THE INTERACTION OF NITRIC OXIDE WITH CONJUGATED DIENES

by

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A thesis presented for the degree of Doctor of Philosophy to the Council for National Academic Awards

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January, 1970

ABSTRACT OF THESIS

The literature dealing with interaction of the dinitrogen tetroxide-nitrogen dioxide equilibrium mixture, dinitrogen trioxide and nitric oxide, with carbon-carbon multiple bonds has been reviewed in detail, with particular reference to the mechanisms which have been suggested at various times. Aspects of the reactions of nitrosyl and nitryl chloride with olefins relevant to this work, have also been mentioned.

The characteristics of the interaction of nitric oxide with a solution of a conjugated diene at moderate temperatures have been found to be the rapid production of a bright blue or green coloured solution, associated with a nitroso monomer, followed by evolution of large quantities of molecular nitrogen. Some dienes precipitated thermally unstable, dimeric, nitro-nitroso compounds during the course of the reaction and all the diolefins used gave considerable amounts of brown, viscous oils as the major reaction product. The evidence relating to the structure of the solid and oil products is considered in detail and it is inferred that the latter consisted largely of low molecular weight polymers containing nitro and nitrate groups, but complete identification of the components was not possible.

From a consideration of the evidence accumulated it is concluded that a free radical mechanism operates during the formation of the afore mentioned compounds. This involves initiation by nitrogen dioxide. The resulting nitro allylic radical can undergo several reactions; combination with nitric oxide to give a nitro-nitroso monomer, which disproportionates nitric oxide into molecular nitrogen and nitrogen trioxide <u>via</u> unconfirmed intermediates; reaction with diene monomer and thus leading to polymerisation; addition of

nitrogen dioxide or nitrogen trioxide to give dinitro and nitronitrate compounds respectively.

Since in many cases the products could not be separated in a pure state, extensive use was made of spectroscopic methods of analysis and the interpretation of these results are explained where relevant.

ACKNOWLEDGEMENTS

The author is extremely grateful to his supervisor, Dr. P.B. Brindley, for continuous help, advice and encouragement during the course of this work.

He would also like to thank Mr. F.J. Bellringer and Mr. P.A. Jenkins of B.P. Chemicals (U.K.) Ltd., for helpful discussions on many occasions. Thanks are also due to B.P. Chemicals for a maintainance grant covering the period of this work.

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POST-GRADUATE STUDIES

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Aspects of Organic Reaction Mechanisms. Chemical Society Symposium, London, 1967.

Some Recent Developments in Free Radical Chemistry. Symposium, Kingston College of Technology, 1969.

Spectroscopic Methods in Organometallic Chemistry. Symposium (2 day), Kingston College of Technology, 1969.

Organic Reaction Mechanisms. Chemical Society Symposium, London, 1967.

Several research colloquia have been attended and two have been given.

CHAPTER 1

The Action of Nitrogen Oxides on Carbon-Carbon Multiple Bonds:

Nitrogen Dioxide

Introduction.

The interaction of the oxides of nitrogen with carbon-carbon multiple bonds has attracted much attention for a number of years and has been the subject of several reviews among which are those of Riebsomer[1], Levy and Rose[2] and more recently of Stacey and Harris[3], Sosnovsky[4] and Shechter[5]. Although the most investigated system has been that of the nitrogen dioxide - dinitrogen tetroxide equilibrium mixture and olefins, some interest has been shown in the other principal oxides of nitrogen or their derivatives.

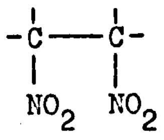
Nitric oxide is frequently used as a trapping agent for free radicals especially in pyrolysis studies[6] and also has industrial applications.

The use by Tilden[7] of nitrosyl chloride for the identification of double bonds was an early technique in terpene chemistry while in recent years the photo initiated reaction with cyclohexane[8] has been used as an industrial route to caprolactam. Dinitrogen trioxide[4] has also found use in natural product chemistry.

The mechanism of the interaction of the principal oxides of nitrogen with unsaturates is not clearly understood although there is increasing evidence that it may be homolytic in nature in keeping with the free radical properties of these oxides[5]. However, in some instances this may not be the case and the mechanism could equally well be interpreted as proceeding ionically. This is especially true of dinitrogen tetroxide and dinitrogen trioxide and emphasis will be placed on the mechanistic aspect of these oxides in the subsequent pages.

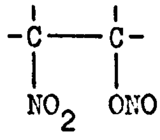
The products of olefin and nitrogen oxides interactions are often thermally unstable and great care and special techniques, developed by Levy and associates[9], are needed when attempting purification because straight forward distillations or column chromatography, often lead to low order explosions or 'fume offs'. The techniques often include hydrolysing the nitrite ester to the alcohol.

Early investigations of nitrogen oxide and olefin interactions were unreliable for three reasons. Firstly, mixtures of oxides (NO_2, N_2O_3, NO) were used, secondly, very often the reaction conditions were not clearly stated and thirdly the nomenclature used was inconsistent. The accepted nomenclature now for the addition products of nitrogen oxides and olefins is; dinitro (I), nitro-nitrite (II), nitro-nitrate (III), nitro-nitroso (IV), nitroso-nitrite (V), nitroso-nitrate (VI), dinitrite (VII) and nitrite-nitrate (VIII).



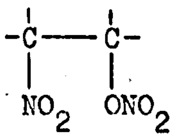
$-\underset{NO_2}{\overset{|}{C}}-\underset{NO_2}{\overset{|}{C}}-$

(I)



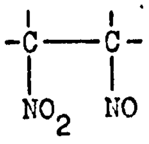
$-\underset{NO_2}{\overset{|}{C}}-\underset{ONO}{\overset{|}{C}}-$

(II)



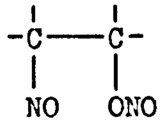
$-\underset{NO_2}{\overset{|}{C}}-\underset{ONO_2}{\overset{|}{C}}-$

(III)



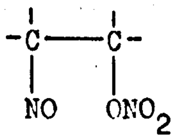
$-\underset{NO_2}{\overset{|}{C}}-\underset{NO}{\overset{|}{C}}-$

(IV)



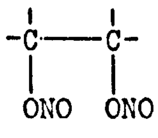
$-\underset{NO}{\overset{|}{C}}-\underset{ONO}{\overset{|}{C}}-$

(V)



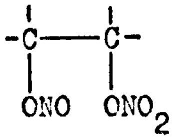
$-\underset{NO}{\overset{|}{C}}-\underset{ONO_2}{\overset{|}{C}}-$

(VI)



$-\underset{ONO}{\overset{|}{C}}-\underset{ONO}{\overset{|}{C}}-$

(VII)



$-\underset{ONO}{\overset{|}{C}}-\underset{ONO_2}{\overset{|}{C}}-$

(VIII)

<u></u>**Structure and Physical Properties of Nitrogen Dioxide and Dinitrogen Tetroxide:-** For a clear understanding of the possible modes of interaction of the nitrogen dioxide - dinitrogen tetroxide equilibrium mixture with carbon-carbon multiple bonds, it is necessary to consider the temperature dependence of the equilibrium, the structure and modes of dissociation of the dimer, and lastly, the structure and nature of nitrogen dioxide.

Dinitrogen tetroxide has long been known to be an equilibrium mixture:-

$$N_2O_4 \rightleftharpoons 2NO_2 \qquad \Delta H = -14.7 \text{ kcal}^4 \text{ (SI unit equivalent } -61.5 \text{ kJ)} \qquad (1)$$

The temperature dependence of this equilibrium is shown in Figure 1.

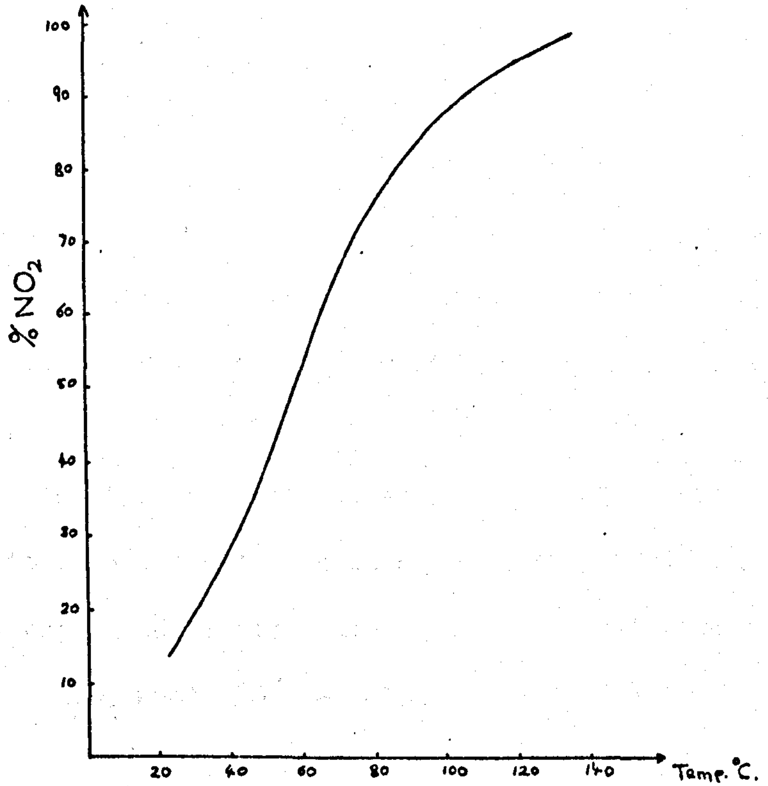
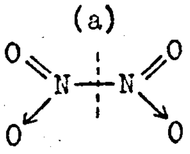


Figure 1

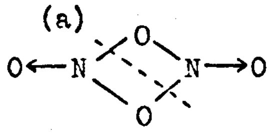
Approximate % NO_2 in $N_2O_4 \rightleftharpoons 2NO_2$ at 1 Atmosphere[29].

The solid melts at -11.3° and the liquid boils at 21.1° at one atmosphere pressure[10]. Most of the reported reactions of unsaturated compounds, with the exception of some halogeno-olefins, have been carried out at temperatures between -20 and +25°. It is therefore clear that a dinitrogen tetroxide rich mixture was used.

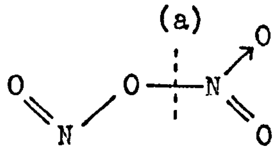
An excellent review on the structure and chemical properties of dinitrogen tetroxide has been given by Gray[11]. Of the wealth of evidence available concerning the structure, Gray, from a consideration of electron diffraction, X-ray diffraction, infrared and Raman spectroscopy, calorimetry and dielectric constant measurements, concludes that formula (IX) is the correct one of the four possible structures (IX - XII).



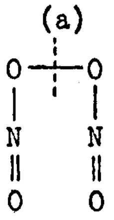
(IX)



(X)



(XI)



(XII)

The chemical evidence is equivocal. The most important aspect is the ready homolytic fission (at (a) in structures IX - XII), to form two NO_2 radicals. None of the formulae imposes any steric difficulties on the homolysis or on the reverse action. On the other hand heterolysis to give the nitrosonium nitrate ions (Equation 2), is more readily explained by structures (XI) and (XII) than by (IX) or (X).

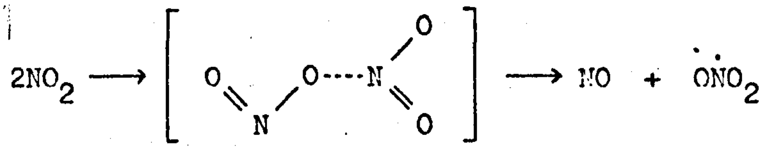
$$N_2O_4 \rightleftharpoons NO^+ + ONO_2^- \qquad (2)$$

Addison and Lewis[12] however, consider that heterolysis takes place firstly to nitronium and nitrite ions, which is the third method of dissociation open to the dimer, followed immediately by oxidative transfer of an oxygen atom:-

$$N_2O_4 \rightleftharpoons NO_2^+ + ONO^- \longrightarrow NO^+ + ONO_2^- \qquad (3)$$

It is probably preferable however, to think in terms of partial polarisation, $\overset{\delta+}{ON}\cdots\overset{\delta-}{ONO_2}$ in liquid dinitrogen tetroxide and solvents of low dielectric constant, rather than the presence of ions.

The very ease of homolysis adds a problem. Since there is always rapid production of nitrogen dioxide radicals there are always pairs of nitrogen dioxide molecules in the act of collision. Gray has suggested that these colliding pairs could show the orientations (IX to XII). That is, whichever structure is correct for the dimer, there is a population, probably small but constantly renewed, of the other forms. There is then a reasonable possibility that homolysis to nitric oxide and nitrogen trioxide also occurs if structures (X to XII) have any significance:-



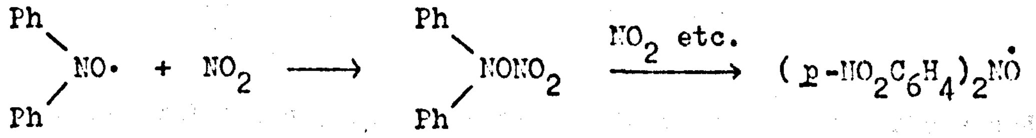
(4)

It is from these considerations that the difficulty of interpreting the chemical evidence stems.

Nitrogen dioxide is a non-linear molecule[13] with an oxygen-nitrogen-oxygen bond angle[13] of 132°. It is an odd electron species and the electron is delocalised at the oxygen and nitrogen atoms:-

$$:\ddot{O}=\dot{N}=\ddot{O}: \longleftrightarrow :\underset{\cdot}{\ddot{O}}=N=\ddot{O}: \qquad (5)$$

Its free radical nature is illustrated by its ready combination with triphenyl methyl radicals[14] in solution to give both nitrite and nitro compounds, with diphenyl nitroxide[15] in chloroform solution to give, <u>via</u> a complicated reaction sequence, 4,4'-dinitrodiphenyl nitroxide (Equation 6) and the fact that it has an e.s.r. spectrum which is a triplet.



$$Ph_2NO\cdot + NO_2 \longrightarrow Ph_2NONO_2 \xrightarrow{NO_2\ etc.} (p\text{-}NO_2C_6H_4)_2N\dot{O}$$

(6)

Influence of the Solvent, Temperature and Oxygen:- During the 1940's the reactions of nitrogen dioxide - dinitrogen tetroxide and simple olefins were extensively studied by Levy, Scaife and co-workers[9,16,17]. In this now classical work it was shown that the reactions were influenced by four factors:-

a) the purity of the dinitrogen tetroxide,

b) solvent,

c) temperature,

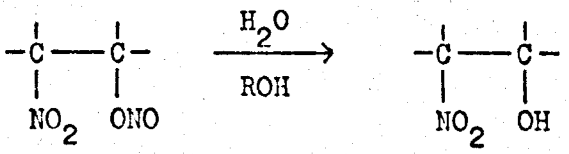
d) the presence or absence of molecular oxygen.

Thus it was found that best results were obtained when addition was effected with pure dinitrogen tetroxide at relatively low temperatures (-10 to +25°) in the presence of oxygen containing solvents, such as ethers, and very often with the addition of molecular oxygen.

Under these conditions the only products formed were the vicinal dinitro (XIII), nitro-nitrite (XIV), and nitro-nitrate (XV) compounds:-

$$RCH = CH_2 \xrightarrow{N_2O_4} \underset{(XIII)}{RCHNO_2CH_2NO_2} + \underset{(XIV)}{RCH(ONO)CH_2NO_2} + \underset{(XV)}{RCH(ONO_2)CH_2NO_2} \qquad (7)$$

Levy et al also found that frequently the nitro-nitrite compound was thermally unstable and prevented the successful separation of the products. This was overcome by hydrolysis of the nitro-nitrite with either water or an alcohol to give the stable nitro alcohol (XVI).

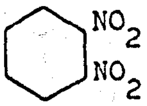
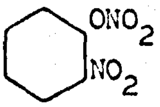


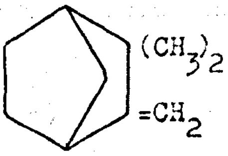
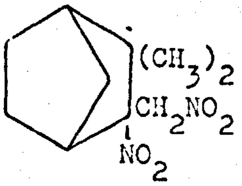
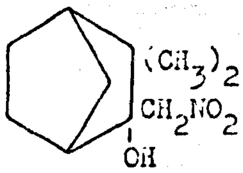
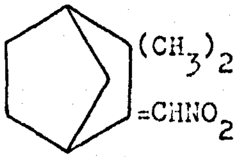
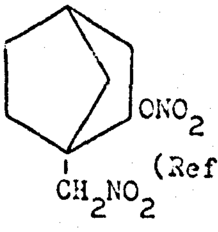
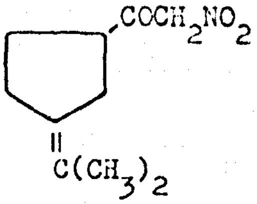
$$\underset{NO_2}{-\overset{|}{\underset{|}{C}}}-\underset{ONO}{\overset{|}{\underset{|}{C}}-} \xrightarrow[ROH]{H_2O} \underset{NO_2}{-\overset{|}{\underset{|}{C}}}-\underset{OH}{\overset{|}{\underset{|}{C}}-} \quad (XVI) \qquad (8)$$

In general these procedures are followed by later workers and the reports since the work of Levy et al have confirmed the scheme given above. Some typical reactions of simple olefins are collected in Table 1.

TABLE 1

Reaction of Nitrogen Dioxide - Dinitrogen Tetroxide with Simple Olefins.(a)

Olefin	Conditions	Product (% yield)	Ref.
$CH_2=CH_2$	CCl_4/press/40 - 60°	$O_2NCH_2CH_2NO_2$(b)	54
		$O_2NCH_2CH_2OH$(c)	
	O_2	$O_2NCH_2CH_2NO_2$(b) (35 - 40)	9
		$O_2NCH_2CH_2OH$(c) (12 - 20)	
		$O_2NCH_2CH_2ONO_2$ (12 - 20)	
$CH_3CH=CH_2$	Ether/10°/O_2	$CH_3CH(NO_2)CH_2NO_2$ (20 - 30)	9
		$CH_3CH(OH)CH_2NO_2$(c) (35 - 40)	
		$CH_3CH(ONO_2)CH_2NO_2$ (2 - 20)	
$(CH_3)_2C=CH_2$	Olefin condensed over N_2O_4(d)/10-15°	$CH_3CH(ONO_2)CO_2C_2H_5$	28b see also Table 2
$C_2H_5CH=CH_2$	Ether/O_2/0°	$C_2H_5CH(NO_2)CH_2NO_2$ (39)	9, 16
		$C_2H_5CH(OH)CH_2NO_2$(c) (33)	
	Olefin condensed over N_2O_4/10-15°(d)	$C_2H_5CH(ONO_2)CO_2H$(c) (50)	28b
$(CH_3)_2C=CHCH_3$	Hydrocarbon solvent	$(CH_3)_2C(ONO)CHCH_3NO_2$	24b
		$[(CH_3)_2C(ONO_2)CHCH_3NO]_2$ (50)	
	Ether solvent	$(CH_3)_2C(NO_2)CHCH_3NO_2$ (35)	24b
$C_2H_5C(CH_3)=CH_2$	N_2O_4 in 50% HNO_3/N_2/10-15° (d)	$C_2H_5CCH_3(OH)CO_2H$(c) (43)	28b
$(CH_3)_2C=C(CH_3)_2$	Hydrocarbon solvent/no solvent	$(CH_3)_2C(NO_2)C(CH_3)_2NO_2$ (5)	24c
	Ether solvent	$(CH_3)_2C(NO_2)C(CH_3)_2NO_2$ (19-22)	24c
	N_2O_4 to olefin in ether	   (30) (54) (2)	9, 16
	Olefin to N_2O_4 in ether	(42) (25) (18)	9, 16
$(C_2H_5)_2C=CH_2$	Ether/0°/N_2	$(C_2H_5)_2CNO_2CH_2NO_2$ (36)	30a
		$(C_2H_5)_2C(OH)CH_2NO_2$(c) (41)	

Olefin	Conditions	Product (% yield)	Ref.
$\underline{n}$-$C_3H_7C(CH_3)$=CH_2	N_2O_4 in 50% $HNO_3/N_2/$ 0-15° (d)	$\underline{n}$-$C_3H_7C(CH_3)(OH)CO_2H^{(c)}$ (60)	28b
$(CH_3)_3CCH_2C$-(CH_3)=CH_2	N_2O_4 to olefin in ether	$(CH_3)_3CCH_2C(CH_3)NO_2CH_2NO_2$ (30-44) $(CH_3)_3CCH_2C(CH_3)(OH)CH_2NO_2$ (42-43)	17
$\underline{t}$-C_4H_9CH=$C(CH_3)_2$		$\underline{t}$-$C_4H_9CHNO_2C(CH_3)_2NO_2$ (48) $\underline{t}$-$C_4H_9CHNO_2C(CH_3)_2OH^{(c)}$ (32)	17
$\underline{n}$-$C_8H_{17}CH$=CH_2	Ether/0°/N_2	$\underline{n}$-$C_8H_{17}CH(OH)CH_2NO_2^{(c)}$ $\underline{n}$-$C_8H_{17}CHNO_2CH_2NO_2$ inseparable mixture	30a
PhCH=CH_2	CCl_4/-5°/O_2	$PhCOCH_2NO_2$ (47)	31
	N_2O_4/N_2	 (30)  (35)  (Ref.32a) (5)  (Ref.32a,c) (5)	32a
		 (22)	32a,c
$PhCH_2CH$=CH_2	N_2O_4/N_2	$PhCH_2CHNO_2CH_2NO_2$ (34) $PhCH_2CH(OH)CH_2NO_2^{(c)}$ (45)	32b
	N_2O_4/O_2	$PhCH_2CH(ONO_2)CH_2NO_2$ (13) $PhCOCH_2NO_2$ (20) $PhCH_2CH(OH)CH_2NO_2^{(c)}$ (27) $PhCH_2CHNO_2CH_2NO_2$ (4)	32b

Olefin	Conditions	Product (% yield)	Ref.
$PhCH{=}CHPh$	$N_2O_4/5^\circ/N_2$	$PhNO_2CHCHPhNO_2$ (53) $Ph(OH)CHCHPhNO_2$[c] (23)	32c
	$N_2O_4/5^\circ/O_2$	$PhNO_2CHCHPh(ONO_2)$ (25) $PhNO_2CHCHPh(OH)$[c] (29) $PhCOCHNO_2Ph$ (24)	32c
$\underline{n}\text{-}C_{14}H_{29}CH{=}CH_2$		See Tables 3 and 4	
$\underline{n}\text{-}C_{16}H_{33}CH{=}CH_2$	Olefin to N_2O_4 in ether at -10°	$\underline{n}\text{-}C_{16}H_{33}CH(OH)CH_2NO_2$[c] (43) $\underline{n}\text{-}C_{16}H_{33}CHNO_2CH_2NO_2$[e] (49)	30b
	Olefin to N_2O_4 in ether at -80°	$\underline{n}\text{-}C_{16}H_{33}CH(ONO)CH_2NO_2$ product identified by i.r.	55

(a) Table covers the period 1937 to 1969.

(b) Highly explosive.

(c) Formed by subsequent hydrolysis of the nitro-nitrite compound.

(d) Excess N_2O_4/NO_2 .

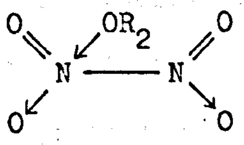
(e) Contaminated with 1-nitro-octadec-1-ene.

b) Solvent. The role of the solvent appears to be two-fold. On the one hand some solvents are able to form a complex with dinitrogen tetroxide, and on the other, some influence the degree of dinitrogen tetroxide dissociation.

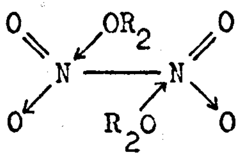
The choice of a suitable solvent is frequently critical to the subsequent product composition when the tetroxide and olefins or acetylenes interact. In general, solvents which favour the production of dinitro and nitro-nitrite compounds are of the ether or ester type such as diethyl ether, benzyl methyl ether, 1,4-dioxane and ethyl acetate. Unsatisfactory solvents include chloroform, carbon tetrachloride and 2,2'-dichlorodiethyl ether. It was suggested by Levy et al[9] that the satisfactory solvents reduce the oxidising tendency of dinitrogen tetroxide as a result of the formation of a complex with the oxide. In fact a white solid adduct of dinitrogen tetroxide and 1,4-dioxane was isolated[9].

This postulate of complex formation was further investigated by Shechter et al[18] who showed from a consideration of the phase diagrams, at temperatures below -10°, that ether solvents formed either a mono-ether or a diether complex with dinitrogen tetroxide. The ethers studied were tetrahydrofuran, tetrahydropyran, and diethyl ether. The dibasic ether 1,4-dioxane was also studied and was particularly stable. 2,2'-Dichlorodiethyl ether did not form a complex of this type and Shechter suggested that this was owing to both steric factors and to the electron withdrawing effect of the chlorines reducing the basicity of the oxygen. It would therefore seem that complex formation of the solvent with dinitrogen tetroxide is a necessary function of the solvent for a successful addition reaction under typical Levy conditions.

The suggested structures for the one to one and two to one complexes were (XVII) and (XVIII) respectively.



(XVII)



(XVIII)

The adduct of 1,4-dioxane[19] is thought to be polymeric.

There was no evidence from either Raman[18] or infrared spectroscopy[18] at temperatures up to 25° that the complexes contained ions such as NO^+, NO_2^+, NO_2^- or ONO_2^-. Magnetic susceptibility measurements[18] showed that below a temperature of -4.4°, they were diamagnetic and thus not addition compounds containing an unpaired electron (presumably indicating the absence of NO_2), but above this temperature the solutions of the complexes became paramagnetic. Since liquid dinitrogen tetroxide itself becomes paramagnetic at -2.4° Shechter concluded that co-ordination of the oxide with these solvents had little effect on the homolytic dissociation of dinitrogen tetroxide.

It is also noteworthy that aromatic hydrocarbons[20] such as benzene, mesitylene (and benzaldehyde) form stable one to one solid adducts with dinitrogen tetroxide at low temperatures. These are π complexes and crystallographic studies[21] have shown that the significant structural feature is plane to plane packing of the donor (aromatic hydrocarbon) and acceptor (N_2O_4) molecules, arranged alternately. The solid derived from benzene is colourless at its melting point (-7°), but it is pale orange[20] at -50°. On the other hand the benzaldehyde mixture is colourless at all temperatures[20].

The second effect of the solvent would seem to be the extent to which it can influence the dissociation of the dinitrogen tetroxide, by favouring either homolysis or heterolysis.

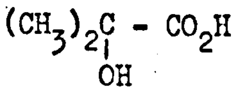
Addison and Sheldon[22] have observed that dissociation of the tetroxide to nitrogen dioxide is increased by such solvents as hexane, carbon tetrachloride and chloroform. On the other hand those solvents which act as electron donors towards the tetroxide, such as diethyl ether, suppressed homolysis. However, no quantitative measurements of these observations were made. Solutions of dinitrogen tetroxide in pure nitric acid are known[23] to be completely dissociated to nitrosonium (NO^+) and nitrate (ONO_2^-) ions.

This influence that the solvent has on the dissociation of the oxide and its effect on the reaction product distribution is illustrated by isobutene. The products when diethyl ether was used as solvent at -10° in the presence or absence of oxygen are shown in Table 2[9,16]. The major product can be seen to be the dinitro compound. The variance of the yields with added oxygen will be discussed later (p. 15).

Michael and Carlson[24a] found that distilling less than an equivalent of dinitrogen tetroxide into a hydrocarbon solution of isobutene at -10° resulted in an inseparable oil and the dimeric nitroso-nitrate (XIX) (7 - 12%).

$$\left[(CH_3)_2C(ONO_2)CH_2NO\right]_2 \qquad \text{(XIX)}$$

In the case of trimethyl ethylene Michael and Carlson[24b] also reported a different product when hydrocarbon solvents were used instead of ether (Table 1). On the other hand several investigators[25-28a] have reported that the reaction of isobutene with dinitrogen tetroxide without solvent or in nitric acid solution at low temperatures and subsequent hydrolysis, resulted in high yields of ∝-hydroxy butyric acid (XX).



$$\underset{\displaystyle OH}{(CH_3)_2\overset{}{C}} - CO_2H$$

(XX)

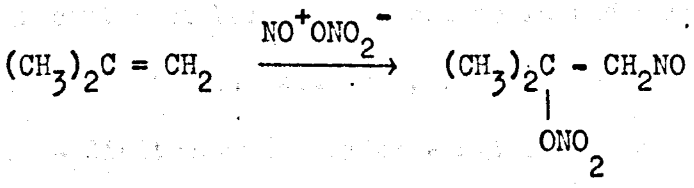
TABLE 2

Nitrogen Dioxide - Dinitrogen Tetroxide with Isobutene[9,16] in Diethyl Ether at -10°.

Product	Yield without O_2 %	Yield with O_2 %		
		O_2/C_4H_8=0.27	=1.09	=3.2
1,2-Dinitroisobutane	42.6	36.2	25.7	18.3
Nitro-tert-butanol[(a)]	27.8	26.5	28.7	26.7
Nitro-tert-butyl nitrate	1.9	7.8	11.8	30.0

(a) formed by subsequent hydrolysis of the nitro-nitrite compound.

Gardner[27] and Faberov et al[28a] have made a detailed study of this reaction and have concluded that under these conditions the reaction initially involves addition of nitrosonium nitrate ions leading to the nitroso-nitrate derivative (XXI):-

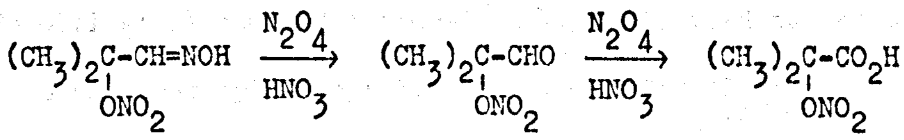


$$(CH_3)_2C = CH_2 \xrightarrow{NO^+ONO_2^-} (CH_3)_2\underset{ONO_2}{C} - CH_2NO \qquad (9)$$

(XXI)

The nitroso compound then tautomerised to the oxime which was converted by excess dinitrogen tetroxide or nitric acid to the aldehyde (XXII). Further oxidation and hydrolysis accounted for the observed product via α-nitratoisobutyric acid (XXIII):-

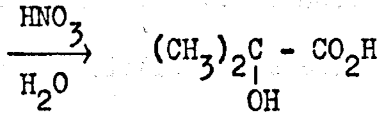
(XXI)



$$(CH_3)_2\underset{ONO_2}{C}\text{-}CH{=}NOH \xrightarrow[HNO_3]{N_2O_4} (CH_3)_2\underset{ONO_2}{C}\text{-}CHO \xrightarrow[HNO_3]{N_2O_4} (CH_3)_2\underset{ONO_2}{C}\text{-}CO_2H \qquad (10)$$

(XXII) (XXIII)

(XXIII)



$$\xrightarrow[H_2O]{HNO_3} (CH_3)_2\underset{OH}{C} - CO_2H \qquad (11)$$

(XX)

Russian workers have obtained similar results under similar conditions using propene, but-1-ene, 2-methyl but-1-ene, 2-methyl pent-1-ene (Table 1) and methallyl chloride[28b] (Table 6, p. 31).

c) Temperature. Although the temperature range of the scheme worked out by Levy et al (-10 to +25°), where a dinitrogen tetroxide rich mixture was used, has been adhered to by most investigators, recently Bonetti et al[29] have claimed that elevated temperatures of between 50° and 102° had advantages. This higher range is comparable to the temperatures commonly used for halogenated olefins (p. 29).

From a consideration of the equilibrium(1)and its temperature dependence (Figure 1), these authors suggested that it might be preferable to use elevated temperatures where the equilibrium lies well towards nitrogen dioxide. The effect of temperature on the product distribution ratio of the addition of nitrogen dioxide to hexadec-1-ene in iso-octane in the absence of oxygen is shown in Table 3, the significant fact being the increase in the amount of nitro-nitrate at lower temperatures. All the products can be seen to be typical of an olefin - dinitrogen tetroxide - nitrogen dioxide equilibrium interaction.

On the basis of an examination of the infrared spectra, the formation of nitro-nitrate (up to 6%) at low temperatures in the absence of oxygen appeared to be general for a variety of solvents including complexing examples such as tetrahydrofuran, ethyl acetate, dioxane and diethyl ether. At elevated temperatures only trace quantities of nitro-nitrate were present (up to 1%).

Bonetti et al concluded therefore, that elevated temperatures and the use of non-complexing solvents were preferable because little or no nitro-nitrate adduct was formed thus giving a simpler product in high overall yield. This conclusion must be viewed with some caution since only two olefins were used and the reduction in nitro-nitrate yield was not great but the earlier work of Porter and Wood[30a,b] tends to bear out their conclusion. These latter authors found that dec-1-ene and octadec-1-ene under typical Levy conditions in the presence of traces of oxygen, gave, in both cases, products that were not completely separable (Table 1). No nitro-nitrate adducts were isolated however.

d) Oxygen. In order to explain the presence of typical dinitrogen trioxide - olefin adducts (Ch. 2) in some of their reaction products, Levy et al[9] suggested that these occurred by addition of the lower oxide which may have arisen by reduction of the tetroxide when the latter oxidised a nitrite group to a nitrate group:-

$$-\overset{|}{\underset{|}{C}}-ONO + N_2O_4 \longrightarrow -\overset{|}{\underset{|}{C}}-ONO_2 + N_2O_3 \qquad (12)$$

TABLE 3

Nitrogen Dioxide - Dinitrogen Tetroxide with Hexadec-1-ene in Iso-octane[29].

Temperature °	% Nitro alcohol[(a)]	% Dinitro	% Nitro-nitrate
90 - 102	47	45	0
72 - 80	54	41	1
49 - 56	53	40	3
25 - 33	52	38	5
1 - 13	52	37	6

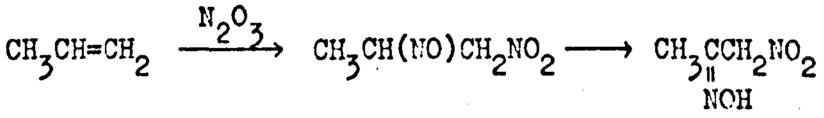
(a) formed by subsequent hydrolysis of the nitro-nitrite compound.

Additionally this scheme explained the production of the observed nitro-nitrate adducts. This complication was overcome by the addition of a small amount of oxygen which oxidised the trioxide back to the tetroxide. This is typically illustrated by the case of propene[9] which was found to react rapidly with dinitrogen tetroxide in ether at 0°, in the presence of oxygen, to yield 70 - 75% products overall:-

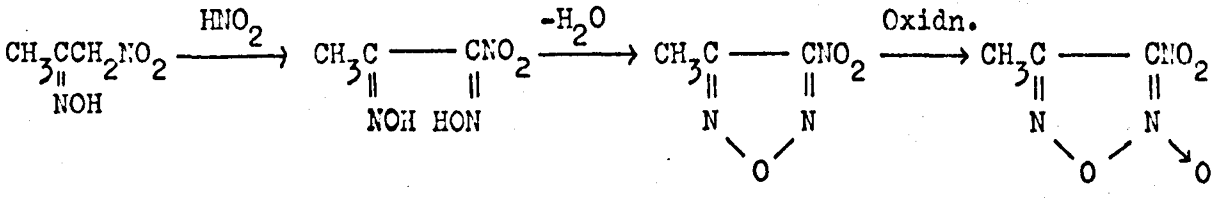
$$CH_3CH{=}CH_2 \xrightarrow{N_2O_4} \underset{(18 - 20\%)}{CH_3CH(NO_2)CH_2NO_2} + \underset{(34 - 41\%)}{CH_3CH(ONO)CH_2NO_2} \qquad (13)$$

$$CH_3CH(ONO)CH_2NO_2 \xrightarrow{N_2O_4} \underset{(21\%)}{CH_3(ONO_2)CH_2NO_2} \qquad (14)$$

Without added oxygen some 4-nitro-3-methyl furazan oxide (XXIV) (5 - 8%) was formed (Equations 15 and 16). The active methylene group resulting from the adjacent nitro and nitroso groups undergoes the well known condensation reaction with nitrous acid to give a second oximino group. The two oximino groups then intramolecularly condense to give, after further oxidation, the furazan oxide:-



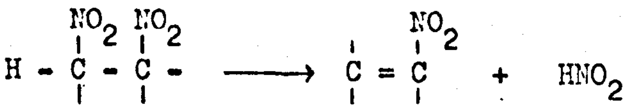
$$CH_3CH{=}CH_2 \xrightarrow{N_2O_3} CH_3CH(NO)CH_2NO_2 \longrightarrow CH_3\underset{\underset{NOH}{\|}}{C}CH_2NO_2 \qquad (15)$$



(16)

(XXIV)

The nitrous acid was probably produced by elimination from the vicinal dinitro adduct to give the α-nitro olefin:-



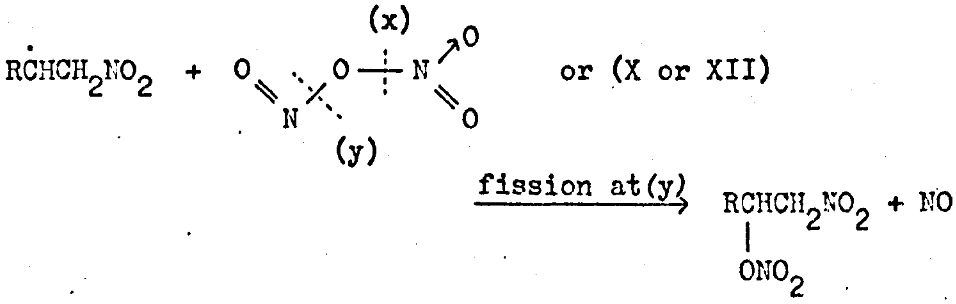
$$H-\underset{|}{\overset{\overset{NO_2}{|}}{C}}-\underset{|}{\overset{\overset{NO_2}{|}}{C}}- \longrightarrow \underset{|}{\overset{|}{C}}=\underset{|}{\overset{\overset{NO_2}{|}}{C}} + HNO_2 \qquad (17)$$

An important observation made by Levy et al was that nitro-nitrate adducts were formed in relatively small amounts unless oxygen was deliberately added to obviate the formation of dinitrogen trioxide.

This can be seen in the cases of isobutene[16] (Table 2) and hexadec-1-ene[29] (Table 4) where the yield of nitro-nitrate increased with added oxygen. This was at the expense of the dinitro compound and not at the expense of the nitro-nitrite, which remained essentially constant. Therefore, in contrast to the case of propene, in these cases the addition of oxygen was undesirable.

The explanation of the production of nitro-nitrate adducts given by Levy _et al_[9] needs careful examination. These authors preferred to suggest that; a) in the absence of added oxygen the nitro-nitrite group was oxidised by dinitrogen tetroxide (Equation 12) and b) in the presence of oxygen, by both oxygen and the tetroxide. It was pointed out however, that b) could not explain the concurrent reduction of the dinitro compound noted in the case of isobutene. There would seem to be a number of arguments against both of these simple explanations. One significant observation is by Bonetti _et al_[29] who showed that 1-nitro-2-nitrite hexadecane was oxidised only very slowly by either pure dinitrogen tetroxide (at 10°) or by air or oxygen alone (at 20 and 75°). Therefore Levy's claim for extensive oxidation of nitro-nitrite to nitro-nitrate by either dinitrogen tetroxide, a), or oxygen, b), would seem to be unjustified.

Bonetti _et al_[29] have suggested another mechanism to account for nitro-nitrate production in the absence of added oxygen which involves the interaction of a 2-nitro alkyl radical (formation of this radical is discussed in a later section), with the alternative forms of dinitrogen tetroxide given on page 4.



(18)

TABLE 4

Nitrogen Dioxide - Dinitrogen Tetroxide with Hexadec-1-ene in Iso-octane[29] at 75°.

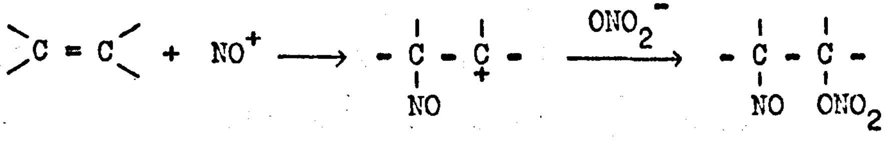
Product	Yield without O_2 %	Yield with O_2, %	
		NO_2:O_2, 18:1	NO_2:O_2, 6:1
1,2-Dinitro hexadecane	46.5	43	42
1-Nitrohexadecanol[(a)]	52.1	52	48
1-Nitro-2-nitrate hexadecane	0.2	5	10

(a) formed by subsequent hydrolysis of the nitro-nitrite compound.

If fission was at (x) then the products would be the normal nitro-nitrite and nitrogen dioxide and if at (y) as shown in equation (18). The nitric oxide from (y) would either combine with another 2-nitro alkyl radical to give a nitro-nitroso compound or with nitrogen dioxide to give dinitrogen trioxide with the same end result. This suggestion was supported by work at elevated temperatures where amounts of such dimeric forms must be very small. Here nitro-nitrate production was negligible (Table 3).

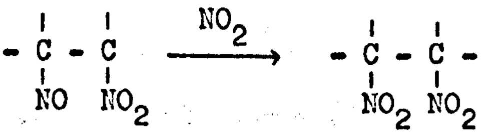
A second alternative explanation for the occurrence of nitro-nitrates in the absence of added oxygen has been postulated[5a] viz., ionisation of dinitrogen tetroxide to nitrosonium nitrate (occurs to a very limited extent in ethers[18]), to give the nitroso nitrate:-

$$N_2O_4 \rightleftharpoons NO^+ + ONO_2^- \qquad (2)$$



$$>C=C< + NO^+ \longrightarrow -\underset{NO}{\overset{|}{\underset{|}{C}}}-\overset{|}{\underset{+}{C}}- \xrightarrow{ONO_2^-} -\underset{NO}{\overset{|}{\underset{|}{C}}}-\underset{ONO_2}{\overset{|}{\underset{|}{C}}}- \qquad (19)$$

followed by oxidation of the nitroso group analogous to the work of Brown[5b] who showed that vicinal nitro-nitroso compounds were oxidised by nitrogen dioxide to dinitro compounds:-

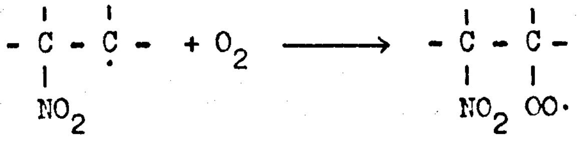


$$-\underset{NO}{\overset{|}{\underset{|}{C}}}-\underset{NO_2}{\overset{|}{\underset{|}{C}}} \xrightarrow{NO_2} -\underset{NO_2}{\overset{|}{\underset{|}{C}}}-\underset{NO_2}{\overset{|}{\underset{|}{C}}}- + NO \qquad (20)$$

There is no published data on this type of oxidation however, but if it is as slow as the oxidation of a nitrite group then the mechanism is unlikely to be important. Evidence presented later also argues against a predominantly heterolytic route in ether-like solvents.

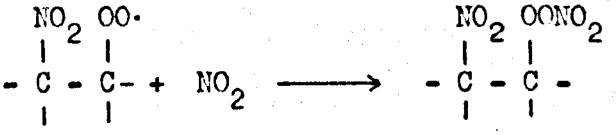
Since neither of these two alternative schemes discussed above depends on the presence of oxygen they cannot be used to explain the very large increases in the yields of nitro-nitrate compound when oxygen was deliberately added. It has been shown by the work of Bonetti et al that the suggestion of Levy and co-workers is unlikely and it is therefore tempting to suggest some type of direct oxidation of the dinitro to nitro-nitrate compound particularly as the amount of dinitro product decreases and the yield of nitro-nitrite remains sensibly constant. However, there is no evidence for this type of oxidation under the requisite conditions. These are therefore not satisfactory explanations for nitro-nitrate production and the mechanisms proposed are incomplete.

Of particular mechanistic interest is the observation that dinitrogen tetroxide and excess oxygen with some olefins yield addition products that are not vicinal dinitro compounds but carbonyl compounds. Thus Baryshnikova[31] and Stevens[32a,b,c] have reported that the use of oxygen and dinitrogen tetroxide with styrene[31], camphene[32a,c], allylbenzene[32b] and stilbene[32c] resulted in the formation of oxidation products, including α-nitroketones, which were not produced in the absence of oxygen. Stevens found that stilbene reacted with dinitrogen tetroxide in ether in the absence of oxygen at 5° to give 1,2-dinitro-1,2-diphenyl ethane (53%) and 1-hydroxy-2-nitro-1,2-diphenyl ethane (23%) (formed by subsequent hydrolysis of the nitrite). In the presence of oxygen no dinitro compound was formed, but 1-nitro-2-nitrato-1,2-diphenyl ethane (25%), α-nitro-α-phenyl acetophenone (24%) and 1-hydroxy-2-nitro-1,2-diphenyl ethane (29%). Some benzoic acid and benzaldehyde were also formed. Similar results were obtained for the other olefins. Baryshnikova and Titov, and Stevens suggested that the effect of the oxygen was the intermediate formation of a 2-nitro alkyl peroxy radical (XXV) or the corresponding peroxy nitrate (XXVI) <u>via</u> the nitro alkyl radical:-



$$-\underset{NO_2}{\overset{|}{\underset{|}{C}}}-\overset{|}{\dot{C}}- + O_2 \longrightarrow -\underset{NO_2}{\overset{|}{\underset{|}{C}}}-\underset{OO\cdot}{\overset{|}{\underset{|}{C}}}- \qquad (21)$$

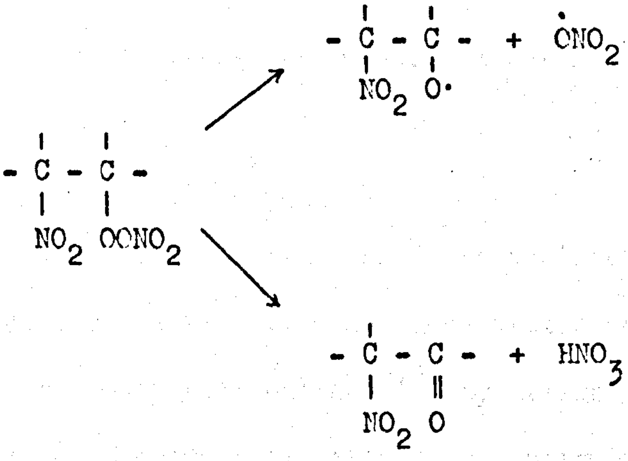
(XXV)



$$-\overset{NO_2}{\overset{|}{\underset{|}{C}}}-\overset{OO\cdot}{\overset{|}{\underset{|}{C}}}- + NO_2 \longrightarrow -\overset{NO_2}{\overset{|}{\underset{|}{C}}}-\overset{OONO_2}{\overset{|}{\underset{|}{C}}}- \qquad (22)$$

(XXVI)

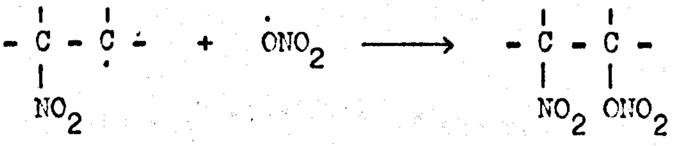
The final products would then result from the decomposition of the intermediates as shown below:-



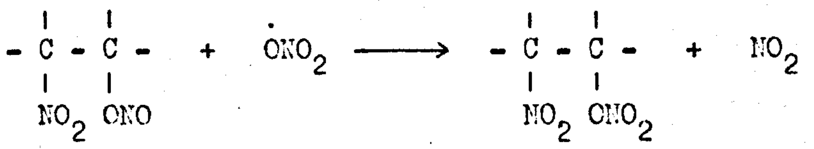
$$-\underset{NO_2}{\overset{|}{\underset{|}{C}}}-\underset{OONO_2}{\overset{|}{\underset{|}{C}}}- \nearrow -\underset{NO_2}{\overset{|}{\underset{|}{C}}}-\underset{O\cdot}{\overset{|}{\underset{|}{C}}}- + \dot{O}NO_2 \qquad (23)$$

$$-\underset{NO_2}{\overset{|}{\underset{|}{C}}}-\underset{OONO_2}{\overset{|}{\underset{|}{C}}}- \searrow -\underset{NO_2}{\overset{|}{\underset{|}{C}}}-\underset{O}{\underset{\|}{C}}- + HNO_3 \qquad (24)$$

but there is no experimental evidence to substantiate this. It has been suggested that the nitrogen trioxide resulting from (23) may then combine with a 2-nitro alkyl radical or oxidise <u>vicinal</u> nitro-nitrites to give nitro-nitrate compounds:- [18]



$$-\underset{NO_2}{\overset{|}{\underset{|}{C}}}-\overset{|}{\dot{C}}- + \dot{O}NO_2 \longrightarrow -\underset{NO_2}{\overset{|}{\underset{|}{C}}}-\underset{ONO_2}{\overset{|}{\underset{|}{C}}}- \qquad (25)$$



$$-\underset{\substack{|\\NO_2}}{\overset{|}{C}}-\underset{\substack{|\\ONO}}{\overset{|}{C}}- \;+\; \dot{O}NO_2 \longrightarrow -\underset{\substack{|\\NO_2}}{\overset{|}{C}}-\underset{\substack{|\\ONO_2}}{\overset{|}{C}}- \;+\; NO_2 \qquad (26)$$

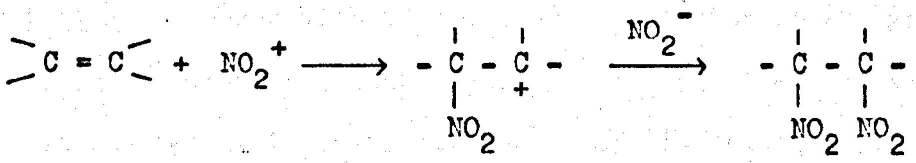
Recently more specific evidence for peroxide intermediates has been given by Lachowicz and Kreuz[33] who treated separately oct-1-ene, octadec-1-ene and docos-1-ene with dinitrogen tetroxide and excess oxygen in hexane solvent at 0°. They found three bands in the infrared at 1724, 1299 and 787 cm^{-1}. which were characteristic of peroxy nitrates[34] and therefore concluded that the principal component of the reaction mixture was a 2-nitro alkyl peroxynitrate.

