}]{BuO^{\ominus}} BuOOC\text{-}CH{=}C(OBu)Me \quad \ldots\ldots 22$$

8.4. THE FORMATION OF VIC-DIESTERS

Since it has been established, both by C.B.Lines[1] and in the present work (Chapter 2.4 (ii), 3.5 (v)) that the vic-diesters were not produced as a result of the carbonylation of monoesters, it seemed consistent with a rational scheme that mono- and diesters should have been produced from a common intermediate.

(i) Formation from a Palladium-Vinyl Intermediate: Applying the carbon monoxide insertion proposal of Heck[23] to the supposed vinyl palladium intermediate, XXVI, formed by nucleophilic attack of carbon monoxide on the acetylene (8.3 (i)), could lead to diester formation:

$$IPd\text{-}CH{=}CR\text{-}COI \xrightarrow{CO} IPd\text{-}CO\text{-}CH{=}CR\text{-}COI \xrightarrow{-Pd^{o}} ICO\text{-}CH{=}CR\text{-}COI \quad \ldots\ldots 23$$

XXVI XXXIV

The predominant formation of trans- diester would thus be explained, though it would be necessary to suppose that cis- monoester was favoured because the extra co-ordination involved in stabilising the cis- intermediate XXVII prevented reaction with a further carbonyl moiety.

The objections that the calculations of Nelson[7] raise for the methylacetylene case, i.e. that nucleophilic attack would lead to an intermediate IPd-CMe=CH-COI (XXXV), are not removed by the fact that XXXV would give the observed diesters, since it would also be expected to give rise to linear monoesters which were not observed in significant amounts.

It is also rather unsatisfactory to require carbon monoxide to react in two different ways to produce one compound.

In view of the above mentioned objections, it does not seem possible that the 'nucleophilic carbon monoxide' mechanism is applicable to the formation of either mono- or diesters.

However, XXVI is identical to the intermediate XXX postulated as arising from the insertion of acetylene into a palladium-carbon monoxide bond (8.3 (iii)). The alternate insertion of acetylene and carbon monoxide, as shown in fig. 8.2, thus appears to be a plausible route to both mono- and diesters:

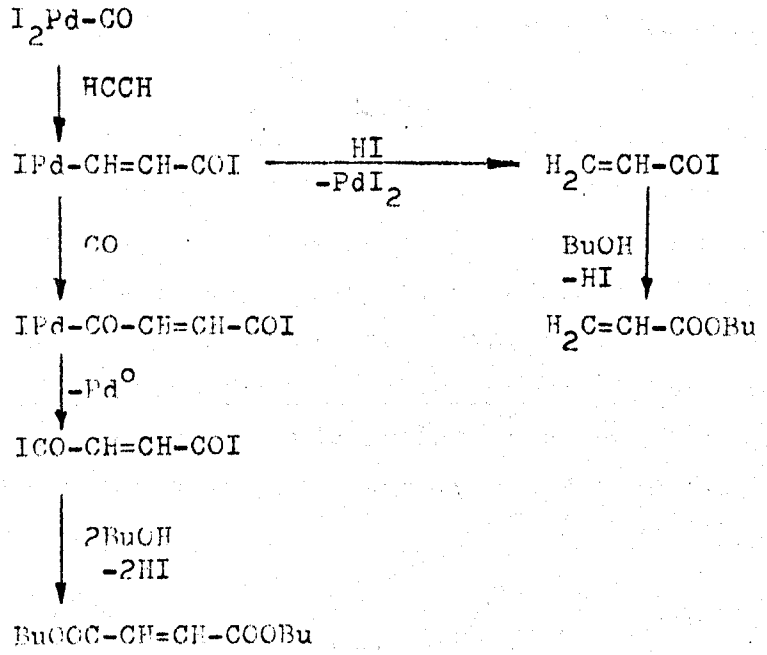
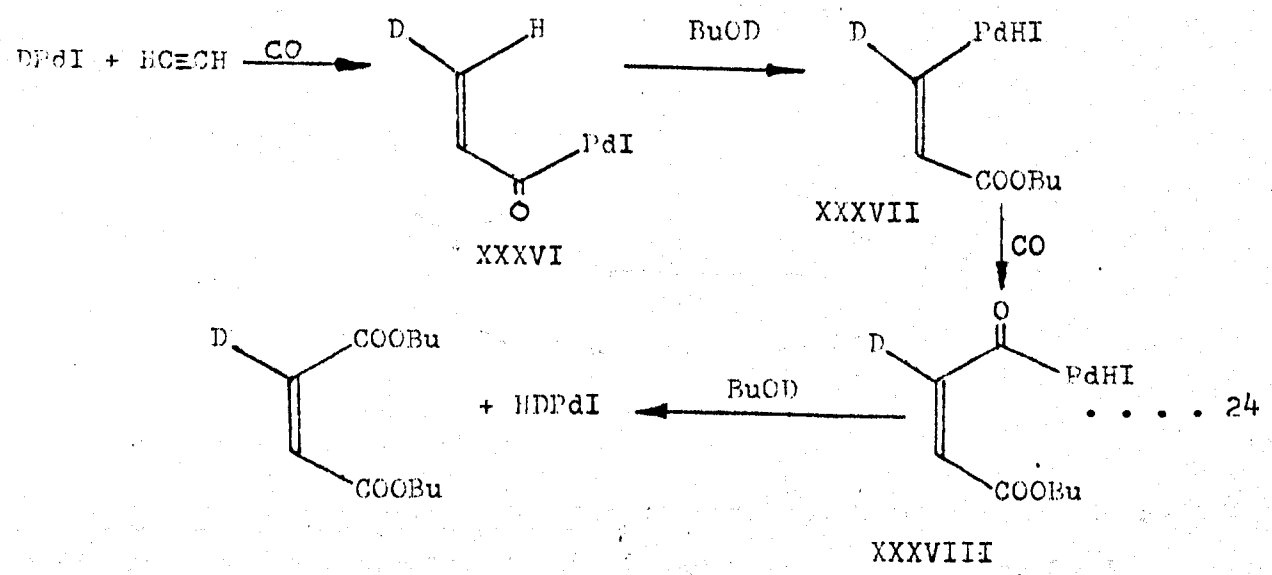


Fig. 8.2: Possible Formation of Mono- and Diesters by Acetylene and Carbon Monoxide Insertion Reactions

A similar mechanism of repeated alternate insertion (followed by hydrogenation) may account for the formation of dimethyl 4-ketoheptanedioate ($MeO\text{-}CO\text{-}CH_2CH_2\text{-}CO\text{-}CH_2CH_2\text{-}CO\text{-}OMe$) reported by Pino and Miglierina[43] as occurring when acetylene was treated with carbon monoxide under pressure in the presence of dicobalt octacarbonyl.

(ii) Formation from a Palladium-Acyl Intermediate: It was proposed by C.B.Lines[1] that diesters were formed from a palladium-acyl intermediate, XXIII, by alcoholysis and re-arrangement, either inter- or intramolecularly, to yield a palladium vinyl system which could insert carbon monoxide and undergo further reaction with alcohol to yield the diester and a palladium dihydride species.

However, formation of a palladium-vinyl system involves the acquisition of a proton from the hydroxyl group of the solvent (since no butyraldehyde was observed, the α-hydrogen atoms of butanol were not affected). Hence, when the reaction was carried out in butanol-O-d, a deuterium atom would be incorporated:



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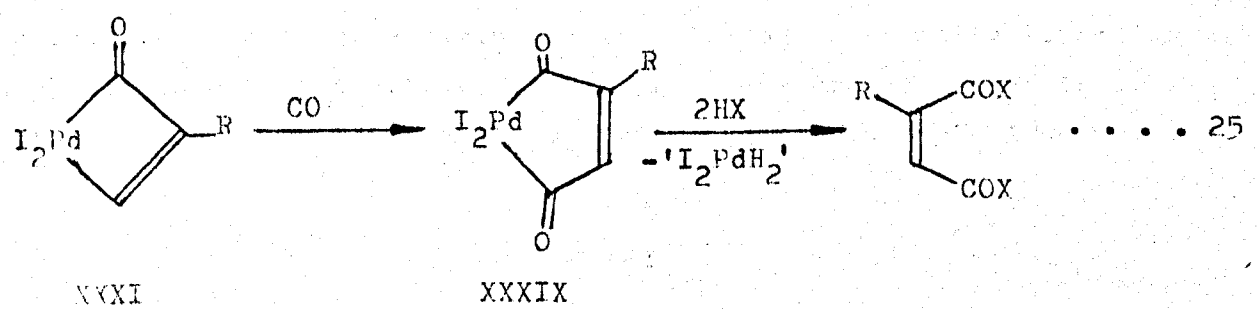
Since the diester from such a reaction was shown to have incorporated no deuterium, the pathway must be discounted. The formation of monoesters by the Heck mechanism however cannot be disproved.

(iii) Formation from a Cyclic Intermediate: The intermediate XXXI can be envisaged as undergoing ring expansion by the insertion of carbon monoxide to form the less strained XXXIX.



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XXXI XXXIX

Stepwise or concerted cleavage by HX (where X=I, Cl or OBu) would then lead to the cis-diester. Isomerisation and preferential reduction of the cis-ester thus need to be invoked. Alternatively, perhaps the partially cleaved intermediate could undergo isomerisation more readily than the ester.

A consistent mechanism for the formation of mono- and diesters can thus be proposed in terms of cyclic intermediates, as shown in fig. 8.3:

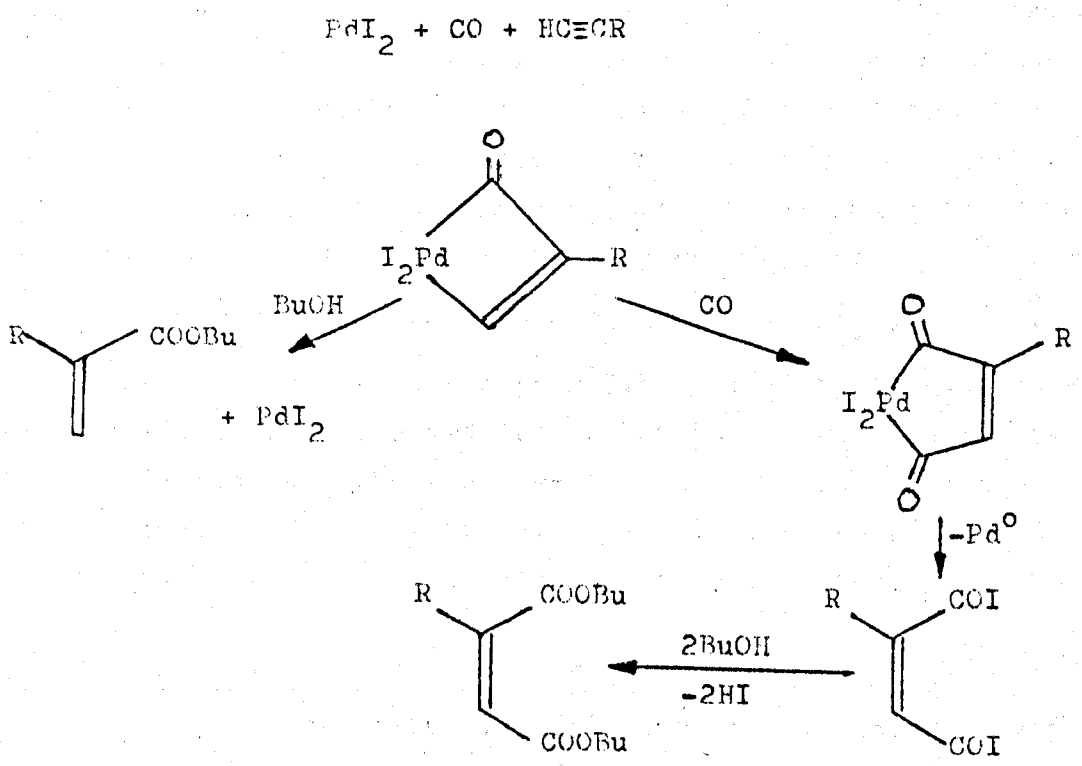


Fig. 8.3: Possible Formation of Mono- and Diesters via Cyclic Intermediates.

(iv) Formation by a Concerted Mechanism: Finally, a mechanism can be proposed wherein concerted insertion of two carbonyl moieties to a co-ordinated acetylene occurs. However, the resulting intermediate would be indistinguishable from XXXIX, and the route will not be considered further.

8.5. THE FORMATION OF SATURATED PRODUCTS

A number of mechanisms were proposed by C.B.Lines[1] to account for the formation of the saturated products, butyl propionate and dibutyl succinate. However, experiments with 'mixed' systems (e.g. adding butyl acrylate to methylacetylene reaction mixtures), showed that propionate could be produced from acrylate, and succinate from maleate

and, to a lesser extent, from fumarate ester under the reaction conditions. There was thus no reason to suppose that the saturated products were produced by any other route. The reducing agent responsible for the phenomenon is not known. Initially, it was supposed that hydrogen iodide in conjunction with metallic palladium could bring about hydrogenation:

$$R_2C{=}CR_2 + 2HI + Pd^{\circ} \longrightarrow R_2HC{-}CHR_2 + PdI_2 \quad \ldots\ldots\ldots 26$$

but anhydrous hydrogen iodide in butanol with palladium/charcoal failed to reduce butyl acrylate, even when warmed at 80°C for several weeks (cf. Chapter 2.4 (v)). Since palladium hydride species have been invoked to account for the formation of the unsaturated products of carbonylation reactions, it is reasonable to assume that they were responsible for the observed reductions:

$$R_2C{=}CR_2 + H_2PdI_2 \longrightarrow R_2HC{-}CHR_2 + PdI_2 \quad \ldots\ldots\ldots 27$$

It has been remarked (Chapter 3.5 (vii)) that branched ester products (i.e. those derived from substituted acetylenes) are much less easily reduced than the parent compounds, and that other unsaturated substances (styrene, acrylonitrile) were not reduced in reaction mixtures. The explanation for such behaviour is not known.

8.6. THE FORMATION OF COUPLED PRODUCTS

The interaction of butyl acrylate with methylacetylene under carbonylation conditions led to 3-substituted hex-2-enedioates.

A coupling reaction between methyl acrylate and acetylene in the presence of nickel carbonyl was demonstrated by Sauer et al.[44], however the product was a conjugated monoester:

$$2HC{\equiv}CH + H_2C{=}CH{-}COOMe \longrightarrow H_2C{=}CH{-}CH{=}CH{-}CH{=}CH{-}COOMe \quad \ldots\ldots\ldots 28$$

An analogy can also be drawn with the reactions of Chiusoli and his co-workers[27] when an allyl compound was linked to acetylene during carbonylation in the presence of nickel compounds, e.g.

$$H_2C{=}CH{-}CH_2{-}Cl + HC{\equiv}CH + CO + MeOH \longrightarrow H_2C{=}CH{-}CH_2{-}CH{=}CH{-}COOMe + HCl \quad \ldots 29$$

Since 3-substituted hex-2-enedioates were obtained, it is clear that (a) the hexenedioates were produced by one unit of acetylene coupling with one unit of butyl acrylate and (b) the compounds were not formed by insertion of an acrylate unit into one of the postulated carbonylation

intermediates, XXVI or XXXI, since such a process would preferentially give the 2-substituted isomer.

The most likely mechanism for the formation of the coupled products appears to be palladium alkyl formation from the acrylate, followed by sequential insertion of acetylene and carbonyl entities, and final cleavage by alcohol or hydrogen halide, as shown in fig. 8.4:

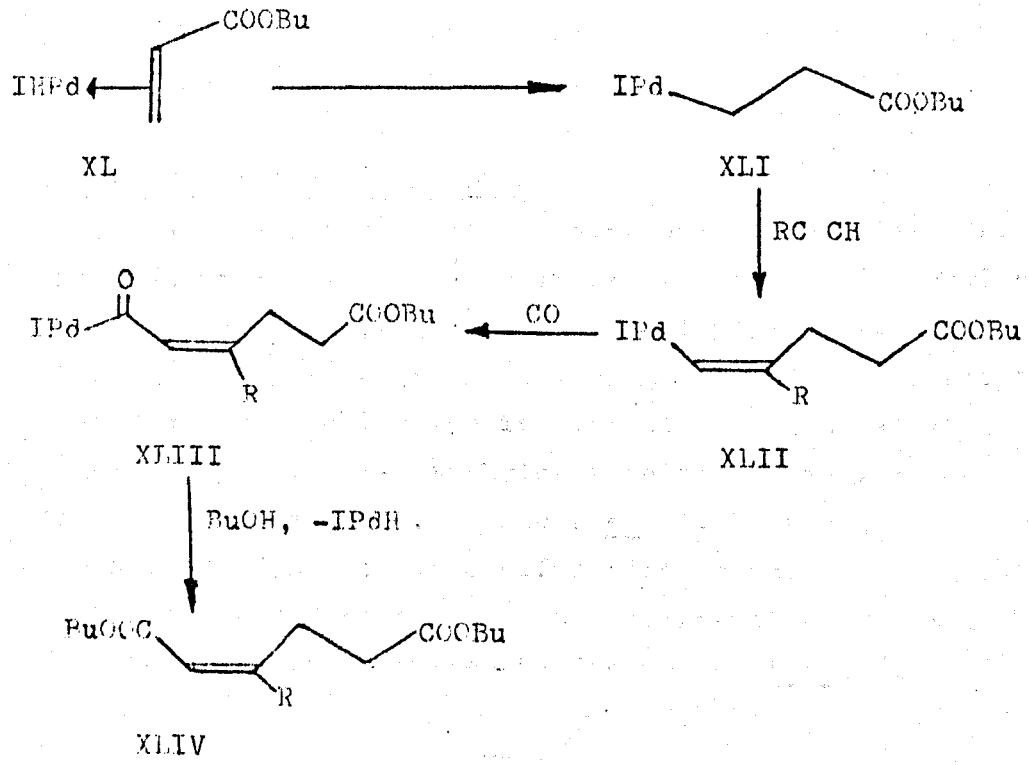


Fig. 8.4: A Possible Mode of Formation of 3-Substituted Hex-3-enedioate Esters

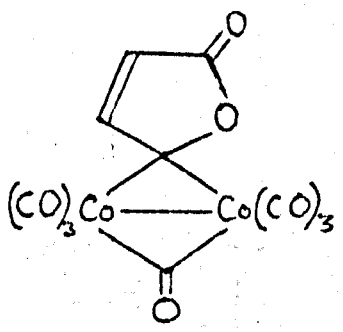
The observed structure was consistent with bond formation between the slightly positive β-carbon of the acrylate ester, and the electron rich[7] carbon of the co-ordinated alkyne. The non-reactivity of substituted acrylates under the conditions used, may be attributable to steric factors, as may the apparently exclusive formation of XLI rather than IPd-CH(Me)COOBu.

In the case of acetylene, not only the cis-hex-2-enedioate ester, but trans-hex-2-enedioate, trans-hex-3-enedioate and trans,trans-muconate were detected. Since large amounts of the latter compounds were observed amongst the products of reactions which had been allowed to continue for extended periods (Chapter 2.3 (v)) it was assumed that

they were derived from the cis-ester by slow secondary reactions. Palladium has been shown to bring about isomerisation amongst hydrocarbons such as butene[45], and such reactions would be expected to give rise predominantly to the trans-hex-2-enedioate. The formation of trans,trans-muconate esters from hex-3-enedioates by reaction with palladium chloride was observed by Tsuji and Imamura[46] (cf. also Chapter 2.3 (v)), andsuch a reaction may account for the muconate observed in acetylene carbonylation mixtures. However no direct evidence was obtained.

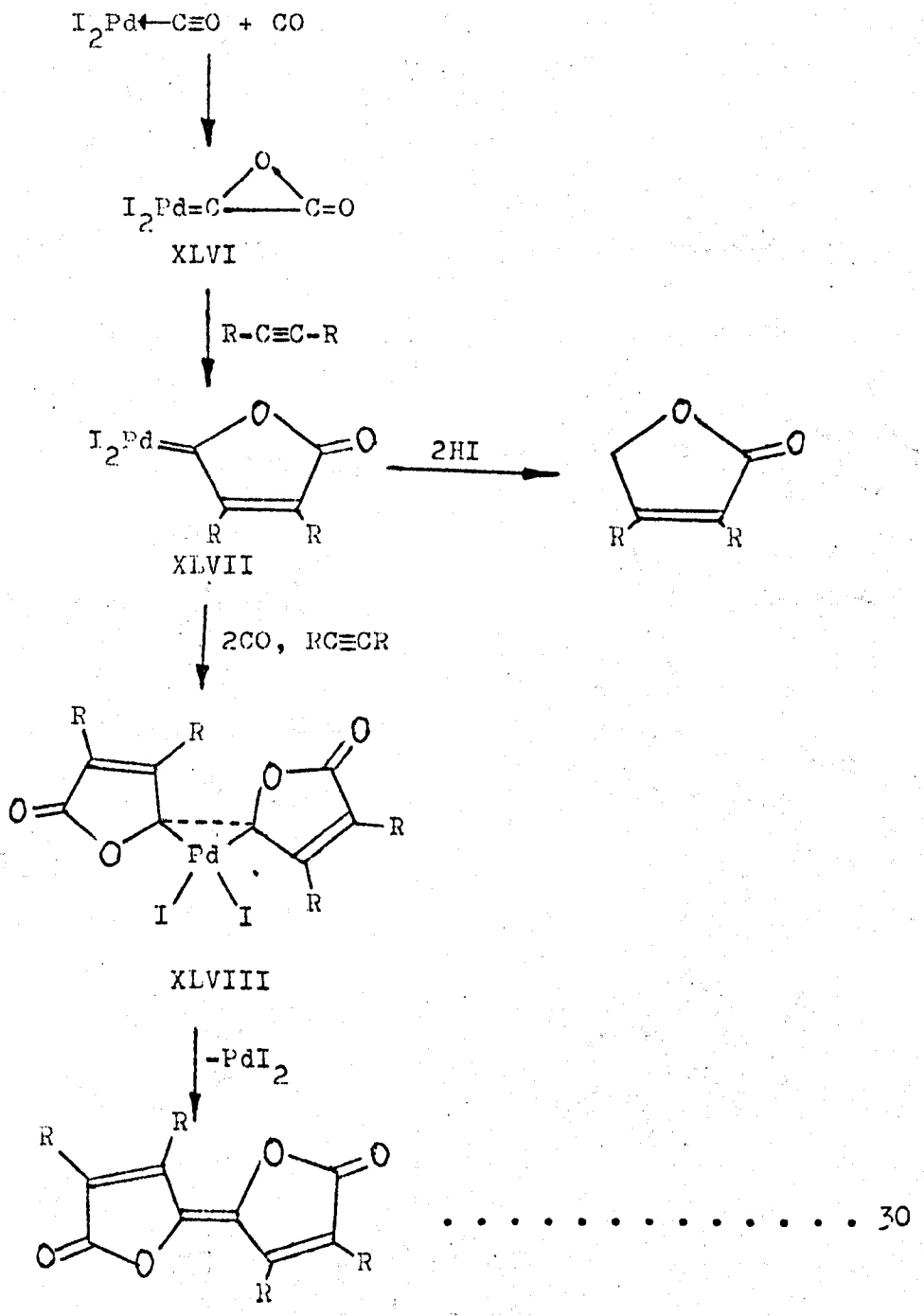
8.7. THE FORMATION OF LACTONES

It is interesting that lactones were formed only from disubstituted acetylenes which were relatively unreactive. Diphenylacetylene yielded 2,3-diphenylcrotonolactone, which had previously been prepared by Tsuji and Nogi[47] using a palladium chloride catalyst, though they advanced no explanation for its formation. Dimethylacetylene yielded the corresponding 2,3-dimethylcrotonolactone as well as tetramethylbifurandione. Sauer et al.[48] have prepared a bifurandione, and a number of substituted bifurandiones using cobalt catalysts, and attributed their formation to the intervention of species such as XLV, which has been prepared by Sternberg et al.[49].



XLV

Thus the most likely route to the formation of lactones appeared to be the insertion of carbon monoxide (occasioned by its high pressure and the unreactivity of the acetylenes) into a palladium carbonyl bond forming an epoxide type structure, XLVI, formally represented as being doubly bonded to palladium. Alternatively the complex might bridge two palladium atoms. Acetylene could then be inserted into the ring to yield a lactonic complex, XLVII. Double cleavage with some species such as butanol or hydrogen iodide would then yield the monocyclic lactone. Further reaction on the same atom or cluster followed by coupling and cleavage could yield the bifurandione:



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8.8. SUMMARY

Although many routes to the observed products have been postulated, and a number of them cannot be discounted, the alternate insertion of acetylene and carbon monoxide into appropriate palladium - carbon σ-bonds offers the most consistent picture. The mechanism is summarised in fig. 8.4:

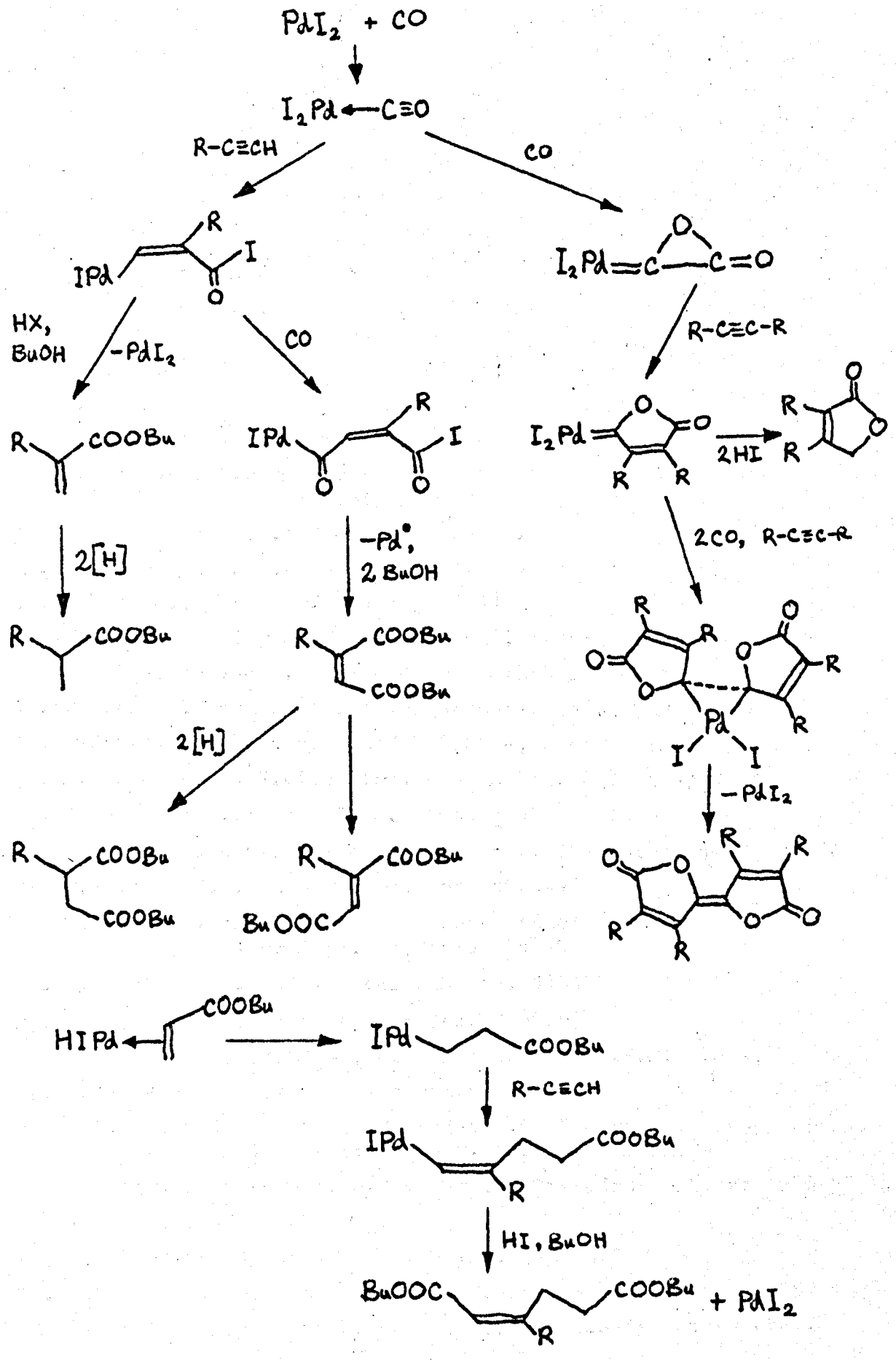

Fig. 8.5: Scheme for a Possible Overall Mechanism

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CHAPTER NINE

Experimental Section

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9.1. MATERIALS

Acetylene was obtained from the British Oxygen Company Limited and freed from traces of acetone by passage through a dry ice trap. Carbon monoxide was obtained from Air Products Limited and Imperial Chemical Industries Limited. The gases were dried by passage over phosphorous pentoxide before use.