It must be noted however, that there is little experimental evidence for the proposed peroxy intermediate and it is significant that Bonetti[29] reported little evidence for a ketone product in his work with hexadec-1-ene.

Evidence for a Free Radical Mechanism:-

The formation of the typical products isolated from the interaction of dinitrogen tetroxide and unsaturates under Levy conditions, were commonly rationalised[9,35] by heterolytic cleavage of the tetroxide and electrophilic attack by a nitronium ion and subsequent addition of a nitrite ion:-

$$N_2O_4 \rightleftharpoons NO_2^+ + NO_2^- \qquad (27)$$



$$>C=C< \;+\; NO_2^+ \longrightarrow -\underset{\substack{|\\NO_2}}{\overset{|}{C}}-\underset{+}{\overset{|}{C}}- \xrightarrow{NO_2^-} -\underset{\substack{|\\NO_2}}{\overset{|}{C}}-\underset{\substack{|\\NO_2}}{\overset{|}{C}}- \qquad (28)$$

More recent studies[5a,36-40,42] of the reactions support a free radical mechanism initiated by nitrogen dioxide produced by homolysis of dinitrogen tetroxide.

$$N_2O_4 \rightleftharpoons 2NO_2 \qquad (1)$$

$$NO_2 + RCH = CH_2 \longrightarrow \dot{R}CHCH_2NO_2 \qquad (29)$$

The resulting nitro alkyl radical may then pair with a second molecule of nitrogen dioxide:-

$$\dot{R}CHCH_2NO_2 + (O\dot{N}O \leftrightarrow \dot{O}NO) \longrightarrow RCHNO_2CH_2NO_2 \text{ or } RCH(ONO)CH_2NO_2 \qquad (30)$$

The principal evidence for the homolytic nature of the addition can be summarised as follows:

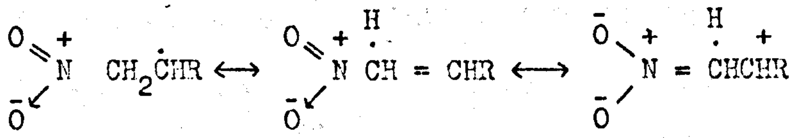
a) The orientation of addition to unsymmetrical olefins is always specific and is not altered by the character of the substituents on the double bond.

b) The products found from the interaction of dinitrogen tetroxide and methyl acrylate were not those expected from an ionic mechanism.

c) In the presence of free radical, chain transfer agents such as bromotrichloromethane, bromoform or iodine, formation of the normal adducts is suppressed and the products obtained are those expected from the interaction of a 2-nitro alkyl radical with the transfer agent.

d) Addition of dinitrogen tetroxide to a number of olefins exhibit a type of stereochemistry associated with homolytic processes.

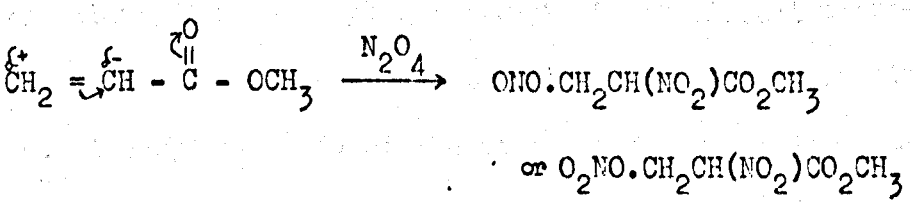
a) Orientation. The addition of dinitrogen tetroxide under typical Levy conditions to terminal olefins always involves the formation of a C-N bond at the terminal position. This could be rationalised by electrophilic attack by a nitronium ion, but Shechter[5a] suggested that the apparent specificity of attack at the terminal position may lie in the greater stability of $O_2NCH_2\dot{C}HR$ due to hyperconjugation involving the nitro group of the type shown below, rather than $ONOCH_2\dot{C}HR$ where the nitrite group does not extend the conjugation:-



$$\overset{O}{\underset{\bar{O}}{\overset{+}{N}}}\;CH_2\dot{C}HR \longleftrightarrow \overset{O}{\underset{\bar{O}}{\overset{+}{N}}}\;\overset{H}{\dot{C}}H = CHR \longleftrightarrow \overset{\bar{O}}{\underset{\bar{O}}{\overset{+}{N}}} = \overset{H}{\dot{C}}H\overset{+}{C}HR \qquad (31)$$

This would lower the activation energy required for the formation of $O_2NCH_2\dot{C}HR$ with respect to $ONOCH_2\dot{C}HR$.

b) <u>Methyl Acrylate</u>. Conrad and Shechter[36] have pointed out that if addition to methyl acrylate under typical Levy conditions, and presumably in the presence of oxygen for the comparison to be valid, occurred by an electrophilic process involving heterolysis of dinitrogen tetroxide, then it would be expected to yield the nitrite and nitrate esters of methyl-3-hydroxy-2-nitropropionate:-



$$\overset{\delta+}{C}H_2 = \overset{\delta-}{C}H - \overset{\overset{\delta O}{\|}}{C} - OCH_3 \xrightarrow{N_2O_4} ONO.CH_2CH(NO_2)CO_2CH_3 \qquad (32)$$

$$\text{or } O_2NO.CH_2CH(NO_2)CO_2CH_3$$

However, reaction of methyl acrylate and dinitrogen tetroxide in ether at 0° with excess oxygen gave, after hydrolysis, methyl-3-nitroacrylate (13%), methyl-2-hydroxy-3-nitropropionate (27%), oxalic acid dihydrate (up to 80%) and nitrogen containing polymers of methyl acrylate. Because the expected products (32) from a heterolytic process were not found it was concluded that the reaction was homolytic in nature.

c) <u>Chain transfer agents.</u> Further evidence for a free radical mechanism has been obtained by the reaction of dinitrogen tetroxide with olefins in the absence of light and in the presence of chain transfer agents such as bromotrichloromethane[37], tribromomethane[31] or iodine[38-40].

Thus dinitrogen tetroxide reacted with cyclohexene[37] in bromotrichloromethane/ether solution at 0° to give a complex mixture of which 2-bromo nitrocyclohexane (30%) was a major component.

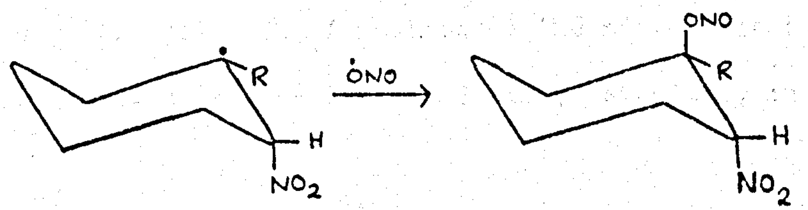
Recently Russian[40] workers have reacted 1,3-butadiene at -10 to -15° in ether solvent in an inert atmosphere with dinitrogen tetroxide in the presence of iodine to give:-

$$O_2NCH_2CH = CHCH_2I$$

2-Methyl-1,3-butadiene, 2,3-dimethyl-1,3-butadiene, chloroprene and 2,3-dichloro-1,3-butadiene were reacted similarly with similar results. No 1,2-adducts were formed (see p. 28).

d) Stereochemistry. Information concerning the mechanism of conversion of intermediate 2-nitro alkyl radicals to their *vicinal* nitro-nitrite or dinitro compounds has been obtained from the stereochemistry of the addition. A complete study of the stereochemistry of the reaction of dinitrogen tetroxide with a specific olefin has been limited, usually by the difficulties in analysing the final products.

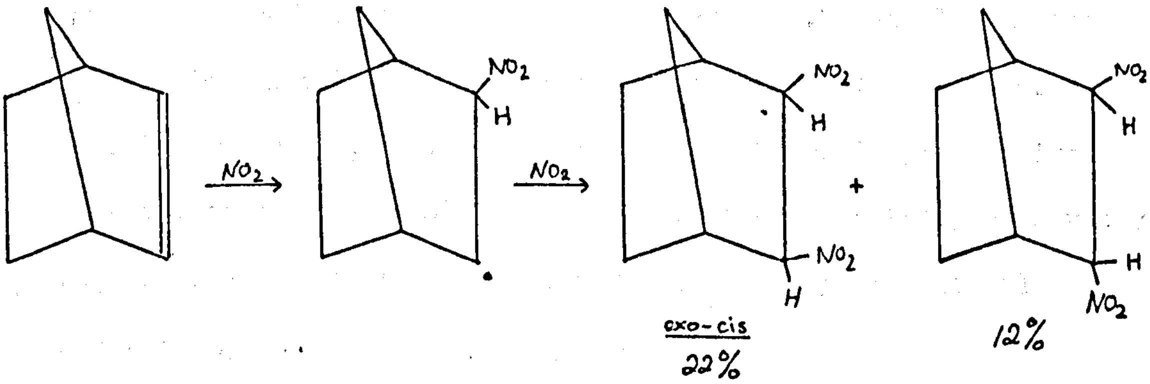
Cyclopentene and cyclohexene[37] in ether solvent yield 2-nitrocyclopentyl nitrites and 2-nitrocyclohexyl nitrites in which the *trans*-isomers predominate (85 and 58 - 65% respectively). More striking stereospecificity was found by Brand and Stevens[37b] with 1-methyl cyclohexene which yielded *trans*-1-methyl-2-nitro cyclohexyl nitrite exclusively. This is in agreement with the, u.v. initiated, free radical, *trans*-addition of hydrogen bromide to the same olefin found by Abell *et al*[41]. Because of this Brand and Stevens interpreted their result in terms of a radical intermediate that was pyrimidal at the odd electron centre:-



(33)

This particular conformation was preferred to the alternative because of the 1,3 repulsions this would incur. It was further postulated that the speed of the ring inversions of these conformers was slow compared to the second step of nitrogen dioxide addition.

Similarly 9,10-octalin gives mainly trans-9,10-dinitro-octalin[42], but the most convincing stereochemical evidence for a homolytic path is that the major attack on norbornene occurs in the exo-cis direction[42],



(34)

the significant point being that there was no Wagner-Meerwein rearrangement which might be expected if an ionic mechanism was operative. Processes involving free radical mechanisms have been observed in reactions of p-thiocresol[43] and ethyl bromoacetate[44] with norbornene, but in these cases addition was exclusively exo-cis. It must be noted that trans-addition of carbon tetrachloride[45] and bromotrichloromethane[46] has recently been observed.

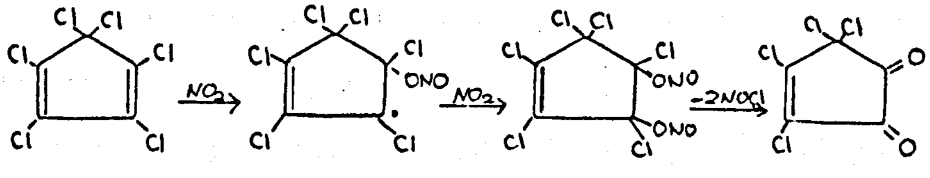
It would seem that under typical Levy conditions the interaction of the nitrogen dioxide - dinitrogen tetroxide equilibrium mixture with olefins may well be predominantly homolytic in nature and that the heterolytic path is negligible. However, under some conditions notably using nitric acid solvent, the alternative ionic addition may become significant. The formation of the nitro-nitrate adduct under conditions favouring homolytic addition, especially in the presence of excess oxygen, is not clearly understood. In this context the synthesis and identification of the products of decomposition of peroxy nitrates is an important field for investigation.

The Interaction of the Nitrogen Dioxide - Dinitrogen Tetroxide Equilibrium Mixture with Conjugated Systems, Halogeno-olefins and Acetylenes:-

a) Conjugated Systems. There are few examples in the literature of reactions between conjugated systems and the equilibrium mixture and those that are reported predictably refer to 1,2- and 1,4-addition.

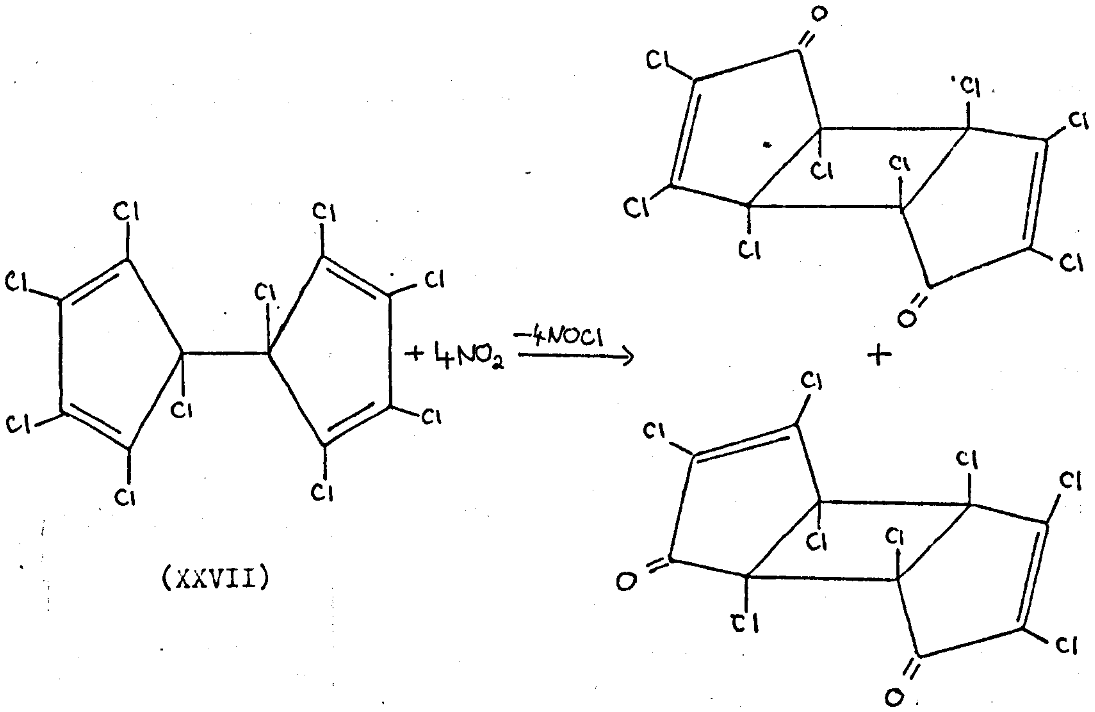
In general those dienes not containing halogens undergo reaction under typical Levy conditions and the only product isolated is the dinitro compound. While those that contain halogens usually require the higher temperatures and pressures typical of halogeno-olefins (p. 29).

Schribner[47] recently reported a novel reaction between hexachlorocyclopentadiene and nitrogen dioxide. When heated together for 9 hours at 60° in an autoclave, they give a yellow solid (ca. 90%), identified by chemical and spectral evidence as tetrachlorocyclopentene-1, 2-dione. The suggested mechanism is shown below:-



(35)

Hexachloro-1,3-butadiene, octachlorocyclopentene and hexachloro-2-cyclopentenone were reported unchanged after similar treatment but decachloro bis-(cyclopentadienyl) (XXVII) reacted to give approximately equal amounts of two isomeric diketones in high overall yield (85 %):-



(XXVII)

(36)

Table 5 is a collection of the other reported reactions of conjugated systems with the equilibrium mixture of dinitrogen tetroxide and nitrogen dioxide.

b) Halogeno-olefins. The reactions of these olefins, with the exception of fluoro-olefins, have been little investigated. The products predictably included the dinitro compound.

The reaction of halogenated olefins would seem to be favoured by higher reaction temperatures. Under these conditions the reacting species must be predominantly nitrogen dioxide and hence the dinitro free radical addition product is usually found. However, even at temperatures in excess of 100° nitrite addition occurs in agreement with the dual radical character of nitrogen dioxide (p. 5).

The reactions of halogeno-olefins are shown in Table 6.

c) Acetylenes. The first recorded reaction of the equilibrium mixture with an acetylene was in 1897 when Biltz^{48} treated di-iodoacetylene in ether with dinitrogen tetroxide to yield tri-iodonitroethylene.

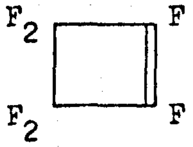
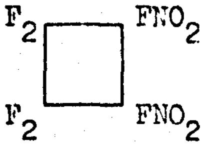
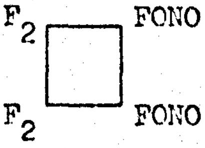
TABLE 5

Reaction of Nitrogen Dioxide - Dinitrogen Tetroxide with Conjugated Systems.

Olefin	Conditions	Product (% yield)	Ref.
PhHC=CH-CH=CHPh	Ether	$PhH(NO_2)CCH=CHC(NO_2)HPh$ (35)	56
Ph(CN)C=CHCH=CHPh	Ether	$Ph(CN)C=CHC(NO_2)C(NO_2)HPh$ (71)	57
$CH_2=C(Ph)C(Ph)=CH_2$	Hexane	$O_2NCH_2(Ph)C=C(Ph)CH_2NO_2$ $CH_2=C(Ph)C(NO_2)(Ph)CH_2NO_2$	58
$CH_2=CHCH=CH_2$	Ether/-30°	$O_2NCH_2CH=CHCH_2NO_2$ (14.5)	30b
$CH_2=CClCH=CH_2$	CCl_4/-5°	$O_2NCH_2CCl=CHCH_2NO_2$ $O_2NCH_2CH_2(NO_2)CCl=CH_2$	59
$CF_2=CFCF=CF_2$	20°/24 hr.	$O_2NCF_2CF=CFCF_2NO_2$ (46.5) $O_2NCF_2CF=CFCF_2ONO$ (15) $F_2C(NO_2)CF=CFCO_2H$ (17.5)	60
$CF_2=CHCH=CF_2$	20°/12 hr.	$O_2NCF_2CH=CHCF_2NO_2$ (47) $O_2NCF_2CH=CHCF_2ONO$ (20) polymer (28)	61

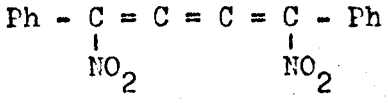
TABLE 6

Reaction of Nitrogen Dioxide-Dinitrogen Tetroxide with Halogeno-Olefins.

Olefin	Conditions	Product (% yield)	Ref.
$Cl_2C=CCl_2$	100°/press/3 hr.	$O_2N(Cl)_2CC(Cl)_2NO_2$ (90)	62, 47
$Br_2C=CBr_2$	100°/press/3 hr.	$O_2N(Br)_2CC(Br)_2NO_2$ (100)	62
$Cl_2C=CHCl$	$CCl_4/20°/AlCl_3$ catalyst	$O_2N(Cl)_2CCClHNO_2$ (16)	63
$Cl_2C=CH_2$	$CCl_4/20°/AlCl_3$ catalyst	$O_2N(Cl)_2CCH_2NO_2$ (22)	63
$BrHC=C(CH_3)_2$	$Ether/0°/O_2$	$O_2N(CH_3)_2CCO_2H$ (8) $[O_2N(CH_3)_2CNO]_2$ (10) $O_2N(CH_3)_2CCHO$ (17) $Br(CH_3)_2CCHBrNO_2$ (26) $Br(CH_3)_2CCH(Br)_2$ (8)	64a
PhCH=CHBr	Ether/-10 to 10°/N_2	$\left.\begin{matrix} O_2NPhC=CBr_2 \\ PnHC=CHNO_2 \end{matrix}\right\}$ (67)	64b 65
$ClCH_2C(CH_3)=CH_2$	Excess N_2O_4 in 50% $HNO_3/N_2/10 - 15°$	$ClCH_2C(OH)(CH_3)CO_2H$ (60)	28b
$F_2C=CF_2$	65°/6 hr/press.	$O_2NCF_2CF_2NO_2$ (53) $ONOCF_2CF_2NO_2$	66, 67 67
$ClFC=CF_2$	65°/6 hr/press.	$O_2NCF_2CFClNO_2$ (51)	67
$CCl_2=F_2$	65°/6 hr/press.	$O_2NCCl_2CF_2NO_2$ (47)	67
$CF_3CF=CF_2$	100°	$CF_3CF(ONO)CF_2$ (90) $CF_3CF(NO_2)CF_2NO_2$	60, 67
$(CF_3)_2C=CF_2$	180°	$(CF_3)_2CNO_2CF_2NO_2$ (<u>ca</u>. 50) $(CF_3)_2C(ONO)CF_2NO_2$ (<u>ca</u>. 50)	67
	130 - 160° explosive > 160°	 	60
$n-C_3F_7CH=CF_2$	100°/halogenated solvent	$n-C_3F_7CH(OH)CF_2NO_2$ (a) $n-C_3F_7CH(OH)CO_2H$ (a)	63
$n-C_3F_7CH_2CF_2CH=CF_2$	100°/halogenated solvent	$n-C_3F_7CH_2CF_2CH(OH)CF_2NO_2$ (a) $n-C_3F_7CH_2CF_2CH(OH)CO_2H$ (a)	63
$CF_3CH=CF_2$	100°/halogenated solvent	$CF_3CH(OH)CF_2NO_2$ (a)	63

(a) Formed by subsequent hydrolysis of the nitro-nitrite compound.

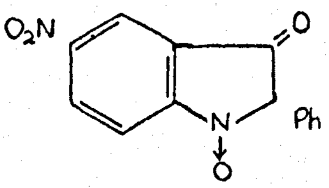
The reactions of propyne and 1,3-butadiyne[49] under various conditions with the equilibrium mixture have been reported to be violent or even explosive. But-2-yne[49] in ether at 0° was found to give cis- and trans-2,3-dinitrobut-2-ene in 30% yield. Diphenyldiacetylene[49] in ether at -25° in the absence of oxygen yielded 1,4-dinitro-1,4-diphenylbutatriene (34%):-



$$Ph-\underset{\underset{NO_2}{|}}{C}=C=C=\underset{\underset{NO_2}{|}}{C}-Ph$$

Emmons[50] found a significant degree of stereospecificity in that 34% of the trans- and only 7% of the cis-2,3-dinitrobut-2-ene were formed by the treatment of but-2-yne with dinitrogen tetroxide in ether at 0°. The trans- isomer[50] also predominated in the reactions of hex-2-yne and hex-3-yne.

The reaction of phenyl acetylene[51] in a hydrocarbon/ether mixture, yielded 1-phenyl-1,2-dinitroethylene. Diphenylacetylene[51,52] reacted at 0° in ether to give three crystalline products in 40% overall yield: cis- and trans-1,2-dinitrostilbene and 5-nitro-2-phenylisatogen[53]:-



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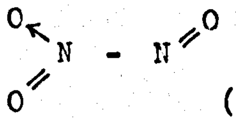
CHAPTER 2

The Interaction of Dinitrogen Trioxide, Nitryl Chloride and Nitrosyl Chloride with Carbon-Carbon Multiple Bonds.

In this chapter it is intended to review the salient points concerning the reaction mechanisms of dinitrogen trioxide, nitryl and nitrosyl chlorides with unsaturated compounds.

Dinitrogen Trioxide:- The interaction of dinitrogen trioxide with olefins and acetylenes has been reviewed by Sosnovsky[1] and earlier by Riebsomer[2]. Sosnovsky in his review pointed out that the discrepancies which are observed with dinitrogen tetroxide also occur with dinitrogen trioxide. This can be attributed to the varying composition of the gas which, depending on the method of preparation, contained besides dinitrogen trioxide, an excess of either nitrogen dioxide or nitric oxide. Where oxygen was not excluded the nitric oxide would have been oxidised to nitrogen dioxide. The interpretation of early results is therefore difficult.

Structure and Physical Properties of Dinitrogen Trioxide:- Dinitrogen trioxide has been described as the Cinderella of the nitrogen oxides since none of its physical properties is known with any degree of certainty owing to its ease of dissociation. The melting point has been variously reported[3] to be between -111 and -90° and the boiling point is thought[4] to be about 3.5° . The structure of the oxide is generally believed to be (I). The evidence for this comes from infrared spectroscopy[5], which indicates a N-N


(I)

bond similar to that found for the tetroxide, and a recent paper by Anderson and Mason[6] has confirmed, by the use of ^{14}N nuclear magnetic resonance, that the structure contains both a nitroso and a nitro group.

Dinitrogen trioxide does not exist in the gaseous state[7] and in the liquid a complicated inter-relationship exists of the following equilibria:-

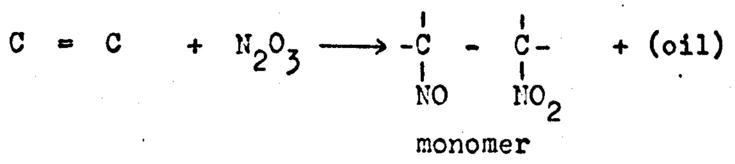
$$N_2O_4 \rightleftharpoons 2NO_2 \qquad -14.7\ \text{kcal}^{1} \quad (-61.5\ \text{kJ}) \qquad (1)$$

$$NO + NO_2 \rightleftharpoons N_2O_3 \qquad + 9.6\ \text{kcal}^{1} \quad (41.8\ \text{kJ}) \qquad (2)$$

The composition of the liquid at any given temperature and pressure depends therefore on the partial pressures of the components. Thus Beattie and Bell[8] have shown that at 25° and one atmosphere pressure only about 20% of dinitrogen trioxide is undissociated. Most reactions with olefins have been carried out in the temperature range -10 to +20° and under atmospheric pressure, hence a mixture rich in nitric oxide and nitrogen dioxide was used.

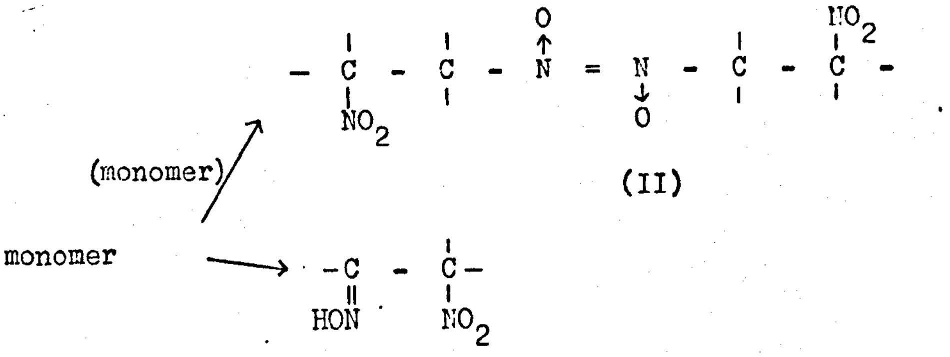
Studies of solvent effects on the equilibria are lacking, but a solvent in which nitric oxide is sparingly soluble will increase the nitric oxide concentration in the gas phase. In paraffinic solvents dinitrogen trioxide is appreciably dissociated and at temperatures above -80° free nitric oxide is evolved; in toluene the nitric oxide is not liberated[9] below -45°.

Simple olefins:- Wieland[10], an early worker in the field, found that dinitrogen trioxide interacted with olefins at low temperatures and in solvents such as diethyl ether, to give colourless solids termed psuedonitrosites, and oils:-



$$C = C + N_2O_3 \longrightarrow \underset{\substack{|\\ NO}}{\overset{|}{-C}} - \underset{\substack{|\\ NO_2}}{\overset{|}{C-}} + (\text{oil}) \qquad (3)$$

monomer



(4)

(5)

The structure (II) was established much later by Gowenlock[11] who pointed out that cis- and trans-isomers were possible.

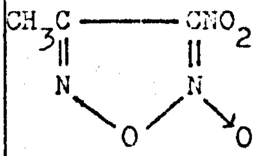
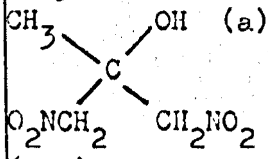
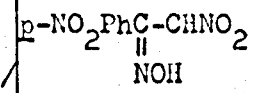
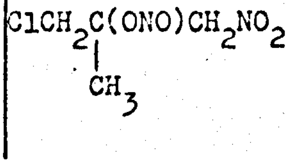
Wieland's experiments have been confirmed by most workers and the addition is generally considered to proceed to give first the monomeric nitro-nitroso compound which can undergo further reaction such as dimerisation (II) or tautomerism to the oxime (III). Some typical reactions of olefins are collected in Table 7 (p. 40).

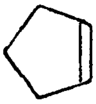
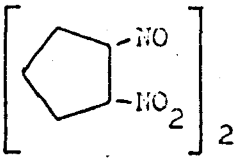
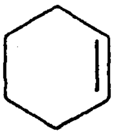
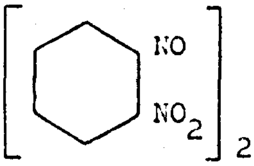
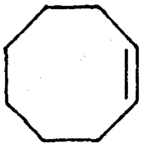
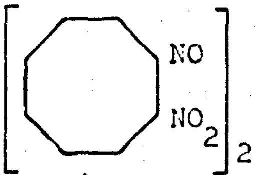
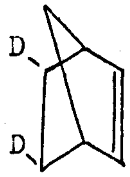
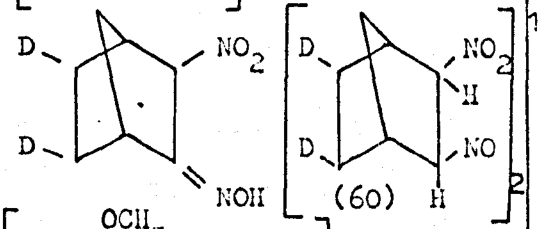
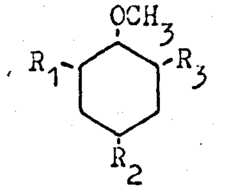
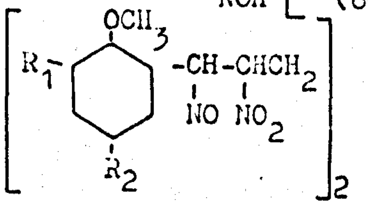
Most workers have not investigated the oil but it has been suggested[12a] that it may arise mainly from dinitrogen tetroxide addition. Indeed in some cases the oil has been shown to consist of typical dinitrogen tetroxide and olefin addition products such as dinitro and nitro-nitrite compounds (Table 7).

The ratio of the solid to oil product varies considerably depending on the particular olefin, the reaction temperature and the solvent. The effect of varying experimental conditions has been studied in the case of cinnamyl acetate. Japanese[13] workers found that cinnamyl acetate when treated with dinitrogen trioxide at unspecified low temperatures gave the nitro-nitroso dimer (IV) and nitro-nitrite (V):-

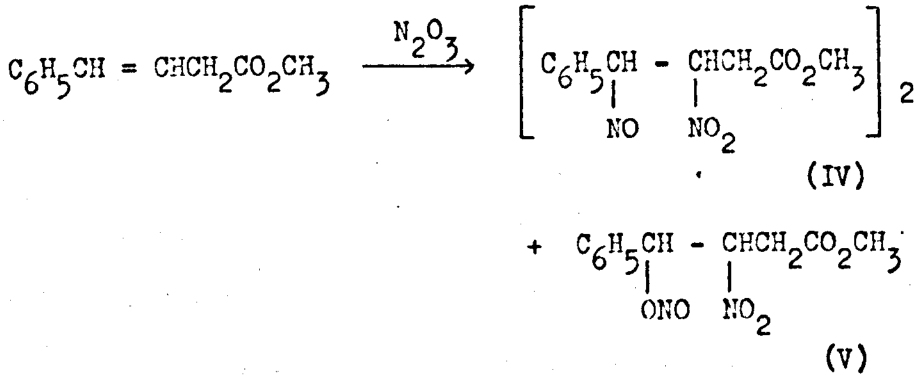
TABLE 7

The Interaction of Dinitrogen Trioxide and Olefins.

Olefin	Conditions	Product (% yield)	Ref.
$CH_3CH{=}CH_2$	0°/ether	 $CH_3CHNO_2CH_2NO_2$ (a) $CH_3CHOHCH_2NO_2$ $[CH_3CHNOCH_2NO_2]_2$ (very little)	14
cis-and trans- $CH_3CH{=}CHCH_3$	-10 to 5°/1:1 pentane-ether/ 2:1 NO-air	$[CH_3CHNOCHNO_2CH_3]_2$ (29) erythreo and threo mixtures	19a,20
$(CH_3)_2CH{=}CH_2$	-5°/ether/N_2O_3 added in ether	$[(CH_3)_2CHNOCH_2NO_2]_2$ $(CH_3)_2CHOHCH_2NO_2$ (a)  (a) $(CH_3)_2CHNO_2CH_2NO_2$ $(CH_3)_2CH{=}CHNO_2$	14
$PhCH{=}CH_2$	60°/2:5 ether-benzene 2:1 NO-air	$[PhCHNOCHNO_2]_2$ (58)	20
p-$NO_2PhCH{=}CH_2$	25°/ether-aq. HNO_2 or -10 to 30°/ether/ N_2O_3	$p\text{-}NO_2Ph\underset{\underset{NOH}{\parallel}}{C}\text{-}CHNO_2$ (32)	18
$CH_3CH{=}CHCO_2CH_3$	0-5°/$NaNO_2$ + H_2SO_4 or -10°/ether/NO-air	$[CH_3CHNOCHNO_2CO_2CH_3]_2$ (47)	18
$PhCH{=}CHCH_2CO_2\text{-}CH_3$	0°/$PhCH_3$	$[PhCHNOCHNO_2CH_2CO_2CH_3]_2$ $PhCHCH(ONO)CHNO_2CO_2CH_3$	13
$ClCH_2CH{=}CH_2$	liq. N_2O_3 or N_2O_3 in ether or $NaNO_2$, acid and H_2O	$ClCH_2CHNOCH_2ONO$	16
$ClCH_2C(CH_3){=}CH_2$	as above	$ClCH_2\underset{\underset{CH_3}{\vert}}{C}(ONO)CH_2NO_2$	16

Olefin	Conditions	Product (% yield)	Ref.
	-10 to 5°/1:1 pentane-ether, 2:1 NO-air	 (20)	19a
	0°/1:1 pentane-ether 2:1 NO-air	 (45-47)	19a,20
	0°/1:1 pentane-ether 2:1 NO-air		20
	0°/1:1 pentane-ether 2:1 NO-air	 (60)	19a,b
 where R_3 was $-CH=CH\ CH_3$	4N H_2SO_4 added to olefin in aq. ether + $NaNO_2$	 where R_1 and R_2 were H H (53) H CH_3 (58) H Cl (64) CH_3 H (20) Cl H (21) OCH_3 H (21)	15
$(C_2H_5)_2C=CH_2$	-10°/ether	$(C_2H_5)_2C(OH)-CH_2NO_2$ (25) $(C_2H_5)_2C(NO_2)-CH_2NO_2$ (39)	21
$CH_3(CH_2)_7CH=CH_2$	-10°/ether	$CH_3(CH_2)_7CHNOCH_2NO_2$ 2 (0.3)	21

(a) formed by subsequent hydrolysis of the nitro-nitrite compound.



$$C_6H_5CH=CHCH_2CO_2CH_3 \xrightarrow{N_2O_3} \left[C_6H_5\underset{NO}{\underset{|}{CH}} - \underset{NO_2}{\underset{|}{CH}}CH_2CO_2CH_3\right]_2 \quad (IV) \qquad (6)$$

$$+ \; C_6H_5\underset{ONO}{\underset{|}{CH}} - \underset{NO_2}{\underset{|}{CH}}CH_2CO_2CH_3 \quad (V)$$

The ratio of (IV) to (V) decreased when the solvent was changed from toluene to diethyl ether or cyclohexane. An increase in olefin concentration in toluene favoured the production of (V) as did the raising of the temperature above 0^o. It would seem therefore that high olefin concentration and increased temperatures favoured nitro-nitrite. This is sufficiently similar to the reaction product of dinitrogen tetroxide to suggest direct reaction by the tetroxide.

<u>Mechanism</u>:- Two of the mechanisms that have been suggested for this reaction envisage heterolysis[14-16] of the trioxide (Equations 7 and 8) and the third mechanism involves homolysis[18,19] to nitrogen dioxide and nitric oxide (Equation 9):-

$$N_2O_3 \rightleftharpoons NO^- + NO_2^+ \qquad (7)$$

$$N_2O_3 \rightleftharpoons NO^+ + NO_2^- \qquad (8)$$

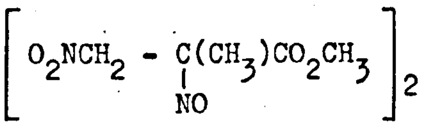
$$N_2O_3 \rightleftharpoons NO + NO_2 \qquad (9)$$

<u>Homolysis</u>. Because nitric oxide and nitrogen dioxide are free radicals, dinitrogen trioxide or its equilibrium mixture would be expected to react with olefins by a homolytic mechanism. The evidence for this can be summarised as follows:-

a) The orientation of addition is independent of the electronic nature of the unsaturated compound.

b) The stereochemistry of the products of the addition to <u>cis</u>- and <u>trans</u>-but-2-ene and to the norbornyl system has been suggested as being consistent with a free radical path.

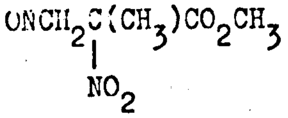
a)Shechter and Ley [18] showed that the nitro-nitroso dimer (VI) (47%) was obtained by the interaction of methyl methacrylate and dinitrogen trioxide in diethyl ether at 0 - 10°.



$$\left[O_2NCH_2-\underset{NO}{C}(CH_3)CO_2CH_3\right]_2 \qquad (VI)$$

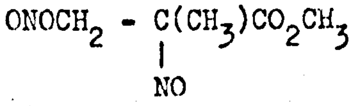
Because neither of the isomers (VII) and (VIII) were found, which were the expected products if heterolysis[(VIII) nitrosonium (NO^+) and nitrite (NO_2^-) ions] was important, it was concluded that addition took place <u>via</u> a homolytic path. Similar results were obtained for

(VII)



$$ONCH_2\underset{NO_2}{C}(CH_3)CO_2CH_3$$

(VIII)

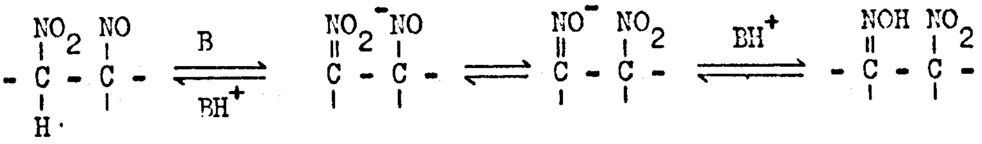


$$ONOCH_2-\underset{NO}{C}(CH_3)CO_2CH_3$$

<u>p</u>- nitrostyrene although the isomeric oxime only was obtained (32%) (Table 7 p. 40).

Additionally, Shechter[12a] has pointed out that in reactions of olefins such as propene, isobutene and styrene the nitro group of the nitro-nitroso product was attached at the terminal rather than the internal position. This would not be expected by an electrophilic process involving the nitrosonium ion (NO^+). (Table 7).

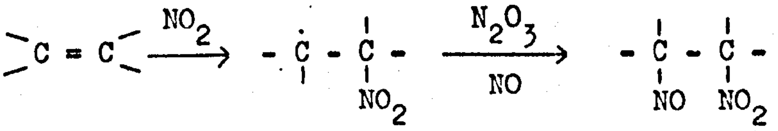
Adducts of other unsymmetrical olefins and dinitrogen trioxide have however been reported[12a] in which the nitro group was attached to the carbon bearing the smaller rather than the greater number of hydrogen atoms. Shechter[12a] has suggested that the structures of these products have been misassigned or else have been derived from base catalysed isomerisation of the initial <u>vicinal</u> nitro-nitroso compounds:-



$$-\underset{H}{\overset{NO_2}{C}}-\overset{NO}{C}- \underset{BH^+}{\overset{B}{\rightleftharpoons}} \overset{NO_2^-}{C}-\overset{NO}{C}- \rightleftharpoons \overset{NO^-}{C}-\overset{NO_2}{C}- \overset{BH^+}{\rightleftharpoons} -\overset{NOH}{C}-\overset{NO_2}{C}- \qquad (10)$$

The source of the base is not clear, neither is the magnitude of the base catalysed nitroso oximino tautomerism considered.

Thus Shechter[12a,18] envisaged addition to take place by initial attack by nitrogen dioxide to give an intermediate 2-nitro radical and subsequent pairing with nitric oxide or exchange with dinitrogen trioxide to give the observed nitro-nitroso product:-



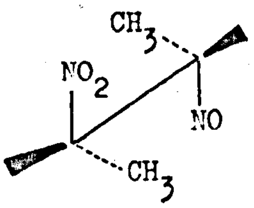
$$>C=C< \xrightarrow{NO_2} -\dot{C}-\underset{NO_2}{C}- \xrightarrow[NO]{N_2O_3} -\underset{NO}{C}-\underset{NO_2}{C}- \qquad (11)$$

The occasionally observed dinitro or nitro-nitrite products were derived by reaction of the intermediate radical with nitrogen dioxide. The dinitro compound could also be produced by oxidation of the nitroso group by nitrogen dioxide[12b].

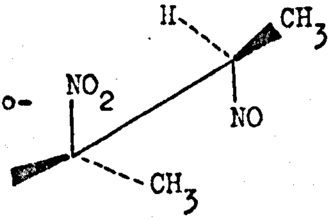
b) Scheinbaum[19a] has recently investigated the stereochemistry of the reaction products of the interactions of _cis_- and _trans_-but-2-ene and _exo_, _exo_-5,6-dideuteronorbornene with dinitrogen trioxide.

The reaction product of but-2-ene has been shown to be the expected nitro-nitroso dimer[20]. It was pointed out that if the reaction involved a concerted _cis_- addition the adducts obtained from _cis_- and _trans_-but-2-ene would be the erythro and threo isomers respectively. If addition was stereospecifically _trans_- the results would have been reversed. However, addition of dinitrogen trioxide to the two butenes

erythro-



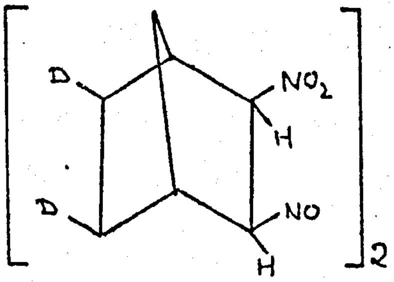
threo-



in a one to one mixture of pentane and diethyl ether solvent at -10 to 5° resulted in identical mixtures of both erythro- and threo-products. Also some isomerisation of cis- to trans-but-2-ene and vice versa was found on examination of the unreacted olefin.

Scheinbaum concluded that these results were in agreement with a two step homolytic path involving the initial reversible addition of nitrogen dioxide with the formation of an intermediate nitro alkyl radical. This radical, in either its isomerised or initial forms, then combined with nitric oxide to give the observed products.

Addition of dinitrogen trioxide to exo, exo-5,6-dideuteronorbornene[19a,b] gave besides the tautomeric oxime, 60% of the nitro-nitroso dimer (IX) formed by exo-cis-addition of the reagent. No skeletal rearrangement was observed as indicated by proton nuclear



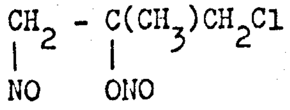
(IX)

magnetic resonance. This result is in agreement with those found for the addition of dinitrogen tetroxide and other free radical systems to norbornene (Ch. 1 p.27)

Heterolysis. The evidence presented in favour of an ionic addition path is rather nebulous.

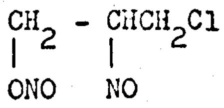
Of those authors who have postulated a mechanism at all, some[14,15] have regarded the nitro-nitroso adduct as arising by attack ofa nitronium ion (NO_2^+) followed by reaction with the hyponitrite ion (NO^-). There is no specific evidence for this ionic path other than the identification of products which fit this scheme.

Recently Park and Williams[16] have found that the treatment of methallyl chloride or allyl chloride with, a) pure liquid dinitrogen trioxide, b) the oxide in diethyl ether solvent, and c) the oxide produced from sodium nitrite and acid in water, resulted in the isolation of the nitroso-nitrite adducts (X), and (XI) respectively.



$$\underset{\mathrm{NO}}{\mathrm{CH_2}} - \underset{\mathrm{ONO}}{\mathrm{C}}\mathrm{(CH_3)CH_2Cl}$$

(X)



$$\underset{\mathrm{ONO}}{\mathrm{CH_2}} - \underset{\mathrm{NO}}{\mathrm{CH}}\mathrm{CH_2Cl}$$

(XI)

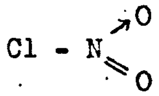
The authors suggest that addition took place as nitrosonium (NO^+) and nitrite ions (ONO^-). This was supported by the fact that addition of hypochlorous acid to allyl chloride is also anti-Markovnikoff[17]. It is unlikely that the observed addition products occurred by direct homolytic addition of the trioxide since a terminal nitro group would have resulted.

Summary:- The evidence in favour of either ionic or free radical paths is inconclusive and the question must still be regarded as open. It is likely though that the mechanism is dependent on the reaction conditions and more information concerning the influence of the solvent on the trioxide is called for. It is also noteworthy that there is no report of the use of radical transfer agents.

Since there is some limited evidence for homolytic addition of nitryl and nitrosyl chloride it is considered relevant to record an outline of the work of this nature.

Nitryl Chloride:- The interactions of nitryl chloride with olefins and acetylenes has been comprehensively reviewed by Stacey and Harris[22] and by Sosnovsky[1].

Structure and Physical Properties of Nitryl Chloride:- Microwave measurements established[23] the structure as the planar form:-



The liquid boils[24] at -15.9° at normal pressures to give a colourless gas that begins to decompose at 120° according to the equation[24]:

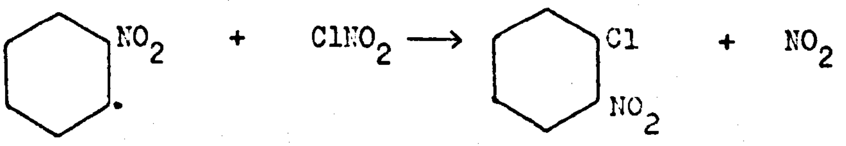
$$NO_2Cl \rightleftharpoons NO_2 + Cl + 32\ \text{kcal}\ (134\ \text{kJ}) \qquad (12)$$

which is followed by the secondary reaction[24]:

$$NO_2Cl + Cl \rightleftharpoons NO_2 + Cl_2 \qquad (13)$$

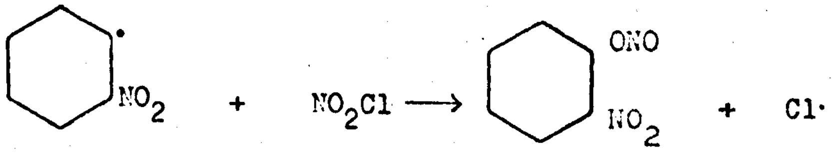
Mechanism:- Shechter[25], from a consideration of the published data[1,22] and from his own results with methylacrylate and acrylonitrile, pointed out that the orientation of addition was independent of the electronic nature of the substrate. In the cases of terminal olefins such as acrylonitrile and methylacrylate[25] addition of a nitro rather than a nitrite group was observed in the terminal position.