Butylacetylene was obtained from Koch-Light Laboratories Limited, phenylacetylene from Ralph N. Emanuel Limited and diphenylacetylene from Harrington Brothers Limited.

Deuterium oxide was obtained from Koch-Light Laboratories Limited and tributyl borate from Kodak Limited.

Palladium iodide and ruthenium trichloride were obtained from Johnson Matthey & Company Limited, and palladium acetate from Engelhard Industries Limited.

Triphenyl- and tributyl phosphine were obtained from Imperial Chemical Industries Limited.

Butyl methacrylate was obtained from Koch-Light Laboratories Limited, and dibutyl itaconate from Charles Pfizer & Company Incorporated. Butyl esters of acrylic, propionate, maleic and fumaric acids were prepared by C.B.Lines[1] according to standard literature procedures.

Butanol-O-d, and solutions of hydrogen iodide and hydrogen chloride in butanol were prepared by the methods described by C.B.Lines[1].

Atropic acid was prepared by the method of Normant[2] (i.e. carbonation of the Grignard reagent from α-bromostyrene) as a white powder, yield = 16% (based on styrene), m.p. = 103 - 105°C (106 - 107°, Beilstein[3]). The other acids used were commercially available.

Esterification was normally performed as follows: Acid (1 mol) was refluxed with butanol (2 mols for monobasic, 4 mols for dibasic acids), toluene (an equal volume) and concentrated sulphuric acid (1 cc per mole of acid) for 2-3 hours, water being removed as an azeotrope with a Dean and Starck apparatus. The reaction mixture was washed with water, dried with anhydrous magnesium sulphate and distilled , under vacuum if required, or recrystallised (as indicated in table 9.1.). In the case of trans-hex-3-enedioic and trans,trans-muconic acids, the acid (1 mol) was refluxed with thionyl chloride (4 mols) for two hours and the acid chloride distilled off

and added to butanol (2 mols), briefly refluxed, washed with aqueous sodium carbonate and distilled under vacuum.

Acetaldehyde dibutylacetal was prepared from paraldehyde by the method of Vogel[4].

Butyl β-butoxycrotonate was prepared from ethyl acetoacetate by the method of Carrol[5], and purified by preparative gas chromatography.

Dibutyl butylsuccinate was prepared by the hydrogenation of dibutyl cis- and trans- butylbutenedioate obtained by carbonylation of butylacetylene (cf. Chapter 4.2 (ii); 9.4.).

Dibutyl trans-hex-2-enedioate was prepared from butyl acrylate by a modification of the method of Alderson, Jenner and Lindsey[6], i.e. butanol (50 g), butyl acrylate (107 g) ruthenium trichloride (1 g) and hydroquinone (1 g) were rocked in an autoclave at 21° C for ten hours.

Dibutyl cis-hex-2-enedioate was obtained in an impure form by ultraviolet light induced isomerisation of the trans- ester (cf. Section 5 (ii)). Butyl allocinnamate was similarly obtained from the cinnamate ester, and purified by preparative scale gas chromatography.

Compound	Yield(%)	$I^{S.E.30}$	B.P.(°C/mmHg)	Reference
Butyl isobutyrate	46	937(130°)	153-6	154.5-155.5; 3
Butyl n-butyrate	76	980	160	164.8; 3
Butyl crotonate	56	1029	180, 60/5	179.5, 55/4; 3
Acetaldehyde dibutylacetal	25	1084	185.5	186.5-187.5; 4
Butyl tiglate	55	1124	105/40	189-191; 11
Butyl oenanthate	65	1268(200°)	221,128-130/37	225; 9
Butyl hydratropate	82	1463	180/3	A
Butyl β-butoxycrotonate	12	1494	160/4	258-265; 5
Butyl atropate	36	1528	240,110/10	B
Dibutyl succinate	56	1540	123/3	120/3; 4
Butyl hydrocinnamate	90	1545	117/4	123/11; 4
Dibutyl pyrotartrate	70	1558	140/10	147/10,115/3; 7,8
Butyl allocinnamate	-	1563	-	*
Dibutyl citraconate	90	1570	132/4	152/10; 7
Dibutyl dimethylsuccinate	96	1605	255	C
Dibutyl mesaconate	75	1629	284-6(d),123/3	D
Butyl cinnamate	85	1672	130/4	162/12; 4
Dibutyl cis-hex-2-enedioate	-	1738	-	*
Dibutyl trans-hex-3-enedioate	50	1744	143/4	E
Dibutyl adipate	91	1750	189/28	165/10; 10
Dibutyl trans-hex-2-enedioate	21	1784	200/35	F
Dibutyl butylsuccinate	-	1805	-	*
Dibutyl trans,trans-muconate	85	1858	m,37(Aq.EtOH)	G
Dibutyl phenylsuccinate	60	2023(230°)	149/2	H
Butyl α-phenylcinnamate	88	2151	m,31-4(Aq.MeOH)	I
Dibutyl 1,2-diphenylsuccinate	43	R_F^{**}= 0.58	m,94-6(Aq.MeOH)	100-101; 10

* Not obtained in sufficient amounts to permit further work

**Alumina/Benzene:Petrol (2:1)

A found C,75.2; H,8.9 $C_{13}H_{18}O_2$ requires C,75.7; H,8.8%

B found C,76.0; H,8.0 $C_{13}H_{16}O_2$ requires C,76.5; H,7.9%

C found C,64.8; H,9.7 $C_{14}H_{26}O_4$ requires C,65.1; H,10.1%

D found C,64.2; H,9.1 $C_{13}H_{22}O_4$ requires C,64.4; H,9.1%

E found C,64.2; H,9.5 $C_{14}H_{24}O_4$ requires C,65.6; H,9.5%

F found C,64.8; H,9.2 $C_{14}H_{24}O_4$ requires C,65.6; H,9.5%

G found C,65.1; H,8.6 $C_{14}H_{22}O_4$ requires C,66.1; H,8.7%

H found C,70.4; H,8.7 $C_{18}H_{26}O_4$ requires C,70.5; H,8.9%

I found C,79.8; H,6.9 $C_{19}H_{20}O_2$ requires C,81.5; H,7.15%

Table 9.1. Substances Synthesised in Connection with the Present Work % Yield Based on the Acid (or other Starting Material). The Retention Index of Kovats Measured on a Dimethylsilicone, S.E.30 Stationary Phase. The Boiling or Melting Points and Combustion Analyses Where Appropriate.

9.2. GAS CHROMATOGRAPHY

(a) Qualitative Gas Chromatography: Gas chromatographic work was carried out on a Perkin Elmer F.11 instrument. The columns used are shown in table 9.2:

Column	Stationary Phase	Loading %	Dimensions (m x ins(o.d.))	n^A	h.e.t.p.^{B} (mm)
'Old'silicone	dimethyl silicone,SE.30	2.25	4 x $\frac{1}{8}$	3900	1.01
'New'silicone	dimethyl silicone,SE.30	4.0	4 x $\frac{1}{8}$	5200	0.77
Apiezon	apiezon L	5.0	4 x $\frac{1}{8}$	945	4.20
D.t.p.	ditridecylphthalate	5.0	2 x $\frac{1}{8}$	2540	0.79
P.e.g.	poly(ethylene glycol)	5.0	2 x $\frac{1}{8}$	278	7.20
N.p.g.s.	neopentylglycol succinate	1.0	1 x $\frac{1}{8}$	97	10.30

A n = plate efficiency derived from the formula $n = 16 \left(\frac{r}{W_b}\right)^2$
(where r = retention distance and W_b = peak width at base)

B h.e.t.p. = height equivalent to a theoretical plate, i.e. $\frac{l}{n}$
(where l is the length of the column)

Table 9.2: Gas Chromatographic Columns Used in the Present Work

Substances were identified, when necessary, by comparison of their retention times with those of authentic compounds on as many columns as possible. However, good agreement on two columns is sufficient to provide unambiguous proof of identity under favourable circumstances[11].

The retention index of Kovats[13] was quoted for compounds produced in the present work, since its value is only dependant on the substance to which it applies, and the stationary phase on which it is measured[14]. The retention indices were measured by the following procedure: members of a series of normal paraffins, C_nH_{2n+2}, were arbitrarily assigned the retention indices 100n. A straight line plot was then obtained, of $\log_{10}$[retention time] (measured from a volatile solvent-front) against the retention index values of the hydrocarbons. Values of $\log_{10}$[retention time] for the substances under study were then interpolated, and retention indices obtained directly. The values are said to change slightly with temperature in practice[12] and the temperature at which the retention index was determined is therefore

recorded in the form: $I^{\text{STATIONARY PHASE}}_{\text{TEMPERATURE}}$. However, a number of duplicate measurements were carried out on the 'old' and 'new' silicone columns, under widely differing conditions of temperature, flow rate and column loading, and were found to agree to within 0.5%.

(b) Quantitative Gas Chromatography: Reaction products were analysed quantitatively, usually using a silicone column, by one of two methods. In the first and best method, used when the products were known and available in pure form, an internal marker was added in known amount to the mixture. The marker was chosen so as to give a peak at a convenient retention time, close to the peaks being measured. The ratios of product peak-heights to marker peak height were then measured, and converted to weight ratios by reference to previously prepared calibration curves. Thence the W/W% of the products could be calculated. It was necessary at intervals to revise the calibration curves since stationary phase 'bleed' and other factors might have caused a slow change in the relative responsiveness of the instrument to different substances[15].

In the second method, an internal marker was also used, and assumed to have a detector response factor close to those of the substances being determined. It was therefore necessary to choose as marker, a substance which not only eluted from the chromatographic column at a suitable point in relation to the other components of the mixture, but also possessed a chemical constitution similar to that of the other substances. The above conditions being fulfilled, the ratio of marker to substance would be equal to the peak area ratio, peak area being conveniently regarded as proportional to the product of peak height and retention distance[15].

A possible random error of about 5% is expected for the first method, somewhat more for the second.

(c) Preparative Scale Gas Chromatography: Initially, preparative gas chromatography was carried out on a Wilkins Aerograph 'Autoprep' using 20 ft. x $\frac{3}{8}$ in o.d. columns packed with 10% silicone oil S.E.30 and apiezon L stationary phases on celite. However, it was found more convenient to modify a Perkin Elmer F.11 instrument for preparative work. A splitter and heated outlet were fitted and a 4m x $\frac{1}{4}$ in o.d. column was packed with 20% silicone oil 'M.F.C.' on celite; its plate efficiency under the normal overloaded conditions was 82, the h.e.t.p. being 49 mm.

9.3. OTHER ANALYTICAL TECHNIQUES

Infrared spectra were run on Unicam S.P.200 and Perkin Elmer 457 spectrophotometers, usually as liquid films or potassium bromide discs, using polystyrene to calibrate the instrument.

Mass spectra were run on A.E.I. M.S.2 and M.S.9 instruments

N.m.r. spectra were run on a Perkin Elmer R.10 machine using tetramethylsilane(t.m.s.) as an internal reference ($\tau = 10$).

Combustion analyses for carbon/hydrogen determination were carried out by Beller, Mikroanalytisches Laboratorium.

Halide (chloride and iodide) determinations were carried out by a gravimetric method, silver nitrate being used to precipitate the halide as its silver salt[16].

Palladium was determined gravimetrically as its dimethylglyoximate[16].

9.4. HYDROGENATION TECHNIQUES

Except in the special case of the diphenylbutenedioates, where more vigorous treatment was required, hydrogenations were performed as follows: The substrate (100 mg), Adams' catalyst, PtO_2 (10 mg) and ethanol or methanol (1-2 ml) were placed in a 20 ml flask, equipped for magnetic stirring, and exposed to an atmosphere of hydrogen for 3-5 hours as determined by the uptake of hydrogen. When the substrate contained a double bond conjugated with a phenyl group, it was necessary to heat the flask at about 80°C in an oil bath. The reduced product was recovered by filtering off the platinum and evaporating the solvent.

9.5. ISOMERISATION TECHNIQUES

(a) To Obtain the Trans- form of an Unsaturated Ester: The substrate (0.1 g) was dissolved in petrol (4 mls) saturated with nitric oxide, and heated at 80°C in a sealed tube for about an hour. The trans- isomer was then recovered by evaporating the solvent. Nitric oxide is well known to promote the transformation of cis- compounds to their thermodynamically more stable trans- isomers[17].

(b) To Obtain the Cis- form of an Unsaturated Ester: The substrate (0.5 g) was dissolved in alcohol (10mls) (preferably butanol to prevent premature evaporation) and exposed to the radiation from a 1000W Hanovia mercury vapour lamp for 1-2 hours. The cis- isomer

was then recovered by evaporation of the solvent and, if necessary, preparative scale gas chromatography. Ultraviolet light is well known to bring about isomerisation of an isomer to the thermodynamically less favoured cis- form[17].

9.6. THE APPARATUS USED FOR THE CARBONYLATION REACTIONS:

(a) Carbonylation at Atmospheric Pressure: The reactor (fig. 9.1) consisted of a multinecked flask fitted with a dropping funnel, a serum cap for sampling, a stirrer and a condenser. In order to achieve a high specific gas surface, the vessel was fitted with baffles and was designed so that its diameter was approximately equal to the liquid depth. The reactant gases were introduced through the hollow-shafted stirrer which reached to about half the depth of the liquid[18]. The unreacted gases were passed first through a water cooled condenser, then through a trap cooled in dry ice, to prevent the escape of volatile materials. The reactor was heated in an oil bath, the chosen temperature being controlled to ± 1°C.

(b) Carbonylation Above Atmospheric Pressure: Reactions at moderate pressure (< 20 atmos.) were conducted in a reactor of 10 ml capacity, made from a length of ½ in. i.d. copper tubing, fitted with a magnetic stirrer. Higher pressures (ca. 100 atmos.) were used in a stainless steel rocking autoclave of 400 ml capacity, manufactured by Chas. W. Cook & Sons, Limited. Alternatively a reactor of 100 mls capacity manufactured from 1 in. i.d. mild steel tubing was employed.

9.7. EXPERIMENTAL FOR CHAPTER 2, THE CARBONYLATION OF ACETYLENE

(a) Gas Chromatography: Quantitative work was carried out using the silicone cclumn, with diethyl adipate as an internal marker for the diesters at 160°C (formerly 190°C on the 'old' column) and propylbenzene for the monoesters at 60°C (formerly toluene at 90°C).

(b) Introduction (2.1.):

The 'standard' reaction (i).- Butanol (60 g), palladium iodide (4 m mols) and sodium iodide (8 m mols) were placed in the multinecked reactor held at 75°C. Acetylene and carbon monoxide were passed through the solution, each at 3 litres per hour. The duration of the experiments was usually seven hours.

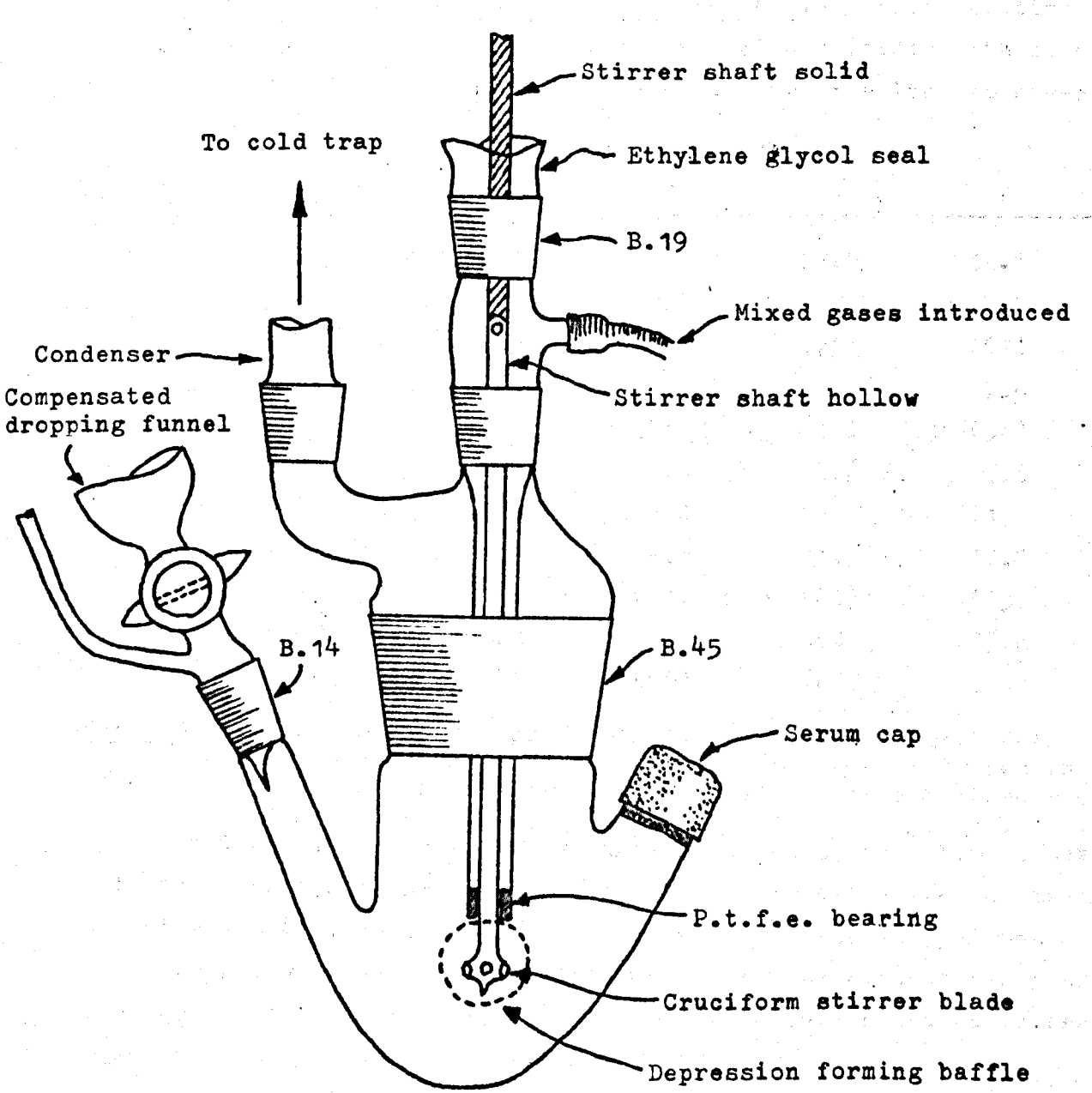

Fig. 9.1: APPARATUS FOR CARBONYLATION AT ATMOSPHERIC PRESSURE

(c) Carbonylation Under a Variety of Conditions (2.2.):

Carbonylation under neutral conditions (i).- Four reactions (rns. 2.1) were carried out under 'standard' conditions with reaction times of 1, 3, 5 and 7 hours respectively. The results are given in table 9.3:

Reaction time (hours)	1	3	5	7
Wt. Increase (g)	5.1	14.9	22.5	32.5
Butyl acrylate, g	3.9	9.0	9.5	7.8
(m mols)	(31)	(71)	(75)	(62)
Butyl propionate, g	1.0	3.7	4.5	7.6
(m mols)	(8)	(28)	(35)	(58)
Dibutyl maleate, g	2.0	3.1	3.6	3.5
(m mols)	(9)	(14)	(16)	(15)
Dibutyl fumarate, g	2.2	9.3	13.6	12.0
(m mols)	(10)	(41)	(60)	(53)
Dibutyl succinate, g	3.2	12.7	19.8	20.2
(m mols)	(14)	(55)	(85)	(88)

Table 9.3: Reactions 2.1, The Carbonylation of Acetylene Under 'Standard' Conditions. (Amounts of Product Esters in Grams and Mols, Initial Weight of Reaction Mixture = 60 g)

Reaction 2.2 was carried out under 'standard' conditions, but allowed to continue for 18 hours, samples being withdrawn and analysed at intervals (cf. table 9.4). The reading designated 'pH' was obtained using universal indicator paper, and comparing the colour developed after five minutes with standard colours provided by the manufacturers.

Reaction time (hours)	1	3	4.75	7	8	11	12	14	16	18
'pH'	4.0	4.0	4.5	4.5	5.0	-	5.0	5.0	-	-
Butyl acrylate	1.0	4.6	6.2	6.8	6.6	5.9	5.0	5.0	4.7	4.6
Butyl propionate	0.0	0.7	1.9	2.9	3.8	4.9	4.9	5.5	5.7	6.0
Dibutyl maleate	1.0	2.7	3.6	3.8	3.3	3.2	2.8	2.9	2.5	2.4
Dibutyl fumarate	1.5	4.2	5.7	7.0	7.5	8.6	9.7	9.8	10.8	9.7
Dibutyl succinate	1.0	5.4	8.3	10.8	11.7	13.6	14.5	15.0	16.8	16.7

Table 9.4: Reaction 2.2, The Carbonylation of Acetylene Under 'Standard' Conditions, but Continued for an Extended Period. (Amounts of Product Esters Expressed as W/W% of the Reaction Mixture, Initially 60 g; Wt. Inc. = 23.5 g)

Carbonylation in the presence of oxidising agents (iii).- Reaction 2.4 was carried out under 'standard' conditions, but with air passing at 1-1.5 l/h. The results are summarised in table 9.5:

Reaction Time (hours)	1	3	5	7
Butyl acrylate	1.1	5.6	8.1	5.7
Butyl propionate	0.3	0.9	1.9	2.0
Dibutyl maleate	1.0	4.0	6.4	7.6
Dibutyl fumarate	0.8	3.7	6.7	9.3
Dibutyl succinate	0.5	3.3	6.4	9.6

Table 9.5: Reaction 2.4, The Carbonylation of Acetylene in the Presence of Air. (Amounts of Product Esters Expressed as W/W% of the Reaction Mixture, Initially 60 g, Wt. Inc. = 16.2 g)

Reaction 2.5 was carried out under 'standard' conditions, but with air (1-1.5 l/h) introduced and anhydrous hydrogen chloride (10 m mols) present. The product analysis was: butyl acrylate, 12.7%; propionate, 1.9%; dibutyl maleate, 7.2%; fumarate, 5.1% and succinate, 4.1% W/W. The sticky black sediment (2.6 g) was boiled in water (100 mls) for 30 minutes, filtered and the filtrate evaporated yielding a white infusible solid (1.2 g) containing sodium and chloride ions, found Cl, 56.4, NaCl requires Cl, 60.7%.

The residue was refluxed with chloroform (50 mls) for 30 minutes, filtered and the filtrate evaporated yielding a viscous material (0.1 g) shown to be poly(butyl acrylate). The remainder was probably palladium iodide for it contained palladium and iodide ions; an analysis gave Pd, 28.3%, PdI_2 requires Pd 29.4%.

Reaction 2.7 was carried out under standard conditions, but with the addition of p-benzoquinone (5.4 g). The results are given in table 9.6.

Reaction Time (hours)	1	3	5	7
Butyl acrylate	0.0	0.5	0.4	6.2
Butyl propionate	0.0	0.0	0.0	1.5
Dibutyl maleate	0.3	1.2	2.6	4.7
Dibutyl fumarate	0.3	2.2	5.3	7.0
Dibutyl succinate	0.0	0.0	0.3	5.3

Table 9.6: Reaction 2.7, The Carbonylation of Acetylene in the Presence of Benzoquinone. (Amounts of Product Esters Expressed as W/W% of the Reaction Mixture, Initially 60 g, Wt. Inc. = 8.8 g)

Reaction 2.8 was carried out under 'standard' conditions, but in the presence of benzoquinone (2.5 g) and with air passing at 1-1.5 l/h. The results are given in table 9.7:

Reaction time (hours)	1	3	5	7
Butyl acrylate	0.0	0.0	0.1	2.6
Butyl propionate	0.0	0.0	0.0	0.5
Dibutyl maleate	0.0	0.5	0.1	3.6
Dibutyl fumarate	0.3	0.3	2.4	5.1
Dibutyl succinate	0.4	0.5	1.1	6.6

Table 9.7: Reaction 2.8, The Carbonylation of Acetylene in the Presence of Benzoquinone and Air. (Amounts of Product Esters Expressed as W/W% of the Reaction Mixture, Initially 60 g, Wt. Inc. = 5.3 g)

Carbonylation in the presence of hydrogen (iv).- Butanol (10 mls), palladium iodide (0.5 m mols), sodium iodide (1.0 m mol), butyl acrylate (0.5 g), dibutyl maleate (0.5 g) and dibutyl fumarate (0.5 g) were placed in a two-necked flask and held at 75°C for 7 hours with hydrogen passing through the solution at 0.5 l/h. The mixture was then analysed by gas chromatography, no change in the product ratios being detectable.

Reaction 2.9 was carried out under the 'standard' conditions but with hydrogen passing at 1.8 l/h. The results are shown in table 9.8:

Reaction time (hours)	1.25	3	5	7
Butyl acrylate	1.3	5.9	7.3	9.4
Butyl propionate	0.3	1.3	1.9	3.0
Dibutyl maleate	1.1	3.0	4.1	4.5
Dibutyl fumarate	1.1	3.2	5.5	7.0
Dibutyl succinate	2.0	4.8	8.0	10.9

Table 9.8: Reaction 2.9, The Carbonylation of Acetylene in the Presence of Hydrogen. (Amounts of Product Esters Expressed as W/W% of the Reaction Mixture, Initially 60 g, Wt. Inc. = 11.4)

(d) Minor Products of the Carbonylation of Acetylene (2.3.):

Butyl iodide(ii) was identified by the following retention times (table 9.9):

	Silicone	D.t.p.	Apiezon	P.e.g.
Butyl iodide	8.6	10.6	12.4	8.4
'A'	8.6	10.8	obsc.	8.4

Table 9.9: Retention Time Comparison of 'A' with Butyl Iodide. (Retention Times in Minutes, Column Temperature = 90°C)

Acetaldehyde dibutylacetal (iii) was identified by the following retention times (table 9.10):

	Silicone	D.t.p.	Apiezon	P.e.g.
Acetal	11.6	13.0	13.8	6.8
'D'	11.4	12.8	14.2	6.6

Table 9.10: Retention Time Comparison of 'D' with Acetaldehyde Dibutylacetal. (Retention Times in Minutes, Column Temperature = 100°C)

Dibutyl adipate, the hexenedioates and muconate (v) were identified by the following retention times (table 9.11):

Dibutyl Ester	Silicone	D.t.p.	Apiezon	P.e.g.
	(180°C)	(185°C)	(200°C)	(185°C)
Adipate	10.6	18.1	16.2	33.2
Hydrogenated 'I','J','K'	10.6	17.9	16.6	33.2
	(170°C)	(195°C)	(205°C)	(190°C)
trans-hex-3-enedioate	11.8	25.0	14.3	19.0
'I" '	11.8	25.0	14.3	18.9
cis-hex-2-enedioate	11.4	24.2	14.8	15.9
'I' '	11.4	obsc.	obsc.	16.2
trans-hex-2-enedioate	13.5	31.5	18.7	22.6
'J'	13.4	31.5	18.6	22.9
trans,trans-muconate	17.4	43.5	25.1	29.3
'K'	17.2	42.8	25.6	29.0

Table 9.11: Retention Time Comparison of 'I', 'J', 'K' and the Hydrogenation Product with Authentic C_6-Diesters (Retention Times in Minutes)

The attempted oxidation of dibutyl hex-3-enedioate to muconate was carried out as follows: Dibutyl hex-3-enedioate (0.5 g), butanol (10 g), palladium iodide (0.25 g) and sodium iodide (0.4 g) were placed in a two-necked flask, held at 75°C in an oil bath, and carbon monoxide was bubbled through the mixture at 0.5 l/h for 5 hours. The mixture was then analysed by gas chromatography and shown not to contain any muconate or hex-2-enedioate esters.