Brand and Stevens[26] found that the principal products from the nitrylchloride - cyclohexene interaction at 0° in diethyl ether in the presence of oxygen, were 1-chloro-2-nitrocyclohexane (41.6%), and trans-1,2-dichlorocyclohexane (26.6%). Some 2-chlorocyclohexanol (6.2%), 2-nitrocyclohexanol (5.4%) (both formed by subsequent hydrolysis of the corresponding nitrite) and 2-chlorocyclohexyl nitrate (6.4%) were formed. The products were rationalised by a mechanism involving initiation by nitrogen dioxide followed by transfer with nitryl chloride in either of two ways:-



(14)

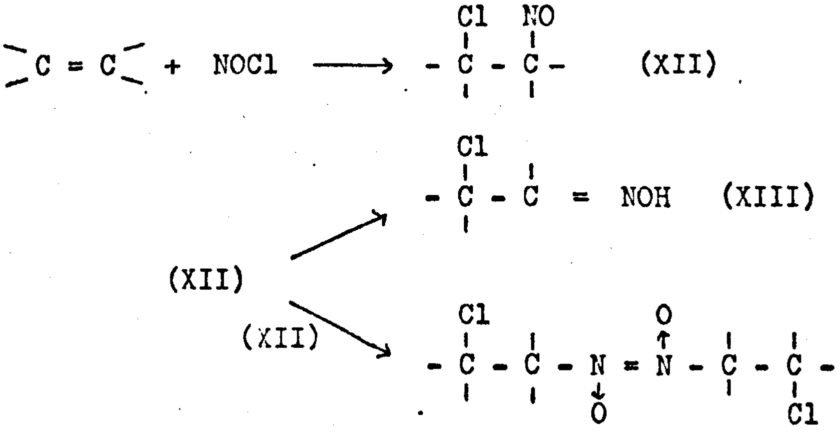
or



(15)

The formation of 2-chlorocyclohexanol indicated that some initiation must have occurred by atomic chlorine because initial attack by nitrogen dioxide always results in a C-N linkage (Ch. 1 p. 24). The formation of dichlorocyclohexane was stereospecifically trans- and could have arisen either by initiation by a chlorine atom or by normal heterolytic addition of molecular chlorine.

Nitrosyl Chloride:- In 1877 Tilden[27] established that nitrosyl chloride added to a carbon - carbon double bond to give nitrosochlorides of the type (XII), which were able to tautomerise to the oxime (XIII) or dimerise (XIV):-



$$>C=C< + NOCl \longrightarrow -\overset{Cl}{\underset{|}{\overset{|}{C}}}-\overset{NO}{\underset{|}{\overset{|}{C}}}- \quad (XII) \qquad (16)$$

$$(XII) \longrightarrow -\overset{Cl}{\underset{|}{\overset{|}{C}}}-\overset{|}{C}=NOH \quad (XIII) \qquad (17)$$

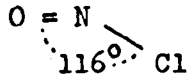
$$(XII) + (XII) \longrightarrow -\overset{Cl}{\underset{|}{\overset{|}{C}}}-\underset{|}{\overset{|}{C}}-\underset{\downarrow O}{N}=\overset{O \uparrow}{N}-\underset{|}{\overset{|}{C}}-\underset{Cl}{\overset{|}{C}}- \qquad (18)$$

(XIV)

This reaction, termed nitrosochlorination, has played an important part in terpene structure determination. In some cases[28] the nitroso compounds were sufficiently stbble to exist as blue monomers, steric factors preventing dimerisation as in the case of tetramethylethylene[29]. In some other cases anomalous products such as chloro-nitro and dichlorides were isolated and it is these that are relevant to this present work because a free radical path has been proposed[30] to account for their formation.

Several reviews[1,31,32] have been published on the preparation, properties and reactions of nitrosyl chloride. The recent exhaustive review of Kadzyaukas and Zefirov concentrated on the mechanism and stereochemistry of the reaction.

Structure and Physical Properties of Nitrosyl Chloride:- Electron diffraction measurements[24] have shown that nitrosyl chloride has the non-linear structure:



The solid melts at -59.6° and the liquid has b.p. -5.8° at normal pressures[24].

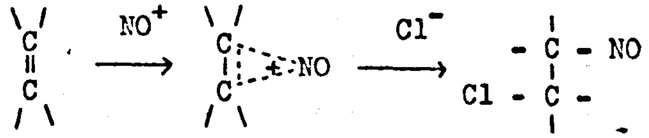
Nitrosyl chloride undergoes thermal decomposition according to the equilibrium[24]:

$$2NOCl \rightleftharpoons 2NO + Cl_2 \qquad (19)$$

and it has been calculated that it is only 0.6% dissociated at 25° at one atmosphere which increases to 6.9% at 125° under one atmosphere[24].

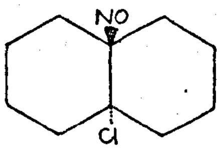
Mechanism and stereochemistry of Nitrosochlorination:-

Considerable experimentation[31,32] has shown that the addition of nitrosyl chloride follows Markovnikoff's rule with the nitroso group adding to the more hydrogenated carbon atom. This indicates that the initial attack is by the nitrosonium ion (NO^+) and Ingold[33] and others[28,34,35] have suggested that addition took place according to the ususl scheme for electrophilic attack on a double bond:-

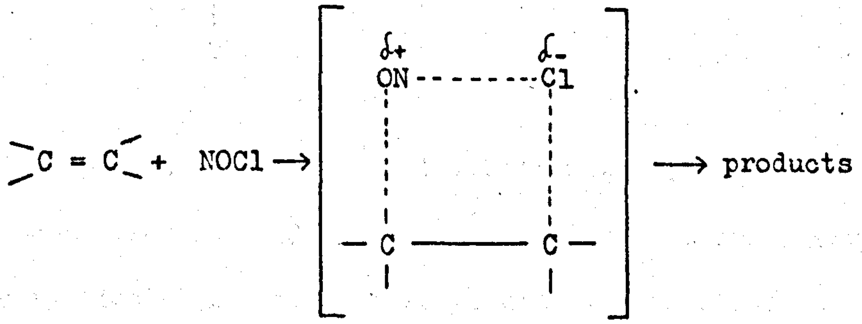


(20)

In agreement with the two stage electrophilic addition Meinwald[36] has found that 9,10-octalin gave a trans-nitrosochloride:



On the other hand norbornene and norbornadiene[36] both gave dimeric nitrosochlorides that had exo-cis-stereochemistry. The lack of skeletal rearrangement, cis-addition and the lack of incorporation of a nucleophilic solvent (ethanol and acetic acid) into the products, led Meinwald to conclude that in these cases a two stage electrophilic addition was inoperative. A free radical mechanism initiated by nitric oxide was ruled out because nitric oxide was known to be unreactive towards norbornadiene[37]. A four centred cyclic transition state (XV) was suggested to account for the observed products:-



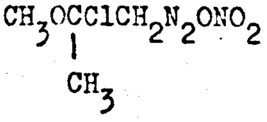
(21)

(XV)

Anomalous Products:- The most commonly occurring anomalous products of nitrosochlorination are vicinal dichlorides, dichloronitroso and chloronitroso compounds.

Ogloblin et al[30] have explained the formation of dichloro and nitrochloro derivatives in terms of the stability of the initially formed nitroso compounds. The formation of stable and insoluble dimers were envisaged as decreasing the yields while nitroso compounds that did not readily dimerise and were soluble would increase the yields by further reaction by a radical mechanism involving the formation of an unstable diazonitrate. This type of intermediate and its formation are discussed more fully in Chapter 3. Thus, Ogloblin found that pent-1-ene[30] in ether solution, when treated with nitrosyl chloride initially at -50° - but stored overnight at -15° - gave the dichloro (43%) and the chloronitro (26%) compounds.

Temperature dependence and the possible involvement of diazonitrates is illustrated by 2-methoxy propene[38]. Treatment of this olefin in ether with nitrosyl chloride at -60° gave the expected dimeric nitroso-chloride which decomposed explosively at room temperature. On the other hand it was implied that 2-chloro-2-methoxy propane diazonitrate (XVI) was present, because, on warming the product formed at 10 - 15°, nitrogen was evolved and on hydrolysis nitrate ions were identified.



$$\underset{\displaystyle CH_3}{CH_3OCClCH_2N_2ONO_2} \qquad \text{(XVI)}$$

The possible initiation of addition by nitrogen dioxide has also been discussed. Jones _et al_[39] found that cholesteryl acetate reacted very slowly with pure nitrosyl chloride in ether in an inert atmosphere at -50° to give the nitro chloride (53%) in two months. When nitrogen dioxide was added at -15° the same product (72%) was formed in only two hours.

Photolysis:- The first photochemical reaction with a hydrocarbon was reported in 1919 by Lynn[40] who found that nitrosyl chloride readily reacted with normal heptane in sunlight giving a transient blue solution. In later papers Lynn and coworkers identified the products as hydrogen chloride and heptanone oxime[41], _via_ the nitroso compound:-

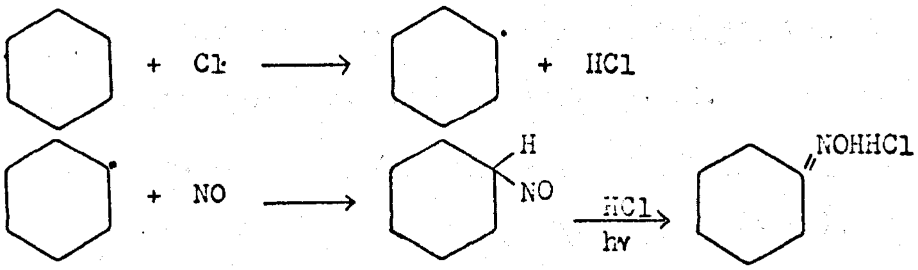
$$C_7H_{16} + NOCl \xrightarrow{h\nu} C_7H_{15}NO + HCl \qquad (22)$$

$$C_7H_{15}NO \longrightarrow C_7H_{14}NOH\ , \qquad (23)$$

and they extended the work to toluene[42].

In 1953 an analogous reaction of cyclohexane was reported[43] and it is on this reaction that the recent industrial process[44] for the production of caprolactam is based. A mixture of cyclohexane, nitrosyl chloride and hydrochloric acid is irradiated[45] with light of wave length 4,050 Å. (SI equivalent 405 nm) at less than 20°:-

$$NOCl + h\nu \longrightarrow NO + Cl\cdot \qquad (24)$$



(25)

(26)

A recent paper[46] has determined the quantum yield as 0.72 indicating that a chain reaction is unlikely.

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CHAPTER 3

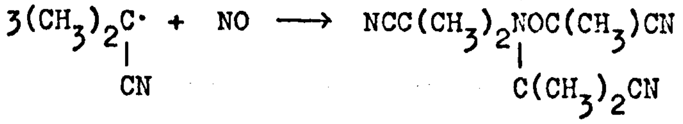
The Interaction of Nitric Oxide with Organic Compounds

Nitric oxide is the simplest of the paramagnetic nitrogen oxides and despite the presence of an odd electron it has little tendency to dimerise except at low temperatures in the liquid (b.p. -151.7°)[1] and solid (m.p. -163.5°) forms. The liquid is reported[2] as being 97% dimeric at its freezing point. Its lack of colour and its low reactivity towards many materials under ordinary conditions suggest an inherently greater stability than is characteristic of many odd electron molecules. Pauling[3] has suggested resonance between the following structures:

$$:\dot{N}::\ddot{O}: \longleftrightarrow :\overset{\cdot\bar{}\cdot}{N}::\overset{\cdot +}{O}: \longleftrightarrow :\dot{N} \equiv \ddot{O}:$$

Green and Linnet[4] have considered the three electron bond from a molecular orbital approach and report a bond order of 2.5.

Examination of the electron paramagnetic resonance spectrum[5] has indicated that the greater part of the spin density (ca. 60%) is centred on the nitrogen atom. Its activity as a free radical is illustrated by its ready combination with 2-cyano-2-propyl radicals in boiling benzene to give tris-(2-cyano-2-propyl) hydroxylamine in 50% yield:[6]



$$3(CH_3)_2\underset{CN}{\underset{|}{C}}\cdot + NO \longrightarrow NCC(CH_3)_2\underset{C(CH_3)_2CN}{\underset{|}{N}}OC(CH_3)_2CN \qquad (1)$$

The high thermal stability - little decomposition[2] even at 500° - of nitric oxide has resulted in its use as a vapour phase inhibitor of radical polymerisation[7] and also as a free radical trap in pyrolysis studies[8].

Inhibition of Gas Phase Reactions. The studies which have been carried out using nitric oxide as a gas phase inhibitor provide a clear picture of the reactivity of this stable free radical and bearing in mind the problems that occur when extrapolating vapour phase results into the liquid phase it is of value to consider those parts of such work relevant to the content of this thesis.

Nitric oxide has long been used as a free radical trapping agent in the gas phase and a considerable number of pyrolytic studies have been carried out in the presence of the oxide[8]. The presence of short lived organic radicals have been deduced from an examination of the kinetics or of the final reaction products[8]. Rice and Polly[9] first pointed out that initiation by nitric oxide was possible and the suggested step was a hydrogen abstraction:-

$$RH + NO \longrightarrow R\cdot + HNO \qquad (2)$$

This idea has been developed into a general theory of inhibition of organic compounds by Laidler, Wojciechowski and coworkers. Two papers[10] survey the general theory in which it is proposed that initiation is by a hydrogen abstraction step and termination involves reaction between the most abundant chain carrier and either nitroxyl (HNO) or nitric oxide. Later[11] it was suggested that species such as a monomeric nitroso compound - or the corresponding oxime - arising by the combination of nitric oxide with an alkyl radical:-

$$R\cdot + NO \longrightarrow RNO \longrightarrow R'CH = NOH \qquad (3)$$

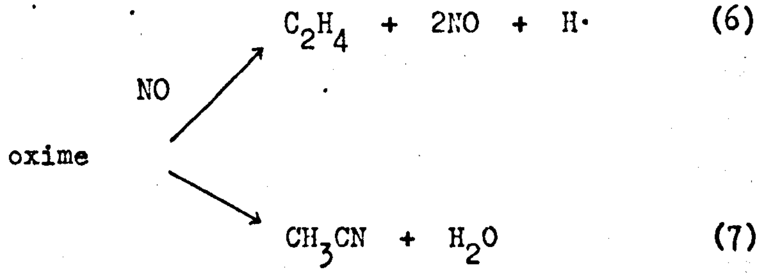
would also take part in the termination step regenerating nitric oxide:

$$R\cdot + R'CH = NOH \longrightarrow RR'H + NO \qquad (4)$$

On the other hand Norrish and Pratt[12] do not consider that nitric oxide abstracts hydrogen atoms, rather that it adds to radicals with the eventual formation of an oxime:

$$C_2H_5\cdot \;+\; NO \longrightarrow C_2H_5NO \longrightarrow CH_3CH = NOH \qquad (5)$$

These oximes undergo decomposition in two ways; by reaction with nitric oxide or by direct unimolecular decomposition:-



$$\text{oxime} \xrightarrow{NO} C_2H_4 \;+\; 2NO \;+\; H\cdot \qquad (6)$$

$$\text{oxime} \longrightarrow CH_3CN \;+\; H_2O \qquad (7)$$

Of particular significance is the fact that of the theories advanced to account for the inhibiting effect of nitric oxide, most have involved disproportionation of nitric oxide to nitrogen and nitrogen dioxide by reaction with nitroso compounds[8]. Batt and Gowenlock[13] have proposed formation of N-nitroso-N-alkyl hydroxylamine nitrite $\left[RN(NO)ONO\right]$, <u>via</u> the nitroso intermediate, which rearranges to a diazonitrate (RN_2ONO_2), and then decomposes. This can explain the formation of nitrogen in the reaction of nitrosomethane with nitric oxide at high temperatures and is analogous to Brown's[14] suggested mechanism for the interaction of nitric oxide with liquid isobutene discussed later (p. 63). Christie[15] has also discussed the possible formation of the substituted hydroxylamine during the room temperature photolysis of methyl iodide in the presence of nitric oxide.

A further significant reaction is between ethoxy radicals and nitric oxide at 181° to give ethyl nitrite which has been studied by Levy[16], and Arden and Phillips[17]:-

$$C_2H_5OO\,C_2H_5 \;\overset{181^{\circ}}{\rightleftharpoons}\; 2C_2H_5O\cdot \qquad (8)$$

$$C_2H_5O\cdot \;+\; NO \longrightarrow C_2H_5ONO \qquad (9)$$

Levy[18] later reported identification of nitrous oxide, ethanol and acetaldehyde formed by the decomposition of ethyl nitrite in the presence of nitric oxide:-

$$C_2H_5ONO \xrightleftharpoons{181^\circ} C_2H_5O\cdot + NO \qquad (10)$$

$$C_2H_5O\cdot + NO \longrightarrow HNO + CH_3CHO \qquad (11)$$

$$2HNO \longrightarrow N_2O + H_2O \qquad (12)$$

$$C_2H_5O\cdot + HNO \longrightarrow C_2H_5OH + NO \qquad (13)$$

Arden and Phillips[17] also found nitrogen and nitrogen dioxide in the early stages (<u>ca</u>. 15%) of the pyrolysis of diethyl peroxide in the presence of nitric oxide at 95°. This was explained by the reaction of nitric oxide with nitroxyl:

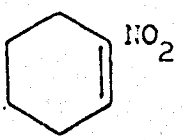
$$HNO + 2NO \rightleftharpoons \left[HN(NO)ONO\right] \longrightarrow H\cdot + N_2 + \dot{O}NO_2 \qquad (14)$$

$$\dot{O}NO_2 + NO \longrightarrow 2NO_2 \qquad (15)$$

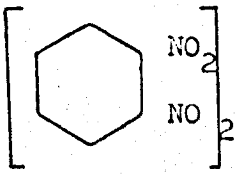
Liquid phase reactions of nitric oxide:-

Simple olefins. The reports in the literature concerning the action of nitric oxide on simple olefins are few and as late as 1949 Sidgwick[19] stated that such reactions did not occur.

The first workers to identify any products were Bloomfield and Jeffrey[20] who obtained from cyclohexene, 1-nitro cyclohexene (I) and dimeric nitro-nitroso cyclohexane (II) without recording yields or reaction conditions.



(I)



(II)

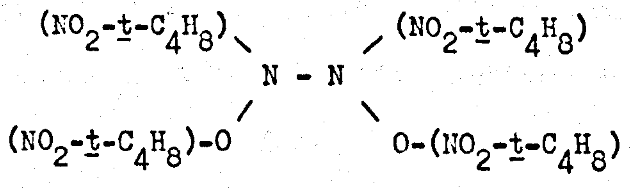
The most comprehensive study of an olefin and nitric oxide interaction was made by Brown[14] in 1957 using liquid isobutene at 28°. Three characteristics of such reactions were established. Firstly when pure nitric oxide was used there was an induction period and the reaction could be initiated by admitting either a small quantity of air or by adding reaction products from an earlier experiment. The method of purification of the oxide was not stated. Secondly a product of a nitric oxide - olefin interaction was usually a dimeric nitro-nitroso adduct, nitrogen and an unstable viscous oil. The latter underwent a "fume off" on attempted separation by distillation or column chromatography. It was found that the decomposition of this liquid could be controlled by steam distillation or passage through a falling film still, but no method of separating the constituents of the oil in significant quantity was discovered. Thirdly, those samples which it had been possible to separate, usually consisted of nitro olefins and were thus typical of adducts formed from other nitrogen oxides and olefins.

Some dimeric nitro-nitroso isobutane (III) (1.2%) and nitrogen were identified.

$$\left[(CH_3)_2C(NO)CH_2NO_2 \right]_2$$

(III)

The structure of the major component (66.4%) of the oil product was postulated as being:-



which arose by the following steps:-

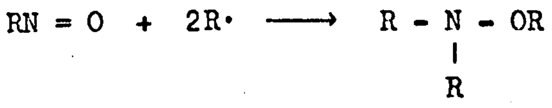
$$(CH_3)_2C = CH_2 \xrightarrow{NO_2} (CH_3)_2\dot{C} - CH_2NO_2 \quad \text{initiation} \tag{16}$$

$$R\cdot + NO \longrightarrow RNO \qquad \left[\text{where } R\cdot = (CH_3)_2\dot{C}CH_2NO_2\right] \tag{17}$$

$$RNO + R\cdot \longrightarrow R\dot{N}OR \xrightarrow{R\dot{N}OR} (RNOR)_2 \tag{18}$$

By fractional crystallisation at low temperatures (-78°) Phillips and Coyne[21] later isolated 34 - 45% of tris-(nitro-_t_-butyl) hydroxylamine (IV) from a similar oil derived from a nitric oxide-isobutene reaction. According to them this arose from the reaction sequence:-

$$R\cdot + NO \longrightarrow RN = O \tag{19}$$



$$RN = O + 2R\cdot \longrightarrow R - \underset{\displaystyle R}{\underset{|}{N}} - OR \tag{20}$$

(IV)

The substituted hydroxylamine was found to decompose rapidly at moderate temperatures to O, N-bis-(nitro-_t_-butyl)-hydroxylamine $(RNOR)_2$, a mixture of nitroisobutenes and traces of acetone, nitromethane and O-(nitro-_t_-butyl) acetoxime, and they are therefore in agreement with Brown who isolated the same compounds by fractional distillation of his oil product (Table 8).

Burkhard and Brown[22] have carried out similar studies using tri- and tetramethyl ethylene with results essentially similar to those above except that considerable quantities of unreacted monomeric nitro-nitroso adducts were found. The constitution of the oils derived from these two olefins and from isobutene could not accurately be determined and was only estimated on the basis of isolation of a few pure compounds and on infrared analysis of the fractions collected.

TABLE 8

Estimated Composition of the Product from the Reaction of Isobutene and Nitric Oxide at 28°.

Compound	% Initially present	% After fractionation(a)
(Nitro-t-butyl)$_4$N$_2$O$_2$ (Crude Oil)	66.4	
N-(Nitro-t-butyl)-hydroxylamine		1
O,N-Bis-(nitro-t-butyl)-hydroxylamine		0.4
Nitromethane		1.8
Acetone		0.8
Acetoxime		0.2
O-(Nitro-t-butyl)-acetoxime		2.3
Regenerated isobutene		ca. 1
1,2-Dinitroisobutane		0.8
1-Nitroisobutene		49.7
2-Nitroisobutene	21.8	24.2
Dimer nitronitrosoisobutane	2.1	2.7
Nitro-t-butanol(b)	8.8	8.8
Nitro-t-butyl nitrate	0.6	0.6
α-Hydroxyisobutyraldoxime	0.3	0.3
Liquids b.p.> 100° (1 mm.)		7.3

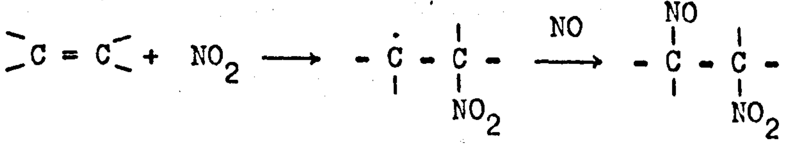
(a) The compounds not initially present arose by decomposition of (nitro-t-butyl)$_4$N$_2$O$_2$ and by further reaction of the decomposition products.

(b) Formed by subsequent hydrolysis of the nitro-nitrite compound.

There are few other significant reports of liquid or gas phase interactions of nitric oxide with simple olefins.

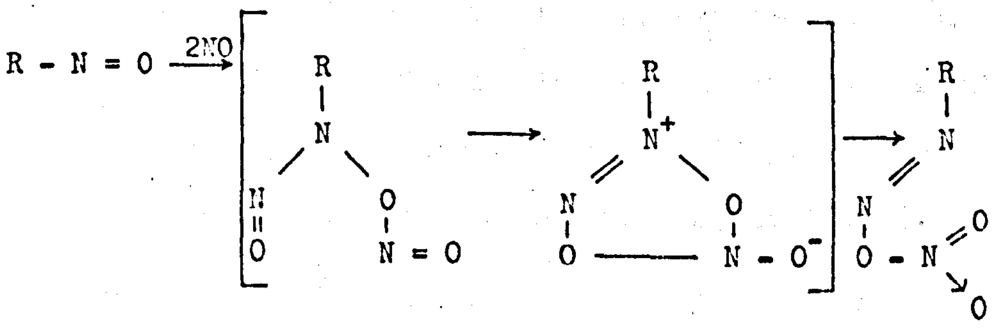
Mechanism: The mechanism of the liquid isobutene, nitric oxide reaction, as postulated by Brown[14], was based on three considerations. The first of these was the need for a catalytic quantity of nitrogen dioxide. The second was the similarity of the structures of the products with those obtained from olefin and other nitrogen oxide additions. Thirdly, the available information on the action of the higher oxides (Ch. 1 and 2), which indicated that products such as 2-nitroisobutene, dimeric nitro-nitroso isobutane and nitro-t-butanol were formed mainly by a homolytic path involving nitrogen dioxide, while those such as nitro-t-butyl nitrate and ∝-hydroxy-isobutyraldoxime arose by an ionic process involving attack by the nitrosonium ion (NO^+).

The first step in Brown's reaction scheme was attack by nitrogen dioxide on the double bond to give a nitro alkyl radical which then paired with nitric oxide to give the initial nitro-nitroso adduct:-



$$>C=C< + NO_2 \longrightarrow -\overset{\cdot}{C}-\underset{NO_2}{C}- \xrightarrow{NO} -\overset{NO}{C}-\underset{NO_2}{C}- \qquad (21)$$

The basic problem became that of accounting for the production of nitrogen dioxide in the reaction. Brown proposed that this occurred by the action of nitric oxide on the nitro-nitroso adduct to form an unstable diazonitrate (V):-



(22)

(V)

It was further postulated that this intermediate diazonitrate could decompose by either homolytic or heterolytic bond rupture. The homolytic process regenerated the original radical and hence accomplished a simple disproportionation of the nitric oxide into nitrogen and nitrogen dioxide:

$$R\cdot + 3NO \longrightarrow RN_2ONO_2 \qquad (23)$$

$$RN_2ONO_2 \longrightarrow R\cdot + N_2 + O\dot{N}O_2 \qquad (24)$$

$$O\dot{N}O_2 + NO \longrightarrow 2NO_2 \qquad (25)$$

The heterolytic route yielded sequentially diazonium nitrate, nitro-olefin and nitric acid. A conversion of nitric oxide to nitrogen dioxide was also envisaged but by a less efficient path than by the homolytic route:

$$RN_2ONO_2 \longrightarrow \left[RN_2^+NO_3^- \right] \longrightarrow \left[R^+NO_3^- \right] + N_2 \qquad (26)$$

$$\left[R^+NO_3^- \right] \longrightarrow C_4H_7NO_2 + HNO_3 \quad (R = C_4H_8NO_2) \qquad (27)$$

$$2HNO_3 + NO \longrightarrow H_2O + 3NO_2 \qquad (28)$$

That nitroso monomers react with nitric oxide was first shown by Bamberger[23], in 1897 who obtained phenyl diazonium nitrate by treating nitrosobenzene with nitric oxide in chloroform. While a wide range of saturated[24] and unsaturated compounds[24,25], and free radicals undergo extremely facile addition to the nitroso group, there is no direct evidence that nitric oxide does so. Recently evidence has been presented[26] for an N-nitroso-N-alkyl hydroxylamine nitrite $\left[RN(NO)ONO \right]$ (<u>c.f.</u> p. 58). One mole of trifluoronitrosomethane, when treated with nitric oxide at -110° in methanol, absorbed exactly two moles of gas, and on warming the solution to -55° gases were evolved, one of which was identified as methyl nitrite (CH_3ONO). The trifluorohydroxylamine was isolated as its methyl ester when diazomethane was passed into a similar solution at -70°, methyl nitrite and O,N-dimethyl-N-trifluoromethyl hydroxylamine (VI) being obtained. Ginsburg interpreted his results according to the scheme:-

$$CF_3NO + 2NO \longrightarrow \left[CF_3N(NO)ONO \right] \xrightarrow{CH_3OH} CF_3NHCH + 2CH_3ONO \qquad (29)$$

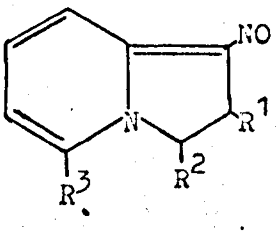
$$CF_3NHOH + 2CH_2N_2 \longrightarrow \underset{(VI)}{CF_3N(CH_3)OCH_3} \qquad (30)$$

Evidence for aliphatic diazonium nitrates has been produced by Tedder[27] who found that a yellow solution was produced by passing nitric oxide into a methylene dichloride solution of 1-nitroso-hex-1-yne at -78°. On warming this solution evolved nitrogen and by treatment with 2-naphthol and dimethylaniline azo coupling products were obtained that gave indirect evidence that an unstable diazonium salt was formed <u>in situ</u>; this was assumed to be the nitrate.

$$BuC \equiv CNO \xrightarrow{2NO} BuC \equiv C - \overset{+}{N} \equiv N\,NO_3^- \qquad (31)$$

A case has already been cited where treatment of 2-methoxypropene with nitrosyl chloride gave an isolatable diazonitrate[28] (p. 51).

Much more recently Tedder[29] has isolated stable heterocyclic diazonium nitrates of some nitroso substituted indolizines (VII), quinilizines (VIII) and pyrrolathiazoles (IX).



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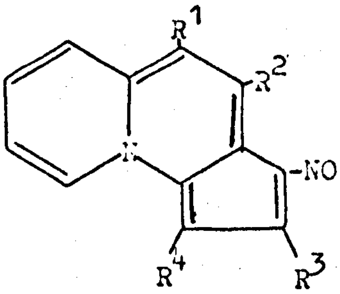

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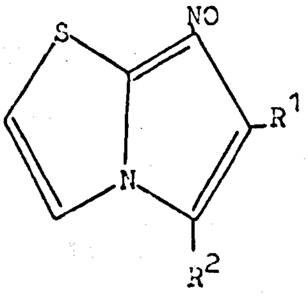


(IX)

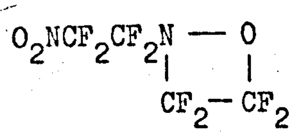
This was done by passing nitric oxide into cold chloroform solutions of these compounds for two hours in the absence of light, when the corresponding yellow diazonium nitrates were deposited. The salts were stable in the solid state and the aqueous solutions could be boiled for some minutes without decomposition, and are typical of other aromatic diazonium salts and in sharp contrast to the highly unstable aliphatic diazonium salts.

It has already been noted that the transient existence of aliphatic diazonitrates or their precursors, has been suggested for gas phase reactions of nitric oxide with nitroso compounds. However, the evidence for their existence in either gas or liquid phases is by no means strong and comes mainly by extrapolation from aromatic chemistry.

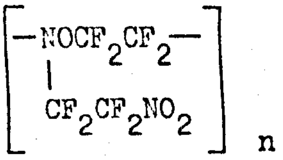
Halogeno-olefins:- Some gas phase studies of the interaction of halogeno-olefins - mainly fluoro-olefins - and nitric oxide have been undertaken by Hazeldine[30-33] and co-workers (other workers are listed in refs. 34 - 36).

Hazeldine[30] in 1959, in a German Patent, showed that polyhalo-olefins reacted with nitric oxide when irradiated and/or heated (100 - 200°) to form resinous or oily polymers of good stability. Typical olefins were $CF_2=CFCl$, $CF_2=CHF$, $CF_3(CF_2)_nCF=CF_2$ (where $n = 0 - 2$), $CF_2=CFCF=CF_2$, $CF_2=CClCH=CF_2$ and $CF_2=C(CF_3)CF=CF_2$.

Later Hazeldine[31] et al reported that tetrafluoroethylene (2 mol.) reacted slowly with nitric oxide (1 mol.) in the gas phase, at room temperature, in the dark to give the stable monomeric tetrafluoro-1-nitro-2-nitrosoethane (68%) and tetrafluoro-1,2-dinitro ethane (15%). Some perfluoro-2-(2-nitro tetrafluoroethyl)-1,2-oxazetidine (X) (5%) and polymer (XI) were also isolated.



(X)



(XI)

These last two compounds arose by the known addition[37] of tetrafluorethylene across the nitrogen oxygen double bond of the nitroso group. Monomeric tetrafluoro-1-nitro-2-nitroso ethane would be expected because nitroso compounds having an α-halogen atom and no α-hydrogen atoms are known not to dimerise[38]. Since no dinitroso compound was found nor were products isolated that may have been derived from it (such as a dioxazetidine), Hazeldine _et al_ concluded that nitric oxide was not the initiating radical and proposed that the reaction was initiated by nitrogen dioxide which was present in the nitric oxide as an impurity. A reaction scheme was therefore proposed that was analogous to Brown's[14] suggestion for the reaction of nitric oxide and isobutene. The nitrogen dioxide so produced gave rise to the observed dinitro product by combination with the initial nitro fluoro alkyl radical.

Partial confirmation of this scheme was obtained when it was found that tetrafluoro-1-nitro-2-nitroso ethane and nitric oxide gave a rapid reaction at room temperature to yield 1,2-dinitrotetrafluoroethane (_ca_. 50%), nitrogen and dinitrogen tetroxide. Again the formation of a diazonitrate and its homolytic decomposition was used to explain the formation of these products.

The same mechanism was accepted by Park _et al_[35] who also examined the reaction of tetrafluoroethylene under similar conditions to those of Hazeldine and found identical products. Additionally these authors used trifluorochloroethylene at 22° (24 hr.) to give a large amount of nondistillable material (_ca_. 50%) and small amounts of the compounds:-

$ClCF_2CFClNO$, $ClCF_2CFCl_2$, $O_2NCF_2CFCl_2$

(XII) (XIII) (XIV)

These latter arose by attack of a chlorine atom which itself was formed from a nitro-nitrite compound as shown below.

$$O_2NCF_2CFClONO \longrightarrow O_2NCF_2CFClO\cdot + NO \qquad (32)$$

$$O_2NCF_2CFClO\cdot \longrightarrow O_2NCF_2COF + Cl\cdot \qquad (33)$$

The acetyl fluoride was probably lost to the water used to wash the reaction product.

The reaction of hexafluoropropene and nitric oxide has also been examined[33,34]. In contrast to tetrafluoroethylene, Hazeldine et al[33] found that hexafluoropropene reacted very slowly with nitric oxide in the gas phase. This was in accord with the known reactivities of the two olefins towards free radicals which was explained by the electron withdrawal by fluorine and by steric interference[39]. At 65° and six atmospheres pressure a three to one nitric oxide hexafluoropropene mixture reacted over 48 hours to give hexafluoro-1-nitro-2-nitroso propane (17%), hexafluoro-1,2-dinitro propane (10%) and pentafluoro acetone (4%). Higher temperatures decreased the yield of the nitro-nitroso compound while increasing the amount of the dinitro adduct. This reflects the thermal instability of the nitro-nitroso compound.

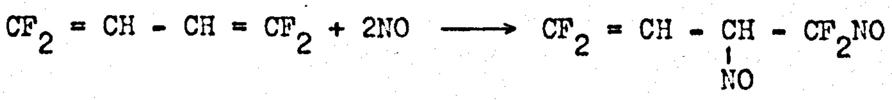
Park et al[36], in addition to the work already described, made an interesting study of the reaction of nitric oxide with tetrafluoroethylene, trifluorochloroethylene and 1,1-difluoro-2,2-dichloroethylene using a flow system and Lewis acids as catalysts at various temperatures. Lewis acids of trivalent cations in the solid state are known to absorb nitric oxide reversibly. It was hoped that an elevated temperature could be found where the complex was appreciably dissociated so that the nitric oxide would be sufficiently activated to behave as a typical free radical initiator. In which case addition to the olefinic bond might be expected to form a 1,2-dinitroso adduct. Of the Lewis acids tried, only finely divided ferric chloride gave suitable results; this supplied chlorine to the system as it was reduced to ferrous chloride. At 45 - 75° the major products were the corresponding chloro-nitroso compounds (71 - 76%) and were thus typical adducts of the nitrosyl chloride reaction (p.49). In the presence of a fluoro-olefin it was suggested that nitric oxide and ferric chloride reacted in the following manner to form nitrosyl chloride.

$$FeCl_3 + NO \rightleftharpoons FeCl_3.NO \qquad (34)$$

$$FeCl_3.NO + NO \longrightarrow FeCl_2NO + NOCl \qquad (35)$$

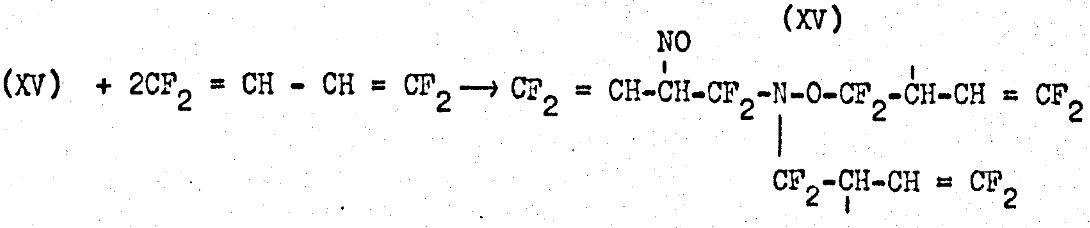
$$FeCl_3 + NOCl \longrightarrow FeCl_4NO \xrightarrow{2NO} FeCl_2NO + 2NOCl \qquad (36)$$

Recently, Putnam and Starkey[40] have isolated a white stable cross linked polymer when nitric oxide and liquid 1,1,4,4-tetrafluoro-1,3-butadiene interacted at room temperature over several hours in a stainless steel reactor. The structure was assigned on the basis of the infrared spectrum and elemental analysis. It was suggested that the polymer was formed via a dinitroso adduct (XV) which copolymerised with excess diene (shown for a 1,2-adduct only):-



$$CF_2 = CH - CH = CF_2 + 2NO \longrightarrow CF_2 = CH - \underset{\underset{NO}{|}}{CH} - CF_2NO \qquad (37)$$

(XV)



$$(XV) + 2CF_2 = CH - CH = CF_2 \longrightarrow CF_2 = CH\text{-}\overset{\overset{NO}{|}}{C}H\text{-}CF_2\text{-}\underset{\underset{CF_2\text{-}\underset{|}{C}H\text{-}CH = CF_2}{|}}{N}\text{-}O\text{-}CF_2\text{-}\overset{|}{C}H\text{-}CH = CF_2 \qquad (38)$$

Summary. Apart from reactions in the presence of ferric chloride it seems that the major products from the interaction of nitric oxide and olefins are unstable oils. In the case of olefins that readily polymerise this oil is largely polymeric and could not be purified. Other products arise by addition of nitrogen dioxide which many authors believe arises *via* an unidentified diazonitrate. The reaction has every indication of being essentially a free radical process probably initiated by nitrogen dioxide. Fluoro-olefins are less reactive towards nitric oxide than their purely hydrogen containing counterparts and the fluorinated adducts are more easily separated.

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CHAPTER 4

Preparation of Solvents, Reagents, Olefins and Chloroprene Dimers, and Methods of Analysis.

a) Solvents and Reagents:-

Fractional distillations were carried out using jacketed Fenske helices packed columns, 0.3 or 0.5 metres in length, the reflux ratio being controlled manually by means of a narrow bore stop-cock through which the condensate flowed.

1) n-Hexane, n-Heptane and Dichloromethane. The liquids were passed through a silica gel column, shaken with successive small portions of concentrated sulphuric acid until the lower layer was colourless, washed successively with water, sodium carbonate solution and water, and then dried over anhydrous magnesium sulphate. The hydrocarbons were finally distilled at atmospheric pressure and collected over 4A molecular sieve. *n*-Hexane b.p. 68.9°; *n*-heptane b.p. 98°; dichloromethane b.p. 40°. The hydrocarbons showed no absorption in the ultraviolet.

2) Chlorobenzene. Chlorobenzene was distilled at atmospheric pressure, the fraction b.p. 130.5° was stored over 5A molecular sieve in the dark.

3) Tetrahydrofuran. Tetrahydrofuran was dried successively with 4A molecular sieve, sodium wire and by refluxing over calcium hydride and finally distilled from calcium hydride and stored under nitrogen. b.p. 65°/729 mm.

4) Sulpholane was dried by standing over 4A molecular sieve and then distilled using an electrically jacketed, one metre long fractionating column packed with Fenske glass helices. The distillation was carried out under reduced nitrogen pressure in order to remove traces of water

and sulpholene. The column was operated at a reflux ratio of 10:1 and the fraction b.p. 97°/2 mm. was collected under nitrogen and stored in a desiccator. In order to prevent solidification in the exit from the magnetically operated still-head, lines were traced with low voltage nichrome heaters. No peaks attributable to water were found in the i.r.

5) Other Solvents. Ether, pentane and benzene (Analar) were dried by standing over sodium wire. Toluene (Analar) was dried by standing over 4A molecular sieve and acetone (Analar) dried by standing over calcium sulphate.

6) Levulinic Acid, (3-Acetyl propionic acid). This was prepared according to the method in Organic Syntheses[1] by acid hydrolysis of cane sugar. The reaction product was fractionally distilled to yield colourless levulinic acid, (19.5 g., 26%) b.p. 136 - 138°/10 mm. (Lit. b.p. 137 - 139°/10 mm)[1]. The acid was solid at 20° and the ^{1}H n.m.r. spectrum, singlet at 7.96 τ, intensity 3; multiplet centred at 7.45 τ, intensity 4 ; a singlet at -5.6 τ of intensity 1, showed no detectable enol or lactone form.

7) Anhydrous p-Toluene Sulphonic Acid. A benzene solution of p-toluene sulphonic acid monohydrate was distilled using a Dean and Starke distillation head until the solution was anhydrous. The solution volume was reduced by further distillation until crystals of the anhydrous acid were just precipitated, when the hot solution was decanted under nitrogen onto a glass sinter and allowed to crystallise. The anhydrous acid crystals were collected and dried in a stream of nitrogen. m.p. 38° (Lit. m.p. 38°)[2].

8) 2-Methallyl Chloride. 2-Methallyl chloride was refluxed over magnesium oxide (0.2% w/w) and then distilled collecting the fraction b.p. 70.5°/733 mm. which was stored over 4A molecular sieve.

9) m-Dimethoxy Benzene. The ether was distilled at atmospheric pressure and the fraction b.p. 214 - 215° collected.

10) Methanol. Methanol was first dried with 3A molecular sieve and further dried by treatment with magnesium activated with iodine after the method given by Vogel[3]. The fraction b.p. 65°/760 mm. was collected and stored over 3A molecular sieve.

11) Molecular Sieves. Linde molecular sieves, when required for drying oxygen-sensitive compounds, were twice degassed by prolonged pumping (ca. 1 mm., 4 hr) at 100° and brought back to atmospheric pressure under nitrogen.

12) Acetophenone. Acetophenone was dried by standing over calcium sulphate (24 hr.) and then distilled under reduced nitrogen pressure. The fraction b.p. 57°/2.5 mm. was collected and stored under nitrogen.

13) Methylene-p-Chloroaniline. p-Chloroaniline (20 g.) was dissolved in ethanol (60 ml.) and 40% formalin (15 ml.) added. This was left standing overnight when the deposited white needles were filtered off, washed with a little ethanol and recrystallised from n-hexane. m.p. 139 - 140° (Lit. m.p. 142°)[4].

14) Nitrogen. White spot nitrogen (British Oxygen Co.) was freed from possible traces of other gases by either passage over Badische (B.A.S.F.) catalyst (finely divided copper) to remove oxygen, followed by sodium hydroxide pellets and finally magnesium perchlorate, or by passage through vanadous sulphate solution to remove traces of oxygen, followed by concentrated sulphuric acid, silica gel and finally 4A molecular sieve.

15) Argon. The gas (British Oxygen Co.) was subjected to the second purification treatment given for nitrogen.

16) Nitric oxide. Nitric oxide (Matheson, U.S.A.) was freed from possible higher nitrogen oxides by passage via glass sinters through concentrated

sodium hydroxide solution, concentrated sulphuric acid, over sodium hydroxide pellets and finally 3A molecular sieve. This purification train formed part of the apparatus discussed later in more detail (p. 99).

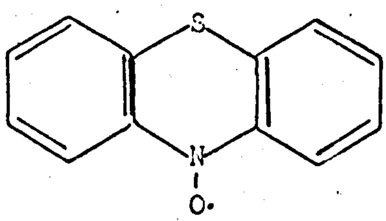
17) Nitrogen Dioxide. When required for injection this was prepared in a syringe by combining 1 vol. of oxygen with 2 vol. of nitric oxide.

18) Cyclohexene. The olefin was freed from peroxides and moisture by refluxing over sodium wire and then fractionally distilled in a nitrogen atmosphere. The fraction b.p. 82.8°/760 mm. was stored under nitrogen in the dark. G.l.c. (Apiezon L at 80°) showed only one component.

b) Inhibitors:-

1) Galvinoxyl. Galvinoxyl was recrystallised from benzene, yielding dark blue crystals of galvinoxyl m.p. 152°, (Lit. m.p. 153.2 - 153.6°)[5]. A very intense maximum was observed in the visible spectrum at 431 nm in agreement with the literature[5].

2) Phenothiazine. The dark green powder was boiled with toluene (charcoal) under reflux and then filtered. On cooling the filtrate deposited pale yellow crystals which were collected, dried and stored under nitrogen. m.p. 181 - 182°, (Lit. m.p. 182 - 183°)[2]. On standing and exposure to the air the mother liquor became pink possibly due to the formation of the nitroxide:-[6]



3) 2,2,6,6-Tetramethyl Piperid-4-one Nitroxide.

i) Triacetonamine. This was prepared from acetone and ammonia by the method of Hall[7]. After working up the product and subjecting it to careful fractional distillation through a 1 metre column packed with Fenske helices, there was obtained triacetonamine (2,2,6,6-tetramethyl piperid-4-one) (258 g., 8%), b.p. 97 - 100°/18 mm., m.p. 36° (Lit. b.p. 102 - 105°/18 mm., m.p. 34 - 36°)[7]. The pale yellow crystals were kept under nitrogen at -20°.

ii) Oxidation to the nitroxide. This was carried out according to the method of Brindley and Allies[8]. Recrystallisation from n-heptane gave the pure compound (9.6g.) m.p. 42 - 44° (Lit. m.p. 36°)[9]; light orange crystals with i.r. spectrum identical to that of an authentic specimen[10], and shown iodometrically to be 99% pure.

4) 2,2,6,6-Tetramethyl Piperidine Nitroxide.

i) 2,2,6,6-Tetramethyl piperidine. The amine was obtained by a modified Wolff-Kishner reduction of triacetonamine after the method of Leonard and Nommensen[11]. After careful fractionation of the product there was obtained 2,2,6,6-tetramethyl piperidine (48 g., 60%) b.p. 152 - 154°/760 mm. (Lit. b.p. 151 - 152°/750 mm.)[11].

ii) Oxidation to the nitroxide. 2,2,6,6-Tetramethyl piperidine nitroxide was obtained by oxidation of 2,2,6,6-tetramethyl piperidine using an analogous procedure as that for 2,2,6,6-tetramethyl piperid-4-one nitroxide. Recrystallisation from n-heptane gave the pure compound (12 g., 32%) m.p. 37° (Lit. m.p. 35°)[12]; red crystals with an i.r. spectrum identical to that of an authentic specimen[10] and shown iodometrically to be 99% pure. The e.s.r. spectrum was a triplet with hyperfine splitting a_N = 15.5 gauss (SI equivalent is 155 mT) arising through coupling of the unpaired electron with the nitrogen atom (Fig. 2).