(e) Miscellaneous Reactions Designed to Elucidate Aspects of the Mechanism of the Carbonylation Reaction (2.4):

Reaction of the catalyst with carbon monoxide (i).- Butanol (10 g), palladium iodide (0.25 g) and sodium iodide (0.2 g) were placed in a Buchner flask fitted with a stopcock. The flask was flushed several times with carbon monoxide and charged to just above atmospheric pressure. After 20 minutes with occasional shaking, a colour change from wine - to blood red had taken place.

In a second reaction using palladium iodide (0.15 g), the sodium iodide was omitted and the flask left for several days. A blood red colour gradually appeared. The residue (0.11 g) gave a correct analysis for palladium iodide, found I,68.3 PdI_2 requires, 70.5%. The supernatant liquid on evaporation yielded palladium iodide (0.03 g).

In a third experiment, a mild steel syphon was charged with butanol (30 g), palladium iodide (0.75 g), sodium iodide (0.6 g) and carbon monoxide at about 2 atmospheres pressure. After three days a pale red liquid containing a residue of palladium iodide could be obtained from the syphon.

The reaction of acetylene with the catalyst solution (ii).- A Buchner flask was charged with catalyst solution as in (i) above. It was flushed with acetylene and charged to just above atmospheric pressure. After 5 days with occasional shaking, the colour of the solution was unchanged, but by means of thin layer and column chromatography, a yellow oil, R_F = 8.6, could be extracted. Thin layer chromatography was carried out on 10 cm. alumina plates, column chromatography on a 30 x 1 cm. alumina column. In both cases the mobile phase was benzene.

Carbonylation in the presence of various esters (iii).- Ethyl acrylate: reaction 2.31 was carried out under 'standard' conditions, but with ethyl acrylate (9.8 g) present. Final analyses were: ethyl acrylate, 9.6%; ethyl propionate, 2.9%; butyl acrylate, 5.7%;

butyl propionate, 3.4%; dibutyl maleate, 4.4%; fumarate, 7.4% and succinate, 8.2% W/W.

Ethyl propionate was identified by the following retantion times (table 9.12):

	Silicone	D.t.p.	Apiezon	P.e.g.
	(20°C)	(30°C)	(30°C)	(30°C)
Ethyl propionate	7.5	11.1	10.9	10.2
Reaction product	7.5	11.0	11.1	10.3

Table 9.12: Retention Time Comparison of the Product from Reaction 2.31 with Ethyl Propionate (Retention Times in Minutes)

Dibutyl citraconate: Reaction 2.32 was carried out under 'standard' conditions, but with dibutyl citraconate (9.6 g) present at the outset. At the end of the reaction, gas chromatographic analysis showed the presence of dibutyl citraconate (6.9 g) and mesaconate (2.2 g).

Dibutyl mesaconate: Reaction 2.33 was carried out under 'standard' conditions, but with dibutyl mesaconate (9.6 g) present initially. At the end of the reaction, gas chromatographic analysis showed the presence of the unchanged ester (9.1 g).

The Attempted Reaction of Acetylene with Cyanide Ion (vii): Sodium Cyanide (10 g) and butanol (60 g) were heated together at 75°C, and acetylene was passed at 3 l/h for 7 hours with vigorous stirring. Dibutyl oxalate was detected at a concentration of 8.9% W/W (5.3 g) by gas chromatography at the end of the reaction. In reaction 2.17, the conditions were as described above, but the carbonylation catalyst, palladium iodide (4 m mols) and sodium iodide (8 m mols), was also present. Dibutyl oxalate was detected at a level of 7.5% W/W (4.5 g).

The carbonylation of acetylene-d_2 (viii).- Acetylene-d_2 was generated in a steady stream by dropping water-d_2 (40 g) onto technical calcium carbide (80 g), purified by passage through a dry ice trap and an alumina tower, and dried by passage over phosphorous pentoxide. The reaction with D-C≡C-D was carried out in the 'standard' manner for 5 hours (rn. 2.16). Product analyses were as follows (table 9.13):

Reaction time (hours)	1	3	5
Butyl acrylate	0.5	4.1	5.6
Butyl propionate	-	0.6	0.5
Dibutyl maleate	1.3	2.9	3.5
Dibutyl fumarate	1.3	4.6	6.7
Dibutyl succinate	1.4	3.7	6.6

Table 9.13: Reaction 2.16, Carbonylation of Acetylene-d_2. (Amounts of Product Esters Expressed as W/W% of the Reaction Mixture, Initially 60 g, Wt. Inc. = 6.2 g)

(f) Attempted Carbonylation Using Other Catalyst Systems (2.5):

Bis(triphenylphosphine)palladium(II) Iodide (i) was prepared by mixing palladium iodide (2.0 g), sodium iodide (5.0 g) and triphenylphosphine (2.5 g) in methanol (150 ml), briefly boiling, cooling and filtering. The crude complex was recrystallised from toluene as deep red crystals, m.p. 265°C (decomp.) (decomposes above 200°C, Senise and Levi[19]). Yield = 2.4 g (53% based on palladium iodide). Infrared (KBr disc) ν (cm^{-1}) = 697 (s), 710 (s), 755 (s), 830 (s), 890 (m), 1005 (m), 1035 (w), 1107 (s), 1160 (w), 1190 (w), 1312 (w), 1440 (s), 1490 (m).

Bis(tributylphosphine)palladium(II) Iodide (ii) was prepared by mixing palladium iodide (4.0 g), sodium iodide (3.5 g) and tributylphosphine (4.0 g) in methanol (100 mls)and briefly boiling. Cooling and double recrystallisation from methanol yielded the complex as orange needles, m.p. 61.5 - 62°C (64 - 65°C, Mann and Purdie[20]) yield = 3.4 g (49% based on palladium iodide). Infrared (KBr disc), ν (cm^{-1}) = 725 (m), 792 (m), 912 (s), 975 (w), 1010 (w), 1055 (m), 1095 (s), 1203 (m), 1305 (w), 1383 (w),1420 (w), 1470 (m), 2820 (m), 2900 (m), 2930 (m).

Bis(diphenylphosphino)ethanepalladium(II) Iodide (iii) was prepared by the general method of Booth and Chatt[21], i.e. palladium iodide (1.5 g), sodium iodide (1.0 g) and 1,2-bis(diphenylphosphino)ethane (1.5 g) were mixed in dimethyl formamide (50 mls) and briefly boiled. Addition of methanol caused the precipitation of the complex as a dark orange powder, m.p. 310-320°C (decomp), yield = 1.0 g (70% based on the phosphine) found C,40.5; H,3.3 $C_{26}H_{24}I_2P_2Pd$ requires C,41.2; H,3.2% Infrared (KBr disc), ν (cm^{-1}) = 691 (s), 706 (s), 750 (s), 820 (s), 887 (m), 1005 (m), 1032(w), 1103 (s), 1160 (w), 1185 (m), 1310 (w),

1410 (w), 1440 (s); 1485 (m).

9.8. EXPERIMENTAL FOR CHAPTER 3, THE CARBONYLATION OF METHYLACETYLENE

(a) Exploratory Reactions (3.2):

The carbonylation of methylacetylene under the conditions used for acetylene (i).- The attempted carbonylation of methylacetylene was carried out as follows: butanol (60 g), palladium iodide (1.5 g) and sodium iodide (1.2 g) were placed in the multinecked reactor and heated at 75°C for 7 hours whilst carbon monoxide and methylacetylene were passed, each at 3 l/h, into the well stirred solution (rn. 3.1).

The effect of varying the reaction temperature (ii).- A reaction was carried out as above, but with the temperature reduced to 65°C (rn. 3.2). The results of analyses are given in table 9.14: (chromatographic analyses were performed under the same conditions as were used for the acetylene products (cf. Chapter 9.7 (a)).

Time (hours)	1	3	5	7
Butyl isobutyrate	0.1	0.4	0.3	0.4
Butyl methacrylate	0.2	1.2	2.7	4.2
Butyl crotonate	0.0	0.5	0.7	0.6
Dibutyl citraconate	0.5	1.6	2.1	2.6
Dibutyl mesaconate	1.0	3.2	4.2	5.0
Dibutyl pyrotartrate	0.3	0.9	0.8	1.0

Table 9.14: Reaction 3.2, The Carbonylation of Methylacetylene at 65°C. (Amounts of Product Esters Expressed as W/W% of the Reaction Mixture, Initially 60 g, Wt. Inc. = 7.2 g)

Acetone was identified by the following retention times:

	Silicone	Apiezon	P.e.g.
Contents of trap	3.3	4.5	2.6
Acetone	3.3	4.4	2.6

Table 9.15: Retention Time Comparison of Acetone with a Product Condensed in the Cold Trap During the Carbonylation of Methylacetylene. (Retention Times in Minutes, Column Temperature = 70°C)

Acetone dinitrophenylhydrazone had an m.p. = 123-4°C (126°C, Haynes[22]), its structure was confirmed by mass spectrometry, parent peak $\frac{m}{e}$ = 238.

Butyl iodide was identified by the following retention times:

	Silicone	D.t.p.	Apiezon	P.e.g.
'A'	8.6	10.7	obsc.	8.4
Butyl iodide	8.6	10.6	12.4	8.4

Table 9.16: Retention Time Comparison of 'A' with Butyl Iodide. (Retention Times in Minutes, Column Temperature = 70°C)

Trans-1,2-Diiodopropene was obtained from reaction 3.2 and identified by spectroscopic methods (cf. Chapter 3.3 (v)). It was shown to occur in typical reactions by the following gas chromatographic comparison:

	Silicone	D.t.p.	Apiezon	P.e.g.
'B'	8.7	14.1	18.2	14.8
trans-1,2-diiodopropene	8.6	obsc.	18.0	14.9

Table 9.17: Retention Time Comparison of 'B' with trans-1,2-Diiodopropene. (Retention Times in Minutes, Column Temperature = 90°C)

Butyl isobutyrate, methacrylate and crotonate were identified by the following retention times:

	Silicone	D.t.p.	Apiezon	P.e.g.
'C'	5.9	6.1	5.7	obsc.
Butyl isobutyrate	5.9	6.0	5.7	5.1
'D'	6.2	7.0	6.6	6.0
Butyl methacrylate	6.2	7.0	6.6	6.0
'E'	7.7	9.6	-	8.4
Butyl crotonate	7.7	9.7	-	8.4

Table 9.18: Retention Time Comparison of 'C', 'D' and 'E' with the Respective Monoesters (Retention Times in Minutes, Column Temperature = 150°C)

Dibutyl pyrotartrate, citraconate and mesaconate were identified by the following retention times:

	Silicone	D.t.p.	Apiezon	P.e.g.
'F'	13.1	24.1	19.7	16.2
Dibutyl pyrotartrate	13.2	24.0	19.6	16.2
'G'	13.8	28.4	21.3	20.4
Dibutyl citraconate	13.8	28.6	21.0	20.4
'H'	16.0	34.2	28.8	21.8
Dibutyl mesaconate	15.9	34.0	28.6	22.0

Table 9.19: Retention Time Comparison of 'F', 'G' and 'H' with the Respective Diesters (Retention Times in Minutes, Column Temperature = 200°C)

The carbonylation of methylacetylene at a reduced flow-rate (iii).- The results of reactions with a methylacetylene flow-rate of 1.5 l/h are summarised in tables 9.20, 9.21, 9.22:

Reaction time (hours)	1.5	2.5	4	5.5	7
Butyl methacrylate	0.9	1.7	3.3	4.6	5.6
Dibutyl citraconate	1.4	2.7	3.8	3.6	4.2
Dibutyl mesaconate	2.2	3.8	5.2	6.0	6.3
Dibutyl pyrotartrate	0.8	1.3	1.9	1.9	2.2

Table 9.20: Reaction 3.4 (weight increase = 7.5 g)

Reaction time (hours)	1	3	5	7
'pH'	3.5	3.5	5.0	6.0
Butyl methacrylate	0.0	0.6	2.3	4.0
Dibutyl citraconate	0.8	2.2	4.6	6.0
Dibutyl mesaconate	1.0	4.5	6.8	7.1
Dibutyl pyrotartrate	0.4	1.4	2.6	2.8

Table 9.21: Reaction 3.5 (weight increase = 6.8 g)

Reaction time (hours)	1	3	5	7
Butyl methacrylate	0.0	0.5	2.1	3.5
Dibutyl citraconate	1.4	2.0	3.1	4.0
Dibutyl mesaconate	0.7	3.8	5.6	6.3
Dibutyl pyrotartrate	0.0	1.0	1.7	2.3

Table 9.22: Reaction 3.6 (weight increase = 7.7 g)

Carbonylation of Methylacetylene at a Flow-Rate of 1.5 l/h. (Amounts of Product Esters Expressed as W/W% of the Reaction Mixture, Initially 60 g)

The 'standard' methylacetylene reaction (iv) was defined as differing from that described above for acetylene (Chapter 9.7 (b)) only in that the temperature used was 65°C, and the methylacetylene flow-rate was 1.5 l/h.

Carbonylation at a reduced temperature (v).- A reaction (rn. 3.7) was conducted under 'standard' conditions, but with the temperature reduced to 40°C. The results are given in table 9.23:

Reaction time (hours)	1.25	3	5.25	7
Butyl methacrylate	0.1	1.4	4.3	4.8
Dibutyl citraconate	0.4	1.1	1.8	2.4
Dibutyl mesaconate	1.1	3.1	4.5	5.2
Dibutyl pyrotartrate	0.3	0.5	0.7	0.7

Table 9.23: Reaction 3.7, Carbonylation of Methylacetylene at 40°C. (Amounts of Product Esters Expressed as W/W% of the Reaction Mixture, Initially 60 g, Wt. Inc. = 6.2 g)

Carbonylation for an extended period (vi).- Reaction 3.8 was carried out for a period of 11 hours under otherwise 'standard' conditions. The results are given in table 9.24:

Reaction time (hours)	1	3.25	5	7.25	9	11
Butyl methacrylate	0.3	1.0	2.7	4.1	6.0	6.1
Dibutyl citraconate	1.0	2.2	2.9	3.5	4.0	3.9
Dibutyl mesaconate	2.2	5.8	6.4	6.9	7.2	7.0
Dibutyl pyrotartrate	0.5	0.8	1.0	1.2	1.2	1.0

Table 9.24: Reaction 3.8, Carbonylation of Methylacetylene Under 'Standard' Conditions, but Allowed to Continue for 11 hours. (Amounts of Product Esters Expressed as W/W% of the Reaction Mixture, Initially 60 g, Wt. Inc. = 9.1 g)

(b) Carbonylation of Methylacetylene in the Presence of Oxidising Agents (3.3):

The effect of air (i).- Reaction 3.9 was carried out under the conditions used initially, i.e. methylacetylene passing at 3 l/h, the temperature being 75°C, otherwise as 'standard', but the supply of methylacetylene was exhausted after 3 hours, and the system opened to the air for two days whilst a further stock was obtained.

Variation of air flow-rate (ii).- A series of reactions was carried out under the same conditions as used in (i) above, but with air passing at 0.5, 1.5, 4.0 and 8.0 l/h respectively.

Variation of the temperature with air passing (iii).- Reactions 3.15 - 3.20 were carried out under the 'standard' conditions with air passing at 1 - 1.5 l/h. The results are shown in table 9.25:

Reaction No	3.15	3.16	3.17	3.18	3.19	3.20
Reaction Temperature (C)	0	30	40	60	86	117
Wt. increase (g)	2.6	5.4	6.1	7.0	2.9	0.5
Butyl methacrylate	0.1	4.5	5.6	1.1	0.6	0.0
Dibutyl citraconate	1.1	3.9	3.1	2.6	2.6	0.3
Dibutyl mesaconate	0.7	3.7	4.7	5.5	3.1	0.3
Dibutyl pyrotartrate	0.0	0.0	1.1	1.0	0.8	0.0

Table 9.25: Carbonylation Reactions Carried Out at Various Temperatures in the Presence of Air. (Amounts of Product Esters Expressed as W/W% of the Reaction Mixture, Initially 60 g)

The carbonylation of methylacetylene under 'standard' conditions but with air passing (iv).- Reaction 3.11 was carried out under 'standard' conditions with air passing at 1 - 1.5 l/h. The results are given in table 9.26:

Reaction 3.12 was carried out as above but with air passing at 2.0 l/h. The results are given in table 9.27:

Reaction time (hours)		1	2	3	4.25	5	6	7
Butyl methacrylate	(W/W%)	0.2	0.5	1.0	1.0	1.2	1.4	1.8
	(g)	0.2	0.3	0.6	0.7	0.8	1.0	1.3
Dibutyl citraconate	(W/W%)	0.8	1.8	2.6	3.1	4.4	5.1	5.8
	(g)	0.5	1.1	1.8	2.2	3.0	3.6	4.2
Dibutyl mesaconate	(W/W%)	1.9	3.7	6.1	6.9	9.2	10.5	11.3
	(g)	1.2	2.3	4.0	4.6	6.3	7.3	8.1
Dibutyl pyrotartrate	(W/W%)	0.4	0.5	1.0	1.2	1.4	1.6	2.0
	(g)	0.2	0.3	0.6	0.8	1.0	1.1	1.4

Table 9.26: Reaction 3.11, Carbonylation of Methylacetylene under 'Standard' Conditions, but with Air Passing at 1-1.5 l/h. (Amounts of Product Esters Expressed as W/W% of the Reaction Mixture, Initially 60 g, Wt. Inc. = 15.0 g; and in Grams.)

Reaction time (hours)	1	2	3	4	5	6	7
Butyl methacrylate	0.0	0.1	0.2	0.3	0.4	0.5	0.6
Dibutyl citraconate	0.6	2.1	2.8	4.1	5.9	6.3	7.0
Dibutyl mesaconate	0.8	2.6	3.1	4.7	6.8	7.7	8.5

Table 9.27: Reaction 3.12, Carbonylation of Methylacetylene Under 'Standard' Conditions, but with Air Passing at 2 l/h. (Amounts of Product Esters Expressed as W/W% of the Reaction Mixture, Initially 60 g, Wt. Inc. = 11.1 g)

The effect of benzoquinone (vi).- Reaction 3.23 was carried out under 'standard' conditions but with benzoquinone (10.0 g) present. The results are given in table 9.28:

Reaction time (hours)	1	3	5	7
Dibutyl citraconate	0.5	1.2	2.0	2.6
Dibutyl mesaconate	0.0	0.0	0.2	0.6
Butyl β-butoxycrotonate	-	-	-	2.0

Table 9.28: Reaction 3.23, Carbonylation of Methylacetylene in the Presence of Benzoquinone (10.0 g) (Amounts of Product Esters Expressed as W/W% of the Reaction Mixture, Initially 60 g, Wt. Inc. = 3.8 g)

Butyl β-butoxycrotonate was identified by the following retention times:

	Silicone	D.t.p.	Apiezon	P.e.g.
Reaction Product	10.9	20.3	20.2	10.3
Butyl β-butoxycrotonate	10.8	20.2	20.5	10.5

Table 9.29: Retention Time Comparison of a Product from Rn. 3.23 with Butyl β-Butoxycrotonate. (Retention Times in Minutes, Column Temperature = 200°C)

Reaction 3.24 was carried out under 'standard' conditions but with benzoquinone (1.0 g) present. The results are given in table 9.30:

Reaction time (hours)	1	3	5.5	7
Butyl methacrylate	0.0	0.6	5.0	8.2
Dibutyl citraconate	0.2	1.1	3.3	4.4
Dibutyl mesaconate	0.0	1.3	5.9	6.6
Dibutyl pyrotartrate	0.0	0.4	1.0	1.1
Butyl β-butoxycrotonate	-	-	-	1.5

Table 9.30: Reaction 3.24, Carbonylation of Methylacetylene in the Presence of Benzoquinone (1.0 g). (Amounts of Product Esters Expressed as W/W% of the Reaction Mixture, Initially 60 g, Wt. Inc. = 9.8 g)

Reaction 3.25 was carried out under 'standard' conditions but in the presence of benzoquinone (1.2 g) and allowed to continue for 22 hours. The results are given in table 9.31:

Reaction time (hours)	1.25	3	5	7	9	10	12	14	16	18	20	22
Butyl methacrylate	0.0	0.0	1.4	5.2	9.1	10.1	12.2	12.4	11.1	10.2	11.0	10.8
Dibutyl citraconate	0.4	0.9	2.2	3.1	3.9	4.7	4.5	3.3	4.2	4.6	5.1	4.7
Dibutyl mesaconate	0.0	0.4	3.9	5.2	5.7	6.5	6.1	5.8	5.7	6.0	5.6	6.1
Dibutyl pyrotartrate	0.0	0.0	0.5	0.9	1.1	1.2	1.2	1.1	1.2	1.1	1.0	1.2
Butyl β-butexycrotonate	0.7	1.3	1.3	1.3	1.3	1.5	1.4	1.2	1.3	1.4	1.6	1.5

Table 9.31: Reaction 3.25, Carbonylation of Methylacetylene in the Presence of Benzoquinone (1.2 g), Continued for 22 hours. (Amounts of Product Esters Expressed as W/W% of the Reaction Mixture, Initially 60 g, Wt. Inc. = 10.4 g)

The attempt to react butyl crotonate (1.0 g) and butanol (3 g) was carried out in the presence of benzoquinone (0.2 g), palladium iodide (0.18 m mol) and sodium iodide (0.36 m mol) in a sealed tube held at 90°C for 6 hours. No products were detected by gas chromatography.

(c) The Carbonylation of Methylacetylene in the Presence of Acid (3.4):

Standard Reactions in the Presence of Acid (i).- Two reactions (Rns. 3.27 and 3.28) were carried out under 'standard' conditions, but with the addition of hydrogen chloride (10 m mols) and only allowed to continue for 6 hours. The results are shown in tables 9.32 and 9.33:

Reaction time (hours)	1	2	3	4	5	6
Butyl methacrylate	0.2	0.8	1.6	2.1	2.3	3.9
Dibutyl citraconate	1.2	1.9	2.5	2.3	2.5	2.9
Dibutyl mesaconate	0.6	6.4	7.9	7.6	7.6	7.9
Dibutyl pyrotartrate	0.6	1.0	1.2	1.5	1.7	1.9

Table 9.32: Reaction 3.27 (Weight Increase = 7.6 g)

Reaction time (hours)	1	2	3	4	5	6
Butyl methacrylate	0.0	0.6	1.5	1.6	2.4	3.0
Dibutyl citraconate	0.1	0.8	1.3	2.0	2.8	2.7
Dibutyl mesaconate	0.5	3.3	5.1	6.9	7.8	7.9
Dibutyl pyrotartrate	0.2	0.6	0.7	1.5	1.8	1.8

Table 9.33: Reaction 3.28 (Weight Increase = 6.9 g)

Carbonylation of Methylacetylene in the Presence of Hydrogen Chloride (10 m mols). (Amounts of Esters Expressed as W/W% of the Reaction Mixture, Initially 60 g)

(d) Miscellaneous Reactions Intended to Elucidate Aspects of the Mechanism of Carbonylation (3.5):

The reaction of methylacetylene with the catalyst solution (ii).- Methylacetylene was bubbled slowly into butanol (50 g) for several hours and the weight increase (0.5 g) was noted. A quantity of Na_2PdI_4 solution was then added with a microlitre syringe to bring the final concentration to 8.0×10^{-5} molar w.r.t. Pd^{II}. The solution was immediately placed in the ultraviolet spectrometer, and spectra run at intervals.

In a second experiment, palladium iodide (0.55 m mols), sodium iodide (1.1 m mols) and butanol (10 mls) were placed in a Buchner flask fitted with a stopcock, which was then flushed with methylacetylene and allowed to stand for three days with occasional shaking.

In a third reaction, a solution of the same composition as above was placed in a mild steel container which was charged with methylacetylene at 5 atmospheres and held at room temperature for 24 hours. Thin layer chromatography was carried out using 10 cm. plates, and column chromatography using a 30 cm x 1 cm column. In both cases the stationary phase was alumina and the mobile phase was benzene. A yellow spot was observed in the thin layer chromatogram of the above reaction mixtures; a yellow oil corresponding to the spot was separated by column chromatography.

The attempted decarbonylation of butyl methacrylate (iii).- A reaction was carried out under 'standard' conditions, but with acetylene substituted for methylacetylene and with butyl methacrylate (11.7 g) present. The reaction was carried on for two hours. The weight increase was 1.6 g and the variation of butyl methacrylate concentration with time was as follows: t = 0, 18.9%; 0.25 hours, 18.9%; 1 hour, 18.8%; 2 hours, 18.6% W/W.

Carbonylation in butanol-O-d (iv).- Palladium iodide (0.75 g), sodium iodide (0.6 g) and butanol-O-d (30 g) were placed in the reactor and held at 65°C for 12 hours, whilst carbon monoxide and methylacetylene were passed at 3 l/h and 1.5 l/h respectively. After a two-day period at room temperature, the reaction was restarted and allowed to continue for a further 6 hours. The results of reaction 3.32 are given in table 9.34:

Reaction time (hours)	1	3	5	7	9	12	18
'pH'	1.0	1.0	1.0	1.5	2.0	3.5	5.0
Butyl methacrylate	0.1	0.5	0.6	0.9	1.1	1.5	2.4
Dibutyl citraconate	1.2	2.3	3.5	4.0	4.3	4.2	7.7
Dibutyl mesaconate	0.1	2.3	4.7	5.2	5.4	5.9	8.0
Dibutyl pyrotartrate	0.1	2.0	2.2	2.2	2.4	2.0	2.1

Table 9.34: Reaction 3.32, Carbonylation of Methylacetylene in Butanol-O-d. (Amounts of Product Esters Expressed as W/W% of the Reaction Mixture, Initially 30 g, Wt. Inc. = 0.6 g)

Reactions involving butyl acrylate (v).- Initially, a reaction was carried out under 'standard' conditions except that butyl acrylate (4.7 g) was present at the outset (Rn.3.33). Butyl propionate was identified by the following retention times:

	Silicone	D.t.p.	Apiezon	P.e.g.
Reaction product	12.5	14.8	14.7	obsc.
Butyl propionate	12.5	14.8	14.8	11.4

Table 9.35: Retention Time Comparison of Butyl Propionate with a Product from Reaction 3.33. (Retention Times in Minutes, Column Temperature = 90°C)

A second reaction (Rn. 3.34) was carried out under 'standard' conditions except that butyl acrylate (4.7 g) was present, air was passed at 1 - 1.5 l/h and the reaction was allowed to continue for 6 hours. Dibutyl 3-methyl-cis-hex-2-enedioate was obtained as a clear oil, b.p. 299° - 301°C (decomp) by Emich's method, $I^{SE\ 30}_{200^{\circ}}$ = 1808, found C, 66.5; H, 9.3 $C_{15}H_{26}O_4$ requires C, 66.4; H, 9.7%.