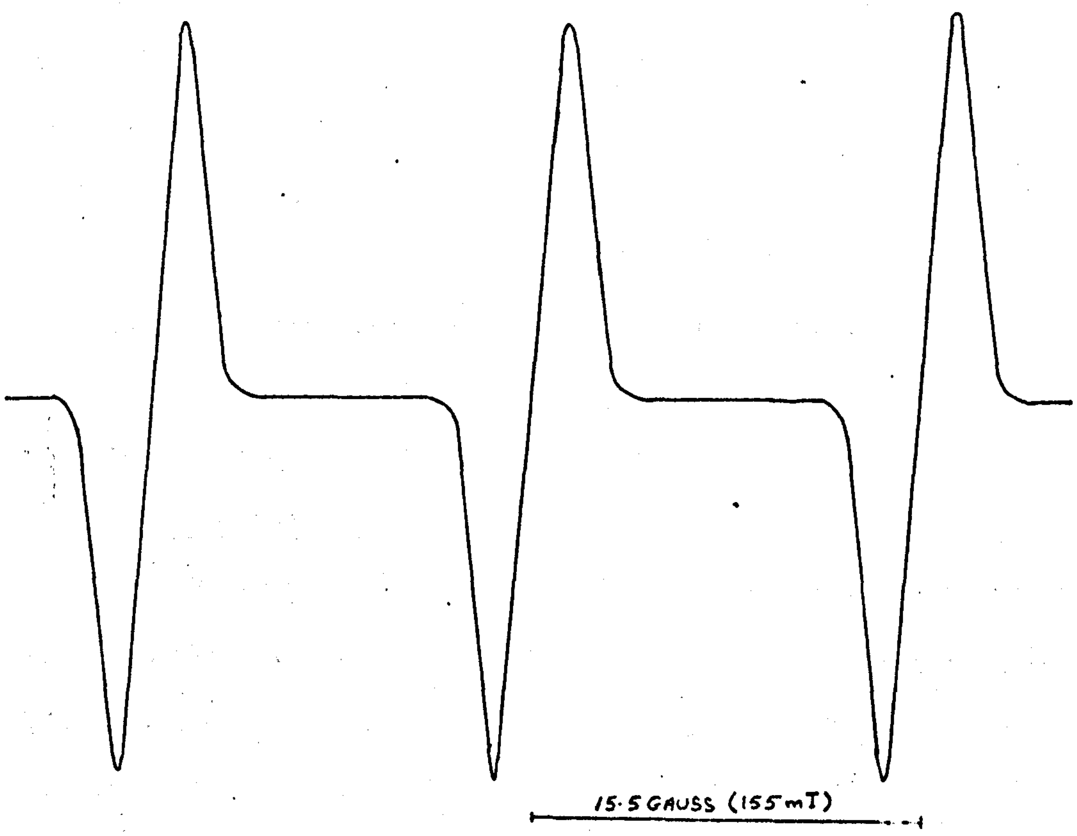


Figure 2 E.S.R. Spectrum of 2,2,6,6-Tetramethyl Piperidine Nitroxide.

5) Diphenylpicryhydrazyl (D.P.P.H.). The stable free radical was obtained commercially and used without further purification.

6) p-t-Butyl Catechol (T.B.C.) The phenol was refluxed with petroleum ether (40 - 60°) and filtered. Cooling (-20°) and seeding caused the deposition of white crystals which were dried and stored under nitrogen. m.p. 54° (Lit. m.p. 55 - 56°)[2].

c) Dienes:-

1) trans,trans-1,4-Diphenyl-1,3-butadiene (D.P.B.). trans,trans-1,4-Diphenyl-1,3-butadiene was recrystallised from toluene. m.p. 152 - 153° (Lit. m.p. 153 - 153.5°)[2]. The white crystals showed purple fluorescence in daylight.

2) Hexachlorocyclopentadiene. The diene was dried by standing over 4Å molecular sieve and then fractionally distilled under reduced nitrogen pressure. The fraction b.p. 79.5 - 80°/1 mm. (Lit. b.p. 80°/1 mm.)[2] was collected and stored under nitrogen in the dark.

3) 2-Methyl-1,3-butadiene (Isoprene). Isoprene was refluxed over sodium (1 hr.) and then distilled at atmospheric pressure under nitrogen using the apparatus described on p.74, operating with a reflux ratio of 15:1. The fraction b.p. 34°/758 mm. (Lit. b.p. 34.5 - 35°/762 mm.)[2] was collected under nitrogen and stored at -20° using phenothiazine as polymerisation inhibitor (0.02% w/v).

4) 2,5-Dimethyl-2,4-hexadiene (1,1,4,4-tetramethyl-1,3-butadiene: T.M.B.)

i) 2,5-Dimethyl-1,5-hexadiene. To a stirred suspension of magnesium turnings (72 g., 3 moles) in tetrahydrofuran (500 ml.) was added bromine (1.5 ml.), and as quickly as possible (ca.2 hr.) a solution of 2-methallyl chloride (540 g., 6 moles), in tetrahydrofuran (1500 ml.) in a nitrogen atmosphere[13]. The solution was allowed to stand (12 hr.). The Grignard was then hydrolysed with 10% acetic acid (100 ml.) and left to stand (24 hr.) when the organic layer was separated. The aqueous layer was saturated with salt, extracted with ether (2 x 250 ml.) and the combined organic layers washed twice with 10% sodium carbonate and finally water (500 ml.) before drying ($MgSO_4$). The dried extract was filtered and distilled in a nitrogen atmosphere to yield 2,5-dimethyl-1,5-hexadiene b.p. 114 - 115°/760 mm.(249 g., 74%) Lit. b.p. 115 - 117°/760 mm.)[4].

ii) Isomerisation of 2,5-dimethyl-1,5-hexadiene. 2,5-Dimethyl-1,6-hexadiene (200 g.) and anhydrous p-toluene sulphonic acid (2 g.) under nitrogen were heated together until reflux and then just sufficiently to maintain reflux until the temperature rose to 132° (ca. 1 hr.)[13].

After refluxing for a further hour the solution was allowed to cool, washed twice with 10% sodium hydroxide solution (150 ml.), water and then dried over magnesium sulphate. G.l.c. analysis on an Apiezon L column at 150° showed better than 95% conversion. Distillation under reduced nitrogen pressure yielded 1,1,4,4-tetramethyl-1,3-butadiene b.p. 75 - 75.5°/100 mm. (158 g., 79%), (Lit. b.p. 75°/100 mm.)[14], stored under nitrogen at -20°. The ^{1}H n.m.r. spectrum showed a doublet at 8.60 τ (split 1:1) and a singlet at 4.39 τ, of relative intensity 1:6.

5) <u>1,4-Diphenylcyclopentadiene</u>.

i) <u>3-Benzoyl propionic acid</u>. 3-Benzoyl propionic acid was prepared by a Friedel Crafts acylation using succinic anhydride (85 g.), benzene (440 g.) and anhydrous aluminium chloride (250 g.) after the procedure given by Vogel[3]. Excess benzene was used as solvent. After work up and drying in a desiccator there was obtained 2-benzoyl propionic acid (142 g., 94%), m.p. 115° (Lit. m.p. 115°)[3].

ii) <u>Ethyl-3-benzoyl propionate</u>. 3-Benzoyl propionic acid (51 g.) was converted to its ethyl ester by refluxing with excess absolute ethanol (150 ml.) using concentrated sulphuric acid (3.6 g.) as catalyst (2 hr.). The excess alcohol was removed by distillation and the product washed successively with water, sodium bicarbonate solution, and finally water. Carbon tetrachloride was added to improve the separation of the organic and aqueous layers. After drying over magnesium sulphate and concentration using a rotary evaporator the liquid was distilled under reduced nitrogen pressure to give ethyl-3-benzoyl propionate (44 g., 60%) b.p. 120 - 121°/<u>ca</u>. 1 mm.

iii) 1,4-Diphenylcyclopentadiene. Ethyl-3-benzoyl propionate (44 g.) was converted to 1,4-diphenyl cyclopentadiene by the base catalysed (sodium ethoxide from 0.42 mole sodium), condensation with acetophenone (25.5 g.) and subsequent warming to 60° to induce decarboxylation, after the method of Adams and Drake[15]. Recrystallisation from a benzene/hexane mixture gave 1,4-diphenyl cyclopentadiene (14 g., 30%) as white needles m.p. 157 - 157.5° (Lit. m.p. 158 - 158.5°)[15], which showed purple fluorescence in benzene solution in daylight but not in chloroform solution. The ^1H n.m.r. spectrum had singlets at 6.23 τ and at 3.05 τ both of intensity 2 and a multiplet centred at 2.81 τ of intensity 10.

6) 2,3-Dichloro-1,3-butadiene (D.C.B.). To a vigorously stirred nitrogen flushed solution of sodium hydroxide (30 g.) in water (400 ml.) at 60° in a nitrogen atmosphere[16], was added 2,3,4-trichlorobut-1-ene (100 g.) supplied by B.P. Chemicals (U.K.) Ltd., containing phenothiazine (0.25% w/w) (12 min.). Stirring was continued (1¼ hr.) and then the mixture was steam distilled to give crude 2,3-dichloro-1,3-butadiene (57.9 g.), and a polymer residue (8 g.). After drying over magnesium sulphate in the presence of phenothiazine (ca. 0.25% w/v) under nitrogen and in the dark, the product was fractionally distilled under reduced nitrogen pressure, using a short helices packed column, with a total reflux/partial take-off head, to give 2,3-dichloro-1,3-butadiene (46.4 g., 60%) b.p. 40.5 - 41°/85 mm., $n_D^{20^\circ}$ 1.4889, (Lit. b.p. 40 - 43°/85 mm., $n_D^{20^\circ}$ 1.4890)[17], collected over phenothiazine (0.02% w/v). G.l.c. analysis on tri-cresyl phosphate at 56° showed only one peak even after running for 4 hours. The product was then transferred to a high-vacuum line, degassed, twice distilled below 0° and stored at -20° under nitrogen in the dark using phenothiazine (0.02% w/v) as inhibitor.

7) 1-Chloro-1,3-butadiene (1-CP.). 1-Chloro-1,3-butadiene, ex. B.P. Chemicals (U.K.) Ltd., was distilled in a nitrogen atmosphere collecting the fraction b.p. 68 - 69° over phenothiazine. The product was then treated on the high-vacuum line and stored as described above.

8) 2-Chloro-1,3-butadiene (Chloroprene; CP.) Chloroprene containing T.B.C. and phenothiazine as inhibitors was degassed under high-vacuum and then three times distilled below 0° the last 10% being rejected, in each case. The product (containing ca. 1% 1-chloro-1,3-butadiene impurity) was stored as described above.

d) Chloroprene Dimers:-

An attempt to bring about the dimerisation of chloroprene using t-butyl catechol (0.5 - 1.0% w/w) as inhibitor at low temperatures (20 - 35°) under nitrogen, had resulted in low yields (ca. 1%) even after 49 days.

The procedure subsequently adopted was analogous to that given by Robb et al[18]. The reaction flasks which were two necked and of ca. 100 ml. capacity, were charged simultaneously with the purified monomer. One neck was closed by a break-seal to which was attached a B19 joint. Inhibitor (Table 9) was introduced through the second neck which was then attached to the high-vacuum line (the inhibitors were predried by high-vacuum pumping). Monomer (ca. 50 ml.) was distilled into each of the vessels which were then sealed off and thermostatted for 14 days (until the D.P.P.H. showed signs of colour change from violet to brown). The flasks were then removed and stored at -78° until required.

The dimer mixture was isolated by attachment of the vessel to the high-vacuum line, cooling to -20°, fracturing the break-seal and removal of excess monomer by high-vacuum distillation. The flask was then allowed to warm to room temperature and the dimers removed by prolonged high-vacuum pumping into a nitrogen trap. The dimer mixtures were stored under nitrogen at -20°. Table 9 is a summary of the experimental details.

The recovered monomer was gas chromatographed using a 2 metre Apiezon L column at 60° and was shown to be pure monomer (+1-chloro-1,3-butadiene impurity). Each dimer mixture was chromatographed using the same column at 100° and 300 ml./min. carrier gas flow (H_2) and was found to consist of 1,2-dichloro-1,2-divinyl cyclobutane (Ret. time 29.5 min.), together with a possible mixture of 1-chloro-4-(α-chloro vinyl)-cyclohexene-1, and 2-chloro-4-(α-chlorovinyl)-cyclohexene-1 (Ret. time 79 min.), in an approximate ratio of 3:2. The chromatogram also showed some residual monomer (<u>ca</u>. 7%) and the presence of two small (less than 2%) unidentified peaks after 31.5 and 33.5 min. The i.r. spectra of the separated dimers are shown in Figures 3 and 4. The ^{1}H n.m.r. spectrum of the cyclobutane derivative showed quartets centred at 3.79 and 4.7 τ and a multiplet centred at 7.5 τ of relative intensity 1:2:2; and that of the cyclohexene derivative singlets at 4.24 and 4.82 τ and a multiplet centred at 7.85 τ of relative intensity 1:2:7. The mass spectra of the individual dimers were recorded on A.E.I. M.S.9, by B.P. Chemicals (U.K.) Ltd., and A.E.I. M.S.2 spectrometers. The cracking pattern of these dimers under varying conditions and that of 1,6-dichloro-1,5-cyclo-octadiene [prepared by B.P. Chemicals (U.K.) Ltd.], are shown in Table 10 along with that of chloroprene for comparison. The temperature of the mass spectrometer sources was <u>ca</u>. 200°.

TABLE 9

Chloroprene Dimerisation at 35°.

Inhibitor 0.127 mM	% Recovered monomer (w/w)	% Dimer mixture (w/w)	% Residue (w/w)
TBC.	66.8	17.7	15.5[a]
Nitroxide[b]	78.5	14	7.5
DPPH.	79.5	6.5	14.0
Galvinoxyl	79.5	6.2	14.3

a Includes 4.3% 'popcorn' polymer.

b 2,2,6,6-Tetramethyl Piperid-4-one Nitroxide.

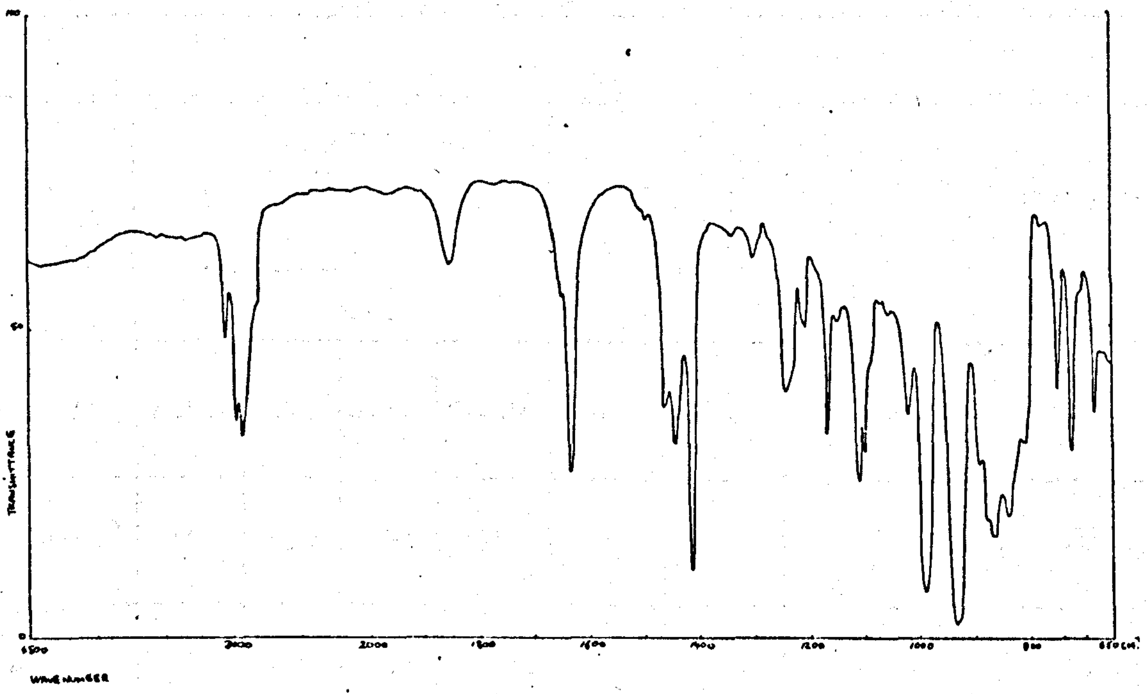


Figure 3 Infrared Spectrum of 1,2-Dichloro-1,2-divinylcyclobutane.

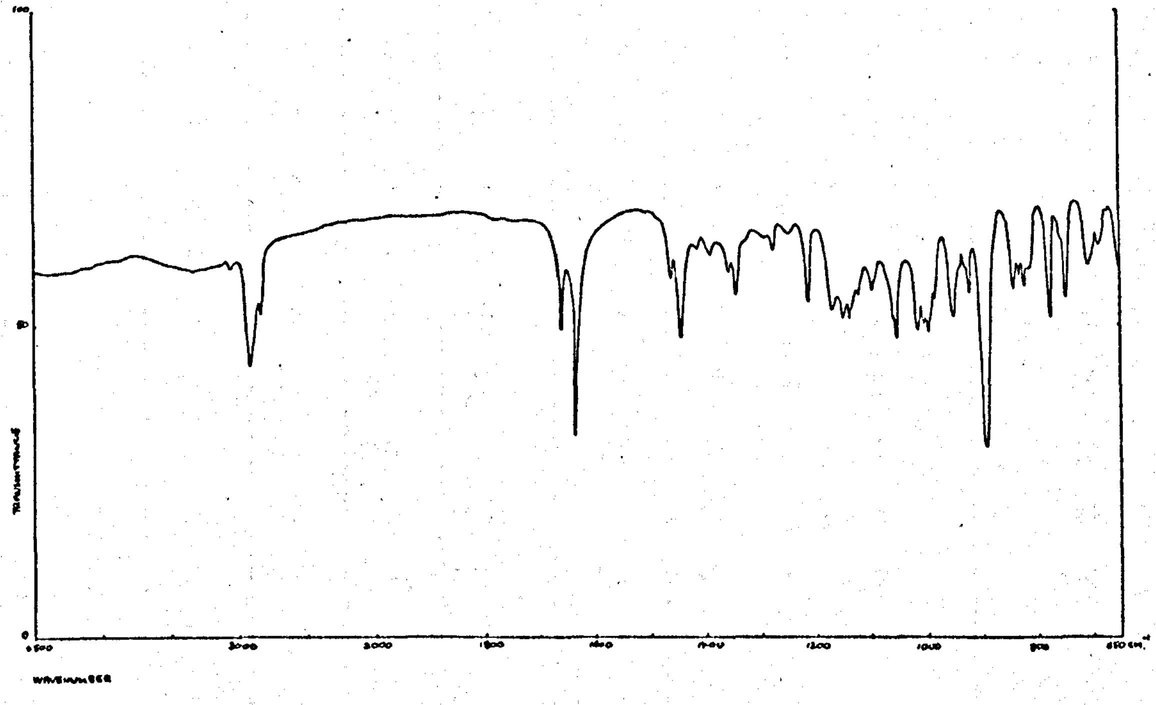
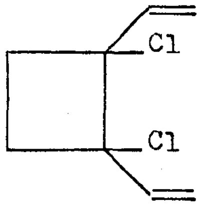
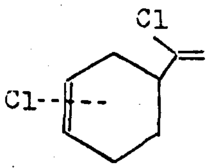
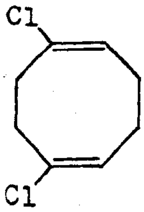


Figure 4 Infrared Spectrum of a Possible Mixture of 1-and 2-Chloro-4-(α-chlorovinyl)-cyclohexene-1.

TABLE 10

Mass Spectra of Chloroprene Dimers (70 ev) (Relative Intensity m/e 88=100)^{a}.

Compound								Chloroprene
Instrument	M.S.2	M.S.9	M.S.9	M.S.9	M.S.2	M.S.9	M.S.9	M.S.2
Inlet Temp.°	80	65	100	175	80	80	175	80
m/e								
37	2	7	4	11	2	-	-	6
38	5	13	10	22	4	4	-	4
39	21	92	83	100	73	15	14	8
40	5	7	4	11	4	4	2	-
41	-	18	19	18	4	7	4	-
42	-	12	-	-	-	-	-	-
43	6	12	-	-	7	7	-	-
49	4	7	8	14	3	1	2	10
50	77	33	52	79	11	8	5	28
51	35	87	110	52	23	18	15	32
52	22	59	55	61	17	13	11	29
53	62	93	54	112	42	44	37	140
54	3	13	9	7	2	4	2	7
58	2	-	-	-	2	-	-	-
60	-	3	6	-	-	-	-	-
61	3	5	8	11	2	-	2	6

m/e	80	65	100	175	80	80	175	80
62	5	13	11	18	4	2	2	10
63	7	21	15	36	5	4	3	3
64	2	5	6	7	-	-	-	3
65	11	35	33	39	2	6	8	-
66	4	9	8	7	-	2	-	-
73	3	15	8	18	3	2	2	4
74	3	18	13	25	2	2	2	-
75	6	-	17	36	5	3	2	-
76	2	11	8	14	-	-	-	-
77	33	100	111	90	23	19	11	-
78	21	91	62	56	7	7	3	-
79	25	83	73	112	15	15	11	-
80	4	10	8	11	2	5	2	-
87	2	3	4	7	-	-	-	3
88	100	100	100	100	100	100	100	100
89	7	12	8	18	5	6	5	6
90	31	31	21	36	25	32	32	34
91	32	165	85	57	7	9	3	1
92	2	13	6	7	-	-	-	-
93	3	11	-	-	3	7	2	
99	2	5	6	7	2	2	2	

m/e	80	65	100	175	80	80	175	80
101	3	11	6	14	2	3	3	
102	2	8	9	18	2	1	-	
103	2	36	48	100	9	7	3	
104	5	13	19	39	3	3	-	
105	65	165	191	360	45	35	24	
106	19	92	54	43	5	6	2	
112	4	13	23	50	4	5	2	
113	7	13	15	21	7	10	7	
114	4	11	9	21	4	4	4	
115	3	5	6	7	3	4	2	
116	-	-	-	-	-	-	2	
125	13	13	23	43	9	6	2	
127	7	8	13	21	5	5	2	
140	16	66	66	126	15	11	1.7	
141	21	25	13	36	18	19	52	
142	4	15	21	43	6	6	4.6	
143	4	8	6	14	6	6	16	
148	-	-	1	1.5	-	-	1.7	
156	-	-	0.4	1	-	-	1.1	
152	-	-	0.2	0.4	-	-	0.1	
176	4.3	3.6	0.9	3.2	3.9	2.6	4	

m/e	80	65	100	175	80	80	175	80
178	2.6	1.8	0.9	2.2	2.6	1.3	1.7	
180	0.4	0.9	0.4	0.8	0.4	0.2	0.6	

a Source temperature *ca*. 200°; apart from peaks 91 (chloroprene only), 140 (cyclo-octadiene only) and 148 to 180, only peaks of relative intensity to the base peak = 100%, greater than or equal to 2%, are recorded.

e) Analyses:-

1) Free Radicals. The sample (ca. 0.1 g.) was shaken under nitrogen for a few minutes with glacial acetic acid (25 ml.), benzene (25 ml.) and sodium iodide (1 g.), then diluted with water (100 ml.) and the liberated iodine titrated with N/10 sodium thiosulphate.

2) Elemental Analysis. Elemental analysis was carried out by B.P. Chemicals (U.K.) Ltd.

3) Analysis of Off Gases. Early in the course of this investigation it was necessary to analyse mixtures of gases containing nitrogen and oxides of nitrogen. Attempts to analyse mixtures of nitrogen and nitric oxide by mass spectrometry proved unreliable since nitric oxide disproportionated into nitrogen dioxide and nitrogen in the instrument and resulted in a false analysis[19]. It was found that nitric oxide and nitrogen could be separated by gas-solid absorption chromatography (g.s.c.) using a Porapak 'Q' column. (Porapak 'Q' is a polymer of ethyl vinyl benzene with divinyl benzene cross links[20] supplied by Waters Associates Inc.). A 2 metre analytical column (5 mm. diameter) was made up. Before use the column was fitted into a Perkin Elmer 451 Fractometer and purged with hydrogen at 100° (36 hr.). A typical trace obtained by these columns using a hot wire detector with a hydrogen flow of 35 ml/min. at 20° is shown in Figure 5.

4) Infrared spectra. The infrared spectra of solids were recorded as nujol and hexachlorobutadiene mulls, and oils as thin films, between sodium chloride plates on a Unicam S.P.200 spectrometer. Polystyrene bands at 1603 $cm.^{-1}$ and 2851 $cm.^{-1}$ were used as calibration marks.

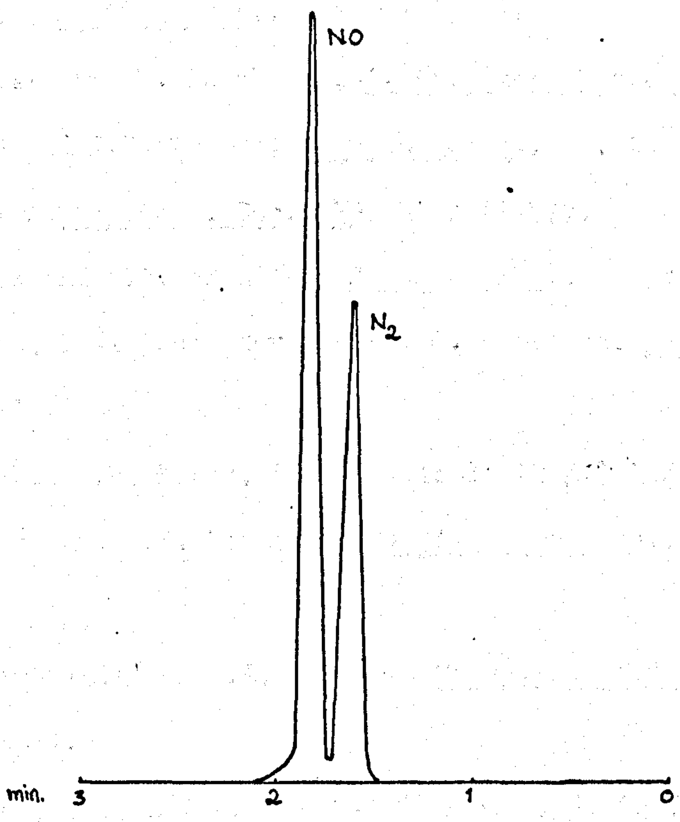


Figure 5 Porapak 'Q' Trace.

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CHAPTER 5

Studies on the Interaction of Nitric Oxide with Olefins.

a) Experimental Technique:- Since in most cases the conjugated olefins were exceedingly oxygen sensitive (chloroprene[1,2]), extensive precautions were taken to exclude air both in their preparation, purification (p.78) and in subsequent manipulations. All solvents were subjected to prolonged bubbling with nitrogen and all operations such as filtration were conducted under nitrogen. Ground glass joints were lubricated with silicone grease and spring loaded. Particular attention was paid to the cleansing of the reaction vessels (Figs. 6 and 7). These were first rinsed well with solvent and then scoured by prolonged contact with strong alkali. Periodically chromic acid was used after alkali treatment. The flasks were then rinsed well with water, dried in an oven at 140° and allowed to cool in a stream of inert gas.

i) Chloroprene, 1-chloro-1,3-butadiene, 2,3-dichloro-1,3-butadiene, 1,1,4,4-tetramethyl-1,3-butadiene, isoprene and cyclohexene.

Immediately before use these olefins were degassed under high-vacuum and then trap to trap distilled twice at less than 0°. The distillate was collected in the apparatus shown (Fig. 8) which had been thoroughly flushed with nitrogen before it was attached to the vacuum line at the joint A, with tap B closed, and then evacuated. The olefin was distilled into the bulb C (ca. 15 ml. capacity), allowed to warm to approximately 0° and brought up to atmospheric pressure with nitrogen. After closure of tap D, the apparatus was removed from the vacuum line and with B open, the pressure inside the vessel increased to a little above atmospheric by insertion through S of the hyperdermic needle connected to the nitrogen supply. This ensured that there was no ingress of air

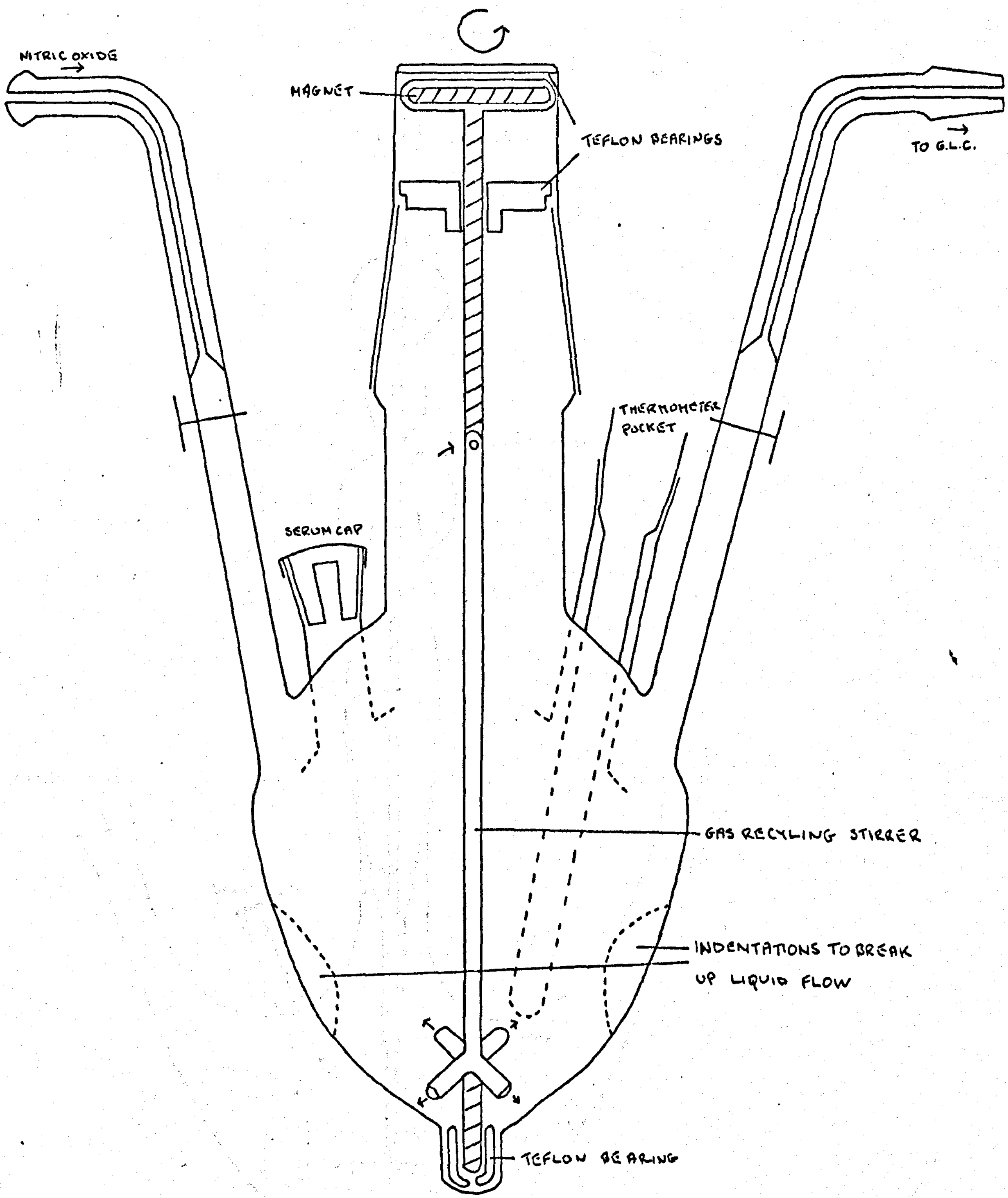


Figure 6 Small Reaction Flask.

(*ca.* 100 ml.)

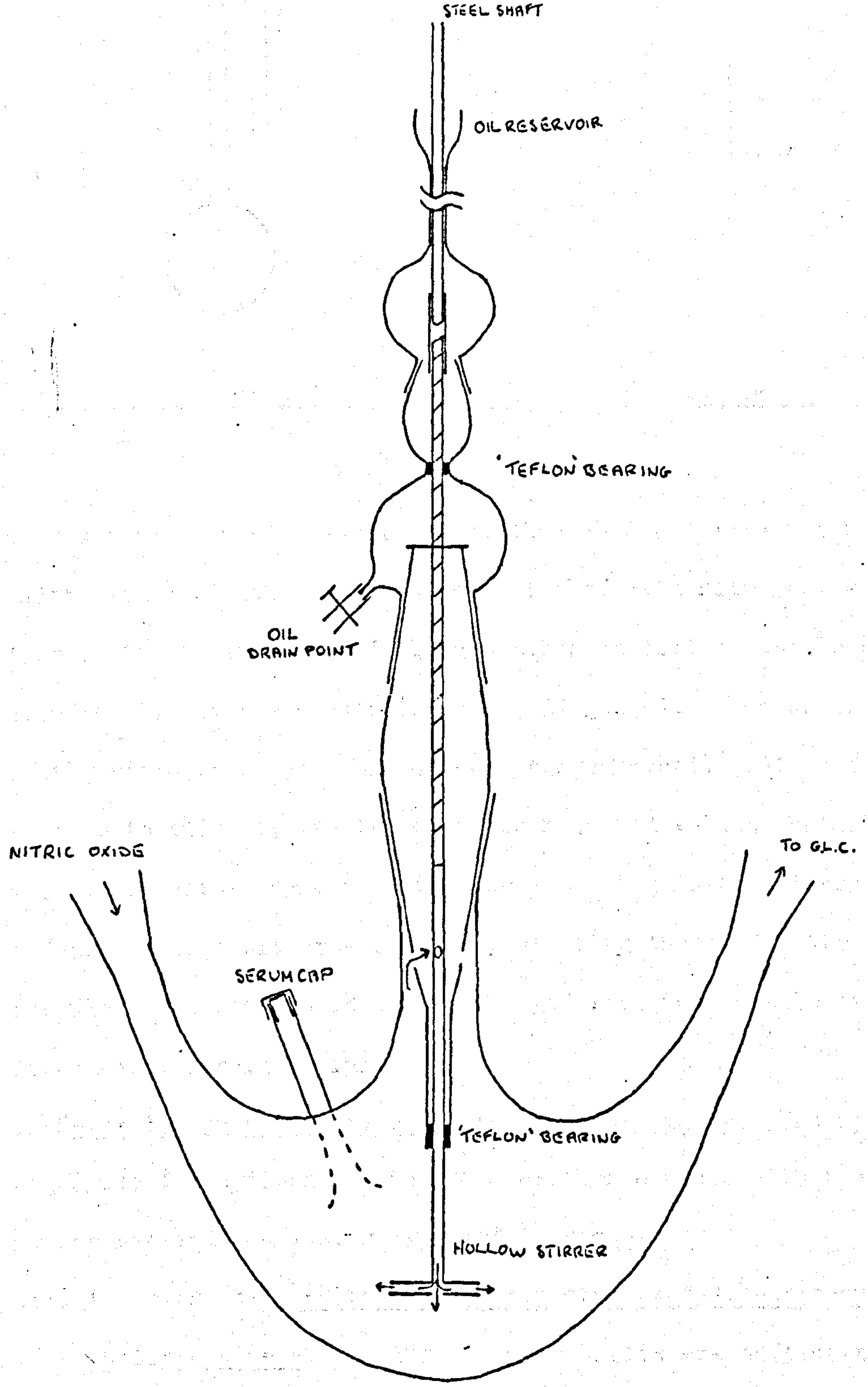


Figure 7 Large Reaction Flask.

(*ca*. 500 ml.)

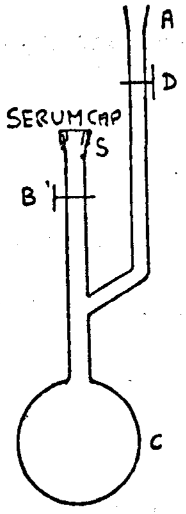


Figure 8 Olefin Collection Flask.

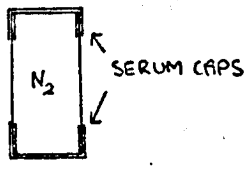


Figure 9 Nitrogen Capsule.

when a syringe needle was inserted through S and into the bulb C. The calibrated syringe, which had been flushed with nitrogen, was protected from contact with air by fitting a nitrogen filled capsule (Fig. 9) over the tip of the needle (22.5 cm, 23 gauge). The diene was forced by the nitrogen pressure into the syringe barrel. After filling the syringe to slightly greater than the required volume the apparatus was depressurised by means of a three way tap in the nitrogen inlet and the syringe withdrawn, again protecting the needle tip with the capsule. Excess liquid was discharged into the capsule leaving the diene ready for injection.

ii) Hexachlorocylopentadiene and chloroprene dimers. The apparatus of Figure 8 was flushed with nitrogen then charged with the olefin by syringe and the latter degassed *in vacuo*.

iii) trans,trans-1,4-Diphenyl-1,3-butadiene and 1,4-diphenylcyclopentadiene. Because neither olefin was sufficiently soluble in a suitable solvent to allow handling in the above manner the following procedure was adopted. Stirred benzene solutions were flushed with argon (2 - 3 hr.). The stirrer was then stopped and nitric oxide passed through the system until gas analyses (g.s.c.) showed that all argon had been displaced (ca. 1 hr.). Zero reaction time was taken as the point when the stirrer was restarted (c.f. injection of olefin p. 99). This procedure was justified for the following reasons:

1) No alteration of gas analysis was noticed when nitric oxide was passed over such solutions at 15° for twice the normal reaction time.

2). No colouration of the solution was produced. (Slight darkening of a solution of trans,trans-1,4-diphenyl-1,3-butadiene was noted after 3.5 hr. nitric oxide flow).

3) trans,trans-1,4-Diphenyl-1,3-butadiene was recovered unchanged as shown by i.r. after similar treatment (2 hr.).

4) Nitric oxide is almost insoluble in benzene (0.02% w/w at 5°)[3a].

5) Argon is stated as being 8% (v/v) soluble in benzene[3b] and, although gas analysis was unable to distinguish between argon and nitrogen, the release of this small volume of gas dissolved in the benzene solvent would not significantly affect the analyses.

iv) The reaction system:- Early experiments using the static system of a gas burette were unsatisfactory since nitrogen was continuously produced.

A dynamic system was therefore designed. Argon, for flushing purposes, or nitric oxide at a known rate (measured by a flow meter), was introduced via a three way tap, to a vigorously stirred solution of the olefin (solvent usually benzene). The system was protected by a mercury safety valve on the inlet side.

The stirrer in the reaction flask consisted of a shaft running in two 'Teflon' bushes and bearing on a similar disc at the top. (Fig.6). A small glass encased magnet was attached to the top of the shaft as shown and was activated from above by an 'Eclipse' horseshoe magnet, centrally mounted and driven up to 6,000 r.p.m. (measured with a stroboscope) by an Anderman multi-speed stirrer. The lower part of the shaft was hollow and thus gas was recycled through the liquid.

The off gases were led in 2 mm. O.D. stainless steel pipe <u>via</u> a trap (-78°), which condensed volatile materials including the higher nitrogen oxides, to a gas sampling valve. This enabled a sample (<u>ca</u>. 0.5 ml.) of gas to be injected into the Porapak 'Q' columns described earlier (p. 90). The length of pipe was kept as short as possible in order to reduce the dead space between the reaction vessel and point of injection. Glass to metal connections were butt joined using short lengths of 'polythene' tubing and the joints sealed with 'Araldite' resin. A silicone oil bubbler allowing the gases to escape to waste completed the system.

b) <u>Experimental Procedure</u>:-

A typical run was performed as follows:- Benzene (50 ml.) was placed in the reaction flask, the stirrer started (usually 1000-2000 r.p.m.) and the solvent degassed by prolonged flushing with argon (2-3 hr.). The argon flow was then stopped and the system flushed with nitric oxide (2-3 hr.) at the desired flow rate (usually 50 ml./min.). A Dewar flask (-78°) was placed around the trap and after approximately 1 hour a series of gas samples was taken and analysed by g.s.c. to ensure that all argon had been displaced. The solvent was then cooled (usually 6°) by immersion in an ice/water bath and the stirrer stopped. The liquid olefin, prepared as described earlier (p. 94), was injected below the solvent surface, stirring recommenced and a stop clock started. Generally there was a rapid, slightly exothermic, absorption of gas and the solution simultaneously became blue or green. In some cases, there was precipitation of a white solid after a few minutes and the solution went from blue/green to amber and this was accompanied by evolution of nitrogen. Gas samples were taken at intervals of about 2 minutes throughout the experiment which was terminated when the analyses showed that nitrogen evolution had ceased. Careful note was made of the times when the above phenomena occurred.

At the end of the experiment the nitric oxide flow was halted and the system flushed with argon (1-2 hr.). The product was worked up in the following manner; during the flushing period, if the olefin was originally a liquid, the reaction solution was examined by g.l.c. for unreacted olefin. The contents of the cold trap were similarily examined at the end of the flushing period. Occasionally the trap contained a very small amount of oil. After flushing, any precipitate formed during the reaction was filtered (under nitrogen cover) and the reaction flask rinsed with ether or acetone. The solid was dried by suction in a stream of nitrogen. Evaporation of the filtrate on a rotary evaporator (down to 10^{-2} mm./20^{o}) left a brown viscous oil. When a solid diolefin was used that part unreacted was recovered at this stage.

In view of the known hazards associated with certain compounds formed by reaction of organic compounds with oxides of nitrogen, all experiments were carried out (a) on a small scale, (b) behind safety screens and (c) using thick leather gloves during manipulations. Differential scanning calorimetry (d.s.c.) and hammer tests were carried out on all products before the above safety precautions were relaxed.

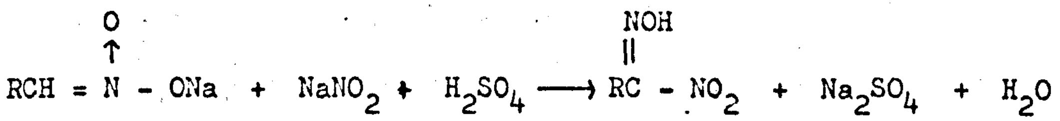
Attempts were made to distil some of the oil adducts under reduced nitrogen pressure behind safety screens. In most cases this gave no volatile material except nitrogen oxides, and in one, that of isoprene, this led to a 'fume off' as benzene solvent was being removed at 80^{o}.

Typical experimental details for the olefins used are summarised in Table 11. Elemental analyses for the oil adducts are collected in Table 12.(p. 112).

c) Examination of Reaction Products:-

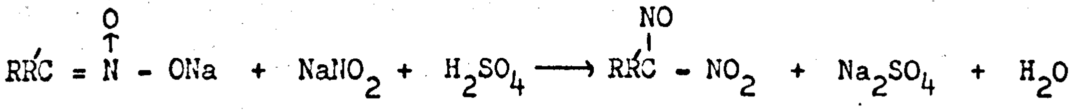
1) Differential Scanning Calorimetry (d.s.c.). Small quantities (1-2 mg.) of the adducts - both solid and viscous liquid adducts - obtained in these experiments were examined by d.s.c. using a Perkin Elmer D.S.C. 1B. Sealed pans, a nitrogen flow of 15 ml./min., and a heating rate of 8°/min. were used. The results are given in Table 13.

2) Alkali. The adducts (ca. 0.1 g.) were treated with concentrated sodium hydroxide, excess sodium nitrite solution and cautiously acidified with dilute sulphuric acid. Table 14 is a summary of the results obtained. Primary nitro compounds give an intense red colour disappearing on acidification. The colouration is that of the sodium salt of the nitrolic acid:-



$$RCH = \overset{O}{\overset{\uparrow}{N}} - ONa + NaNO_2 + H_2SO_4 \longrightarrow \overset{NOH}{\overset{\|}{RC}} - NO_2 + Na_2SO_4 + H_2O \quad (1)$$

Secondary nitro compounds give dark blue or green colours due to the nitro-nitroso derivative:-



$$RR'C = \overset{O}{\overset{\uparrow}{N}} - ONa + NaNO_2 + H_2SO_4 \longrightarrow RR'\overset{NO}{\overset{|}{C}} - NO_2 + Na_2SO_4 + H_2O \quad (2)$$

Tertiary nitro compounds give no colouration.

The oil adducts derived from chloroprene and 2,3-dichloro-1,3-butadiene were treated with anhydrous sodium methoxide in methanol, but no sodium salts were precipitated.

3) Gel Permeation Chromatography (g.p.c.). Attempts to separate the constituents of nitric oxide/chloroprene oil adducts by thin layer and column chromatography gave unsatisfactory results. Some resolution was

achieved by g.p.c. run by B.P. Chemicals (U.K.) Ltd., on a Waters G.P.C. 200 instrument. A series of five columns was used with upper permeability limits of 10^4, 10^3, 10^3, 10^2 and 10 Å (1Å = 10^{-1}nm) consisting of polystyrene, cross linked with divinyl benzene. The chromatograms obtained for the oil adducts from chloroprene (1% in tetrahydrofuran; 35°) and 2,3-dichloro-1,3-butadiene (1% in toluene; 25°) are shown in Figures 10 and 11.

4) Vapour Phase Osmometry. The number average molecular weight ($\bar{M}_n$) of several of the oil adducts was measured with a Hewlett Packard 301A vapour phase osmometer. The results are summarised in Table 15.

5) Infrared Spectroscopy. The spectra of the oil adducts of chloroprene, isoprene, 2,3-dichloro-1,3-butadiene, 1-chloro-1,3-butadiene and 1,1,4,4-tetramethyl-1,3-butadiene are shown in Figures 12 to 16. These all show bands characteristic of nitrate esters (near 1640, 1280, 855, 755 and 700 cm.$^{-1}$) and nitro groups (near 1570 and 1375 cm.$^{-1}$). A further characteristic is a broad band near 3400 cm.$^{-1}$ in the OH or NH stretching range. The 1,1,4,4-tetramethyl-1,3-butadiene oil adduct has additional bands at 1535 (shoulder) and 1400, 1370 and 1350 cm.$^{-1}$ (NO_2 sym. str.) and the 1-chloro-1,3-butadiene adduct an additional band at 1350 (NO_2 sym. str.). Some of the oils have weak bands near 1730 cm.$^{-1}$ due to a carbonyl group, near 1200 cm.$^{-1}$, possibly due to an ester and near 1140 cm.$^{-1}$ possibly due to an ether linkage or tertiary alcohol.

6) Cryoscopy. A cryoscopy apparatus was constructed as described by Finch et al.[4] This was calibrated with pure naphthalene (micro-analytical standard) for both sulpholane and benzene solvents, and dry nitrogen atmospheres were used in all determinations. A molecular weight of 209 was obtained for benzil in sulpholane (Mol. Wt. required = 210).

d) Nitric Oxide-Olefin Reactions.

1) Chloroprene. (ref. Table 11). White crystals of bis-(2-chloro-1-nitro-

4-nitrosobut-2-ene) (0.32g. 18%) m.p. 110° (decomp.) (Found: C,29.2; H,3.0; Cl,20.9; N,17.0. $C_4H_5ClN_2O_3$ requires C,29.2; H,3.0; Cl,21.3; N,17.1%) were isolated from the interaction of nitric oxide and chloroprene (0.98g.). Cryoscopic determination of the molecular weight in sulpholane gave 280 $\left[(C_4H_5ClN_2O_3)_2 \text{ requires Mol. Wt.} = 328 \right]$. The solid was subjected to chemical and physical investigation.

i) Solubility. Chemical investigation of the solid was difficult because of its insolubility in most organic solvents. Solution was observed only with nitromethane and sulpholane which gave pale green solutions. Bases also effected solution but intractable oils were recovered. The solid was recrystallised from a mixture of sulpholane and water.

ii) Nitric Oxide. A suspension of the solid in benzene was shown to be inert towards nitric oxide at 20°. A solution of the solid in sulpholane at 30° was also found to be unreactive towards nitric oxide (6.5 hr.). The pale green solution slowly became brown but no gases were evolved nor were any volatile compounds retained by the cold trap. After flushing with argon, water was added to part of the solution giving a white suspension that could not be separated by filtration or centrifugation. Part of the solution was treated with alkali to give a red colour that faded on acidification. Extraction of the brown sulpholane solution with petroleum ether did not give any further separation.

iii) Levulinic Acid. The solid (0.38g.) was stirred with a mixture of levulinic acid (10 ml.) and 1N hydrochloric acid (1 ml.) in a nitrogen atmosphere, at 20°, in the dark, after the method of De Puy[6]. After two hours there was no indication that the solid was dissolving and so the temperature was increased to 30° (16 hr.). As solid was still evident the temperature was raised to 50° which resulted in complete solution (2.5 hr.). Water (10 ml.) was then added and the solution extracted with ether (4x10 ml.)

The organic layer was washed with saturated bicarbonate solution until the washings were just alkaline (litmus) and then dried (magnesium sulphate). The ether was removed in vacuo to leave a pale yellow oil (0.29g.) whose i.r. was inconclusive but there was a broad band at 3400 cm.$^{-1}$ in the OH region. An attempt to form a benzoate derivative was unsuccessful.

iv) Benzene, toluene. A suspension of the solid in either solvents was slowly heated to reflux under nitrogen to give dark brown solutions. A slow stream of nitrogen swept any evolved gases into wash bottles containing alkali and acidified ferrous sulphate solutions. Chloride (silver nitrate test) or nitrate ions (diphenylamine test) were not detected in the alkali at the end of the experiment and the colour of the ferrous sulphate solution was unchanged. The solvents were removed in vacuo to leave brown gums. D.s.c. analysis of these was not significant. I.r., bands at 1640, 1570 (NO_2 asym. str.); 1380, 1280 cm.$^{-1}$ (NO_2 sym. str.), showed the presence of nitro and nitrate groups. Elementary analysis (Found: C,42.6; H,3.9; Cl,14.7; N,10.5%) corresponded to an empirical formula of $C_4H_{4.5}Cl_{0.5}N_{0.8}O_{1.8}$.

v) Ammonia. The treatment of the solid which was under nitrogen, with dry ammonia gas at room temperature resulted in a 'fume off'. When repeated at -78°, (liquid NH_3) a deep red solution resulted. Evaporation of the excess ammonia led to a brown water soluble solid (Found: C,23.8; H,5.5; Cl,19.9; N,27.4; ionisable Cl,20.2; hydrolysable N,16.9%), showed a weight increase of corresponding to an uptake of 2 mol. of ammonia. Elementary analysis gave $C_4H_{11.1}Cl_{1.2}N_{3.9}O_{2.9}$ as an empirical formula. A small weight loss (less than 1%) occurred on pumping (10^{-3} mm.) at room temperature for several hours. Tituration with chloroform did not lead to extraction of the solid. The i.r. was inconclusive and the ^1H n.m.r. spectrum (in D_2O) had two doublets centred at 1.05 and 2.65 τ (J = 3 Hz) and a singlet at 2.18 τ all of equal intensity. The mass spectrum had few fragments and the highest of m/e 82 had no chlorine.

vi) Sodium Borohydride.[7] To a stirred suspension of the solid (0.62g.) in acetonitrile (20 ml.) at 0° under nitrogen was slowly added (over 0.5 hr.) sodium borohydride (1.0g.) in water (20 ml.) stabilised with alkali. The pH of the suspension was maintained at 3.5-6 by the addition of 3N hydrochloric acid. The suspension was left stirring at 0° (3 hr.) but solution was not realised. Filtration gave a solid (0.56g.) whose i.r. was identical to the original solid.

vii) Catalytic Hydrogenation. Catalytic hydrogenation was attempted at atmospheric pressure and room temperature with either palladium on charcoal, platinum oxide (Adams Catalyst) or Raney nickel in ethanol or acetic acid solvents. Insignificant gas uptake resulted. Using sulpholane solvent at 30°, atmospheric pressure and palladium on charcoal catalyst hydrogen was absorbed (2.7 mol.; 18 hr.) and a brown solution was formed. Additional tests were inconclusive.

viii) Thermal Stability. The thermal stability did not alter markedly over a period of 72 days if stored at room temperature in air, or at -20° under nitrogen. After one year the sample stored in air had become semi-solid while that under nitrogen had retained all its original properties.

ix) Spectra. The i.r. and mass[5] spectra of the white crystalline solid are shown in Figures 17 and 24. The mass spectrum was run at an inlet temperature of 100° using a direct insertion probe and a source temperature of 200°. The i.r. spectrum had bands at 1672 (C = C str.); 1640 (N = N str.); 1550, 1375 (NO_2 asym. and sym. str.); 1425 (CH deformn. of CH_2NO_2); 1235, 1205 (nitroso dimer) and 745 cm.$^{-1}$ (C - Cl str.). The ^1H n.m.r. spectrum $[(CD_3)_2SO]$ - triplet centred at 3.32τ (J = 6Hz), singlet at 4.27τ, doublet centred at 4.85τ (J = 6Hz) - changed slowly with time. These results are considered in Ch. 7.

Distillation of oil adduct. No volatile material was obtained from a chloroprene oil even at 100°/0.05 mm. Molecular distillation of the oil at

10^{-3} mm. gave an appreciable condensate at 40° and a slow evaporation up to 100°. The inability to reduce the pressure further suggested that a slow decomposition was occurring. The i.r. of the distillate showed that the broad band at 3300 cm.$^{-1}$ (OH, NH str.) in the original oil was moved to 3350 cm.$^{-1}$ and a sharp band at 2150 cm.$^{-1}$ ($C \equiv C$, $C \equiv N$ str.) was present. After storing one month under nitrogen at 5° this band was no longer present.

2) <u>2,3-Dichloro-1,3-butadiene</u>. (ref. Table 11). White crystals of bis-(2,3-dichloro-1-nitro-4-nitrosobut-2-ene) m.p. 107° (decomp.). (Found: C,24.3; H,2.0; Cl,34.7; N,13.6. $C_4H_4Cl_2N_2O_3$ requires C,24.3; H,2.0; Cl,35.8; N,14.1%) were isolated from the interaction of nitric oxide with 2,3-dichloro-1,3-butadiene in up to 40% yield. Molecular weight (by cryoscopy in sulpholane) = 196 ($C_4H_4Cl_2N_2O_3$ requires Mol. Wt. 198).

i) <u>Solubility.</u> The solid was insoluble in a wide range of organic solvents (partially soluble in nitromethane), but was recrystallised by dissolution in sulpholane and subsequent rapid additon of water to the pale green solution.

ii) <u>Spectra</u>. The mass (70 and 20 ev) and i.r. spectra are shown in Figs. 25,26 and 18. The i.r. spectrum had bands at 1640 ($N = N$ str.); 1570, 1375 (NO_2 asym. and sym. str.); 1425 (CH deformn. of CH_2NO_2) and 1245, 1210 cm.$^{-1}$ (nitroso dimer). The ^1H n.m.r. spectrum had a singlet at 1.6τ and a series of 6 peaks between 4.08 and 4.62τ. The spectrum was continually changing with time and after 24 hr. the same solution had singlets at 1.48, 1.60, 3.98, 4.05 and 4.20τ. The intensities of both spectra were inconclusive. The results of the spectra are considered in Ch. 7.

iii) <u>Tautomeric Isomerisation to Oxime</u>. The solid (0.4g.) was cautiously warmed (<u>ca</u>. 50°) with nitromethane (40 ml.) until solution was complete. The pale green solution after standing overnight was almost colourless and on cooling (-20°) deposited white crystals of 2,3-dichloro-4-nitrobut-2-enaldoxime (0.38g., 95%) m.p. 120°, which was recrystallised from nitromethane. (Found: C,24.5; H,2.0; Cl,34.5; N,14.4; Mol. Wt. = 194 in sulpholane. $C_4H_4Cl_2N_2O_3$ requires C,24.3; H,2.0; Cl,35.8; N,14.1%; Mol. Wt. = 198). The i.r. and mass spectra are shown in Figures 19 and 27. The i.r. spectrum had bands at 3250 (OH of oxime); 1620 (C = N str.); 1570, 1380 (NO_2 asym. and sym. str.); 1295, 980 (NO); and 670 cm.$^{-1}$ (C - Cl str.). The ^1H n.m.r. spectrum (in $CDCl_3$) had singlets at 1.28, 1.58 and 4.5τ of relative intensity 1:1:2.

Oil Product. During the isolation of the oil adduct in the normal manner (p.100) decomposition of the oil occurred since a blue solid (N_2O_3) was found in the cold trap protecting the pump. A small quantity of water was also trapped. This was acid to litmus but gave no precipitate with silver nitrate indicating the absence of chloride ions.

3) 1,1,4,4-Tetramethyl-1,3-butadiene. The characteristics of the reaction of this olefin are given in Table 11. A small quantity of 1,4-dinitro-1,1,4,4-tetramethylbut-2-ene (0.41g. 4.7%), b.p. 87-95°/1 mm., m.p. 131-133°, was obtained by distillation of an oil adduct (9.6g.) of nitric oxide and 1,1,4,4-tetramethyl-1,3-butadiene. After recrystallisation from ether the solid had the following analysis. (Found: C,47.5; H,7.0; N,13.6. $C_8H_{14}N_2O_4$ requires C,47.5; H,7.0; N,13.9%). The i.r. spectrum (Fig. 20) shows bands at 1540 (NO_2 asym. str.); 1400, 1380, 1350 (the bands are weak due to the low concentration of the hexachlorobutadiene mull) and 860 (NO_2 sym. str.); and 890 cm.$^{-1}$ (out-of-plane = CH deformn. vib. of trans. disub. ethylene). A bright blue solid in the cold trap protecting the pump indicated that decomposition of the oil had occurred during its distillation; the oil having been heated to a maximum of 150°. On warming to 20° the blue solid disappeared leaving two immiscible liquids (1.2g.) which smelt strongly of

acetic acid. One liquid was colourless and the other bright green. The latter quickly changed to brown on standing, under nitrogen at 20°. The combined weight of the kettle residues - a brown tar whose i.r. showed no significant change from the original oil - product and trap contents, indicated a weight loss of 0.07g., this was presumably due to oxides of nitrogen. The ^{1}H n.m.r. (in $CDCl_3$) showed singlets at 3.9τ (ethylenic protons) and 8.28τ (methyl) of relative intensity 1:6. Cryoscopy (sulpholane) gave a molecular weight of 198 ($C_8H_{14}N_2O_4$ requires Mol. Wt. = 202). The mass spectrum is shown in Figure 28.

When nitric oxide interacted with the olefin in higher concentrations (15% w/v soln.) under similar conditions given in Table 11, but over 5 hours, a small amount of a white solid was deposited (<u>ca</u>. 1% of weight of olefin used). The major product was an oil whose i.r. was identical to the oil obtained from more dilute solutions. The solid m.p. 140° (decomp.) (nitromethane) was insoluble in common organic solvents but was soluble in sulpholane. Analysis (Found: C,36.9; H,4.6; N,21.3%), corresponds to an empirical formula $C_8H_{12.1}N_4O_{6.1}$. The mass spectrum is shown in Figure 29 and the ^{1}H n.m.r. spectrum (in trifluoroacetic acid, initial green solution turned rapidly brown) changed slowly with time and had initially singlets at 3.2, 5.26, 5.32, 6.05, 8.38 and 8.6τ of relative intensities 1:1.5 (for combined singlets at 5.26 and 5.32τ):2.7:5.4:2.8. The i.r. spectrum is shown in Figure 21 and showed bands at 1550 (NO_2 asym. str.); 1400, 1380 (shoulder) and 1350 cm.$^{-1}$ (NO_2 sym. str.). The interpretation of these results is considered in Ch. 7.

4) trans, trans-<u>1,4-Diphenyl-1,3-butadiene</u>. The oil (3.2g.) (ref. Table 11) on standing under nitrogen for fourteen days at -20°, deposited white crystals of 1,4-diphenyl-1-nitro-4-nitratobut-2-ene m.p. 102° (decomp.), (ether), (Found: C,61.5; H,4.5; N,9.0. $C_{16}H_{14}N_2O_5$ requires, C,61.3;

H,4.5; N,8.9%). After standing for several weeks, the yield increased to 44%. The mass and i.r. spectra are shown in Figures 30 and 22. The i.r. showed bands at 1640, 1555 (NO_2 asym. str.); 1370, 1270 (NO_2 sym. str.) and 840 $cm.^{-1}$(NO str.). Cryoscopy (benzene) indicated a molecular weight of 298 ($C_{16}H_{14}N_2O_5$ requires Mol. Wt. = 314). The ^1H n.m.r. spectrum was complex and the u.v. spectrum had $\lambda_{max.}^{EtOH}$ 260 nm (ε 3000). The d.s.c. result is given in Table 13 and showed a mild exotherm immediately after melting. The i.r. of the remaining oil shown in Figure 23, had bands at 1640, 1550 (NO_2asym. str.); 1370, 1270 (NO_2 sym. str.); 840 (NO str.); and 740 and 690 $cm.^{-1}$ (aromatic CH out-of-plane deformn.).

5) <u>Isoprene, 1-Chloro-1,3-butadiene, 1,4-Diphenylcyclopentadiene and Hexachlorocyclopentadiene</u>. The results of the interaction of these dienes with nitric oxide are shown Table 11. Hexachlorocyclopentadiene was found to be unreactive toward nitric oxide even at 130°.

6) <u>Chloroprene Dimers and Cyclohexene</u>. A mixture of chloroprene dimers (p. 82), or cyclohexene, reacted slowly when treated separately with nitric oxide (50 ml/min.) at 6° in benzene solvent (50 ml.). The reaction solutions were coloured (Table 16) at the end of the reaction and evolved oxides of nitrogen (brown fumes in reaction vessel) on argon flushing. The reaction variables are summarised in Table 16. D.s.c. of the oil products of both experiments showed no significant change up to 200°. (Dimer product had a series of minor exotherms 136-158°).

G.l.c. analysis (on Apiezon 'L' at 100°) of the reaction solution and cold trap contents at the end of the reaction of chloroprene dimers and nitric oxide, showed no unreacted dimer. The i.r. spectrum was insignificant below 1400 $cm.^{-1}$ but had bands at 3500 (OH, NH str.); 2100 (C = N, C = C str., weak); 1730 (carbonyl) and 1575 $cm.^{-1}$ (NO_2 asym.

str.). The ^{1}H n.m.r. (in $CDCl_3$) showed broad multiplets centred at 2.45, 4.6 and 7.1τ. Elemental analysis (Found: C,34.6; H,3.2; Cl,21.6; N,11.8%), corresponds to an empirical formula of $C_8H_{8.8}Cl_{1.7}N_{2.2}O_{2.5}$.

A similar investigation on cyclohexene gave almost identical results. G.l.c. analysis of the cyclohexene reaction solution (on diethylhexyl sebacate at 80°) showed a trace of unreacted olefin (none in cold trap). The blue oil had i.r. with bands at 3300 (NH,OH str.); 2950, 2900 (CH str.); 1730 (carbonyl); 1640, 1560 (NO_2 asym. str.); and 1380 (broad) and 1275 cm.$^{-1}$ (NO_2 sym. str.).

Table 11 The Interaction of Nitric Oxide (50 ml./min.) with Conjugated Dienes in Benzene Solvent (50 ml.).

Diene (10.8 mM.) g.	Reaction temp.° (hr.).	Time (min.) for appearance of			Product Oil, g. (% w/w) Solid, g. (% w/w)
		N_2 max.	Soln. colour	Precipitate	
Chloroprene^{a} 0.96	6 (1)	14	green, 0.5	2	Oil, 1.80 (85) Solid, 0.32 (15)
Isoprene^{a,b} 0.34	6 (1.5)	14	green^{c}, 10	none	Oil, 0.93 (100)
1-CP.^{a,d,e} 0.96	6 (1.5)^{f}	14.5	blue, 0.5 green^{c}, 3	none	Oil, 2.01 (100)
D.C.B.^{a,d,e} 1.33	6 (1)	13	green, 0.5	2	Oil, 1.94 (69) Solid, 0.86 (31)
D.P.B.^{d} 2.22	15^{g} (1.5)	18	green, 6	none	Oil, 3.27 (100)
T.M.B.^{a,d,e} 1.19	6 (3)^{f}	28	blue^{c}, 1	none	Oil, 2.44 (100)
D.P.C.P.^{d} 2.22	15^{g} (3)	63	pale green^{c}, 2	none	2.31^{h}
Hexachlorocyclopentadiene 2.96	130^{i} (6.25)	none	none	none	unchanged diene

a G.l.c. at end of reaction showed only benzene present.
b Benzene (100 ml.), 5.0 mM.
c Colour remained until degassing started, when solution became amber.
d 1-CP. = 1-chloro-1,3-butadiene; D.C.B. = 2,3-dichloro-1,3-butadiene; D.P.B. = *trans*, *trans*-1,4-diphenyl-1,3-butadiene; T.M.B. = 1,1,4,4-tetramethyl-1,3-butadiene; D.P.C.P. = 1,4-diphenylcyclopentadiene.
e After approximately $\frac{1}{3}$ reaction time a bright blue solid observed in cold trap - this disappeared on warming to 20°.
f Brown gas evolved from solution when degassing started.
g No reaction at 6° after 2.5 hr.
h Benzene (175 ml.) in flask of Fig. 7 , diene (1.08g.) recovered, rest of product was original olefin contaminated with a brown oil, little N_2 evolved.
i No reaction at 20 or 81°, chlorobenzene (50 ml.) solvent, 15 cm. double surface condenser included in gas exit.

TABLE 12

Quantitative Determination of Elements in Oil Products.

Product	Percentage				Empirical Formula
	C	H	Cl	N	
Chloroprene	33.7	2.9	18.9	12.7	$C_4 H_4 Cl_{0.8} N_{1.3} O_{2.9}$
Isoprene	41.1	7.0	-	37.6	$C_4 H_{8.2} N_{1.2} O_{2.7}$
D.C.B.[a]	24.8	1.5	34.2	13.1	$C_4 H_{2.8} Cl_{1.8} N_{1.8} O_{3.2}$
1-CP.[a]	25.9	2.5	16.9	15.1	$C_4 H_{4.6} Cl_{0.9} N_{2.1} O_{4.6}$
T.M.B.[a]	40.8	5.6	-	14.9	$C_8 H_{13.2} N_{2.4} O_{5.9}$

[a] See footnote d Table 11.

TABLE 13

D.s.c. Analyses of Reaction Products[a] (Indium Standard).

Product	Temperature ± 1°		
	Range 30-	Exotherm max. (ΔH cal/mg.)	Endotherm min.
Chloroprene; oil	241	none	none
solid[b,c,d]	120	110 (1.6±0.3) (6.7J)[e]	none
D.C.B.[c]; oil	227	none	none
solid[d]	117	107 (0.2) (0.8J)[e]	none
oxime[d]	149	none	121
1-CP.[c]; oil	237	none	none
T.M.B.[c]; oil	239	none	none
solid	157	141 (0.6) (2.5J)[e]	none
1,4-dinitro-1,1,4,4-tetramethylbut-2-ene	148	none	133
Isoprene; oil	210	none	none
D.P.B.[c]; oil	231	none	none
1,4-diphenyl-1-nitro-4-nitratobut-2-ene	138	108	102

a Only significant deviations recorded; heating rate 8°/min.; Nitrogen flow 15 ml./min.

b Exotherm began at 58°; hydrogen chloride and nitrogen oxides identified as products.

c See footnote d Table 11.

d Hammer test at 20° was negative.

e Δ HJ/mg.

TABLE 14

Observations on Sodium Hydroxide Treatment of Reaction Products.

Product	Colour change		Inference[a]
	alkali	acid	
Chloroprene; oil	deep red	original yellow	RCH_2NO_2 present
; solid	deep red	original yellow	RCH_2NO_2 present
D.C.B.[b]; oil	deep red	original yellow	RCH_2NO_2 present
; solid	deep red	original yellow	RCH_2NO_2 present
1-CP.[b]; oil	deep red	original yellow	RCH_2NO_2 present
T.M.B.[b]; oil	slight darkening[c,d]	original yellow	R_3CNO_2 present RCH_2NO_2; R_2CHNO_2 absent
; solid	pale yellow	no change	R_3CNO_2 present RCH_2NO_2; R_2CHNO_2 absent
1,4-dinitro-1,1,4,4-tetramethylbut-2-ene	pale yellow	no change	R_3CNO_2 present RCH_2NO_2; R_2CHNO_2 absent
Isoprene; oil	deep red	original yellow	RCH_2NO_2 present
1,4-Diphenyl-1-nitro-4-nitratobut-2-ene	solid changed from white to yellow[e]	-	-

---

[a] Nitro group identified by i.r.

[b] See footnote d Table 11.

[c] Only *ca*. 50% of oil was alkali soluble.

[d] No blue or green colour extracted by chloroform.

[e] Yellow solid had m.p. 104° but was not characterised.

TABLE 15

Results of Vapour Phase Osmometry (Benzil Standard).

Product	Solvent	Temperature°	$\bar{M}_n$
Chloroprene oil[a]	benzene	25	240
D.C.B.[b] oil	toluene	65	314, 328[c]
1-CP.[b] oil	toluene	65	220
T.M.B.[b] oil	toluene	65	297

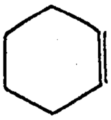
[a] Contained 0.02% w/w phenothiazine.

[b] See footnote d Table 11.

[c] Same solutions run within 24 hr. of each other.

TABLE 16

Reaction of Nitric Oxide with Chloroprene Dimers/Cyclohexene.

Olefin g.	Time for			Product g.
	Colour min.	N_2 max hr.	Reaction hr.	
Chloroprene[a] dimers; 1.11	green, 0.5[b]	small[c],0.25	8	green oil 1.7 solid (5 mg.)[d]
 ; 0.81	blue, 23	small 2.5	5	blue oil, 1.4 trace solid[e]

a Contained *ca*. 1% monomer.

b c.f. time (0.5 min.) for chloroprene in Table 10.

c c.f. 0.25 hr. for chloroprene Table 10; for the remainder of the reaction time there was slow N_2 evolution.

d I.r. corresponded to bis-(2-chloro-1-nitro-4-nitrosobut-2-ene).

e Solid probably nitro-nitroso dimer.

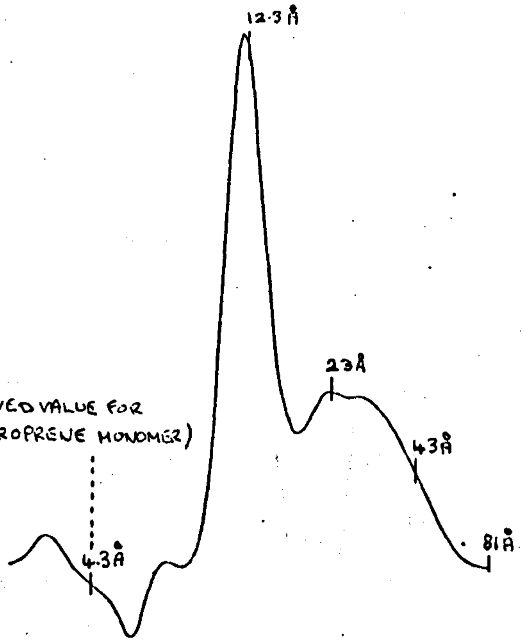


Figure 10 Gel Permeation Chromatogram of Chloroprene/Nitric Oxide Oil.

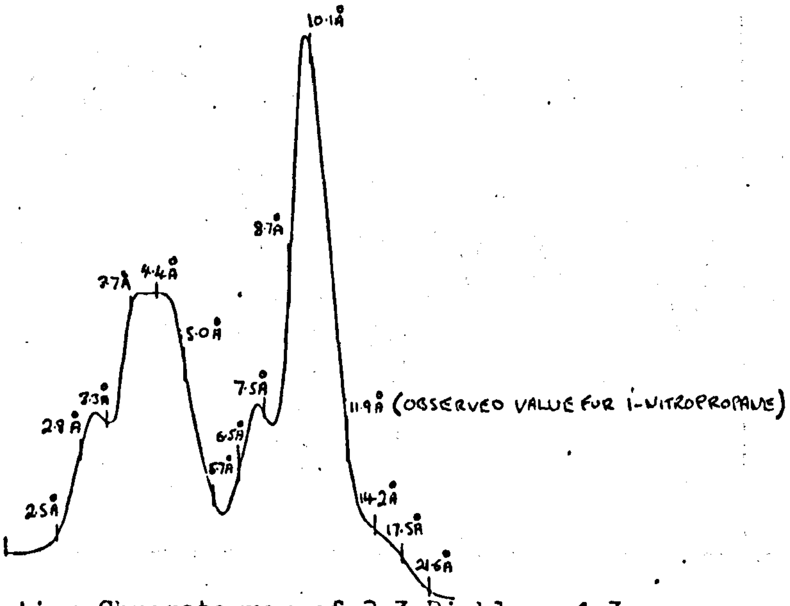


Figure 11 Gel Permeation Chromatogram of 2,3-Dichloro-1,3-butadiene/Nitric Oxide Oil.

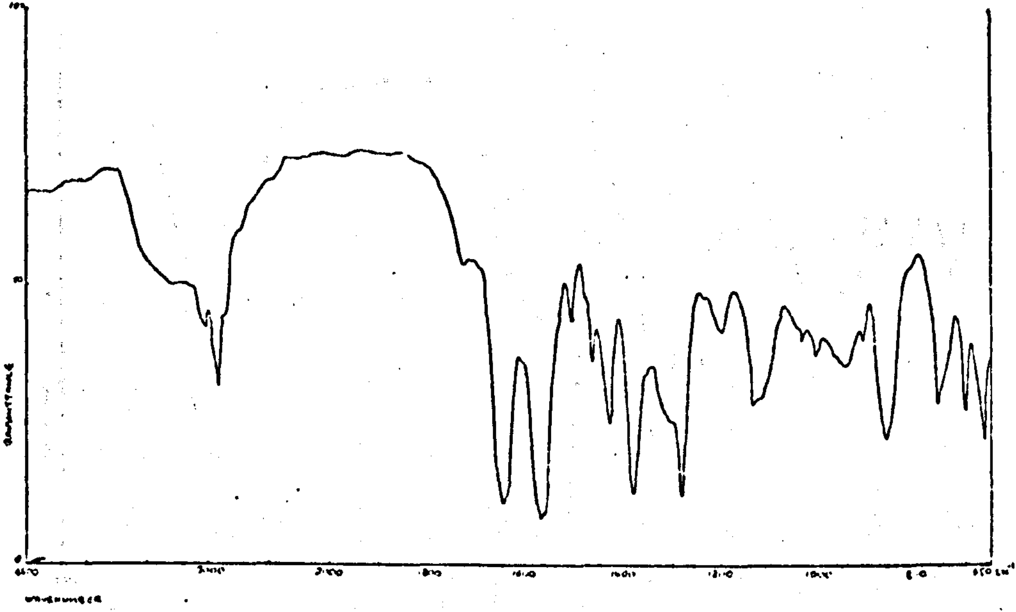


Figure 12 Infrared Spectrum of Chloroprene/Nitric Oxide Oil.

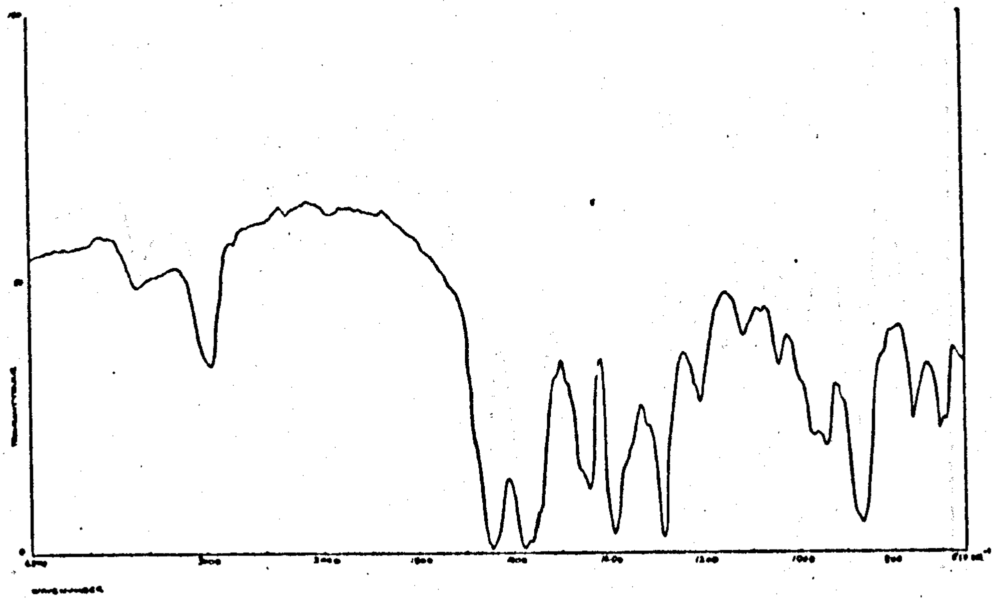


Figure 13 Infrared Spectrum of Isoprene/Nitric Oxide Oil.

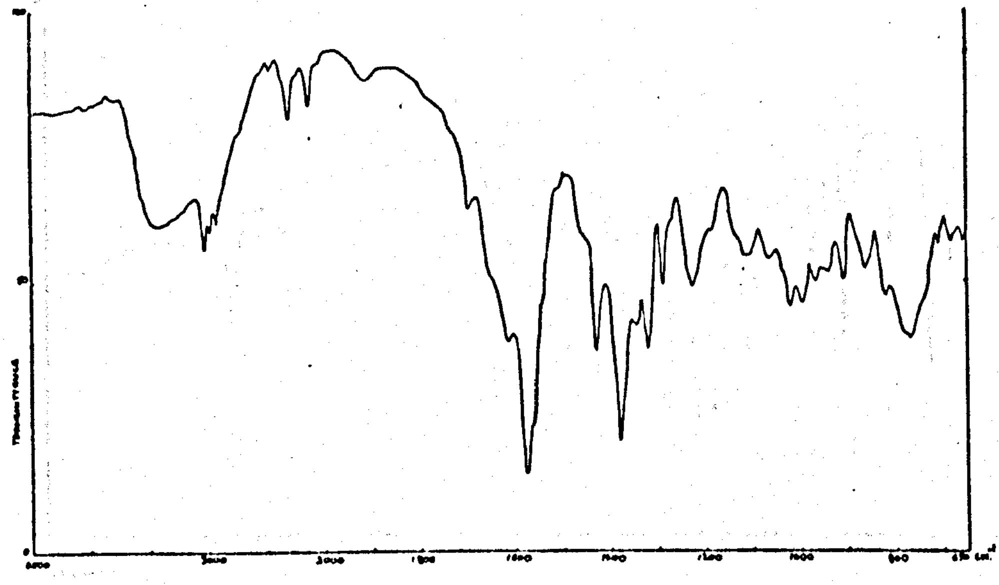


Figure 14 Infrared Spectrum of 2,3-Dichloro-1,3-butadiene/ Nitric Oxide Oil.

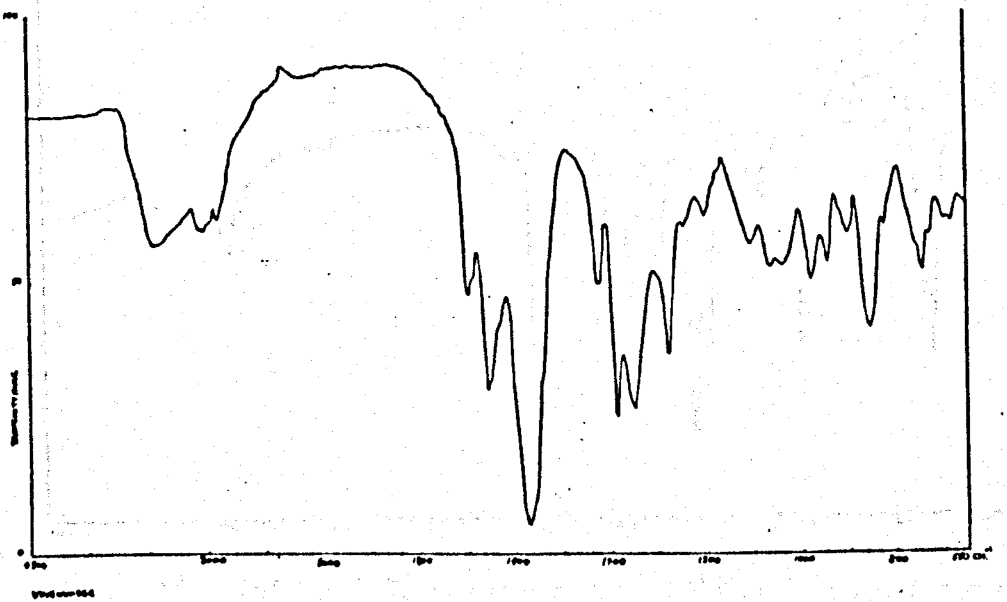


Figure 15 Infrared Spectrum of 1-Chloro-1,3-butadiene/Nitric Oxide Oil.

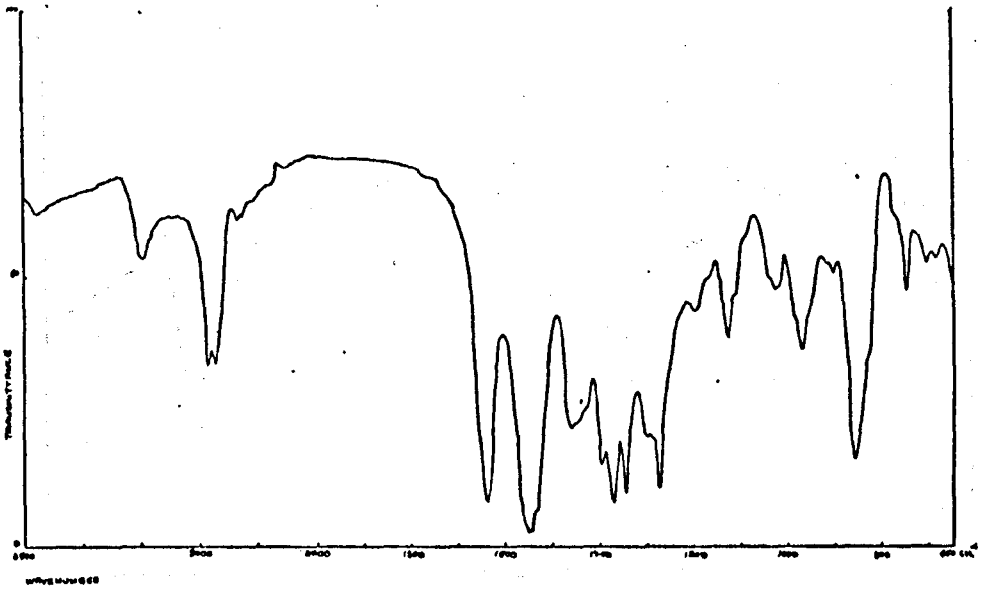


Figure 16 Infrared Spectrum of 1,1,4,4-Tetramethyl-1,3-butadiene/Nitric Oxide Oil.

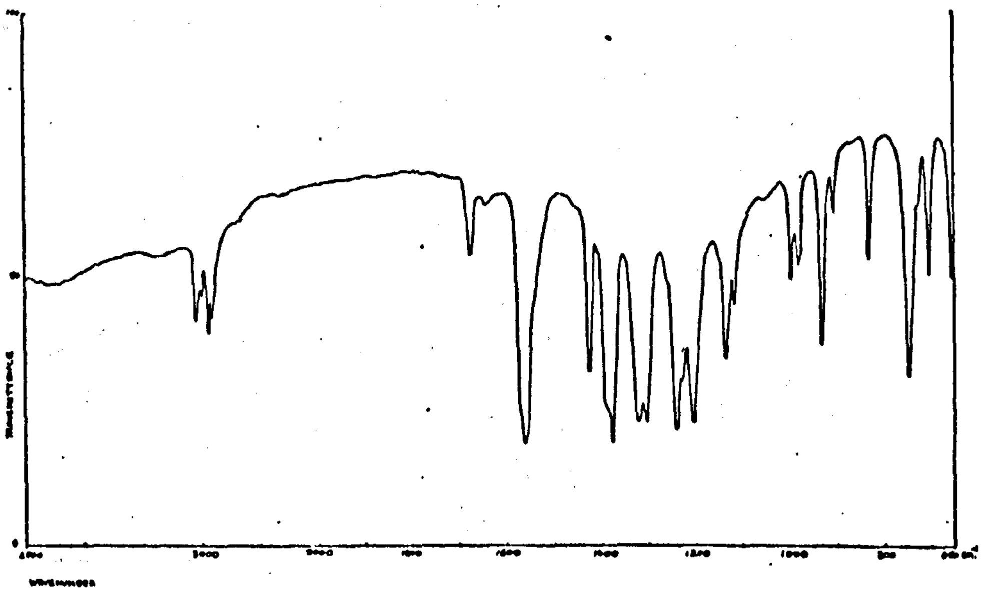


Figure 17 Infrared Spectrum of Bis-(2-chloro-1-nitro-4-nitrosobut-2-ene).

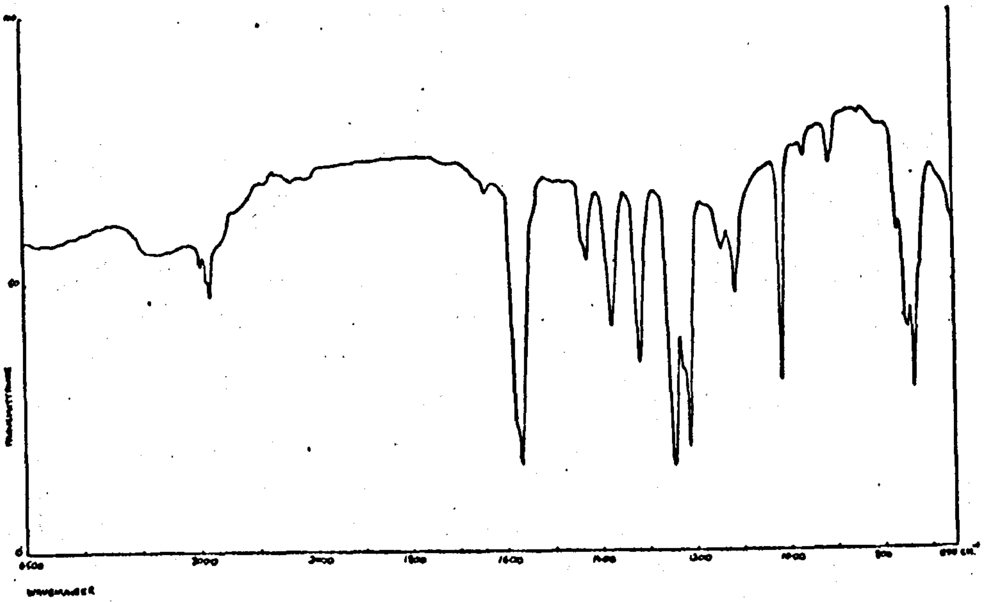


Figure 18 Infrared Spectrum of Bis-(2,3-dichloro-1-nitro-4-nitrosobut-2-ene).

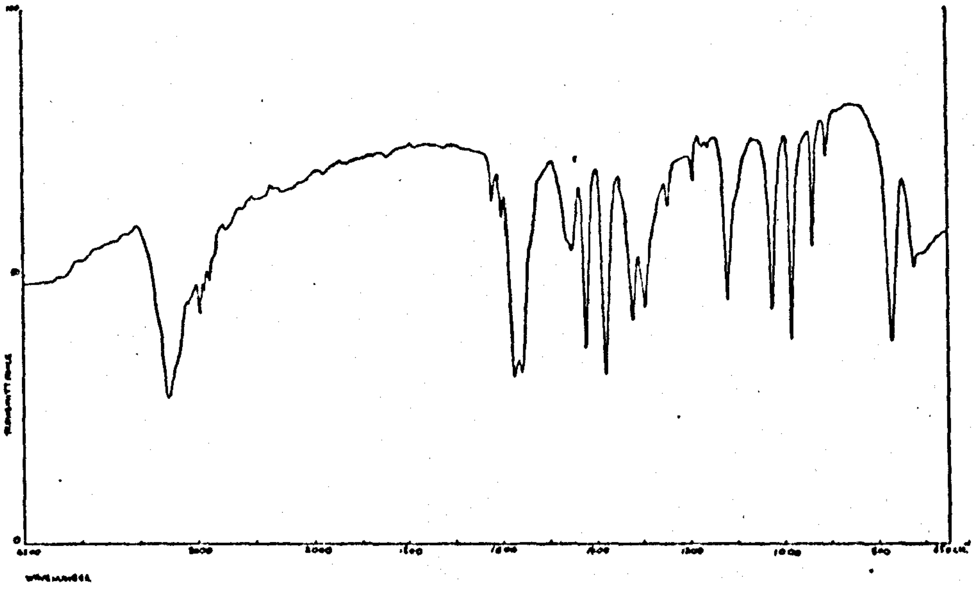


Figure 19 Infrared Spectrum of 2,3-Dichloro-4-nitrobut-2-enaldoxime.

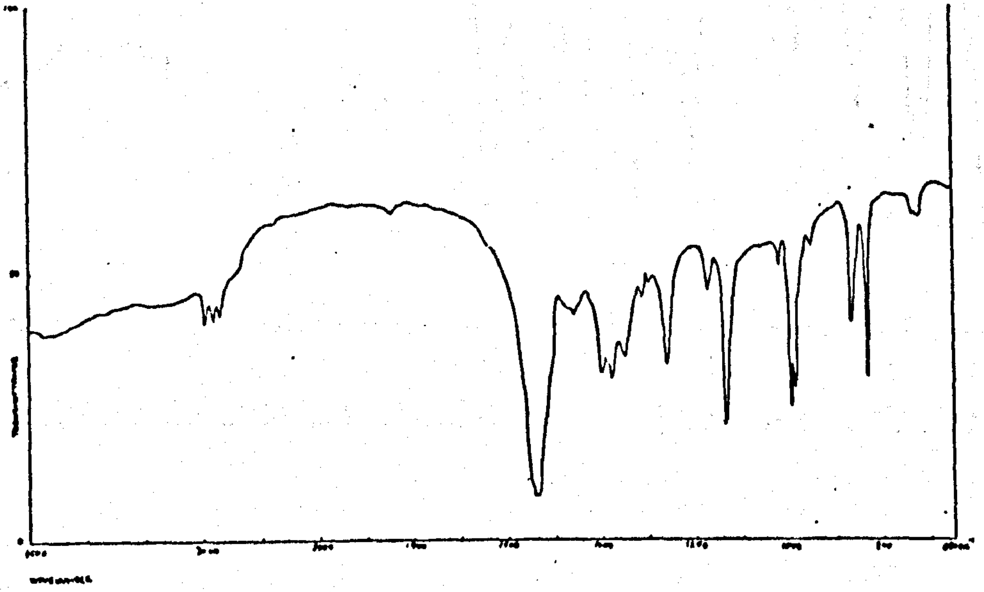


Figure 20 Infrared Spectrum of 1,4-Dinitro-1,1,4,4-tetramethylbut-2-ene.

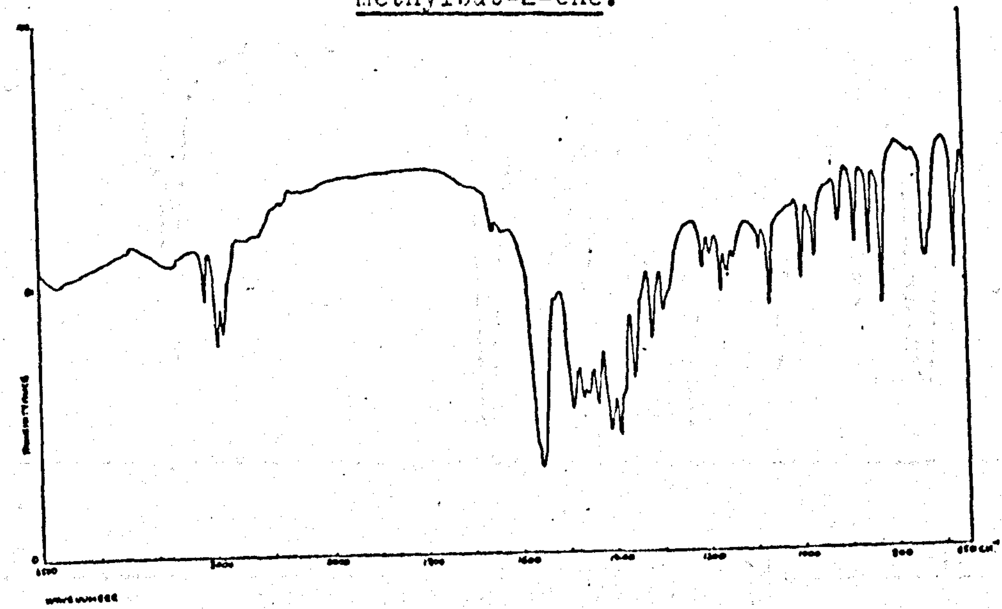


Figure 21 Infrared Spectrum of 1,1,4,4-Tetramethyl-1,3-butadiene/Nitric Oxide Solid.

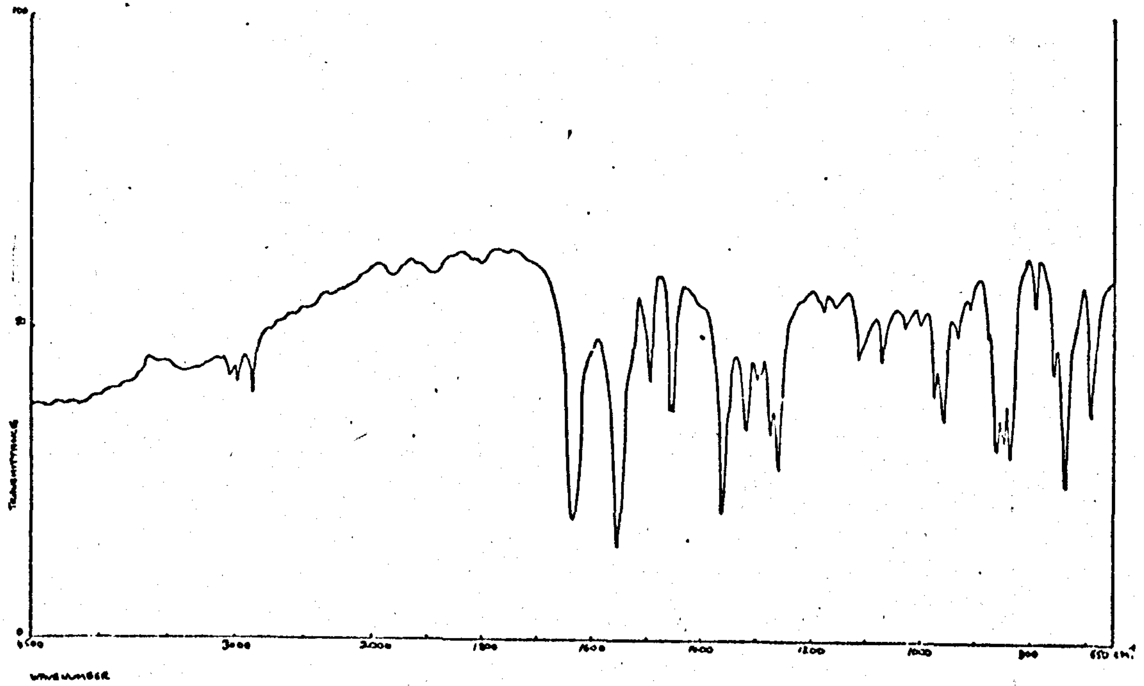


Figure 22 Infrared Spectrum of 1,4-Diphenyl-1-nitro-4-nitratobut-2-ene.