In an attempt to increase the yield of the new diester, 'standard' conditions were varied in that butyl acrylate (40 g) was added from a compensated tap funnel throughout the reaction, and air was passed at 1 - 1.5 l/h. The results are given in table 9.36. The somewhat erratic nature of the results is no doubt due to variations in the rate of addition of the ester.

Reaction time (hours)	1	3	5.25	7
Butyl methacrylate	0.0	0.0	0.2	0.3
Dibutyl citraconate	0.3	0.5	1.7	2.2
Dibutyl mesaconate	0.7	0.8	2.6	3.2
Dibutyl pyrotartrate	0.0	0.0	0.2	0.2
Dibutyl 3-methyl-cis-hex-2-enedioate	0.8	1.2	3.6	4.3

Table 9.36: Reaction 3.36, Carbonylation of Methylacetylene in the Presence of Butyl Acrylate and Air. (Amounts of Product Esters Expressed as W/W% of the Reaction Mixture, Initially 60 g, Wt. Inc. = 10.9 g)

Reactions involving the homologues of acrylate ester (vi).- Reaction 3.37 was carried out under 'standard' conditions, but with butyl methacrylate (8.7 g) present, and air passing at 1 - 1.5 l/h. The results are given in table 9.37.

Reaction time (hours)	1	3	5	7
Butyl methacrylate	[15.4]	[14.5]	[14.4]	[11.9]
Butyl isobutyrate	0.0	0.1	0.2	0.3
Dibutyl citraconate	1.0	3.7	4.7	5.7
Dibutyl mesaconate	2.1	6.0	8.1	9.3
Dibutyl pyrotartrate	0.3	0.7	1.6	2.0

Table 9.37: Reaction 3.37, Carbonylation of Methylacetylene in the Presence of Butyl Methacrylate and Air. (Amounts of Product Esters Expressed as W/W% of the Reaction Mixture, Initially 60 g, Wt. Inc. = 11.3 g)

Reaction 3.38 was carried out as above but with butyl crotonate (5.7 g) present instead of the methacrylate ester. The results are given in table 9.38:

Reaction time (hours)	1	3	5	7
Butyl methacrylate	0.1	0.4	0.8	1.0
Butyl crotonate	[9.7]	[10.5]	[10.8]	[9.9]
Butyl n-butyrate	0.1	0.3	0.5	0.6
Dibutyl citraconate	0.4	2.0	3.0	4.2
Dibutyl mesaconate	0.9	4.3	6.4	8.2
Dibutyl pyrotartrate	0.1	0.5	0.9	1.2

Table 9.38: Reaction 3.38, Carbonylation of Methylacetylene in the Presence of Butyl crotonate and Air. (Amounts of Product Esters Expressed as W/W% of the Reaction Mixture, Initially 60 g, Wt. Inc. = 7.2 g)

Butyl n-butyrate was identified by the following gas chromatographic retention times:

	Silicone	D.t.p.	Apiezon	P.e.g.
Reaction Product	6.4	obsc.	6.8	obsc.
Butyl n-butyrate	6.4	7.2	6.8	6.0

Table 9.39: Retention Time Comparison of Butyl n-Butyrate with a Substance Formed in Reaction 3.38. (Retention Times in Minutes, Column Temperature = 150°C)

Reactions involving diesters (vii).- Reaction 3.39 was carried out under 'standard' conditions but with dibutyl maleate (8.7 g) present. Dibutyl succinate was identified by the gas chromatographic retention times given in table 9.40. The results of analyses are given in table 9.41:

	Silicone (160°C)	D.t.p. (180°C)	Apiezon (200°C)	P.e.g. (170°C)
Substance from Rn. 3.39	10.0	19.1	25.2	17.3
Substance from Rn. 3.40	10.0	19.2	25.2	17.4
Dibutyl succinate	10.0	19.0	25.3	17.3

Table 9.40: Retention Time Comparison of Dibutyl Succinate with Substances Formed in Reactions 3.39 and 3.40. (Retention Times in Minutes)

Reaction Time (hours)	1	3	5	7
Butyl methacrylate	0.0	0.3	0.4	0.4
Dibutyl citraconate	0.9	2.5	4.1	5.5
Dibutyl mesaconate	1.3	4.1	6.6	9.0
Dibutyl pyrotartrate	0.6	1.8	2.9	3.8
Dibutyl maleate	[12.4]	[9.8]	[7.5]	[5.1]
Dibutyl succinate	0.8	2.9	4.8	7.1

Table 9.41: Reaction 3.39, Carbonylation of Methylacetylene in the Presence of Dibutyl Maleate. (Amounts of Product Esters Expressed as W/W% of the Reaction Mixture, Initially 60 g, Wt. Inc. = 5.1 g)

Reaction 3.40 was carried out under 'standard' conditions but with dibutyl fumarate (8.6 g) present. Dibutyl succinate was identified by the gas chromatographic retention times shown in table 9.40. The results are given in table 9.42:

Reaction time (hours)	1	3	5	7
Butyl methacrylate	0.0	0.0	0.0	0.2
Dibutyl citraconate	0.0	0.0	0.4	4.0
Dibutyl mesaconate	0.0	0.1	0.6	4.7
Dibutyl pyrotartrate	0.0	0.0	0.1	0.2
Dibutyl fumarate	[14.2]	[14.1]	[14.1]	[10.2]
Dibutyl succinate	0.0	0.0	0.2	4.4

Table 9.42: Reaction 3.40, Carbonylation of Methylacetylene in the Presence of Dibutyl Fumarate. (Amounts of Product Esters Expressed as W/W% of the Reaction Mixture, Initially 60 g, Wt. Inc. = 1.2 g)

Reactions in the presence of pyrotartrate ester (viii).- Reactions 3.41 and 3.42 were carried out under the 'standard' conditions, but with air passing at 1 - 1.5 l/h and dibutyl pyrotartrate (1.0 g in 3.41 and 0.8 g in 3.42) introduced when the reaction had been under way for 4 and 2 hours respectively. The analyses are shown in tables 9.43 and 9.44:

Reaction time (hours)	1.0	2.0	3.0	4.0	4.5	5.5	6.5
Butyl methacrylate	0.3	0.6	0.9	1.4	1.3	1.3	1.5
Dibutyl citraconate	0.7	1.6	2.3	3.2	3.5	4.2	4.9
Dibutyl mesaconate	1.8	3.8	5.8	7.4	7.8	8.7	11.4
Dibutyl pyrotartrate	0.3	0.6	0.7	1.4	[2.5]	[2.9]	[2.8]

Table 9.43: Reaction 3.41 (Weight Increase = 14.2 g)

Reaction time (hours)	0.5	1.0	1.5	2.0	2.25	2.5	3.0	3.5	4.0	4.5	5.5	6.0
Butyl methacrylate	0.1	0.2	0.3	0.4	0.4	0.5	0.5	0.8	0.8	0.7	0.8	0.8
Dibutyl citraconate	0.5	1.0	1.1	2.1	2.3	2.5	3.0	3.4	4.0	4.3	4.7	5.2
Dibutyl mesaconate	1.4	2.1	2.8	4.2	4.4	4.8	5.6	6.8	7.8	8.3	9.1	9.8
Dibutyl pyrotartrate	0.0	0.1	0.3	0.5	[2.1]	[2.2]	[2.3]	[2.5]	[2.7]	[2.7]	[2.8]	[2.9]

Table 9.44: Reaction 3.42 (Weight Increase = 10.8 g)

Methylacetylene Carbonylation Reactions Carried Out in the Presence of Dibutyl Pyrotartrate and Air. (Amounts of Product Esters Expressed as W/W% of the Reaction Mixture, Initially 60 g)

(e) The Carbonylation of Methylacetylene in the Presence of Various Additives (3.6):

Gases other than air (i).- The results of reaction 3.44 are given in table 9.45 and the results of reaction 3.45 are given in table 9.46:

Reaction time (hours)	1	3	5	7
Butyl methacrylate	0.4	0.9	1.6	2.2
Dibutyl citraconate	0.9	1.7	2.3	2.9
Dibutyl mesaconate	1.6	5.4	5.7	6.5
Dibutyl pyrotartrate	0.7	1.2	1.5	1.9

Table 9.45: Reaction 3.44, Carbonylation of Methylacetylene in the Presence of Hydrogen. (Amounts of Product Esters Expressed as W/W% of the Reaction Mixture, Initially 60 g, Wt. Inc. = 6.1 g)

Reaction time (hours)	1	2	3	4	5	6
Butyl methacrylate	0.1	0.5	0.7	1.2	1.6	2.6
Dibutyl citraconate	0.7	1.3	1.7	2.2	2.2	2.7
Dibutyl mesaconate	2.5	3.9	5.2	5.9	6.4	6.8
Dibutyl pyrotartrate	0.4	0.7	0.9	1.2	1.3	1.5

Table 9.46: Reaction 3.43, Carbonylation of Methylacetylene in the Presence of Nitrogen. (Amounts of Product Esters Expressed as W/W% of the Reaction Mixture, Initially 60 g, Wt. Inc.= 6.0g)

9.9. EXPERIMENTAL FOR CHAPTER 4, THE CARBONYLATION OF BUTYLACETYLENE

(a) Gas Chromatography: The products from the carbonylation of butylacetylene were quantitatively analysed by gas chromatography using butyl methacrylate at 110°C as an internal marker substance for the monoesters on the silicone column, and dibutyl mesaconate at 200°C for the diesters on the apiezon column.

(b) Exploratory Work (4.2):

The 'standard' reaction.- n-Butanol (60 g), palladium iodide (4 m mols) and sodium iodide (8 m mols) were placed in the multinecked reactor, held at 65°C and vigorously stirred, whilst butylacetylene (10 g) was run in over a 7 hour period from a compensated dropping funnel (Rn. 4.1). Carbon monoxide was bubbled through the solution at the rate of 3 litres/hour.

The above conditions will be regarded as 'standard' in the following discussions of butylacetylene carbonylation reactions.

Butylmethyl ketone was identified by the following retention times:

	Silicone	D.t.p	Apiezon	P.e.g.
Butylmethyl ketone	4.1	4.5	4.1	3.2
'B'	4.1	4.5	4.1	obsc.

Table 9.47: Retention Time Comparison of 'B' with Butylmethyl Ketone. (Retention Times in Minutes, Column Temperature = 150°C)

Butyl α-butylacrylate was isolated by preparative scale gas chromatography as a clear oil, b.p. 215°C by Emich's method, $I^{SE\ 30}_{150^{o}} = 1240$, having a smell resembling that of butyl methacrylate, found C, 71.6; H,11.0 $C_{11}H_{20}O_2$ requires C, 71.6; H,10.9%.

Butyl oenanthate was identified by the following retention times:

	Silicone	D.t.p.	Apiezon	P.e.g.
Butyl oenanthate	15.7	23.8	24.8	9.3
'F'	15.7	23.7	25.1	9.3

Table 9.48: Retention Time Comparison of 'F' with Butyl Oenanthate. (Retention Times in Minutes, Column Temperature = 150°C)

Hydrogenation of the reaction mixture required extreme conditions, in view of the presence of iodide ion which is known to inhibit most heterogenious hydrogenation catalysts[23]. The reaction mixture, 4.1 (30 g) was placed in a rocking autoclave with 5% palladium/charcoal (5 g) and hydrogen charged in at 85 atmos. The autoclave was held at 130°C with constant agitation for 2 hours. The diesters were unaffected by such treatment, but the monoesters were largely reduced.

Dibutyl butylbutenedioate was isolated as a clear oil b.p. = 295°C by Emich's method, $I^{SE\ 30}_{230^{o}} = 1812$, found C,68.4; H,10.0 $C_{16}H_{28}O_4$ requires C, 67.7; H,9.9%.

Isomerisation was effected by heating the sample of cis- and trans-diesters (20mg) with a trace of nitric oxide (cf. Chapter 9.5 (a)). The retention indices of the two isomers on an apiezon L stationary phase were as follows: Dibutyl butylmaleate, $I^{APIEZON\ L}_{230^{o}} = 1741$; dibutyl butylfumarate, $I^{APIEZON\ L}_{230^{o}} = 1760$.

Hydrogenation over platinum yielded dibutyl butylsuccinate (cf. Chapter 9.1).

'H' was identified as dibutyl butylsuccinate by the following gas chromatographic retention times:

	Silicone	Apiezon	P.e.g.
Dibutyl butylsuccinate	12.8	16.1	17.4
'H'	12.6	15.8	17.6

Table 9.49: Retention Time Comparison of 'H' with Dibutyl Butylsuccinate. (Retention Times in Minutes, Column Temperature = 230°C)

(c) Carbonylation of Butylacetylene Under Various Conditions (4.3):

Carbonylation in the presence of a high concentration of butylacetylene (iv).- Butanol (4.0 g), palladium iodide (0.27 m mols), sodium iodide (0.54 m mols) and butylacetylene (1 g) were placed in a 50 ml flask equipped for magnetic stirring and attached to a water manometer. The flask was flushed several times with carbon monoxide, then charged to slightly above atmospheric pressure, warmed to 40°C and stirred for 7 hours (Rn. 4.5).

Column chromatography of the product was carried out on a 30 x 1 cm alumina column, using petrol as the mobile phase.

Carbonylation under an elevated carbon monoxide pressure (v).- A solution of the same composition as was used for reaction 4.5, was placed in a mild steel reactor charged with carbon monoxide at 100 atmos. and held at 90°C for 7 hours without agitation (Rn. 4.6).