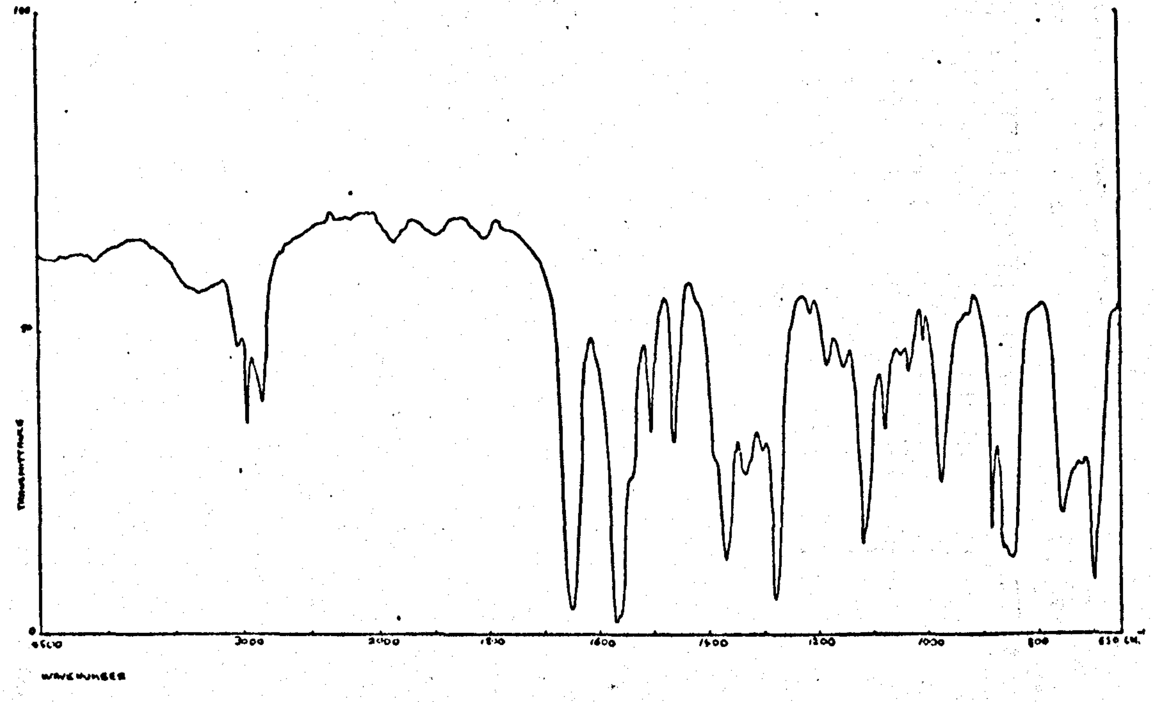


Figure 23 Infrared Spectrum of trans, trans -1,4-Diphenyl-1,3-butadiene/Nitric Oxide Oil.

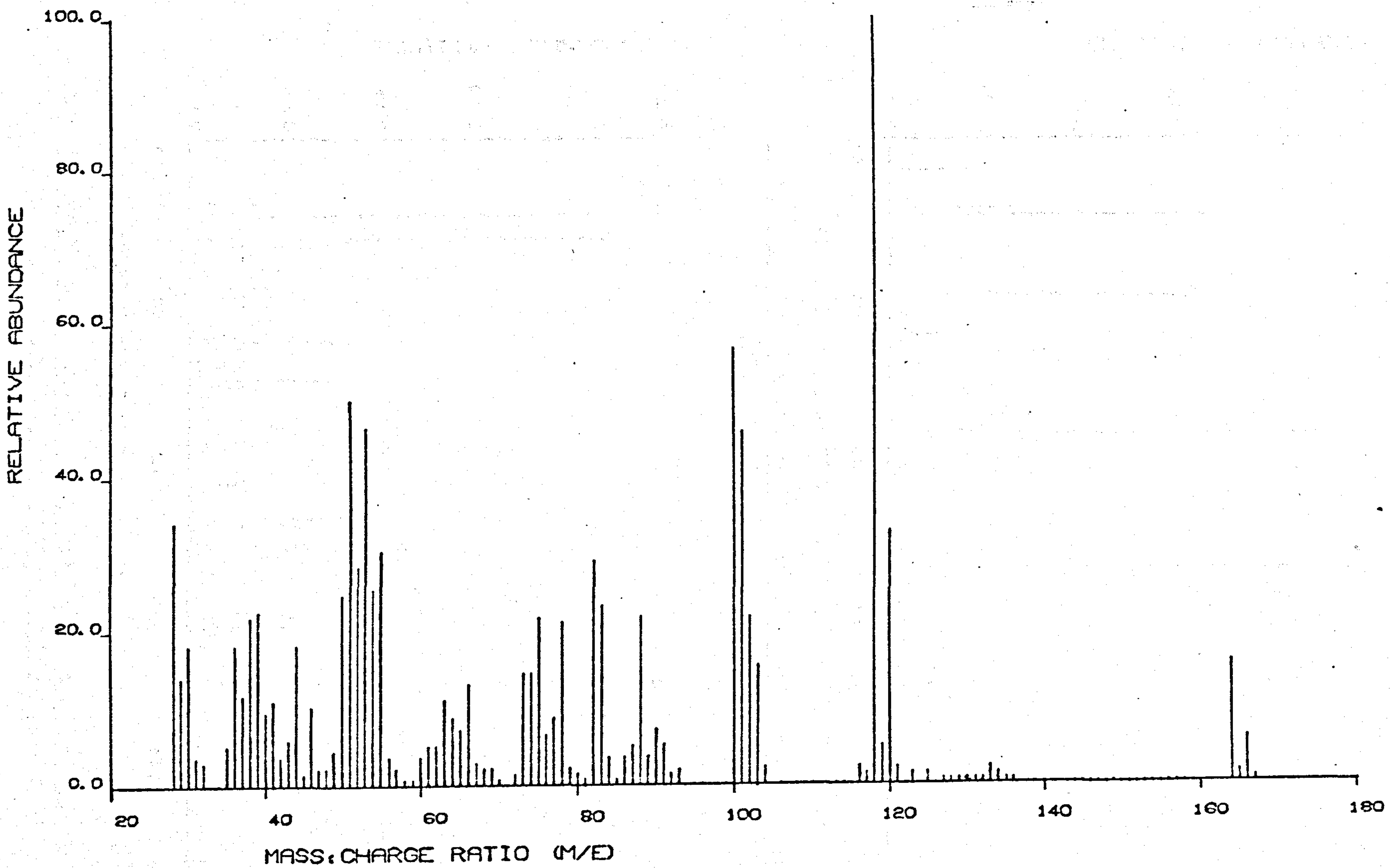


Figure 24 Mass Spectrum (70 ev; M.S.9) of Bis-(2-chloro-1-nitro-4-nitrosobut-2-ene)

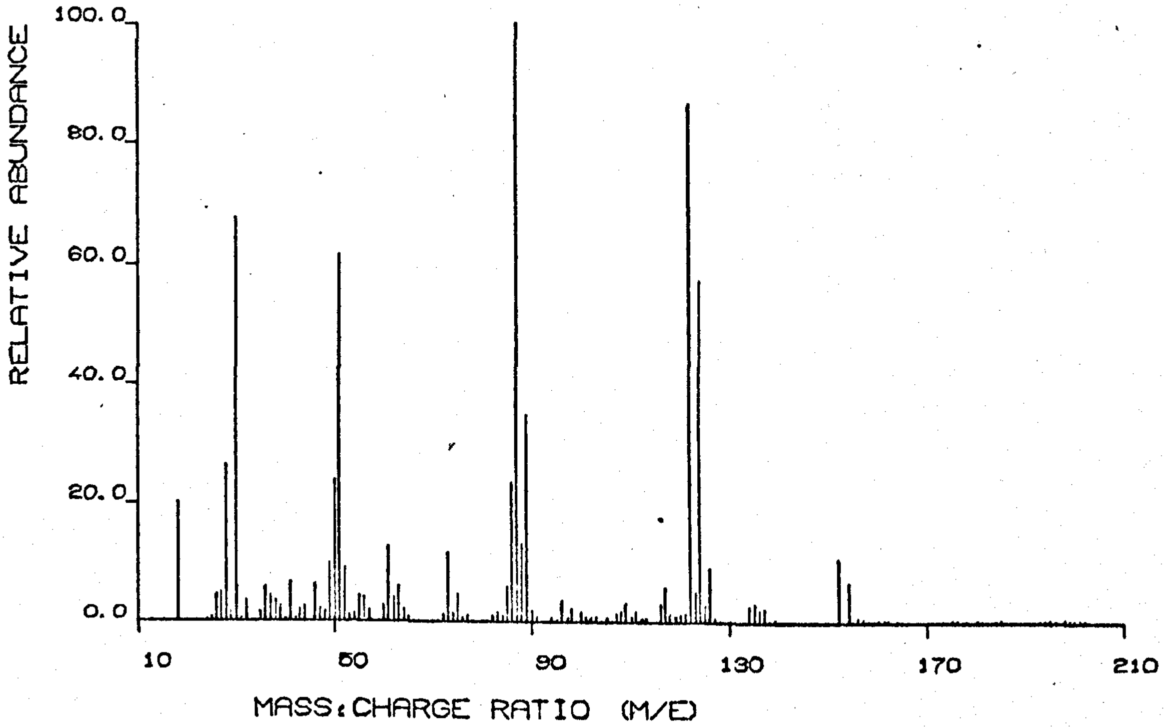


Figure 25 Mass Spectrum (70 ev; M.S.2) of Bis-(2,3-dichloro-1-nitro-4-nitrosobut-2-ene).

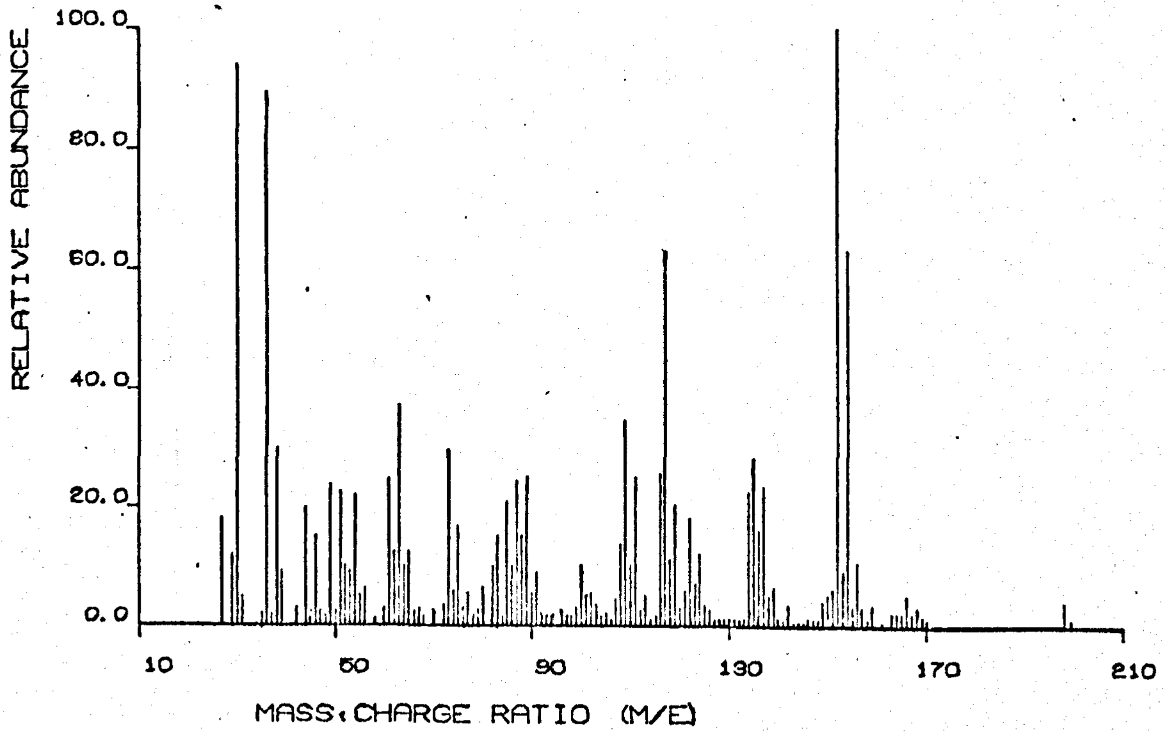


Figure 26 Mass Spectrum (20 ev; M.S.2) of Bis-(2,3-dichloro-1-nitro-4-nitrosobut-2-ene).

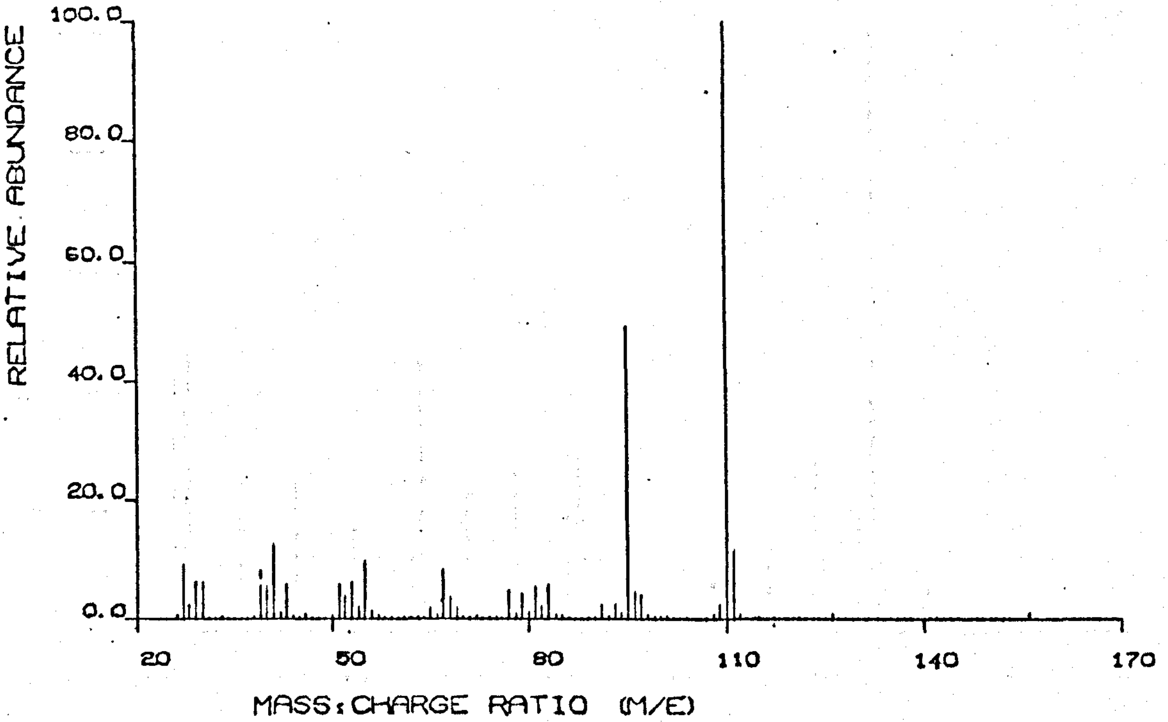


Figure 28 Mass Spectrum (70 ev; M.S.2) of 1,4-Dinitro-1,1,4,4-tetramethylbut-2-ene.

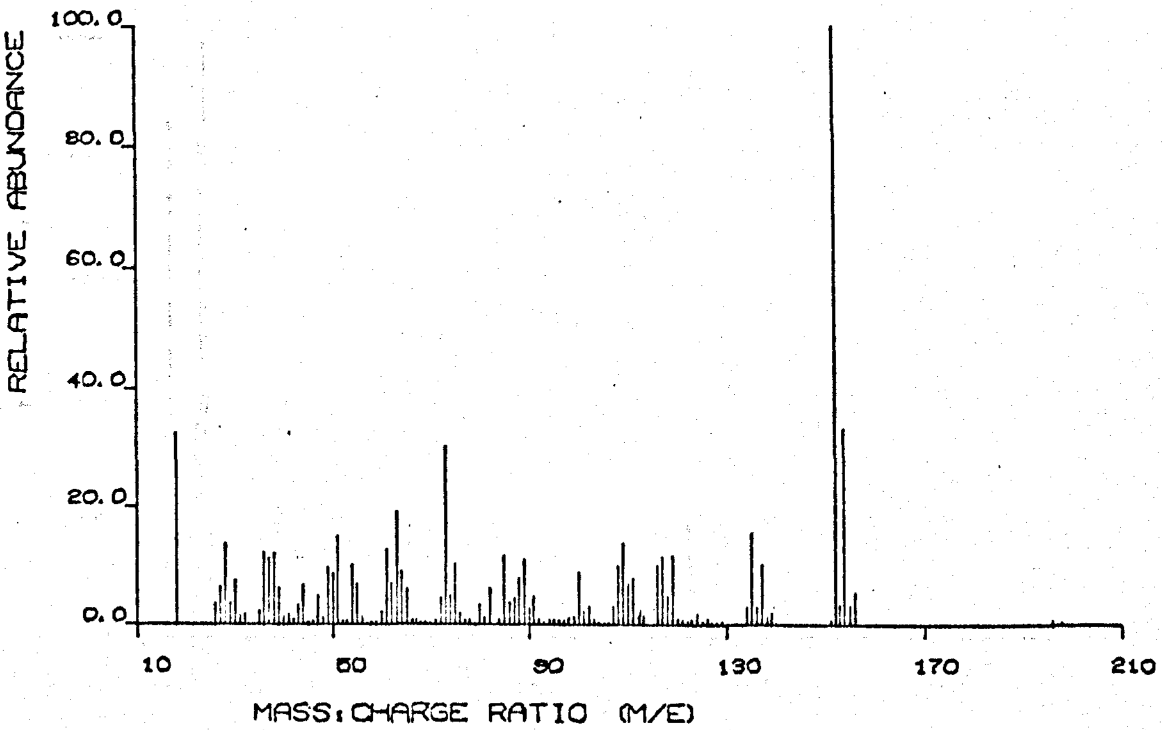


Figure 27 Mass Spectrum (70 ev; M.S.2) of 2,3-Dichloro-4-nitrobut-2-enaldoxime.

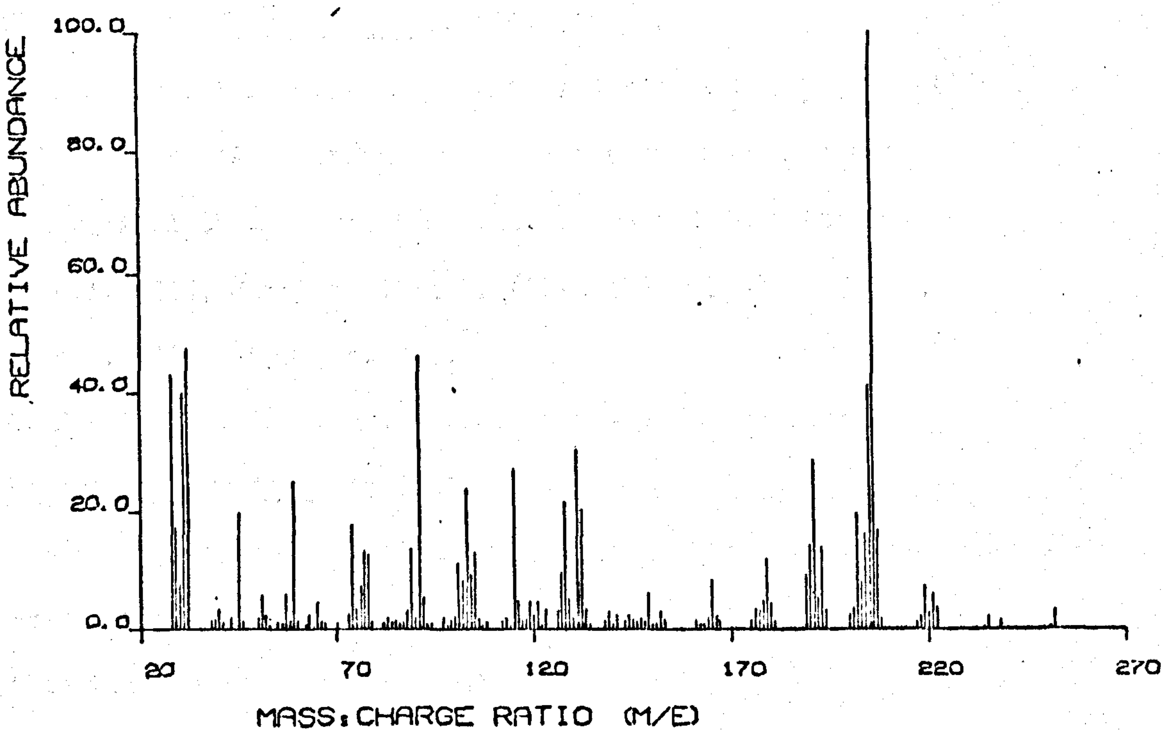


Figure 30 Mass Spectrum (70 ev; M.S.2) of 1,4-Diphenyl-1-nitro -4-nitrato but-2-ene.

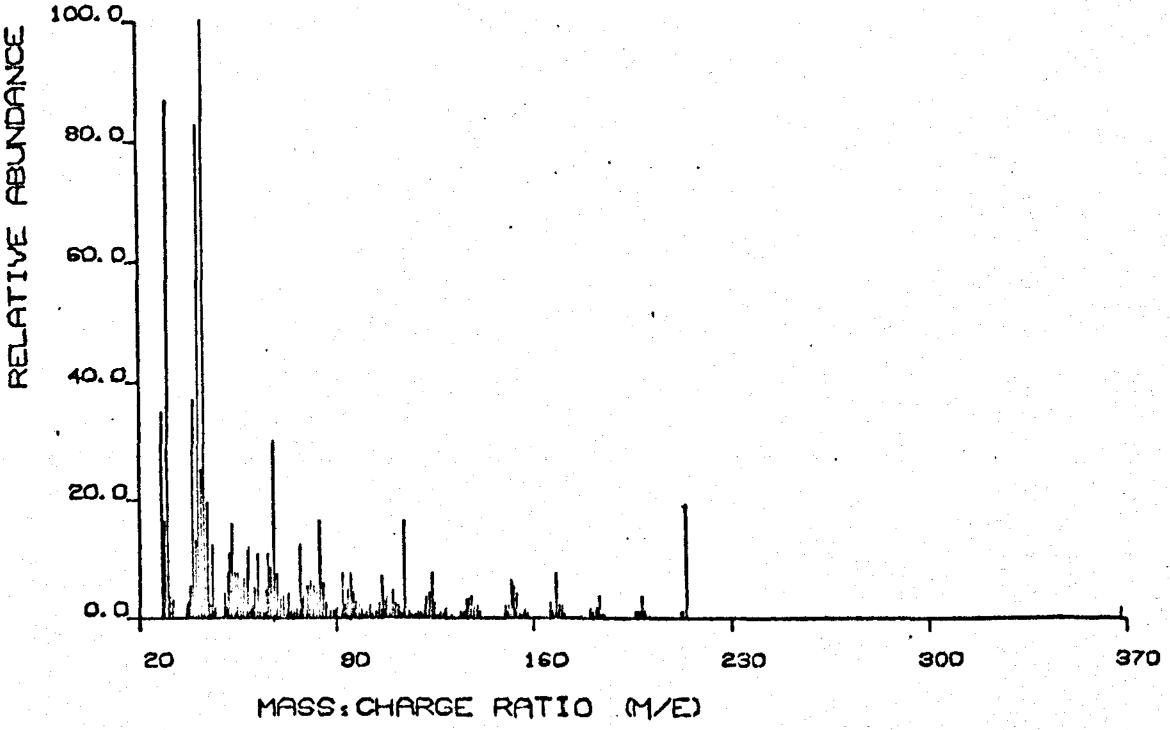


Figure 29 Mass Spectrum (70 ev; M.S.9) of 1,1,4,4-Tetramethyl-1,3-butadiene/Nitric Oxide Solid.

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1. C.E. Hollis, Chem. and Ind., 1030 (1969).
2. H.C. Bailey, 'Advances in Chemistry Series', No. 75, 139 (1968).
3. J.W. Mellor, 'A Comprehensive Treatise on Inorganic and Theoretical Chemistry', Longmans, Green and Co., London,
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   b) Vol. VII, 1930 , p. 943.
4. A. Finch, P.J. Gardiner, R.D.G. Lane and B. Smethurst, Laboratory Practice, April (1965).
5. The histograms were plotted by computer. The use of the program written by J.A. Wilson, Kingston College of Technology, for this purpose is acknowledged.
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CHAPTER 6

Experimental Work Designed to Investigate the Reaction Mechanism.

1) High-Vacuum Line Technique. The high-vacuum line (Fig. 31) was used for the purification of nitric oxide and reaction of the purified gas with the olefinic substrate. Greaseless 'Teflon' taps were used throughout and all glass joints were of the 'Clear Fit' variety and were lightly greased. The system was connected *via* a three way tap to the pumps and to a section used for the purification of chloroprene and degassing of benzene solvent. The flask (Fig. 32) (*ca.* 50 ml. capacity) was used as the reaction vessel and was attached to the B14 joint after the introduction of impure nitric oxide (*ca.* 4 l.) to the system. The operating principle of this flask was identical to that described earlier (p. 99).

Liquid nitrogen and isopentane slush baths (*ca.* -150°) were used in trap to trap distillations of nitric oxide which were continued until all traces of blue solid were absent. Rejected gas was collected in trap A and purified gas in the bulb B (*ca.* 1 l.). Chloroprene was degassed and several times distilled and the final distillate collected in a calibrated tube. The last 10% from each distillation was rejected. Benzene was thoroughly degassed and then distilled into the reaction flask followed by chloroprene (0.5 ml.). After allowing to thaw the reaction solution was maintained at 6° by immersion in an ice/water bath and stirred briefly to complete mixing. Tap 1 was then closed and the section enclosed by taps 1, 2, 3 and 4, and the bulb B, raised to slightly above atmospheric pressure with nitric oxide. With taps 2, 3 and 5 closed, tap 1 was opened and high speed stirring of the reaction solution commenced. The progress of the subsequent reaction was observed by the appearance of a green colouration of the solution and by changes in pressure. When the pressure reading was constant

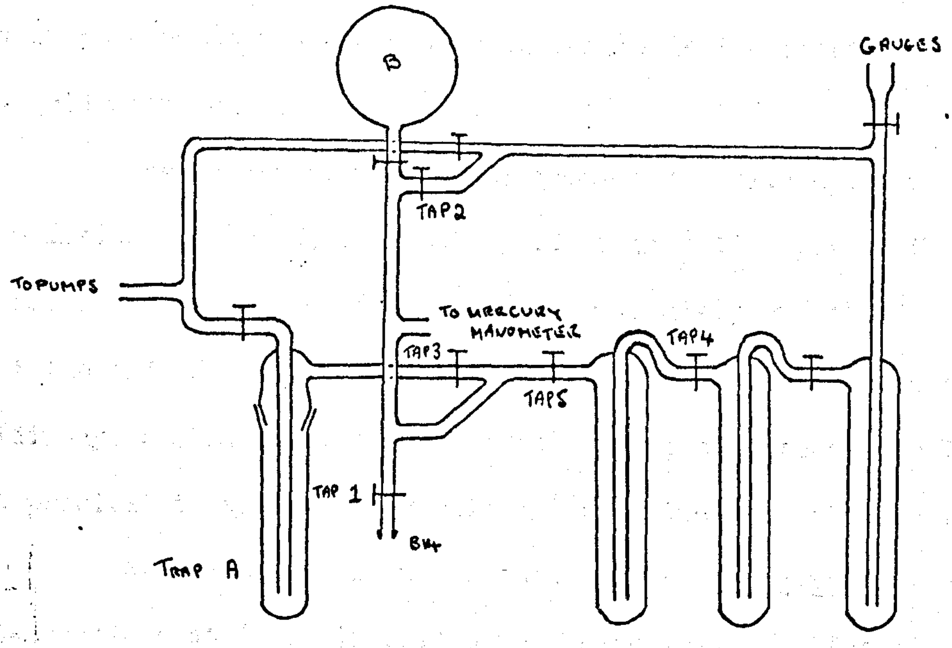


Figure 31 High-Vacuum Line.

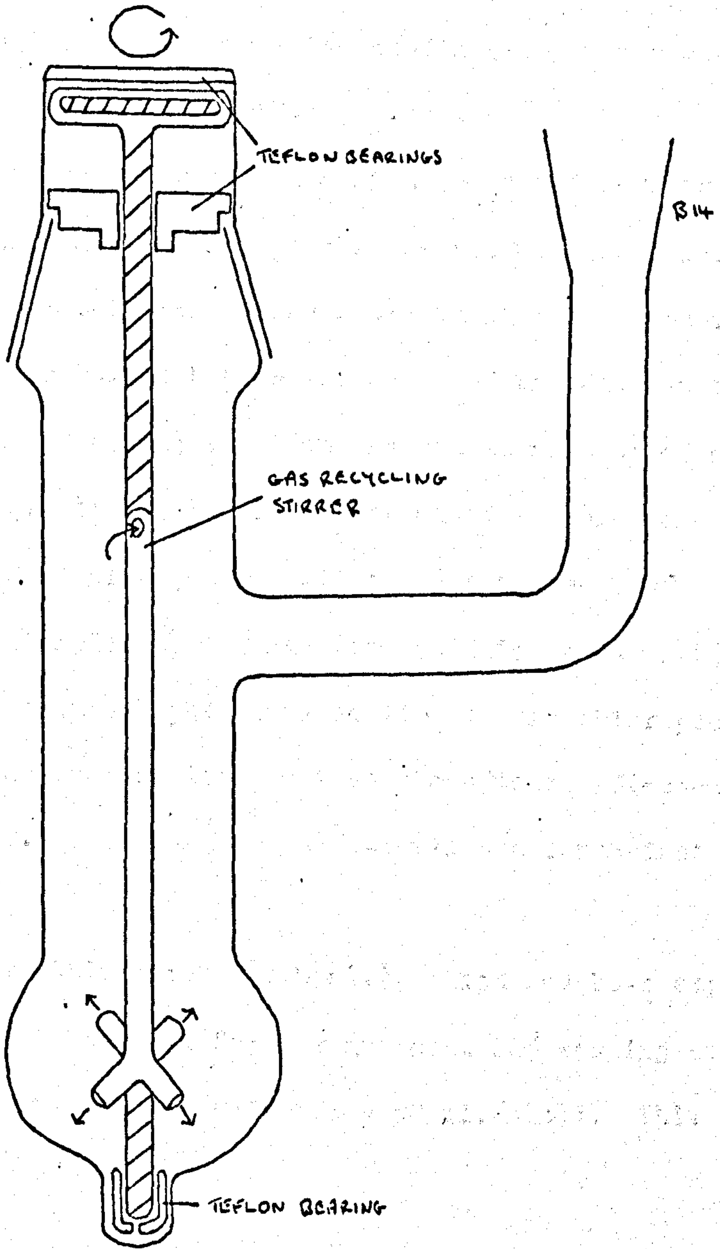


Figure 32 High-Vacuum Line Reaction Flask.

over 30 minutes the gases were condensed in the reaction vessel by liquid nitrogen.

The interaction of chloroprene and nitric oxide under these conditions showed no indications of an induction period for the production of a green solution. Approximately one third of the gas at the end of the experiment (ca. 1.5 hr.) was not condensable. G.l.c. (dinonyl phthalate at 110°) showed a trace of unreacted chloroprene. A precipitate and an amber coloured solution were obtained.

A similar result was obtained using trans,trans-1,4-diphenyl-1,3-butadiene at 15°. In this case the benzene solution of the diene was made up in situ in the reaction flask by distilling degassed benzene onto the solid (1.5 g.). Unreacted olefin (24%) was recovered after 2.5 hours together with an oil (0.8 g.).

2) Nitrogen Dioxide. Using the reaction system described earlier (p. 98), nitrogen dioxide gas was injected below the unstirred surface of benzene solvent immediately before the addition of chloroprene. The nitric oxide flow was halted before injection of the gas and zero reaction time was taken to be the simultaneous recommencement of nitric oxide flow and stirring. At 20° the introduction of nitrogen dioxide affected both the speed of nitrogen evolution and the amount of chloroprene consumed. Samples of the reaction solution were withdrawn and analysed by g.l.c. (dinonyl phthalate at 110°), for chloroprene. The speed of chloroprene consumption was thus shown to be affected in a non-reproducible manner. The experimental details are summarised in Table 17, (p. 137).

3) Chloroprene Peroxide. Chloroprene (1.0 ml.), which had been exposed to, and had air bubbled through it for 2 minutes at 20° was injected into stirred benzene at 6° (nitric oxide flow 50 ml./min.). This had

no significant effect on the reaction variables or product composition as measured by g.l.c. and isolation of products.

4) Dilution. The effect on the reaction with nitric oxide of varying the dilution of chloroprene in benzene has been studied. The substrate was totally consumed in all instances (g.l.c.). A summary of the experimental details are given in Table 18, (p. 138).

5) Trapping of Possible Intermediates:-

a) Nitroso trapping.

i) Diphenyl acetylene. Chloroprene (4.8 ml.) was injected below the surface of stirred, flushed n-heptane (75 ml.) at -40° with a nitric oxide flow of 25 ml./min. (reaction of chloroprene/NO proceeded normally in n-heptane at 6° but the products were insoluble). The gas flow was stopped (6.5 hr.) and the pale yellow solution (a green colour was never obtained) was flushed with argon (15 min.) and an oxygen free solution of diphenyl acetylene (0.5 g., 0.57 mole %) in n-heptane was injected with stirring. The colour remained but slowly faded on being allowed to warm to room temperature. After standing (4 hr.) the volatiles were removed at the pump (g.l.c. on dinonyl phthalate showed a trace of residual chloroprene) to yield diphenyl acetylene (0.4 g.) and a brown oil (3.2 g.).

ii) Methylene-p-chloro aniline. Chloroprene (1 ml.) was injected below the surface of stirred dichloromethane (75 ml.) at -5° with a nitric oxide flow of 50 ml./min. Gas flow was continued until a strong green colour was produced (ca. 2 min.), when the solution was flushed with argon. This discharged the colour and nitric oxide was again passed until a green colour redeveloped. Flushing again discharged the colour and further nitric oxide was introduced (1.5 hr.) to give a permanent yellow solution on flushing. An oxygen free solution of methylene-p-chloroaniline (1 g., 6.9 mole %) in dichloromethane was injected and on standing (3 hr.) at room temperature the yellow colour intensified. The volatile material (g.l.c. on dinonyl phthalate showed traces of residual chloroprene) was removed at the pump to give methylene-p-chloroaniline (0.85 g.) and a brown oil (0.7 g.).

In the hope that the green colour might be more permanent benzene was substituted for methylene dichloride. In this case, although the expected colour was produced, flushing with argon discharged the colour. Under the same conditions but in the absence of chloroprene there was no colour formed even on injection of several aliquots (0.5 ml.) of air both above and below the liquid surface.

b) Diazonium nitrate trapping.

i) Methanol; 2-naphthol. Chloroprene (2 ml.) was injected into n-heptane at -55 to -60° with a nitric oxide flow of 10 ml./min. After 29 hours a small amount of nitrogen was being evolved and methanol (2 ml.) was injected with continuing gas flow. The colour of the solution before injection was yellow/green with a small amount of dark brown semi-solid around the edges of the flask. After injection these colours were discharged and there was no alteration in the level of nitrogen evolution. After a further hour the gas flow was stopped and the solution stirred slowly (12 hr.) at -60°. The gas flow was then restarted and after a further hour the amount of evolved nitrogen had increased slightly. On allowing to stand a pale yellow oil (ca. 0.5 ml.) separated leaving a colourless solution. The gas flow was continued (6 hr.) and the flask left at -60° overnight. Part of the reaction solution (0.9 ml.) was then injected into an oxygen free, alkaline solution of recrystallised 2-naphthol (0.1 g.) in methanol at -78°. No immediate colour developed and on shaking at room temperature a brown colour formed which darkened on standing. The reaction solution was flushed with argon and a second part of the reaction solution (7 ml.), which contained a quantity (ca. 0.2 ml.) of the yellow insoluble oil noted above, was injected into 2-naphthol (0.6 g.) in methanol, under nitrogen at -78°. On standing this became deep red. I.r. spectra of the yellow oil (this turned brown when taken up into a N_2 flushed syringe) and of others run on the 2-naphthol solutions were inconclusive.

ii) m-Dimethoxy Benzene. Chloroprene (3 ml.) was injected into stirred, flushed n-heptane (75 ml.) at -55° with a nitric oxide flow of 25 ml./min. After 3 hours nitrogen dioxide (2 ml.) was injected below the surface of the colourless solution. The liquid immediately became pale blue due to the dissolved dinitrogen trioxide. After a further 2 hours a pale green colour was evident in the solution but there was no significant rise in the level of nitrogen evolution. Nitric oxide flow was continued (30 hr.) without an increase in nitrogen evolution. After 40 hours of gas flow a slight increase in nitrogen content was observed and m-dimethoxy benzene (0.3 ml.) was injected into the argon flushed reaction solution at -47°. On standing and allowing to warm to room temperature the solution became tar-like and was abandoned.

c) Free radical trapping.

i) Iodine. Iodine was unreactive in the dark towards excess, oxygen free chloroprene (24 hr.) (shown colourimetrically using an E.E.L. absorptiometer). The following experiments were carried out in the dark and experimental details are summarised in Table 18. In the first experiment an oxygen free benzene solution of iodine was slowly injected into the reaction solution over a 10 minute period immediately on appearance of the green colour following the introduction of chloroprene. The remaining experiments used iodine <u>in situ</u>. No green colour was produced in the latter experiments and only in the third was there significant lightening of the brown solution (after 6 min.). At the end of the reaction times g.l.c. analysis (Apiezon L at 80°) showed no residual chloroprene and after flushing with argon the volatile materials were removed by prolonged pumping (10^{-2} mm.) at room temperature. The reaction cold trap contents and volatile products were combined and unreacted iodine determined by titration against standard thiosulphate solution. The i.r. spectra of the oil products showed bands at 3400 (OH, NH str., broad); 3005, 2900 (CH str., weak); 1650, 1570 (NO_2 asym.str.); 1380, 1280 (NO_2 sym. str.); and 860 $cm.^{-1}$ (NO str., weak).

ii) <u>Nitroxides</u>. 2,2,6,6-Tetramethyl piperid-4-one nitroxide when stirred with excess chloroprene in benzene at room temperature showed no change in its absorption spectra over 5.5 hours. An oxygen free diethyl ether solution of the nitroxide was found to adsorb exactly 1 mol. of nitrogen dioxide gas to precipitate bright yellow crystals (insoluble benzene), which were collected and stored under nitrogen at -20°. At room temperature, under nitrogen, the crystals rapidly changed to red, to green and finally to a viscous brown oil (benzene soluble). At -20° the crystals slowly changed to a brown oil over a period of <u>ca</u>. 3 weeks. The i.r. of the final oil product had bands at 3040, 2950, 2850 (CH str.); 1705 (carbonyl); 1540, 1355 $cm.^{-1}$ (NO_2 asym. and sym. str.).

A benzene solution of 2,2,6,6-tetramethyl piperid-4-one nitroxide was shown colourimetrically to be unaffected by nitric oxide (4 hr.). Both 2,2,6,6-tetramethyl piperid-4-one nitroxide and 2,2,6,6-tetramethyl piperidine nitroxide were recovered unchanged from their benzene solutions after treatment with nitric oxide (6 hr.) at room temperature. There was no production of nitrogen in this time.

The details of the experiments using the nitroxides in the reaction system are shown in Table 20. The nitroxides were used in situ except for experiment 4 where a benzene solution of the nitroxide was slowly injected over a 10 minute period immediately on appearance of a green colour after the addition of chloroprene. At the end of the reaction times any solid was collected by filtration and the volatile products removed at the pump. G.l.c. analysis (Apiezon L at 80°) of the volatiles of experiments 1, 2 and 7, showed no residual chloroprene. No significant lightening of the initial brown solutions was noted. Unsuccessful attempts were made to form semicarbazone, phenyl hydrazone and 2,4-dinitrophenyl hydrazone derivatives of the oils produced in the presence of 2,2,6,6-tetramethyl piperid-4-one nitroxide.

One attempt to make derivatives by using the benzene reaction solution without isolation of the oil by removal of solvent, was also unsuccessful (Expt. 4). The oil from experiment 7 was extracted with water (very little colouration) and the aqueous solution extracted with ether but no material remained on removal of the ether indicating complete consumption of the nitroxide. A typical i.r. of an oil adduct using 2,2,6,6-tetramethyl piperid-4-one nitroxide is shown in Figure 33, (p. 141). The oils resulting from the use of 2,2,6,6-tetramethyl piperidine nitroxide showed similar infrared spectra but the band at 1705 cm^{-1} (carbonyl) was absent.

The uncertainty of the fate of the nitroxides led to the development of a system designed to follow the reaction colourimetrically. It was hoped by this method to determine the approximate point of consumption of the inhibitor and even the specific rate of consumption. Nitric oxide was passed through a cold trap (ca. -140°), a flow meter (10 ml./min.) and led in a short length of 'polythene' narrow bore tubing via a 12.7 cm., 23 gauge stainless steel hyperdermic needle, to the bottom of nitrogen flushed solvent contained in a 1 cm. path length quartz cell. The latter was held in the cavity of an E.E.L. absorptiometer and was protected from stray light by suitably shaped pieces of blackened cardboard. A piece of card also served to expose the light source when a reading was required. The cell neck supported a narrow bore, solid carbon dioxide condenser (ca. 15 cm.) below which was a side arm stopped with a serum cap through which the needle passed. The cell and condenser were joined by shortened, greased, C10, Quick-fit joints and sprung loaded. The excess gases escaped to waste via a silicone oil bubbler. Nitrogen, for flushing purposes was introduced by a three way tap in the nitric oxide inlet system. After flushing the empty cell, a known volume of degassed (high-vacuum) solvent or standard inhibitor solution was injected into the cell and flushing continued (ca. 0.5 hr.). Nitric oxide was then flowed for a comparable period, the light meter adjusted to zero on the solution or solvent, and a known volume of chloroprene or 1,1,4,4-tetramethyl-1,3-butadiene injected (micrometer syringe) below the liquid surface. The alteration in absorption of the solution was measured as a function of time.

The success of this technique was frustrated by a number of practical problems. The major one was the lack of a suitable solvent. Most solvents tried (e.g. benzene, toluene, dioxane) foamed badly which caused loss of solution by bubbles being carried out with the gas flow. Solvents which did not foam (n-heptane) had another disadvantage - the reaction products were insoluble and formed a film on the cell walls. If the gas flow was kept to a level which gave an acceptable degree of foaming non-reproducible rates of either colour formation or its disappearance were observed. This effect was enhanced by the lack of thermostatting of the cell. A further complicating factor was that both the two nitroxides and the reaction products absorbed in the same filter range of the E.E.L. absorptiometer. Some reaction also took place in the condenser. Attempts to follow the reaction using thermostatted cells and the more sensitive S.P. 500 (nitroxides λ_{max} 235 - 245 nm, chloroprene ca. 225 nm, reaction products - oils - ca.340 nm) was rejected for the same practical reasons. A sampling technique coupled with u.v. measurements was a possible alternative. However it was felt that this would not lead to sufficiently meaningful results to justify the further time necessary to develop the technique.

TABLE 17

Reaction of Nitric Oxide with Chloroprene in the Presence of Added Nitrogen Dioxide[a]

Mole % added NO_2	Time for N_2 max. min.	Oil g.[b]	Solid g.[c]	Ratio oil/solid	% unreacted Chloropren	
					reactor	cold trap
none	28	5.5	0.8	6.6/1	none	1.5
2.4	24	6.4	1.0	6.4/1	5	0.5
2.4	24	7.38	0.32	24/1[d]	none	5
4.8	26	4.55	1.5	3/1	22.5	5
4.8	30	7.84	0.54	14/1	5	1
8.1	22	3.5	1.1	3.2/1	22.5	8
8.1	27	4.3	0.7	6.1/1	12	3

[a] Nitric oxide 50 ml./min; chloroprene 4.8 g; benzene (25 ml.); 20°; 3.5 hr.

[b] I.r. corresponded to typical NO/Chloroprene oil.

[c] I.r. corresponded to bis-(2-chloro-1-nitro-4-nitrosobut-2-ene).

[d] Acetone used instead of ether to rinse reaction flask.

TABLE 18

Reaction of Nitric Oxide with Chloroprene at Different Dilution[a].

% Soln. v/v	Oil g.	Solid g.
2	0.69	0.13
2	0.7	0.1
0.1[b]	1.1	trace
0.1[b]	0.9	none

[a] Nitric oxide 50 ml./min.; chloroprene 0.48 g.;benzene at 6°; 2 hr.

[b] Reaction flask of Figure 7 used.

TABLE 19

The Reaction of Nitric Oxide with Chloroprene in the Presence of Iodine[a].

No.	Chloroprene m M. (g.)	I_2 mole % (g.)	Time for		Product		% I_2 consumed
			N_2 max. min.	Expt. hr.	Oil g.	Solid g.	
1	10.8 (0.96)	2.3 (0.32)	15(small)	3	2.22	0.06[b]	18.8
2	5.4 (0.48)	10.1 (0.57)	none[c]	5.5	1.37	none	64
3	5.4 (0.48)	2.3 (0.16)	none	2.5	1.38[d]	none	75

[a] Nitric oxide 50 ml./min; benzene (50 ml.); 6°.

[b] I.r. corresponds to bis-(2-chloro-1-nitro-4-nitrosobut-2-ene.

[c] Slight increase after 4.5 hr.

[d] Found: C, 29.7; H, 2.5; Cl, 13.4; I, 8.7; N, 12.4%.

TABLE 20

The Reaction of Nitric Oxide with Chloroprene in the Presence of Nitroxide Radicals[a].

NO	Chloroprene m M.(g.)	Nitroxide mole % (g.)	Time for		Product	
			N_2 max. min.	Expt. hr.	Oil g.	Solid g.
1[b]	5.4 (0.48)	5.3[c] (0.04)	2	1.5	0.83	0.07[d]
2[b]	5.4 (0.48)	5.3[c] (0.04)	6	1.5	0.92	trace
3	5.4 (0.48)	51[e] (0.46)	no sampling	4.5	1.31	0.07[d]
4	10.8 (0.96)	26[e] (0.48)	16	2.5	-	0.07[d]
5[f]	10.8 (0.96)	51[e] (0.92)	none	3	0.17	trace[g]
6[f]	10.8 (0.96)	51[e] (0.93)	small 63	3.5	2.18	0.19
7	5.4 (0.48)	92.5[e] (0.83)	19	3	1.01	trace

a Nitric oxide 50 ml./min.; benzene (50 ml.); 20°.

b Temp. 6°.

c 2,2,6,6-Tetramethyl piperidine nitroxide.

d I.r. identical to bis-(2-chloro-1-nitro-4-nitrosobut-2-ene).

e 2,2,6,6-Tetramethyl piperid-4-one nitroxide.

f n-Heptane solvent (50 ml.)

g 80% Nitroxide[e] recovered.

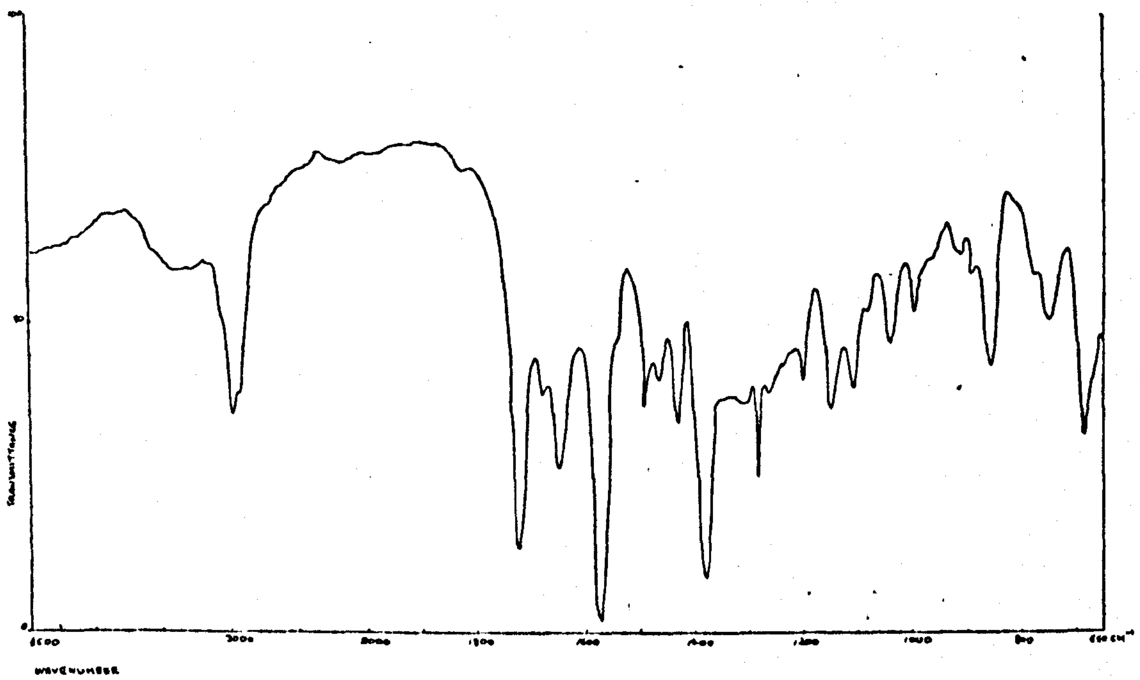


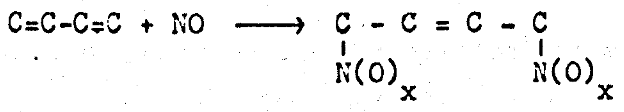
Figure 33 Infrared Spectrum of 2,2,6,6-Tetramethyl Piperid-4-one Nitroxide/Chloroprene/Nitric Oxide Reaction Product.