(d) Miscellaneous Reactions Designed to Elucidate Aspects of the Mechanism of Carbonylation (3.4):

The reaction of butylacetylene with the catalyst solution (i).- The reaction between palladium iodide and butylacetylene was studied as follows: butanol (2.0 g), palladium iodide (0.2 m mols), sodium iodide (0.4 m mols) and butylacetylene (0.3 g) were placed in a tube and shaken at intervals for 2 hours. A yellow colour was produced and separated by thin-layer chromatography (on a 10 cm alumina plate using benzene as the mobile phase) as a spot of R_F = 0.52. The oily yellow substance corresponding to the spot was isolated using the alumina column described above with benzene as the mobile phase.

Carbonylation in butanol-O-d (ii).- The possibility of exchange between butanol-O-d and butylacetylene was checked as follows: a sample of butylacetylene was shaken with deuterium oxide and a trace of acid, and n.m.r. spectra were run at intervals. No diminution of the integral of the acetylenic proton was observed even after three days, and it was concluded that such exchange did not occur to a significant extent.

Carbonylation in the presence of butyl acrylate (iii).- Two new substances (supposed to be isomers) were present amongst the products of reaction 4.8, having retention indices $I^{SE\ 30}_{230^o}$ = 2040 and 2122. The latter was isolated by preparative scale gas chromatography as a clear oil, found C, 70.8; H, 9.5 $C_{18}H_{32}O_4$ requires C, 69.2; H, 10.3%.

9.10. EXPERIMENTAL FOR CHAPTER 5, THE CARBONYLATION OF PHENYLACETYLENE

(a) Gas Chromatography: The products from the carbonylation of phenylacetylene were quantitatively analysed on a silicone column using dibutyl itaconate at 180°C as an internal marker for the monoesters and dibutyl phthalate at 220°C for the diesters. As a check on the reproducibility of the method, butyl cinnamate was also determined relative to dibutyl phthalate on a number of occasions and, though the wide separation of the two substances in the chromatogram is not regarded as favouring an accurate result[12,15], agreement with the value obtained using itaconate ester as the internal marker was always better than 5%.

(b) Exploratory Reactions (5.2):

The attempted carbonylation of phenylacetylene using a high initial concentration (i).- Phenylacetylene (20 g), butanol (40 g), palladium iodide (4 m mols) and sodium iodide (8 m mols) were placed in the multinecked reactor and held at 65°C, the solution being vigorously stirred whilst carbon monoxide was passed at 3 litres/hour for 7 hours. The reaction mixture was concentrated by distillation under reduced pressure to a viscous mass (only butanol and phenylacetylene being detected in the distillate). The mass was triturated with methanol, when a yellow solid separated, was filtered off, and washed with methanol. Thin layer chromatography was carried out using 10 cm alumina plates and a range of solvents from petrol to ethyl acetate. Column chromatography was conducted on a 30 x 1 cm alumina column with the same solvents. The average molecular weight of the mixture was determined by Rast's method based on the depression of the freezing point of camphor[4].

The interaction of phenylacetylene with the catalyst solution (ii).- Phenylacetylene (0.3 g), butanol (2 g), palladium iodide (0.2 m mols) and sodium iodide (0.4 m mols) were shaken together for a few minutes. A reddish yellow substance was produced and separated by thin layer

and column chromatography as described above using benzene as the mobile phase (R_F = 0.75). A catalyst solution consisting of butanol (60 g), palladium iodide (4 m mols) and sodium iodide (8 m mols) was placed in the reactor and held at 65°C with vigorous stirring. Phenylacetylene (10 g) was placed in a bubbler, also held at 65°C, and carbon monoxide was passed, at 9 l/h, through the bubbler and directly into the reactor. The reaction was allowed to continue for 12 hours, during which time, all the phenylacetylene was transferred to the reactor (Rn. 5.2). Products were identified by the following retention times:

	Silicone	D.t.p.	Apiezon	P.e.g.
	(200°C)	(200°C)	(220°C)	(200°C)
'B'	5.0	6.2	6.0	7.5
Acetophenone	5.0	6.2	6.0	7.5
'C'	7.7	14.8	11.2	10.8
Butyl hydratropate	7.7	14.8	11.4	10.7
'D'	11.2	19.8	15.7	15.1
Butyl atropate	11.2	20.0	15.6	14.9
'E'	12.1	22.4	16.5	15.1
Butyl hydrocinnamate	12.0	22.4	16.6	15.2
'F'	16.9	39.2	30.4	28.8
Butyl cinnamate	16.8	39.5	30.6	29.1
	(240°C)		(240°C)	(230°C)
'G'	17.8		34.2	32.6
Dibutyl phenylsuccinate	18.0		34.2	32.4
Hydrogenated 'H' + 'I'	17.9		34.1	32.4

Table 9.50: Retention Time Comparison of Phenylacetylene Carbonylation Products with the Authentic Esters. (Retention Times in Minutes)

The 'standard' reaction (iv).- Butanol (60 g), palladium iodide (4 m mols) and sodium iodide (8 m mols) were placed in the reactor and vigorously stirred at 65°C, whilst phenylacetylene (10 g) was introduced from a compensated tap funnel over a 7 hour period. Carbon monoxide was meanwhile passed at 3 l/h (Rn. 5.3).

(c) Carbonylation of Phenylacetylene in the Presence of Butyl Acrylate (5.5):

Reaction 5.7 was carried out as described for the 'standard' reaction above, but instead of phenylacetylene, a mixture of butyl acrylate

(10 g) and phenylacetylene (10 g) was added from the tap funnel, and air was passed at 1 - 1.5 l/h. Dibutyl 3-phenylhex-2-enedioate was isolated by preparative scale gas chromatography as a clear oil, $I^{SE\ 30}_{230^\circ} = 2336$. Combustion analysis, like the n.m.r. spectrum (fig. 5.7) pointed to the presence of an aromatic or carbon-rich impurity, found C, 77.8; H, 8.9 $C_{20}H_{28}O_4$ requires C,72.4; H, 8.5%, however its molecular formula was obtained by high resolution mass spectrometry, found $\frac{m}{e} = 332.1984$ $C_{20}H_{28}O_4$ requires 332.1987.

9.11. EXPERIMENTAL FOR CHAPTER 6, THE CARBONYLATION OF DIMETHYLACETYLENE

(a) Gas Chromatography: The products from the carbonylation of dimethylacetylene were quantitatively analysed by gas chromatography (where appropriate) on a silicone column at 140°C using diethyl adipate as an internal marker.

(b) Attempts to Carbonylate Dimethylacetylene at Atmospheric Pressure (6.2):

Attempted carbonylation in a closed system (ii).- Butanol (10 g), palladium iodide (0.55 m mols), sodium iodide (1.1 m mols) and dimethylacetylene (1.0 g) were placed in a 50 ml flask, exposed to an atmosphere of carbon monoxide, and stirred magnetically at 16°C for 22 hours. No products were detected by gas chromatography.

(c) Carbonylation of Dimethylacetylene Above Atmospheric Pressure (6.3):

Carbonylation under moderate pressure (i).- Butanol (4.5 g), palladium iodide (0.28 m mols), sodium iodide (0.56 m mols) and dimethylacetylene (0.42 g) were placed in a copper reactor of 10 ml capacity, charged with carbon monoxide at 17 atmospheres and stirred magnetically at 65°C for 15 hours, the reactor occasionally being recharged with carbon monoxide (Rn. 6.4). A second reaction was carried out under similar conditions, but allowed to continue for 28 hours (Rn. 6.5).

Carbonylation under higher pressures (ii).- Butanol (23.0 g), palladium iodide (1.0 m mol), sodium iodide (2.0 m mols) and dimethylacetylene (2.5 g) were placed in a stainless steel rocking autoclave, of 400 ml capacity, charged with carbon monoxide at 100 atmos. pressure. The autoclave was heated at 80°C, with rocking, for 18 hours (Rn. 6.6).

Rn. 6.7: Butanol (21.0 g), palladium iodide (1.4 m mols), sodium iodide (2.8 m mols) and dimethylacetylene (3.0g) were placed in

a mild steel reactor of 100 ml capacity, charged with carbon monoxide at 90 atmos. and held at 75°C for 7 hours without agitation.

Rn. 6.8: Butanol (16.2 g), palladium iodide (0.9 m mols), sodium iodide (1.8 m mols) and dimethylacetylene (3.2 g) were placed in the mild steel reactor, charged with carbon monoxide at 90 atmos. as above and held at 90°C without agitation for 17 hours.

Dimethyl crotonolactone was isolated by preparative scale gas chromatography as white blades, m.p. 27°C (33-34°C, Ames, Bowman and Grey[24]). Retention Index, $I^{SE\ 30}_{105°C}$= 1153.

'B' was isolated by preparative scale gas chromatography as a clear oil, $I^{SE\ 30}_{130°C}$ = 1611; $\frac{m}{e}$ = 256.1710 $C_{14}H_{24}O_4$ requires 256.1675.

Dibutyl dimethylmaleate was isolated by preparative scale gas chromatography as a clear oil, $I^{SE\ 30}_{155°C}$ = 1676, found C, 64.8; H, 9.7 $C_{14}H_{24}O_2$ requires C, 65.6; H, 9.5%.

Trans-tetramethylbifurandione was thrown down during the carbonylation reactions. It was collected and recrystallised from aqueous methanol, as golden yellow feathery crystals, m.p. 222-223.5°C, found C, 65.3; H, 5.9 $C_{12}H_{12}O_4$ requires C, 65.4; H, 5.5%.

9.12. EXPERIMENTAL FOR CHAPTER 7, THE CARBONYLATION OF DIPHENYLACETYLENE

(a) The Carbonylation of Diphenylacetylene Above Atmospheric Pressure (7.3):

The carbonylation reaction (i).- Diphenylacetylene (3 g), palladium iodide (1.5 m mols) and sodium iodide (3 m mols) in butanol (30 mls) were placed in a 400 ml stainless steel rocking autoclave, which was charged with carbon monoxide at 100 atmos. and held at 80°C with constant agitation for 7 hours.

(b) Chromatographic Techniques:

Gas chromatography.- The columns used hitherto were not suitable for analysing the products obtained from diphenylacetylene, since only the monoester was sufficiently volatile to be eluted from the column, even at high temperatures and flow-rates. For the same reason, preparative scale gas chromatography was ruled out. However, a 1m x $\frac{1}{8}$" o.d. column, packed with a 1% neopentylglycolsuccinate (n.p.g.s.) stationary phase was found to be satisfactory. The products were quantitatively analysed using dibutyl phthalate as an internal marker at 170°C.

Thin layer chromatography.- 10 cm plates coated with alumina were found to be satisfactory. The solvent giving best resolution, being a 2:1 mixture of benzene and petrol, was used throughout. Chromatogenesis was achieved by exposing the plates to iodine vapour.

Column chromatography.- Components 'A' and 'C' were isolated from the reaction mixture using a 30 x 1 cm alumina column, eluted with 2:1 benzene:petrol (300 mls) followed by 20:1 petrol:ether (200 mls) and 1:1 petrol:ethyl acetate (150 mls).

The first crude extract, used for mass spectral studies, was obtained using the same column, eluted with chloroform/2% ethanol. The second crude extract, used for n.m.r. hydrogenation studies, was obtained by shaking the reaction mixture (10 mls) with alumina (3 g), adding water (20 mls) and extracting with ether (5 x 20 ml portions).

(c) Reaction Products: Butyl α-phenylcinnamate was identified by the following chromatographic data:

	Retention Time (Minutes)		R_F
	Silicone	Apiezon	Al_2O_3
	(210°C)	(210°C)	Benzene/Petrol
'A'	10.2	48.4	0.64
Butyl α-phenylcinnamate	10.4	48.8	0.64

Table 9.51: Chromatographic Comparison of 'A' with Butyl α-Phenylcinnamate

(d) Hydrogenation of the Diphenylacetylene Carbonylation Products: The second crude mixture obtained as above (10 mg) was placed in a stainless steel reactor of 5 ml capacity with Adams' catalyst (5 mg) and methanol (1.5 mls) and exposed to hydrogen at 20 atmospheres and room temperature for 7 days with magnetic stirring. Platinum was then filtered off and the hydrogenated products concentrated by evaporation. The product from the hydrogenation of 'B' was identified as dibutyl 2,3-diphenylsuccinate on the basis of the following chromatographic data:

	Retention Time (Mins.)	R_F
	n.p.g.s.	Al_2O_3
	(160°C)	benzene/petrol
'B'	12.0	0.26
Component in hydrogenated mixture	10.5	0.58
Dibutyl 2,3-diphenylsuccinate	10.6	0.58

Table 9.52: Chromatographic Comparison of Hydrogenated 'B' with Dibutyl 2,3-Diphenylsuccinate

9.13. REFERENCES

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APPENDIX

The following courses of study were undertaken, and symposia attended, in fulfilment of the requirements of the C.N.A.A.

Unless otherwise stated, the courses were organised within the School of Chemical Science & Technology, Kingston Polytechnic.

SYMPOSIUM ON THE CHEMISTRY OF ACETYLENES, ALLENES & CUMULENES (The Chemical Society) 32 lectures

THE USES & PRODUCTION OF ACRYLATES (The Society for Chemical Industry) 1 lecture

GAS CHROMATOGRAPHY 6 lectures

SYMPOSIUM ON GAS CHROMATOGRAPHY (Techmation Ltd.) 8 lectures

SYMPOSIUM ON QUANTITATIVE GAS CHROMATOGRAPHY 6 lectures

N.M.R. INTERPRETATION 8 lectures

THE THEORETICAL BASIS OF N.M.R. 8 lectures

VIBRATIONAL SPECTROSCOPY 8 lectures

CLASSICAL THEORIES OF MOLECULAR SPECTROSCOPY 8 lectures

PRACTICAL MASS SPECTROMETRY 18 hours

SYMPOSIUM ON MASS SPECTROMETRY 6 lectures

STATISTICS 6 lectures

In addition, a number of colloquia on various research topics, given by members of the School and visiting speakers, have been attended.