Chapter 7

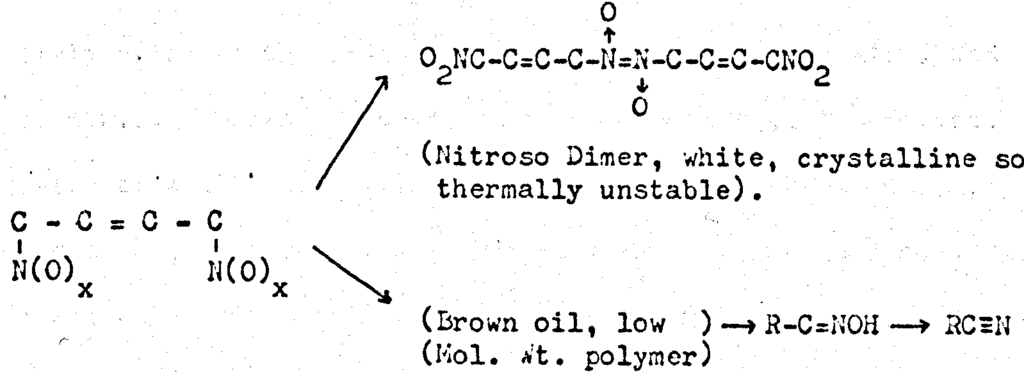
The Nature of the Reaction Products.

During the early stages of this work little was known about the nature and the extent of the action of nitric oxide on chlorinated, conjugated olefins. Reports in the chemical literature (Ch. 3) dealing with mono-olefins suggested that reaction would occur fairly readily in the presence of nitrogen dioxide-dinitrogen tetroxide. Subsequently, it was found at ambient temperature and below, that chloroprene gave rather intractable products if purified nitric oxide was allowed to mix intimately with solutions of the olefin. A specially designed apparatus (Figs. 6,7) to keep the solution saturated with nitric oxide at all times, was essential to bring about the changes indicated below.

At a later stage a pattern of results appeared and in this chapter the experimental evidence leading to compound identification and/or compound speculation will be considered. Because of the unstable, insoluble, often polymeric nature of the products spectroscopic analysis proved a more suitable technique than chemical investigation. Depending on the conjugated olefin, the following types of compounds were obtained and consideration of how they arose will be dealt with in Chapter 8.



$$C{=}C{-}C{=}C + NO \longrightarrow \underset{N(O)_x}{C} - C = C - \underset{N(O)_x}{C} \qquad (1)$$



$$O_2NC{-}C{=}C{-}C{-}\overset{O}{\overset{\uparrow}{N}}{=}\underset{O}{\underset{\downarrow}{N}}{-}C{-}C{=}C{-}CNO_2 \qquad (2)$$

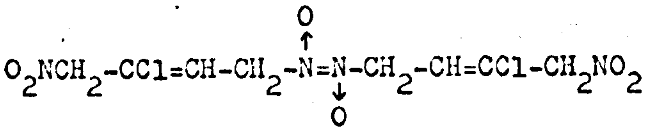
(Nitroso Dimer, white, crystalline solid, thermally unstable).

$$\underset{N(O)_x}{C} - C = C - \underset{N(O)_x}{C}$$

(Brown oil, low) ⟶ R-C=NOH ⟶ RC≡N (3)
(Mol. Wt. polymer)

1) Crystalline Solid Derived from Chloroprene.

This was found to be bis-(2-chloro-1-nitro-4-nitrosobut-2-ene). Owing to the lack of solubility and thermal instability, the evidence for the structure (I) of this solid is drawn mainly from information obtained by physical techniques, mainly infrared studies.



$$O_2NCH_2\text{-}CCl{=}CH\text{-}CH_2\text{-}\overset{O}{\overset{\uparrow}{N}}{=}\underset{O}{\underset{\downarrow}{N}}\text{-}CH_2\text{-}CH{=}CCl\text{-}CH_2NO_2$$

(I)

Much of the spectral information given in these next sections is applicable to the remaining adducts discussed and should therefore be borne in mind.

a) Infrared Spectroscopy. The infrared spectrum (Fig. 17) of the solid shows[1] clearly the presence of a nitro group because of strong bands at 1550 (asym. str.) and 1375 (sym. str.). Conjugated olefins are excluded[1] by the absence of bands in the region 1520-1540 cm.$^{-1}$ similarly dinitro alkenes with the two nitro groups on the same carbon atom are ruled out[1] by the absence of bands at 1575-1580 cm.$^{-1}$ (asym. str.) and 1342 cm.$^{-1}$ (sym. str.). Tertiary nitro groups have an asymmetrical stretching vibration at 1540 cm.$^{-1}$ and a symmetrical stretching vibration at 1340 cm.$^{-1}$; consequently the absence of these bands in the spectrum also excludes a tertiary nitro compound[1]. The presence of a nitro group attached to a chlorine carrying carbon (implying 2,1-addition) is also unlikely owing to the absence of bands at 1565 (asym. str.) and 1342 cm.$^{-1}$ (sym. str.). Brown[1] however, only examined one such compound. The presence of a nitro group in the three position, which would imply 3,4-addition, is also a possibility because of the characteristic bands of a secondary nitro group[1] in the regions 1542-1555 cm.$^{-1}$ (asym. str.) and 1360-1380 cm.$^{-1}$ (sym. str.). Evidence presented later argues against this. It is concluded therefore that a primary ($-CH_2NO_2$) nitro group is present which is further substantiated by the band at 1425 cm.$^{-1}$ resulting from methylene bending vibrations in a primary nitro compound[2]. This conclusion is indicative of 1,4- or 4,1- addition.

Nitrite (-ONO) groups are excluded since they exhibit[3] a double band between 1681-1653 cm.$^{-1}$ (N=O str.) and 1625-1613 cm.$^{-1}$ (N=O str.). These are attributed to the __trans__- and __cis__- forms of the nitrite structure respectively. Nitrate ($-ONO_2$) esters[3] also show a strong band __inter alia__ in the region 1650-1600 cm.$^{-1}$ (NO_2 asym. str.) and are therefore eliminated.

The absorptions attributable to the nitroso group are less readily assigned. The N-O frequencies quoted by Gowenlock and Lüttke[4] for aliphatic __cis__- and __trans__- nitroso dimers are given in Table 21.

__Table 21__

__Characteristic NO Frequencies in Aliphatic $(RNO)_2$[4].__

__cis__-Dimer	__trans__-Dimer
Double band between 1323 and 1344 cm.$^{-1}$ and 1330 and 1420 cm.$^{-1}$	Single band between 1176 and 1290 cm.$^{-1}$

The fact that the range of frequencies is large, combined with the presence of a nitro group, which may well overlie a characteristic band, makes the unambiguous identification of a nitroso group difficult. It is possible that both __cis__- (1322 and 1385 - shoulder - cm.$^{-1}$) and __trans__- (1205 cm.$^{-1}$) [1,4] may be present. Arguing against this suggestion is the presence of a very weak band in the -N=N- stretching range (1640 cm.$^{-1}$) which, besides substantiating a dimeric structure, is evidence for a __trans__- rather than a __cis__- form. The band would be expected to be weak if a <u>trans</u>- structure was present but stronger if the <u>cis</u>- form was present arising from the greater change in dipole moment associated with the latter.[3] As the <u>trans</u>- structure would be favoured on steric grounds it is significant that no alteration in band intensities was observed after repeated recrystallisations. Although cryoscopy has shown that the solid is largely dimeric in sulpholane solution, some dissociation does occur and presumably on being brought out of solution the monomers would larely combine in the sterically preferred <u>trans</u>- arrangement. Brown[1] has examined seven bis-nitroso compounds all of which showed a strong band in the range 1213-1200 $cm.^{-1}$.

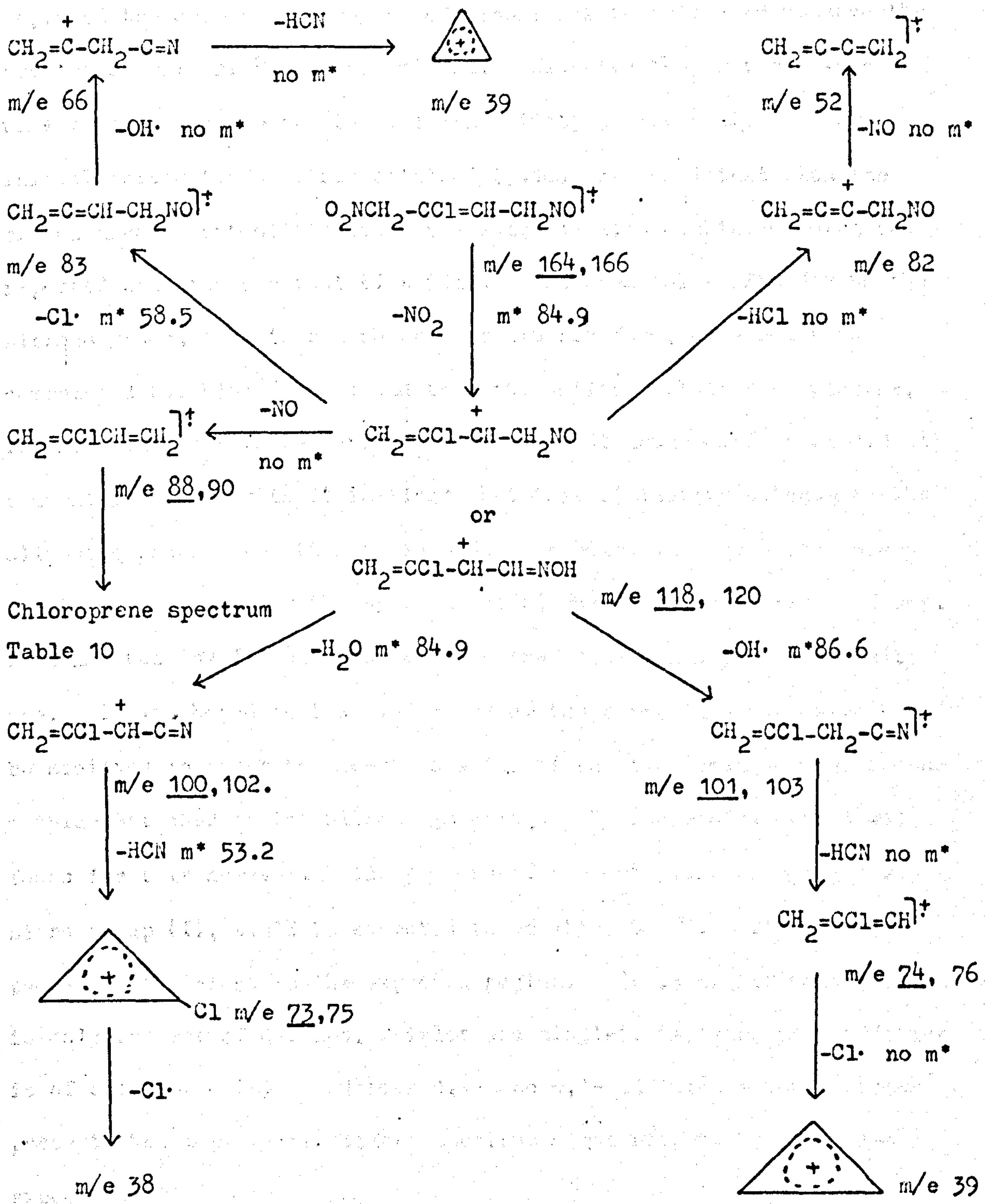
That the molecule contains unsaturation is shown by the band at 1672 $cm.^{-1}$ (C=C str.) and this falls in the range established by Mc.Murry and Thornton[5] for trisubstituted ethylenes, although these authors quote the intensity as very weak. This is not thought to be a serious objection because halogens are known to enhance the intensity of the carbon-carbon double bond stretching frequency[6]. It must be recorded that this band is somewhat higher than is normally expected for a carbon-carbon double bond stretch and is more typical of a carbonyl stretching mode[7]. Of particular significance is the observation that some α,β-unsaturated carbonyl compounds[8] show a strong band near this value and also a weak band near 1640 $cm.^{-1}$ (C=C str.). It is difficult however, to rationalise the presence of a carbonyl group with other data collected on the solid such as elemental analysis, lack of solubility and its method of preparation, which presented no opportunity for hydrolysis of an oxime (formed by tautomerism of a nitroso group) to a carbonyl group. In the absence of any other evidence to the contrary the favoured interpretation is that the unsaturation vibration is shifted by the combined effects of the nitrogen-oxygen groups and chlorine[7] to a value higher than usual.

Further evidence for a trisubstituted ethylene is the band at 828 cm.$^{-1}$ due to a C-H deformation of a trisubstituted double bond[3]. The bands at 926 cm.$^{-1}$ (CH_2 out-of-plane deformn.) and 990 (CH out-of-plane deformn.) are characteristic of a $-CH=CH_2$ group[7] which therefore adds the possibility of some 3,4-addition.

Finally the strong band at 745 cm.$^{-1}$ is assigned to the C-Cl stretching mode[3].

b) <u>Mass Spectrometry</u>. Accurate mass measurement of the parent ion gave a molecular formula $C_4H_5ClN_2O_3$ which is in agreement with the formula derived from elemental micro-analysis. The major fragmentation routes of the compound are shown in Figures 24 and 34. Comparison of the cracking pattern with published data[9] eliminates N-nitroso compounds (R_2NNO) which give an abundant molecular ion and ready cleavage of the carbon nitrogen bond giving the base peak. Further evidence against the presence of alkyl nitrites, besides that of infrared spectroscopy is that these usually give a very large NO^+ (m/e 30) peak owing to the easy breaking of the RO-NO bond[10]. Additionally, the known facile α-cleavage would lead in this case (Structure I) to an abundant peak at m/e 60 ($CH_2=\overset{+}{O}-N=O$). Since there is an absence of peaks attributable to a dimer (even at 20 ev) it is postulated that the dimer fragments to the monomer under the conditions described on p.105. It is significant that dimeric nitroso benzene is not detected by mass spectrometry and the monomer decomposes by loss of nitric oxide[11]. A similar fragmentation was found for dimeric nitro-nitroso cyclohexene, [prepared by the action of N_2O_3 on cyclohexene[12], m.p. 139-140° (decomp.), 38% (Lit. m.p. 142°)[13]; identified by i.r. and ^1H n.m.r.] and in this case the loss of $-NO_2$ took place more readily than -NO.

Figure 34. Major Fragmentation Routes of Bis-(2-chloro-1-nitro-4-nitrosobut-2-ene).



(m/e for major chlorine isotope underlined; assigned metastable peaks are indicated with an asterisk).

c) *Proton Magnetic Resonance*. A spectrum of this adduct and that of 2,3-dichloro-1,3-butadiene was difficult to obtain due to the poor solubility. A similar restriction was found by Scheinbaum[13] who employed the computer averaging of transients technique to observe the spectra of some nitro-nitroso dimers. Elevated temperatures were undesirable owing to the thermal instability of the solids. The initial integrated spectrum obtained (p.105) is consistent with the proton arrangement of structure (I) which is also consistent with the reported coupling constant (J = 6Hz). The chemical shifts due to the nitroso group, in either monomeric or dimeric form, have not been correlated but King[11] has found that the shifts, relative to benzene, for nitroso and nitrobenzene are similar. Although Schienbaum did not comment on his results it is clear that this similarity extends to the aliphatic case. An attempt was made to resolve this question more precisely by examining the spectrum of nitro-nitroso cyclohexane dimer. This had two low field broad peaks centred at 4.4 and 5τ of intensity one. It was hoped that a conversion of the dimer into the oxime could be achieved in order to ascertain which of the two peaks was due to the methine attached to the nitroso grouping. No successful method was found for this however. The protons of the methylene carrying the nitro group (I), would be expected to be about 5.1τ. The observed peaks are therefore in the expected region. It is significant that there is only one set of doublet, triplet and singlet, implying that addition is of one type only. Had both 1,4- and 4,1- addition products been present then a more complicated spectrum might reasonably have been expected.

d) *Supplementary Evidence*. It has been shown by cryoscopy that the solid is only weakly dissociated (*ca*. 15%) at 28° and it is significant that the solutions were coloured pale green. The colour would be expected of a nitroso monomer[4]. Treatment with alkali, sodium nitrite and subsequent acidification (Table 14) indicated the presence of a primary nitro group supporting therefore, the conclusion of infrared studies.

The observed instability of the compound towards light and temperature are in keeping with the similar results that Hazeldine et al[14] found for the case of tetrafluoro-1-nitro-2-nitrosoethane. (p.66). The slow decomposition of dimeric 2-chloro-2-nitrosonorbornane on exposure to daylight at room temperature has also been noted[15].

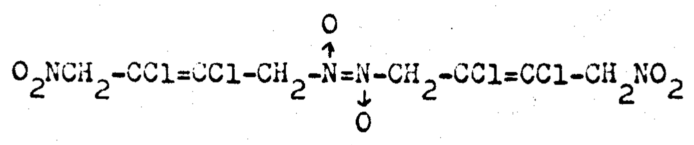
The inertness of a benzene suspension of the solid towards nitric oxide is consistent with the dimeric structure (I) and the findings of Donaruma and Carmody[16] who found that bis-nitrosocyclohexane reacted very slowly with nitric oxide at 25° to give nitrocyclohexene, cyclohexyl nitrite and cyclohexyl nitrate as the major reaction products. The result of the treatment of a sulpholane solution of the solid with nitric oxide is less readily explained. Burrell[17] has shown qualitatively that the addition of nitric oxide to monomeric 1-chloro-1-nitrosocyclohexane was rapid even at -80°. Since cryoscopy has shown that the solid is dissociated (ca. 15% at 28°) in sulpholane, the monomer formed should, on Burrell's evidence, have reacted readily with nitric oxide and have disproportionated the gas to nitrogen dioxide and nitrogen which would have been detected. However, some results of this investigation indicate that the reaction of nitroso monomers with nitric oxide may not always be fast. At the termination of experiments using 1,1,4,4-tetramethyl-1,3-butadiene, isoprene and 1-chloro-1,3-butadiene (Table 11) there remained a blue or green coloured solution. (This colour faded on flushing with argon). It seems probable that the colour was due to a nitroso monomer and if Burrell's observation was applicable this would react rapidly with the excess nitric oxide. Brown[18] also found considerable quantities of unreacted nitroso monomers after tri- and tetramethylethylene were reacted with nitric oxide. Alternatively it must be borne in mind that the monomer may have tautomerised to the oxime more quickly than it reacted with nitric oxide. It is also possible that the evolution of nitrogen, if any, was too slow to be detected.

Neither catalytic hydrogenation, which failed to induce significant gas absorption, (N-O functional groups are only slowly catalytically hydrogenated at room temperature and atmospheric pressure[19]), nor examination of the reaction product after ammonolysis, helped to resolve the question of structure. The action of liquid ammonia is particularly puzzling. Comparison of the micro-analysis values with the figures estimated by titration, indicates that all the chlorine was ionisable and that a little over half of the nitrogen content was liberated by alkali. It seems therefore that the chlorine was stripped from the molecule and that all of it can be accounted for as ammonium chloride.

It is concluded that the structure for the solid isolated from the reaction of chloroprene with nitric oxide is the dimer of 2-chloro-1-nitro-4-nitrosobut-2-ene (I). The point most open to question is the relative positions of the nitro and nitroso groups.

2) Crystalline Solid Derived from 2,3-Dichloro-1,3-butadiene.

i) Bis-(2,3-dichloro-1-nitro-4-nitrosobut-2-ene). The structure (II) of this white solid,



$$O_2NCH_2\text{-}CCl{=}CCl\text{-}CH_2\text{-}\overset{O}{\overset{\uparrow}{N}}{=}\underset{O}{\underset{\downarrow}{N}}\text{-}CH_2\text{-}CCl{=}CCl\text{-}CH_2NO_2$$

(II)

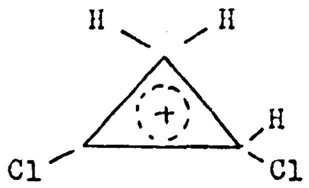
is based on the following interpretation of experimental results.

On the basis of evidence already presented the infrared spectrum shows a primary (or possibly a secondary) nitro group[1]. This is supported by a band (1425 cm.$^{-1}$) due to a methylene of a primary nitro group[2] and by the colour test (Table 14). There is no evidence for the presence of nitro groups in other enviroments.

The bands attributable to the dimeric nitroso group are again less easily assigned. In this connection it is of interest that this spectrum and that of bis-(2-chloro-1-nitro-4-nitrosobut-2-ene) have strong doublets at 1210 and 1245 cm.$^{-1}$, and 1205 and 1235 cm.$^{-1}$ respectively. Although these are not within the range quoted by Gowenlock and Lüttke[4] for nitroso dimers (Table 21) (Brown[1] has identified the band at <u>ca</u>. 1205 cm.$^{-1}$ with the nitroso group), it is significant that the doublet is absent in the spectrum of 2,3-dichloro-4-nitrobut-2-enaldoxime (Fig. 19). A further significant similarity is the weak band tentatively assigned to the -N=N- stretching frequency. This band is also absent in the spectrum of the oxime.

There is no band attributable to carbon-carbon double bond stretch. The intensity of this band in the case of tetrasubstituted ethylenes is however, always low and often absent[3].

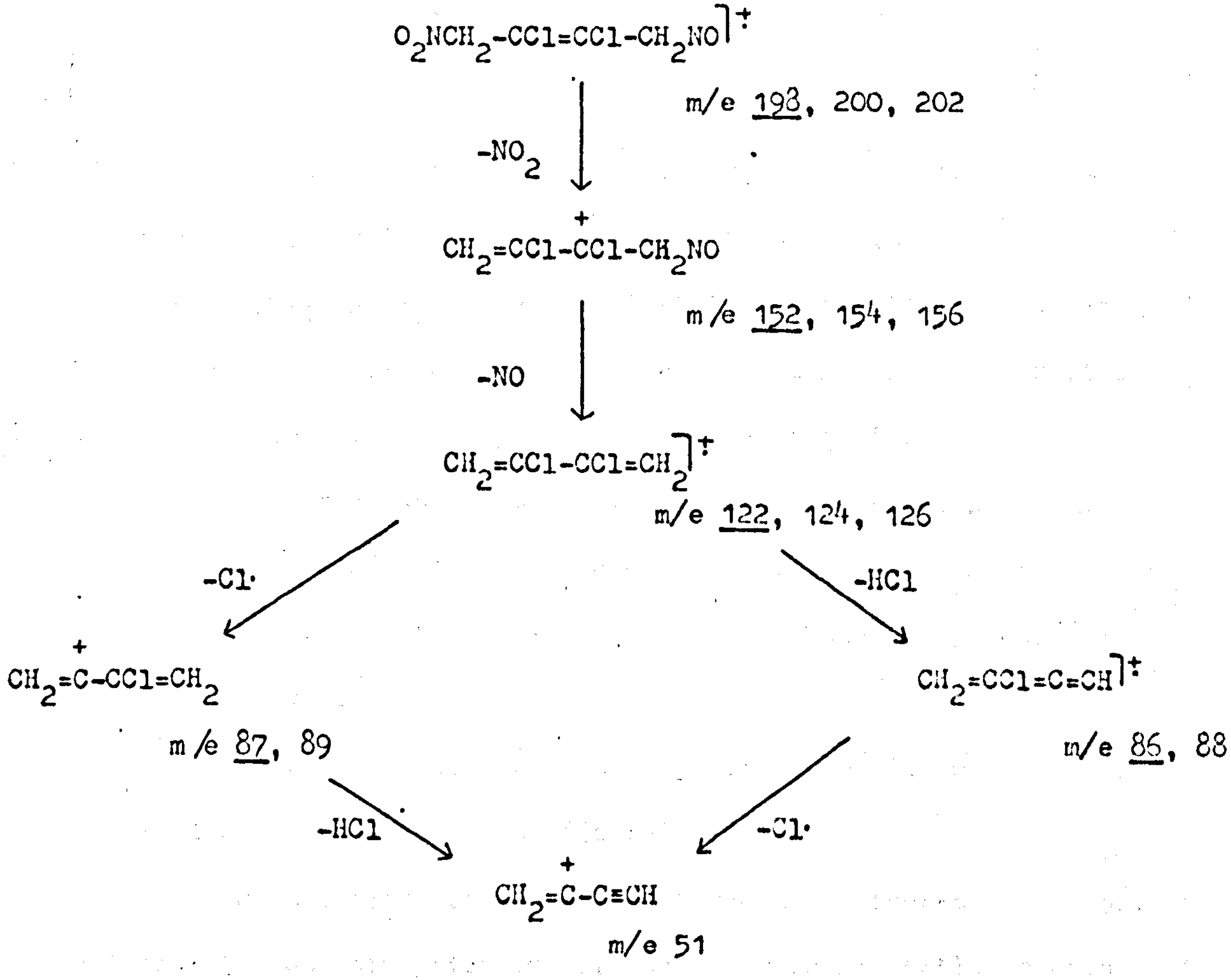
The mass spectra of the solid is shown in Figures 25 and 26. In neither case were there higher molecular weight fragments and again it is postulated the dimer readily fragments to the monomer. An interpretation of the major fragmentation routes (70 ev) of the compound is shown in Figure 35. The spectrum obtained at 20 ev is unusual in that it shows a more complicated fragmentation pattern than at 70 ev. It is interesting to note that loss of OH· and H_2O occurs to a greater extent than at 70 ev. The peaks at m/e <u>109</u>, 111, 113 (Fig. 25) are difficult to rationalise but a plausible structure is,



(III)

and loss of HCl would account for the peaks at m/e <u>73</u> and 75.

Figure 35. Major Fragmentation Routes of Bis-(2,3-dichloro-1-nitro-4-nitrosobut-2-ene).



(m/e for major isotope of chlorine is underlined).

The integrated proton magnetic resonance spectrum could not be interpreted in any meaningful manner owing to its complexity. It is consistent with the instability noted for bis-(2-chloro-1-nitro-4-

nitrosobut-2-ene) in dimethyl sulphoxide solution.

The result of a cryoscopic determination indicates that the solid readily dissociates (100% at 28°) in sulpholane to give a green solution and this is consistent with its subsequent ready conversion to the corresponding oxime.

ii) 2,3-Dichloro-4-nitrobut-2-enaldoxime. The evidence for the structure (IV) of this compound is in two parts.

$$O_2NCH_2\text{-}CCl{=}CCl\text{-}CH{=}NOH$$

(IV)

Firstly, the method of formation, from bis-(2,3-dichloro-1-nitro-4-nitrosobut-2-ene), and the positive nitrous acid test, (Table 14) substantiate a primary nitro group. This together with a molecular weight of 194 (cryoscopy) agrees with the formula given. The rest of the evidence is derived from spectroscopic investigation.

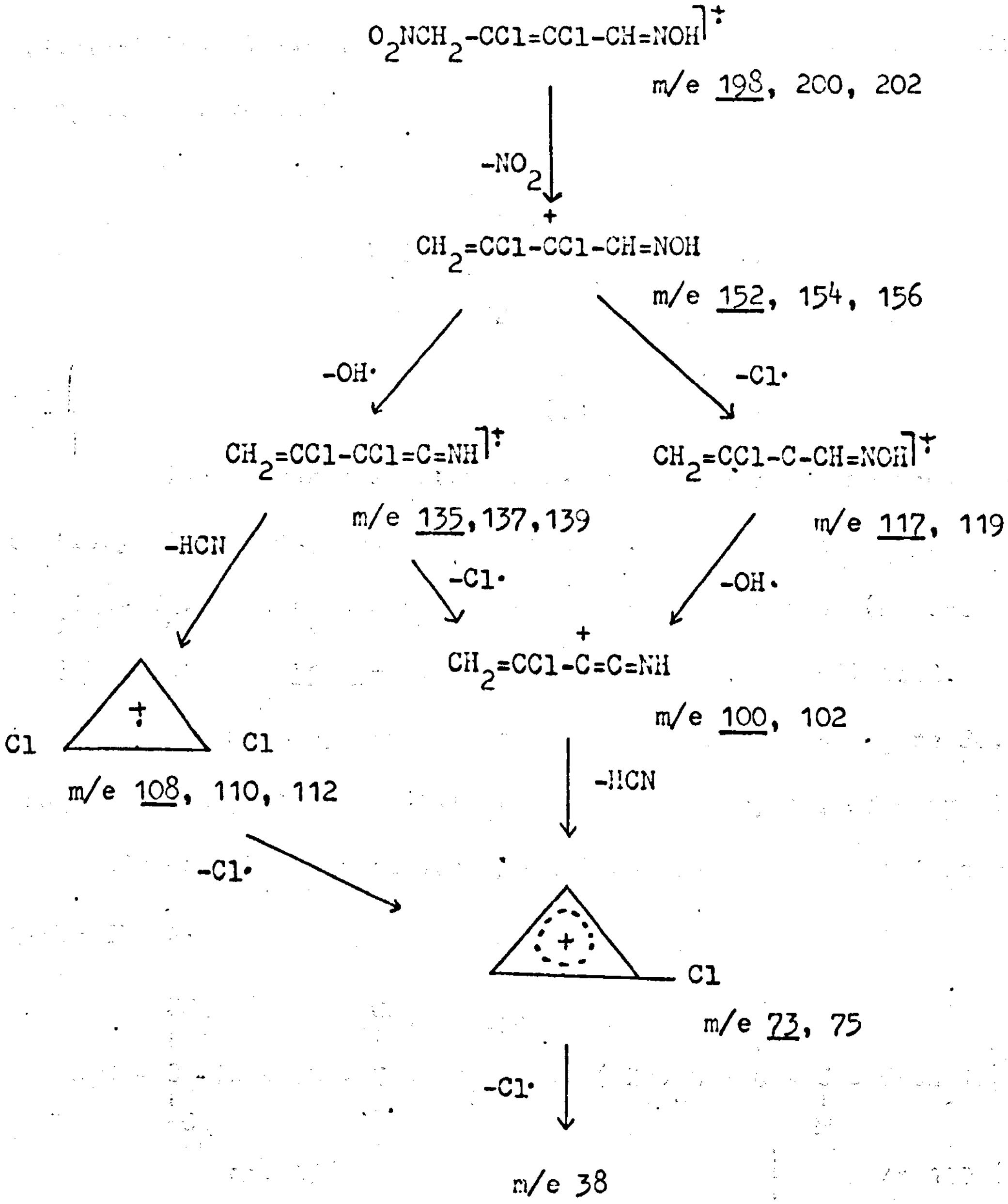
The infrared bands are consistent with the results of Fligge et al[12] for a series of nitro-oximino compounds. Additionally the band at 1620 cm.$^{-1}$ may be due to -C=N-stretch and the band at 670 cm.$^{-1}$ is due to C-Cl stretch[3].

The proton magnetic resonance spectrum (details on p.107 of Experimental Section) are seen to fit this formula.

The mass spectra of the oxime is shown in Figures 27 and 36. The latter shows an interpretation of the major fragmentation routes.

It is concluded that the structure (II) is therefore the correct one for the solid reaction product formed between nitric oxide and 2,3-dichloro-1,3-butadiene and that it readily converts to the oxime (IV) under the conditions described on p.106.

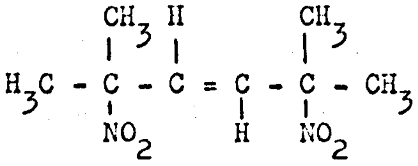
Figure 36. Major Fragmentation Routes of 2,3-Dichloro-4-nitrobut-2-enaldoxime.



(m/e for major chlorine isotope underlined).

3) Identification of 1,4-Dinitro-1,1,4,4-tetramethylbut-2-ene.

Unlike the previous two olefins discussed, a crystalline material was isolated on distillation of the initially formed oil from 1,1,4,4-tetramethyl-2,3-butadiene. The structure (V) was confirmed by spectral investigation.

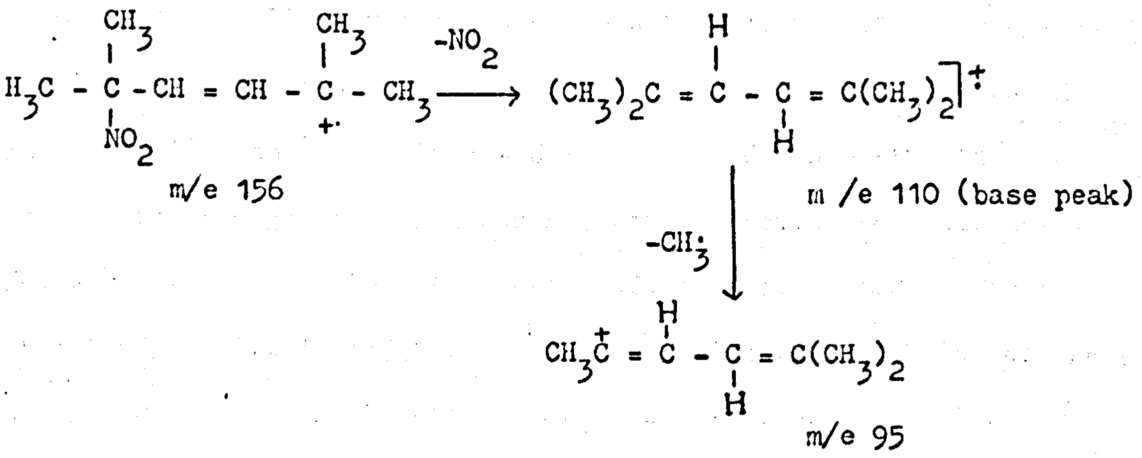


$$H_3C-\underset{NO_2}{\overset{CH_3}{C}}-\overset{H}{C}=\underset{H}{C}-\underset{NO_2}{\overset{CH_3}{C}}-CH_3$$

(V)

The infrared spectrum shows unambiguously the presence of a tertiary nitro group and other bands (p.107) conform to the structure[1] $(CH_3)_2\overset{|}{C}-NO_2$. There was no evidence for 1,2-addition (no trisubstituted C=C) but rather a trans-disubstituted ethylene is indicated.

The mass spectrum of the solid is shown in Figure 28. The fragmentation pattern exhibits no parent ion typical of many nitro compounds and the highest ion m/e 156 corresponds to the loss of one nitro group.

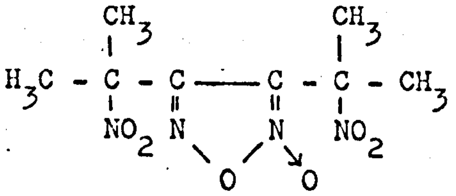


$$\underset{m/e\ 156}{H_3C-\underset{NO_2}{\overset{CH_3}{C}}-CH=CH-\underset{+\cdot}{\overset{CH_3}{C}}-CH_3} \xrightarrow{-NO_2} \underset{m/e\ 110\ (base\ peak)}{\left[(CH_3)_2C=\overset{H}{C}-\underset{H}{C}=C(CH_3)_2\right]^{+\cdot}}$$

$$\xrightarrow{-CH_3^{\cdot}} \underset{m/e\ 95}{CH_3\overset{+}{C}=\overset{H}{C}-\underset{H}{C}=C(CH_3)_2}$$

The proton magnetic resonance spectrum (p.108) can be interpreted successfully in terms of structure (V). The high field singlet indicates that all the methyls are equivalent as are the two ethylenic protons - low field singlet - therefore confirming 1,4-addition. The molecular weight (p.108) helps confirm structure (V).

It was not possible to satisfactorily identify the solid isolated in low yield (*ca.* 1%, p.108) from the interaction of nitric oxide with 1,1,4,4-tetramethyl-1,3-butadiene in concentrated benzene solution. A furazan oxide structure (VI) (p.17 Historical Section) can be eliminated from a consideration of the infrared spectrum (Fig. 21) since furazan oxides exhibit a strong band in the range 1625-1600 cm.$^{-1}$ (C=N str.)[20].



(VI)

Infrared also eliminates nitrate groups but shows the presence of the grouping[1] $(CH_3)_2\overset{|}{C}-NO_2$. There are no strong bands that might be assigned to a nitroso dimer but Brown[1] has observed that tertiary nitroso dimers, a reasonable possibility in this case, do not exhibit absorption *ca.* 1205 cm.$^{-1}$. There are weak bands at 1640 cm.$^{-1}$ - possibly of - N = N - stretching origin and at 1660 cm.$^{-1}$ - possibly - C = C - or - C = N - stretch. An integrated proton magnetic resonance spectrum in trifluoroacetic acid, changed with time and could not be successfully interpreted. The mass spectrometer gave little major fragmentation and a very weak ion of m/e 368 which might correspond to a fragment of a nitro-nitroso dimer (require Mol. Wt. = 372),

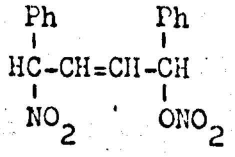
$$\left[O_2N(CH_3)_2C\text{-}CH{=}CH\text{-}C(CH_3)_2NO\right]_2 \qquad \text{(VII)}$$

but this must be excluded if the micro-analysis figures are reliable. The next highest major fragment is at m/e 214 which an accurate mass measurement showed was $C_8H_{12}N_3O_4$. Loss of $-NO_2$ from this would lead to the ion m/e 158. The only metastable evidence is for a loss of mass 30 (NO) from m/e 197, which might have arisen by loss of an OH• radical from m/e 214.

Investigation of the solid was difficult owing to the low yields obtained and the poor solubility. No satisfactory conclusion, on the evidence available, can be made as regards its structure.

4) trans, trans-<u>1,4-Diphenyl-1,3-butadiene</u>.

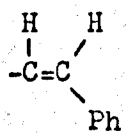
<u>1,4-Diphenyl-1-nitro-4-nitratobut-2-ene</u>. The solid is given the structure:-



$$\underset{NO_2}{\overset{Ph}{HC}}-CH=CH-\underset{ONO_2}{\overset{Ph}{CH}}$$

(VIII)

The infrared of the solid shows clearly the presence of a secondary nitro group[1] (1555 and 1370 cm.$^{-1}$). The bands at 1640, 1270 and 840 cm.$^{-1}$ are diagnostic of a nitrate ester but there is no way of distinguishing between primary, secondary or tertiary groups[1]. The lower frequency bands are probably masked by the C-H out-of-plane bending modes of the monosubstituted phenyl ring[3] (740 and 690 cm.$^{-1}$) as are olefinic bands. The lack[3] of a strong band close to 1625 cm.$^{-1}$ excludes a conjugated phenyl ring which is itself an indication that no 1,2-addition has occurred which would result in conjugation of the type:-



$$-\overset{H}{C}=C\begin{array}{l}\diagup H\\ \diagdown Ph\end{array}$$

(IX)

The mass spectrum (Fig. 30) of the sample showed a molecular ion at m/e 252 corresponding to a loss of $-ONO_2$ and this then lost $-NO_2$ to give m/e 206. The peaks at m/e 30 (7%) and m/e 46 (1%) tend to confirm the presence of a nitro group. Proton magnetic resonance occurred at low field in agreement with structures (VIII) or (IX). Elemental analysis and cryoscopy are in agreement with structure (VIII), and it is concluded that this is correct for the solid isolated from the reaction of nitric oxide with trans, trans-1,4-diphenyl-1,3-butadiene.

5) Oil Isolated from Chloroprene.

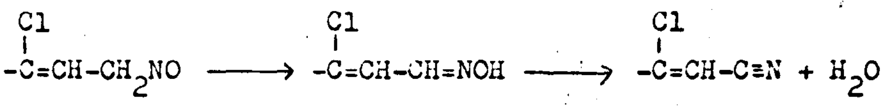
The structure of the oil adduct of nitric oxide and chloroprene is uncertain. Again the most significant information has been obtained from physical techniques.

The infrared spectrum (Fig. 12) of the oil shows clearly the presence of a nitro group. On the basis of evidence presented earlier (p.143) this is assigned as a primary nitro group[1] and is supported by the methylene band of a primary nitro group[2] and by alkali treatment (Table 14). There is no evidence for any other type of nitro group.

The bands at 1645, 1280, 860, 758 and 705 cm.$^{-1}$ are characteristic of nitrate esters[1]. Nitrite esters are unlikely to be present in significant amounts. As pointed out earlier (p.144) these are recognised[3] by a double band in the ranges 1681-1653 cm.$^{-1}$ and 1625-1613 cm.$^{-1}$ attributed to the trans- and cis- forms respectively of the nitrite structure and by a band near 800 cm.$^{-1}$. The broad band ca. 3300 cm.$^{-1}$ is attributed to a hydrogen bonded-OH group[3]. There is little evidence for unsaturation in the oil excepting the band at 3030 cm.$^{-1}$. Other diagnostic bands are either very weak or masked.

In an attempt to purify the chloroprene oil adduct molecular distillation was attempted. This resulted in a distillate that showed absorption due to triply bonded carbon in the infrared. The band

(2150 cm.$^{-1}$) is low even for a conjugated nitrile[3] which might reasonably be expected in this case. The formation of the nitrile would probably be due to the loss of water from an oxime or an amide[21].

 (4)

$$\overset{Cl}{\overset{|}{-C}}=CH-CH_2NO \longrightarrow \overset{Cl}{\overset{|}{-C}}=CH-CH=NOH \longrightarrow \overset{Cl}{\overset{|}{-C}}=CH-C\equiv N + H_2O \qquad (4)$$

The band does fall in the ranges quoted for alkynes[3] which in this case would probably arise by loss of hydrogen chloride.

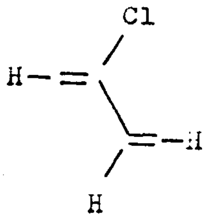
$$-CCl=CH- \longrightarrow -C\equiv C- \qquad (5)$$

The number average molecular weight (240) of the initial oil is too high for 1,2- or 1,4- addition of nitro (Mol. Wt. = 179) or nitrate (Mol. Wt. = 211) groups and too low for the dimeric structure,

$$O_2N(-CH_2-CCl=CH-CH_2-)_2ONO_2$$

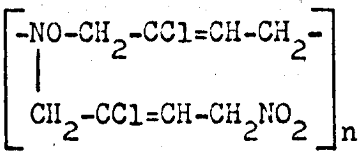
which requires a molecular weight of 317.

Gel permeation chromatography (Fig. 10), using refractive index as the method of detection, shows the presence of at least six components. The chromatogram shows that the major part of the oil consists of structures whose apparent length lies between 4.3 and 81Å. (0.43 and 8.1 nm). Because the observed value for chloroprene monomer 4.3 Å. (0.43 nm) (See Fig. 10), which was run under the same conditions, is less than the value calculated, 6.3Å. (0.63 nm) on the basis of the structure,



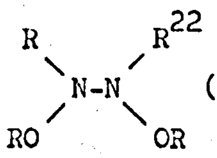
it is tempting to conclude the constituents range from a dimer up to a decamer. This assumes that the refractive indices of the components are similar and that there is ideal behaviour of nitro and nitrate compounds. Evidence is presented later that indicates that this may not be the case (p. 161).

Elemental analysis (Table 12) corresponds to an empirical formula $C_4H_4Cl_{0.8}N_{1.3}O_{2.9}$. This, and the observations of the number average molecular weight and the molecular weight distribution, would seem to exclude a major contribution from the type,

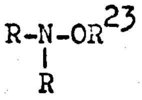


$$\left[\begin{array}{l}-NO-CH_2-CCl=CH-CH_2- \\ \;\;| \\ \;\;CH_2-CCl=CH-CH_2NO_2\end{array}\right]_n$$

analogous to the structure Hazeldine[14] has suggested for the polymer isolated from the interaction of nitric oxide and tetrafluoroethylene (p. 67). Similarly structures such as,



(Mol. Wt. = 598);



$$R-\underset{R}{\underset{|}{N}}-OR^{23}$$

(Mol. Wt. = 433.5)

(where R = $O_2NCH_2CClCHCH_2$-)

suggested for oils isolated from the reaction of isobutene and nitric oxide (p. 60) can also be ruled out as major contributors.

It is therefore concluded that the major part of the oil adduct is a low molecular weight polymer. The main component is likely to be a dimer with nitro or nitrate end groups. By analogy with bis-(2-chloro-1-nitro-4-nitrosobut-2-ene) this was probably formed by 1,4 or 4,1-addition.

6) Oil Isolated from 2,3-Dichloro-1,3-butadiene.

A viscous brown oil formed the major component when 2,3-dichloro-1,3-butadiene reacted with nitric oxide. The infrared spectrum shows the expected bands attributable to nitrate and primary nitro groups. The nitrate bands are relatively weak compared to those of the nitro. This contrasts with the case of the oil derived from chloroprene where they are of approximately equal intensity. A further difference is the presence of triply bonded carbon. This was only observed in the case of chloroprene after molecular distillation of the oil under high-vacuum at temperatures up to 100°. In the case of 2,3-dichloro-1,3-butadiene only a moderate pressure (10^{-2}mm.) and room temperature were sufficient to bring about the same change. This illustrates the contrasting instability of the oil derived from 2,3-dichloro-1,3-butadiene to that of chloroprene.

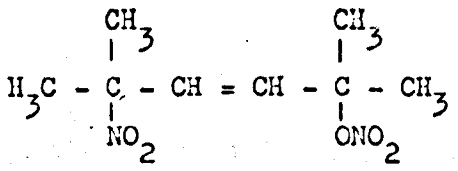
The same considerations as applied to chloroprene, lead to the conclusion that the dimeric structure,

$$O_2N(-CH_2-CCl=CCl-CH_2-)_2ONO_2$$

which requires a molecular weight of 352, is a major component. Gel permeation chromatography (Fig. 11) is rather inconclusive in that the presence of at least six components whose apparent lengths lie between 2.5 and 21.6 Å.(025 and 2.16 nm), are shown. Since a molecule of 2,3-dichloro-1,3-butadiene, depending on its conformation, has a length of between 6.2 and 6.7 Å.(0.62 and 0.67 nm) and there are a number of eluted peaks of size smaller than that of the monomer, it would seem that more complex absorption or association is taking place. It is significant that 1-nitropropane, which is calculated to have a chain length of between 6 and 7 Å. (0.6 and 0.7 nm), run under identical conditions as the oil (See Fig. 11), gave an apparent length of 11.9 Å. (1.19 nm).

7) Oil Isolated from 1,1,4,4-Tetramethyl-1,3-butadiene.

The infrared spectrum of this oil (Fig. 16) shows the expected bands attributable to methyl, nitrate and nitro groups. The latter is further characterised as the grouping[1] $(CH_3)_2\overset{|}{C}-NO_2$. The shoulder at 1530 cm.$^{-1}$ is near the frequency where a secondary nitro group would absorb[1]; the lower frequency band (ca. 1380 cm.$^{-1}$) would overlie that of the tertiary nitro group. This could imply some 1,2-addition. However, there is little evidence for unsaturation excepting for the band at 970 cm.$^{-1}$ generally attributable to a trans- disubstituted ethylene[3]. This supports the possibility of 1,4-addition, but there should be an accompanying band in the region 3040-3010 cm.$^{-1}$ which is absent[3]. The observed molecular weight (ca. 300) eliminates a major contribution from the structure,



$$H_3C-\underset{NO_2}{\overset{CH_3}{C}}-CH=CH-\underset{ONO_2}{\overset{CH_3}{C}}-CH_3$$

which requires a molecular weight of 218. Since the parent olefin would not be expected to polymerise readily it may be that some form of limited copolymerisation with nitric oxide has occurred.

The evidence available on the nature of the oil derived from 1,1,4,4-tetramethyl-1,3-butadiene is inconclusive excepting for the likelyhood of 1,4-addition of nitro and nitrate groups.

8) Other Oil Adducts.

a) trans, trans-1,4-Diphenyl-1,3-butadiene.

The infrared spectrum (Fig. 23) of the oil adduct of the olefin and nitric oxide shows a marked similarity to that of 1,4-diphenyl-1-nitrato-4-nitrobut-2-ene already discussed.

b) 1-Chloro-1,3-butadiene.

An infrared spectrum of a typical oil adduct exhibits bands attributable to nitro and nitrate groups. There is some indication that there are nitro groups in at least two enviroments - the one is primary - and the other is either secondary, or more probably, attached to a chlorine carrying carbon[1]. There is some evidence for a trans-disubstituted ethylene[3] (980 cm.$^{-1}$).

The observed number average molecular weight (ca.220) indicates that a major product may be formed by simple addition of a nitro and a nitrate group. (Mol. Wt. = 196).

c) Isoprene.

The infrared spectrum of the oil shows the customary bands of nitro and nitrate groups.

It is concluded that the coloured, viscous, oil products from nitric oxide and conjugated diene interactions were formed by 4,1-(unsymmetrical diene) or 1,4-addition, although the existence of other isomers in lesser quantities cannot be ruled out. All included substantial amounts of nitro groups and varying amounts of nitrate ester. There is evidence in some cases for a considerable number of components and a major portion of these is likely to be a low molecular weight polymer. The infrared also indicates that there are in some instances compounds containing NH or OH, carbonyl, and tertiary alcohol or ether linkages. There was little evidence for the constitution of some of the oils changing on storage for some months at -20° under nitrogen. However, on storage at room temperature under air in the dark or light the chloroprene oil adduct gradually evolved nitrogen oxides, swelled and became darker and tar-like.

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CHAPTER 8

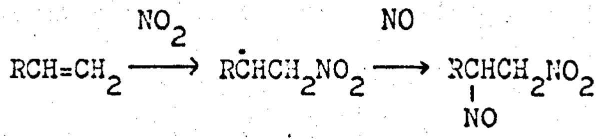
The Mechanism of the Interaction of Conjugated Dienes with Nitric Oxide.

In the previous chapter the compounds formed from purified nitric oxide and readily polymerised, conjugated olefins were identified as far as possible and the stabilities of these compounds described and discussed. Because of the experimental difficulties encountered, certain other conjugated olefins were selected for investigation in the hope that, if the olefins were less susceptible to autoxidation and polymerisation, they would give less complicated products and a clearer idea of the stages involved might result. For this reason olefins such as 1,1,4,4-tetramethyl-1,3-butadiene, trans, trans-1,4-diphenyl-1,3-butadiene, hexachlorocyclopentadiene and 1,4-diphenylcyclopentadiene were also included in the study. A knowledge of the mechanism of these reactions would give a better appreciation of the system under consideration and it was hoped that this would lead to a correlation of steric and polar factors and an understanding of relative reactivities.

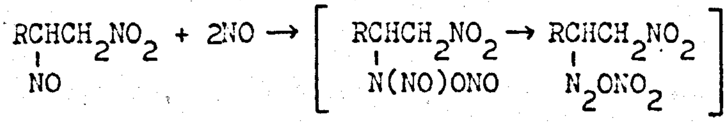
It was clear after a consideration of the work of earlier investigators (Chs. 1,2 and 3) that there was considerable ambiguity as to whether homolytic or heterolytic reactions were involved and so experimental work was carried out with a view to throwing further light on to this aspect of the work. It was disappointing that attempts to put certain measurements such as the rate of absorption of nitric oxide or rate of removal of trapping agents on a quantitative basis proved to be difficult.

The interaction of the conjugated dienes with nitric oxide showed many similarities to the characteristics observed by Brown[1], and Bloomfield and Jeffrey[2] for mono-olefins and nitric oxide reactions.

The products, already discussed in the previous chapter, are those that might reasonably be expected to result from the action of dinitrogen trioxide or nitrogen dioxide on the conjugated systems. Brown[1] postulated a free radical path (p. 63) to account for his major reaction product. This mechanism involved initiation by nitrogen dioxide, combination of the 1-nitro alkyl radical so formed with nitric oxide (Equation 1) and further action of nitric oxide on the nitroso monomer, to give, <u>via</u> a N-nitroso-N-alkyl-hydroxylamine nitrite, an unstable aliphatic diazonium intermediate:-

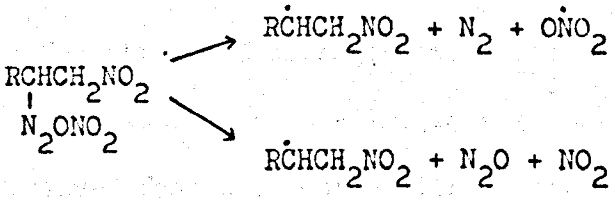


$$\mathrm{RCH{=}CH_2} \xrightarrow{\mathrm{NO_2}} \mathrm{R\dot{C}HCH_2NO_2} \xrightarrow{\mathrm{NO}} \underset{\mathrm{NO}}{\mathrm{RCH}}\mathrm{CH_2NO_2} \qquad (1)$$



$$\underset{\mathrm{NO}}{\mathrm{RCH}}\mathrm{CH_2NO_2} + \mathrm{2NO} \rightarrow \left[\underset{\mathrm{N(NO)ONO}}{\mathrm{RCH}}\mathrm{CH_2NO_2} \rightarrow \underset{\mathrm{N_2ONO_2}}{\mathrm{RCH}}\mathrm{CH_2NO_2} \right] \qquad (2)$$

The latter intermediate was believed to break down by a predominantly homolytic path:-



$$\underset{\mathrm{N_2ONO_2}}{\mathrm{RCH}}\mathrm{CH_2NO_2} \rightarrow \mathrm{R\dot{C}HCH_2NO_2} + \mathrm{N_2} + \mathrm{\dot{O}NO_2} \qquad (3)$$

$$\underset{\mathrm{N_2ONO_2}}{\mathrm{RCH}}\mathrm{CH_2NO_2} \rightarrow \mathrm{R\dot{C}HCH_2NO_2} + \mathrm{N_2O} + \mathrm{NO_2} \qquad (4)$$

$$\mathrm{\dot{O}NO_2} + \mathrm{NO} \longrightarrow 2\ \mathrm{NO_2} \qquad (5)$$

By either route the 1-nitro alkyl radical is regenerated. It is worthwhile recording at this point that in the course of the work described in this thesis no nitrous oxide was detected and therefore it is concluded that reaction 4 is not significant. If this free radical chain reaction does indeed apply then it was considered that it should demonstrate, under suitable circumstances, the phenomena of induction period, initiation by radical sources and inhibition or chain transfer by free radical trapping agents.

1) Induction Period. One of the factors that led earlier workers to suggest a homolytic path for the reaction was the observation of an induction period. Bloomfield and Jeffrey[2] quote a period of between fifteen and thirty minutes for the appearance of a coloured solution, attributed to a nitro-nitroso monomer, when cyclohexene was treated with nitric oxide. Brown[1] on the other hand does not state the magnitude of the induction periods he observed or how they were assessed. Based on the criteria of the times for the appearance of green-blue colours and the rate of nitrogen evolution, the conjugated olefins used in this study can be placed in an approximate order of decreasing reactivity:-

Chloroprene, 2,3-Dichloro-1,3-butadiene, 1-Chloro-1,3-butadiene $>$ Isoprene $>$ 1,1,4,4-Tetramethyl-1,3-butadiene $>$ trans, trans-1,4-Diphenyl-1,3-butadiene $>$ 1,4-Diphenylcyclopentadiene. (Table 11),(p. 111). It can be seen from the table, that in most cases there was a time lag between colour formation and nitrogen evolution to reach a maximum. This favours the suggestion that nitrogen was evolved from some metastable intermediate derived from a coloured nitroso monomer. Hexachlorocyclopentadiene was found to be inert towards nitric oxide even at high temperatures. This is probably a reflection of its lack of reactivity towards nitrogen dioxide as found by Schribner[3] and is therefore consistent with the idea of nitrogen dioxide initiation.

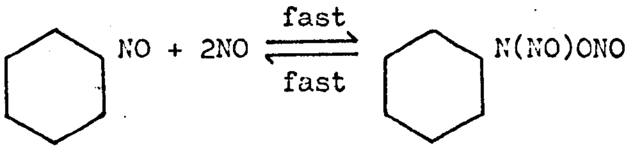
Using the flow system described in the experimental section it was difficult to determine accurately the time when nitric oxide absorption was at its greatest. With the more reactive dienes it was evident that absorption was taking place from the slowing of the bubble rate of the gas exit bubbler and this was simultaneous with the reaction solution becoming coloured. On the other hand with the less reactive olefins this bubbler effect was barely noticeable.

2) Initiation. If we consider the general case of the conjugated diene (I), initiation will take place by attack by a radical $Z\cdot$ to give the allylic radical (Ia) and (Ib), assuming attack in the 1-position.

$$\underset{\text{(I)}}{CR^1_2{=}CR^2{-}CR^3{=}CR^4_2} + Z\cdot \rightarrow \underset{\text{(Ia)}}{ZCR^1_2{-}CR^2{=}CR^3{-}\dot{C}R^4_2} \leftrightarrow \underset{\text{(Ib)}}{ZCR^1_2{-}\dot{C}R^2{-}CR^3{=}CR^4_2} \qquad (6)$$

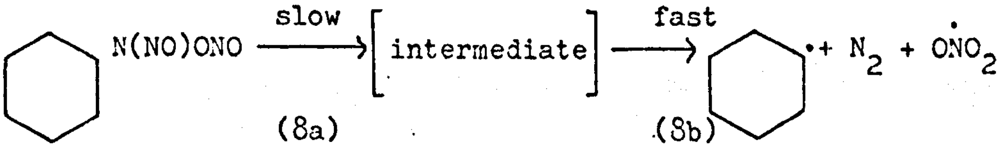
The exact nature of the allylic radical will depend, inter alia, on the nature of $Z\cdot$ and the nature of the R groups. It is therefore relevant to consider the problemn of initiation and in particular the evidence throwing light on the identity of $Z\cdot$.

Brown[1] found that his periods of induction were obviated by the introduction of products of an earlier reaction, or more significantly, by nitrogen dioxide. He is the only author to report that pure nitric oxide does not react with liquid olefins when they were stored in contact for an unspecified time. Hazeldine[4] has attempted purification of nitric oxide by shaking the gas with mercury for four days in order to remove traces of nitrogen dioxide. He was unable to find evidence of a significant induction period when he treated tetrafluoroethylene with gas purified in this manner. In the course of the work described in this thesis it was hoped to prepare the reactants in a high degree of purity by the use of a high-vacuum technique and then study any evidence of inhibition. Despite a thorough preparation of apparatus and purification of reactants, no evidence of an induction period was found even with the relatively unreactive trans,trans-1,4-diphenyl-1,3-butadiene. Because of this it can be concluded that any initiating species was not removed or that its concentration was not reduced to a level which prevented the steps 1 to 5 becoming fully established. If the initiating radical is nitrogen dioxide, then it is possible that traces of oxygen were left occluded to the glass inspite of the considerable conditioning periods and this led to the formation of traces of the higher oxide. This trace amount cannot account exclusively for the occurrence of a high proportion of nitro groups in the products. Hazeldine[4] has noted the slow decomposition of nitric oxide to nitrogen dioxide and nitrogen, a process which was accelerated by heat and pressure. An alternative approach to test for nitrogen dioxide initiation was to add the gas deliberately to the system before the introduction of the chloroprene substrate. It was hoped that a large number of nitro-allylic radicals ($Z\cdot = NO_2$ in Equation 6) would thus be generated quickly and that there would be a significant alteration in the observed reaction variables. This would indicate that either nitrogen dioxide was the initiator or that the oxide participated with an unknown initiator. Although the ratio of solid to oil products did vary, as did the consumption of chloroprene, there was no recognisable trend with increasing amounts of added nitrogen dioxide. (Table 17). Since the time for the formation of nitrogen to reach a maximum did not alter significantly it may be interpreted that either nitrogen dioxide was not an initiator or there was a rate determining formation of some intermediate leading to the release of molecular nitrogen. On the basis of Burrell's[5] work it is suggested that the latter is the more probable explanation. This author examined the reaction that occurred when monomeric nitrosocyclohexane and nitric oxide were irradiated with high energy electrons. Subsequent infrared analysis of the product showed the presence of nitro and nitrate groups which were attributed to nitrocyclohexane and cyclohexyl nitrate. This agreed with the earlier thermal work of Donaruma and Carmody[6]. Burrell was able to show that the rate of disappearance of the nitroso monomer was independent of nitric oxide concentration. It was suggested that the unreacted monomer in the presence of excess nitric oxide was in equilibrium with an unstable intermediate which was thought, by analogy with Brown, to be a substituted hydroxylamine nitrite:-



(7)

Because of this equilibrium the rate of monomer disappearance would be equal to that of the intermediate. Thus the half life of 0.2 sec. (25^{o}) observed for the monomer disappearance was also the half life for the rearrangement of the intermediate, which, again by analogy with Brown, was assumed to be a diazonium nitrate:-



(8)

It was implied that the break up of the diazonium nitrate (Equation 8b) was very rapid since Burrell suggested that reaction 8a was rate controlling and the nitroso monomer was related to the intermediates by the rapidly obtained equilibrium 7.

An alternative is initiation by nitric oxide itself. However, nitric oxide seems to be a particularly unreactive free radical - see the gas phase reactions discussed in Chapter 3. Also there is no evidence from this work that nitric oxide could add to the double bond and the resulting 1-nitroso radical be trapped by a second nitric oxide radical to give a dimeric dinitroso compound $(ONRNO)_2$. This might reasonably be expected to be insoluble in the solvents used although it must be borne in mind that any dinitroso monomer may have rapidly reacted further with nitric oxide.

A third possible type of initiation is that due to homolytic fission or induced decomposition of a peroxidic species. It has recently been demonstrated[7] that <u>t</u>-butyl hydroperoxide rapidly reacted with nitric oxide at 25° to give initially <u>t</u>-butyl nitrate and <u>t</u>-butanol according to the scheme:-

$$\underline{t}\text{-BuOOH} + \text{NO} \longrightarrow \underline{t}\text{-BuO}\cdot + \text{HONO} \qquad (9)$$

$$\underline{t}\text{-BuO}\cdot + \underline{t}\text{-BuOOH} \longrightarrow \underline{t}\text{-BuOH} + \underline{t}\text{-BuOO}\cdot \qquad (10)$$

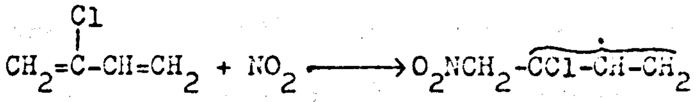
$$\underline{t}\text{-BuOO}\cdot + \text{NO} \longrightarrow \left[\underline{t}\text{-BuOONO}\right] \longrightarrow \underline{t}\text{-BuONO}_2 \qquad (11)$$

The authors suggested that the reaction was an induced decomposition caused by nitric oxide. The reaction was shown to apply only to hydroperoxides. Thus the oxide also reacted with <u>n</u>- and <u>s</u>-butyl hydroperoxides as well as with <u>m</u>-chloroperbenzoic acid, but it was virtually unreactive towards dibenzoyl peroxide, <u>t</u>-butyl peracetate and di-<u>t</u>-butyl peroxide. When one considers chloroprene specifically, we can take advantage of the recent work of Bailey[8], who has made a comprehensive study of the autoxidation of chloroprene and has concluded that the major peroxidic content is in the form of 1,2- and 1,4-dialkyl-polyperoxides - the latter predominating. The possibility of hydroperoxide end groups of the polyperoxide could not be excluded. The chloroprene peroxides are known to decompose even at 0° presumably to alkoxy radicals, and to initiate the facile polymerisation of the monomer. The gas phase reactions of nitric oxide with alkoxy radicals has been discussed in Chapter 3, where carbonyl and nitrite compounds are formed. Therefore there is a real possibility of reaction between nitric oxide and chloroprene peroxides decomposition products with the initial formation of nitrites. It was therefore pertinent to this study to, (a) remove all traces of chloroprene peroxides by thorough purification and (b) to add chloroprene peroxides. Since it was observed by Kern et al[9] and confirmed by Bailey[8], that chloroprene does not form a volatile peroxide, the method of purifying chloroprene described earlier should have removed any traces of peroxide matter and rigourous trap to trap distillation had little effect on the onset of reaction with nitric oxide. Also the introduction of partially oxidised chloroprene had no noticeable effect on the reaction, either with regard to colour changes, gases evolved or product composition. It is therefore concluded that there is no evidence to support chloroprene peroxides or their decomposition products as initiating species.

It can be postulated that nitrogen trioxide is a product of nitric oxide and olefin interactions (Equation 3) and could therefore act as an initiating species, particularly as the oxide is reported to be a more reactive radical than nitrogen dioxide[10], but there is no evidence to support this.

It is therefore concluded that, as there is no evidence to support either nitric oxide, chloroprene peroxides or nitrogen trioxide as initiators and the fact that nitrogen dioxide was shown to have some effect - albeit haphazard - on the reaction of nitric oxide with chloroprene, nitrogen dioxide was the most probable initiating radical.

If then we consider the radical resulting from the initial attack by nitrogen dioxide on chloroprene, this would take place predominantly in the 1-position,



$$\mathrm{CH_2{=}\overset{Cl}{\overset{|}{C}}{-}CH{=}CH_2 + NO_2 \longrightarrow O_2NCH_2{-}\overbrace{\mathrm{CCl{-}CH{-}CH_2}}^{\bullet}} \qquad (12)$$

because this gives an allylic radical which derives additional stability from the chlorine. In the general case of addition of ions or radicals to 1,3 conjugated dienes the thermodynamically stable product is the 1,4-addition product and this is in agreement with the observation of almost exclusive 1,4-addition of nitrogen dioxide and nitric oxide. This can be compared in certain respects to the u.v. initiated addition of thiols to the same olefin which gave predominantly 1,4- (72-95%) as opposed to 4,1- addition products. No 1,2- adducts were found[11]. Similarly, predominantly 1,4-addition might be expected with the other dienes used.

The stability of the intermediate allylic radicals derived from the dienes used can, to a certain extent, explain the order of overall reactivity as measured by the colour formation of nitroso compounds (p. 168). Thus <u>trans</u>, <u>trans</u>-1,4-diphenyl-1,3-butadiene would be expected to react more slowly than chloroprene because of the enhanced stability of the 1-nitro allylic radical due to the phenyl groups.

The initiation reactions in the case of chloroprene are envisaged to be as follows:-

$$\mathrm{CH_2{=}CCl{-}CH{=}CH_2 + NO_2 \longrightarrow O_2NCH_2{-}\overbrace{\mathrm{CCl{-}CH{-}CH_2}}^{\bullet}} \qquad (12)$$

$$\mathrm{R + NO \xrightarrow{fast} \overset{\bullet}{RNO}} \qquad (\text{where } \mathrm{R = O_2NCH_2{-}\overbrace{\mathrm{CCl{-}CHCH_2}}^{\bullet}}) \qquad (13)$$

$$\mathrm{RNO + 2NO \longrightarrow \left[Intermediate\right] \xrightarrow{slow} R + N_2 + O\dot{N}O_2} \qquad (14)$$

If the nitro allylic radical has a relatively long life then the concurrently produced nitrogen trioxide (Equation 14) can escape from its environment and react further with nitric oxide (Equation 5) forming more nitrogen dioxide which can then act as a chain carrier.

$$\dot{O}NO_2 + NO \longrightarrow 2NO_2 \quad \text{propagation} \qquad (5)$$

That nitrogen dioxide is produced in the reactions of this study is inferred from the considerable quantities of nitro groups shown by infrared spectroscopy to be present in the reaction products, and by the appearance of a blue solid - attributed to dinitrogen trioxide - in the cold trap when certain of the dienes were treated with nitric oxide (Table 11).

3) Termination. As the final products of the reactions studied have not been fully characterised the nature of the termination steps must necessarily be somewhat speculative.

A termination of importance when one considers chloroprene and 2,3-dichloro-1,3-butadiene is dimerisation of the nitro-nitroso compound or dimerisation and precipitation, which in this way removes it from the system. Considering the general case of the diene monomer M and its nitro allylic radical R· $(O_2NC\text{-}\overbrace{C\text{-}C\text{-}C}^{\bullet})$, these can polymerise according to the scheme:-

$$M + R\cdot \longrightarrow RM\cdot \xrightarrow{M} RM_x\cdot \quad (x = 2 \text{ to } 10) \qquad (15)$$

Some of the more probable termination steps involving the radicals $RM_x\cdot$, R· and nitrogen oxides are given in reactions 16-20.

$$R\cdot \text{ (or } RM_x\cdot \text{) } + NO \longrightarrow RNO \longrightarrow R'CH{=}NOH \qquad (16)$$

$$R\cdot \text{ (or } RM_x\cdot \text{) } + NO_2 \longrightarrow RNO_2 \qquad (17)$$

$$R\cdot \text{ (or } RM_x\cdot \text{) } + \dot{O}NO_2 \longrightarrow RONO_2 \qquad (18)$$

$$R\cdot + R\cdot \longrightarrow 2R \qquad (19)$$

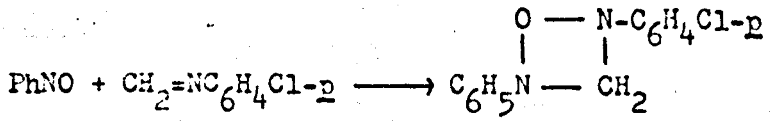
$$RM_x\cdot + R\cdot \longrightarrow R_2M_x \qquad (20)$$

The inclusion of 16 as a termination step is justified by the detection of hydroxyl groups in many of the reaction oils. The most probable steps involved in the formation of the oils are 17 and 18 as this would account for the nitro and nitrate groups and low molecular weight polymers found in most cases. The indications are that none of the dienes gave rise to high molecular weight polymers and therefore reaction 20 is not significant.

A reaction of the type 17 was probably responsible for the formation of 1,4-dinitro-1,1,4,4-tetramethylbut-2-ene which was isolated in low yield (p.107). The low yield is in agreement with the greater reactivity of the ONO_2 radical compared with NO_2. Finally it can be concluded that reaction 18 was of importance for *trans,trans*-1,4-diphenyl-1,3-butadiene where some 1,4-diphenyl-1-nitro-4-nitratobut-2-ene was formed (44%).

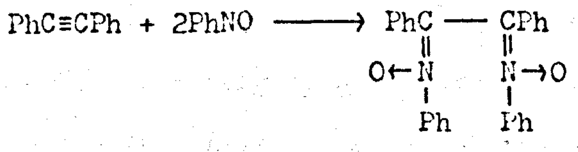
Reaction Intermediates.

It has been pointed out at various stages of this work that metastable intermediates such as nitroso compounds or nitroxides can be given reasonable consideration. Since a dimeric nitroso compound was isolated from chloroprene and 2,3-dichloro-1,3-butadiene and this was associated with the green/blue colour, believed to be a nitro-nitroso monomer, attempts were made to trap the corresponding chloroprene compound. Ingold[12] has reported that monomeric nitroso benzene reacted with the Schiff base *p*-chloro-methylene aniline to give a 1,2,4-oxadiazetidine:-



$$\mathrm{PhNO} + \mathrm{CH_2{=}NC_6H_4Cl\text{-}\underline{p}} \longrightarrow \begin{array}{ll} \mathrm{O} & \!\!\!—\; \mathrm{N\text{-}C_6H_4Cl\text{-}\underline{p}} \\ | & \;\;| \\ \mathrm{C_6H_5N} & \!\!\!—\; \mathrm{CH_2} \end{array} \qquad (21)$$

The reaction of the same nitroso compound with 1,2-diphenylacetylene is reported[13] to give a nitrone:-



$$\mathrm{PhC{\equiv}CPh + 2PhNO \longrightarrow \begin{array}{ccc} PhC & - & CPh \\ \| & & \| \\ O{\leftarrow}N & & N{\rightarrow}O \\ | & & | \\ Ph & & Ph \end{array}} \qquad (22)$$

The separate introduction of these two compounds into the reaction of nitric oxide and chloroprene resulted in high recovery of the reagent - this was probably due to the nitroso compound only being present in low concentrations and the fact that the monomer appeared to be unstable as indicated by the rapid fading of the colour on flushing the solution with argon. It is interesting to consider the fate of the nitroso monomer formed in the reaction of nitric oxide with dienes, particularly as only in two cases were dimeric nitro-nitroso compounds found, viz., chloroprene and 2,3-dichloro-1,3-butadiene. The dimerisation of the nitroso compound is presumably in competition with its tautomerisation to the oxime and this competition will depend on the structure of the particular diene being considered.

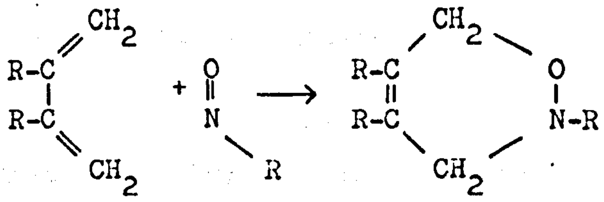
$$2RCH_2NO \rightleftharpoons (RCH_2NO)_2 \qquad (23)$$

$$RCH_2NO \rightleftharpoons RCH{=}NOH \qquad (24)$$

Gowenlock and Lüttke[14] have suggested that when the monomer is present in small concentrations the oxime formation is preferred. On the other hand the same authors have stated that dimer formation is dominant in non-hydroxylic solvents. Since nitric oxide addition to the nitroso monomer is postulated as part of the reaction sequence between olefins and the gas the picture is further complicated by the equilibrium:-

$$RCH_2NO + 2NO \rightleftharpoons \left[RCH_2N(NO)ONO\right] \qquad (25)$$

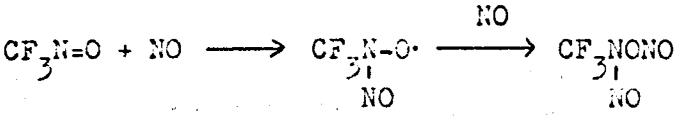
Burrell[5] has suggested that the nitroso monomer and the substituted hydroxylamine are in equilibrium and has shown qualitatively that the addition of nitric oxide to monomeric chloronitrosocyclohexene was rapid even at -80°. Ginsburg et al[15] have similarly found that there was a rapid reaction when trifluoronitrosomethane was treated with nitric oxide even at -100°. There is no evidence for other reactions occurring such as a Diels Alder addition,



(26)

or of radical addition across the nitroso group as suggested by Brown[1], (p. 61) and these are not considered. It may be that, whereas in the cases of chloroprene and 2,3-dichloro-1,3-butadiene, the dimers were insoluble in the benzene solvent, the dimers of the other olefins used were soluble, dissociated to a greater or lesser extent, and therefore reacted further with nitric oxide. A similar explanation has been advanced by Ogloblin et al (p. 50) to explain the formation of anomalous products of nitrosochlorination. It is also reasonable from a consideration of the overall reactivities of the conjugated olefins (p.168) that the nitroso monomers in these two cases were produced rapidly and therefore an appreciable concentration accumulated causing reaction 23 to compete successfully with routes 24 and 25. Only in one case can the failure to isolate a nitroso dimer be attributed to steric hindrance, that of 1,1,4,4-tetramethyl-1,3-butadiene. This is supported by the observation that tetramethylethylene forms only a monomeric nitrosochloride on reaction with nitrosyl chloride[16].

Ginsburg et al[15] have recently suggested that the reaction of nitric oxide with trifluoronitrosomethane proceeds via an intermediate nitroxide radical,

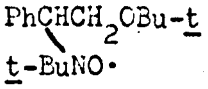


$$CF_3N{=}O + NO \longrightarrow CF_3\underset{NO}{\underset{|}{N}}\text{-}O\cdot \xrightarrow{NO} CF_3\underset{NO}{\underset{|}{N}}ONO \qquad (27)$$

but no radicals were detected by electron spin resonance spectroscopy carried out at an unspecified low temperature. Recently it has been demonstrated by the same technique that nitroxide radicals are produced by the addition of free radicals to nitroso compounds. Thus Perkins[17] has used 2-methyl-2-nitrosopropane (II) as a radical trap in the study of the radicals generated during the t-butylperoxyoxalate initiated polymerisation of styrene at room temperature.

$\underline{t}\text{-BuNO} \qquad (II)$

The e.s.r. spectrum due to (III) was observed:-

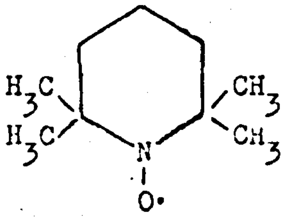


$$Ph\underset{\underline{t}\text{-}BuNO\cdot}{CH}CH_2OBu\text{-}\underline{t} \qquad (III)$$

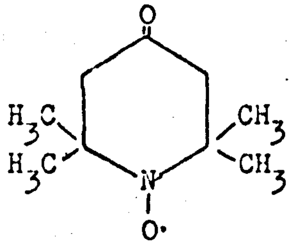
It does seem reasonable that nitroxides are formed in the reaction of nitric oxide with olefins and this can be used to explain the step yielding the N-nitroso-N-alkyl-hydroxylamine nitrite (Equation 2).

A much favoured intermediate has been the diazonium nitrate but when one looks at the evidence it seems that many authors are working by analogy with the work of Bamberger (Ch. 3) who reported on aromatic diazonium nitrate which he deduced after formation of an azo dye with 2-naphthol. In the work described in this thesis addition of such reagents as methanol, 2-naphthol or m-dimethoxy benzene failed to give ethers or azo compounds. The most probable explanation of this is the extreme instability of aliphatic diazonium salts. Two claims [18,19] have been made for the isolation of the possible diazonium salt derived from treatment of ethyl diazoacetate with hexachloroantimonic acid, but the exact structure of the compounds in each case was uncertain. Zollinger[20] has stated that aliphatic diazonium salts are incapable of existence because the $-\overset{|}{\underset{|}{C}}-N=$ bond is not stabilised by resonance. A phenyl group is able to stabilise a diazonium ion to a limited extent through delocalisation of the charge. Such delocalisation cannot occur in an alkyl diazonium ion and decomposition, with the elimination of molecular nitrogen, follows. An aliphatic diazonium nitrate, the suggested reaction intermediate of olefins and nitric oxide, would not therefore be expected to be stable and would have but transient existence even at low temperatures.

Some evidence for the existence of radical intermediates in the reaction of nitric oxide and chloroprene has been obtained in two ways. The first of these involved the use of two stable nitroxides; 2,2,6,6-tetramethyl piperidine nitroxide (IV) and its ketonic analogue (V).

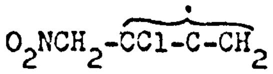


(IV)



(V)

These types of radicals have been shown by Buchachenko et al [21], confirmed later by Ingold[22], to react with alkyl rather than peroxy radicals and have been used by Bailey[8] in his study of the autoxidation of chloroprene. It was hoped by the use of (V) to trap any intermediate radicals, such as



$$O_2NCH_2\text{-}\overset{\bullet}{\overbrace{CCl\text{-}C\text{-}CH_2}}$$

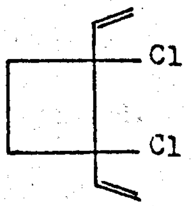
(VI)

and to isolate from the reaction products a suitable derivative of the carbonyl group present in the heterocyclic ring. Examination of the infrared spectra of the resulting oils showed that the characteristic nitroxide absorption was missing suggesting its consumption by some radical intermediate. It is also interesting that only traces of the nitroso dimer were isolated from most of the reactions suggesting that some interception of the radical (VI) may have occurred. It was shown that the nitroxide (V) combined rapidly with nitrogen dioxide to give an unidentified unstable solid (p.133). Since nitrogen dioxide is a likely intermediate in the reaction then it is probable that some of the nitroxide was consumed in this manner. The speed of nitrogen evolution in these experiments appeared to be affected in a haphazard way for which no explanation can be advanced.

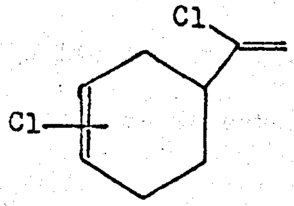
Some additional evidence was obtained for radical intermediates by performing the reaction of nitric oxide with chloroprene in the presence of iodine. Again little or no nitroso dimer was isolated and the major product was an intractable oil. Analysis showed that a considerable quantity of iodine had been consumed (Table 19). The intervention of nitrosyl iodide, formed by the combination of nitric oxide and iodine atoms, is not thought likely as this is reported as being unstable[23]. Porter[23] has postulated its existence to account for the absorption spectrum observed when a mixture of iodine and nitric oxide were subjected to flash photolysis.

Significance of Dimers derived from Conjugated Dienes.

It has been known for some time that chloroprene forms dimers on standing at room temperature. Robb et al [24] have shown that the major components of the dimer mixture are cyclobutane (VII) and vinyl cyclohexene (VIII) compounds, but these are formed only slowly at 35°.



(VII)



(VIII)

Even though the interaction of chloroprene and excess nitric oxide at 6° in non polar solvents is a relatively much faster reaction, it was felt that the effect of nitric oxide on these dimers should be checked. The action of nitric oxide on a mixture of dimers (p.109) under standard reaction conditions was found to be a very slow process giving, after eight hours, a dark green viscous oil. Although there was an early, slight evolution of nitrogen this dropped off quickly and for the remainder of the reaction period there appeared to be a very slow nitrogen evolution. The observed nitrogen maximum and the very small amount of solid isolated can be attributed to the chloroprene monomer impurity (ca. 1%). It would seem therefore, that chloroprene dimers are unlikely to be involved in the reaction of the monomer with nitric oxide under standard conditions. It must also be borne in mind that in this work, reaction solutions are very dilute (ca. 2%) and this must decrease the possibility considerably of chloroprene dimerisation. Some confirmation of the conclusion was obtained for the vinyl cyclohexene component by the observation of a comparably slow reaction, with little nitrogen evolution, of cyclohexene and nitric oxide under the same conditions. Similarly the dimers of isoprene are not likely to play a significant part in the reaction[25] while the relative ease of formation of the dimers of 2,3-dichloro-1,3-butadiene and their reactivities have yet to be determined.

Nitrite Intermediates.

One of the most puzzling facts concerning the constitution of the reaction products of conjugated dienes and nitric oxide is the large amounts of nitrate esters and the virtual non-existence of nitrite groups as shown by infrared spectroscopy. In view of the known dual reactivity (p. 5) of nitrogen dioxide some nitrite esters would reasonably be expected. Since none were detected it suggests that they were intermediary in the formation of other groups. The earlier explanations of Levy et al (p. 18) who suggested nitrogen dioxide oxidation of nitrite to nitrate groups has been questioned by Bonetti and co-workers (p. 18). Shechter[26] has suggested oxidation of the same group by nitrogen trioxide but has no evidence to support this. An alternative explanation is the dissociation of alkyl nitrites into alkoxy radicals and nitric oxide.

$$\mathrm{RONO} \longrightarrow \mathrm{R\dot{O}} + \mathrm{NO} \qquad (29)$$

This has been put forward by Park et al[27] in their study of the interaction of nitric oxide with fluoro-olefins at 22°. The alkoxy radicals so produced could then undergo a number of combination and disproportionation reactions. (Shown for a primary alkoxy radical)[28]:-

$$\mathrm{RCH_2\dot{O}} \longrightarrow \mathrm{R\cdot} + \mathrm{CH_2O} \qquad (30)$$

$$\mathrm{RCH_2\dot{O}} \xrightarrow{\mathrm{R\cdot}} \mathrm{RCHO} + \mathrm{RH} \qquad (31)$$

$$\mathrm{RCH_2\dot{O}} \xrightarrow{\mathrm{RO\cdot}} \mathrm{RCHO} + \mathrm{ROH} \qquad (32)$$

$$\mathrm{RCH_2\dot{O}} \xrightarrow{\mathrm{RH}} \mathrm{RCH_2OH} + \mathrm{R\cdot} \qquad (33)$$

The reactions of the type 31 and 32 could account for the minor amounts of carbonyl groups, and 32 and 33 for the possible hydroxyl groups found to be present in the infrared spectra of some of the oil adducts.

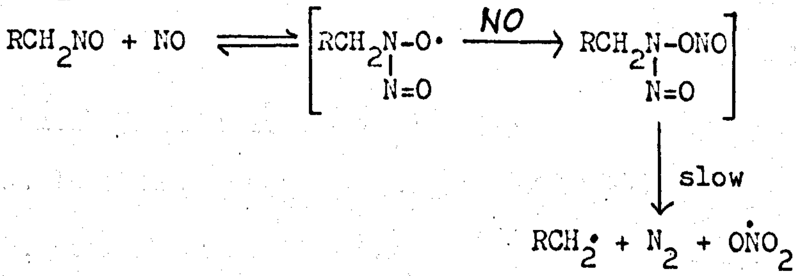
It is has been demonstrated that the reaction between nitric oxide and conjugated olefins under the conditions used led to complex reaction products. Only in a few cases were identifiable solid products formed - the major product in all cases was a brown, viscous, polymeric oil. Evidence was obtained for induction periods leading to an unidentified metastable intermediate, but the data collected from the experiments designed to test initiation do not clearly point to any single species being responsible. In the absence of any contrary evidence it is felt that nitrogen dioxide was the initiator. The work carried out to trap postulated reaction intermediates failed to prove their existence and the participation of aliphatic diazonium intermediates must still be regarded as highly speculative whereas the indirect evidence for free radical intermediates is more satisfactory. The coloured reaction solutions and the isolation of nitro-nitroso dimers give good reason to believe that nitroso monomers are reaction intermediates and the consumption of nitroxide radicals and iodine during the reaction points to the involvement of free radicals. It is considered at this stage of this investigation that the most likely reaction sequence is as follows:-

Diene + $NO_2 \longrightarrow$ Nitro Allylic radical .... initiation

Allylic radical + NO —— 1,4-nitro-nitroso compound (RCH_2NO)

$2RCH_2NO \rightleftharpoons (RCH_2NO)_2$ .... applies to Chloroprene and 2,3-Dichloro-1,3-butadiene

$RCH_2NO \rightleftharpoons RCH{=}NOH$ .... applies to 2,3-Dichloro-1,3-butadiene



$$RCH_2NO + NO \rightleftharpoons \left[RCH_2\underset{N=O}{\underset{|}{N}}\text{-}O^{\bullet} \xrightarrow{NO} RCH_2\underset{N=O}{\underset{|}{N}}\text{-}ONO \right] \xrightarrow{\text{slow}} RCH_2^{\bullet} + N_2 + \dot{O}NO_2$$

$RCH_2^{\bullet} + \dot{O}NO_2 \longrightarrow RCH_2ONO_2$ ....identified for trans, trans-1,4-Diphenyl-1,3-butadiene

$RCH_2^{\bullet} + NO_2 \longrightarrow RCH_2NO_2$ .... identified for 1,1,4,4-tetramethyl-1,3-butadiene and probably occurs with oil products

$\dot{O}NO_2 + NO \longrightarrow 2NO_2$

and where polymerisation occurred

$RM_x^{\bullet} + NO\ (or\ NO_2;\ \dot{O}NO_2) \longrightarrow RM_xNO$ (x = 2 to 10) applies to oil products.

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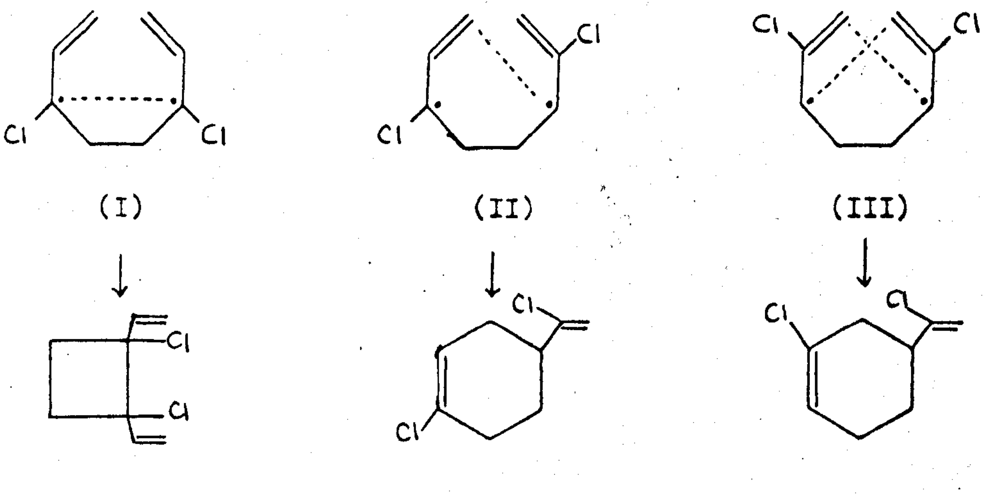
CHAPTER 9

Thermal Rearrangement of Chloroprene Dimers and Their Significance in Mass Spectrometry.

During the course of the work described in this thesis it was necessary to prepare and isolate some dimers of chloroprene (p. 82). Part of the identification procedure adopted involved the use of mass spectral analysis and the results obtained and the conditions used are listed in Table 10.

1) Thermal Characteristics of Chloroprene Dimers.

Recently Robb et al[1] have demonstrated that major components from mild temperature (35-38°), chloroprene, thermal dimerisation are 1,2-dichloro-1,2-divinylcyclobutane and 1- and/or 2-chloro-4-(α-chlorovinyl)-cyclohexene-1. A small amount of 1,6-dichloro-1,5-cyclo-octadiene was also found. The failure of earlier workers to detect the cyclobutane compound was attributed to the higher temperatures (90° or above) previously used in the preparation or isolation of the dimers. At these elevated temperatures Robb et al suggested this derivative might undergo a Cope rearrangement to 1,6-dichloro-1,5-cyclo-octadiene. Indeed, a peak that corresponded to the latter compound was observed in high temperature gas chromatograms of dimer samples that had been shown spectroscopically to contain no cyclo-octadiene before injection. In a later paper[2] it was noted that such thermally induced isomerisation was not quantitative. It was suggested that both trans- and cis-1,2-dichloro-1,2-divinylcyclobutanes were formed, but it was only the cis- form that underwent rearrangement to the cyclo-octadiene. In the same publication evidence was presented which led the authors to propose that the cyclobutane- and cyclohexene-type dimers were formed via isomeric diradical intermediates of very similar free energies:-



(I) (II) (III)

It is apparent that both 1- and/or 2-chloro-4-(α-chlorovinyl)-cyclohexene-1 could be formed. Although the intermediates I to III could give rise to cyclo-octadiene, in fact only minor amounts of this compound were formed. This probably reflects the degree of stability conferred on the radicals by the chlorine substituents. This might be expected to be at a maximum where the chlorine is α to the unpaired electron - thus a high yield of the cyclobutane would be expected from the intermediate (I).

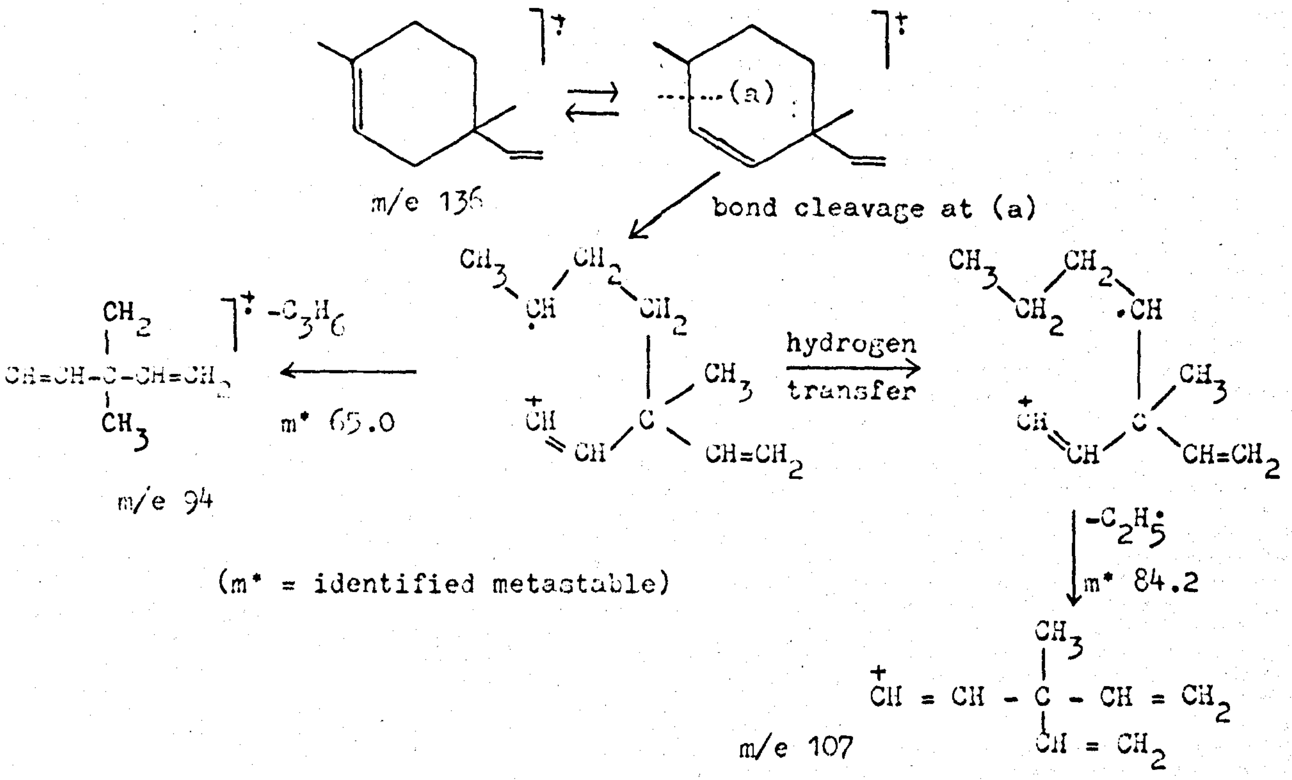
In addition to thermal isomerisation, hydrogen chloride elimination can occur, for when chloroprene dimers were heated for a number of hours at temperatures below 95°, the following compounds were identified[3] as well as the chlorovinyl-cyclohexene and dichloro-cyclo-octadiene:-

1-chloro-4-vinyl-cyclohexa-1,3-diene
1-chloro-4-ethyl benzene
methyl chlorobenzenes

2) <u>Mass Spectra of Isomers; Substituted Cyclobutanes, Cyclohexenes and 1,5-Cyclo-octadiene.</u>

Also of relevance is the recent work of Brittain *et al*[4a,b,c] who have recorded the mass spectra of some of the dimers of isoprene, penta-1,3-diene and buta-1,3-diene. They point out that the fragmentation patterns of the respective cyclobutane and cyclohexene dimers (and 1,5-cyclo-octadiene in some cases) of these compounds are very similar in intensity and that in most cases the isomers showed the same metastable transitions. One result of electron impact on these compounds was ring cleavage leading on the one hand to the corresponding diene monomer fragments and on the other, to the loss of ethylene. No metastable ions corresponding to the loss of ethylene were found and only in two cases[4a] were the metastable ions corresponding to the production of diene monomer recorded. The authors suggested that these facts indicated that processes involved in the cleavage of the ring of the molecular ion were rapid.

In the cases of the cyclohexene derivatives it was found that losses of an ethyl radical and propene occurred (*ca.* 10-20%) and their proposed fragmentation route leading to these is shown in Figure 37 for the typical case of 1,4-dimethyl-4-vinylcyclohexene-1.



(m* = identified metastable)

Figure 37 A Fragmentation Route[3a] of 1,4-Dimethyl-4-vinylcyclohexene-1.

The cyclobutanes and 1,5-cyclo-octadiene also exhibited losses of ethyl radicals and propene and because these could not be readily explained by a direct route from the respective molecular ions, Brittain et al[4b,c] postulated that some isomerisation of the molecular ions of the cyclobutanes and 1,5-cyclo-octadiene, to their corresponding cyclohexene isomers, had occurred in the mass spectrometer under the influence of electron impact. Rearrangement followed by bond cleavage as described above then gave rise to the observed losses. That such a rearrangement to a six-membered ring can occur - at least in the case of the thermal isomerisation of trans-1,2-dimethyl-1,2-divinylcyclobutane - is illustrated by the work of Trecker and Henry[5] who have observed isomerisation of this compound at 98-130° to 1,4-dimethyl-4-vinylcyclohexene-1 (70-77%; 25hr.). It is interesting to note that the other major products were isoprene (ca. 18%) and 1,6-dimethyl-1,5-cyclo-octadiene (ca. 6%).

3) The Mass Spectra of Chloroprene Dimers.

Bearing in mind the work outlined in Sections 1) and 2) above, it was of interest to examine the mass spectra of some dimers of chloroprene. In this work the dimers were introduced into the spectrometers (M.S.2 or M.S.9) using heated, glass, gas inlet systems (for temperatures see Table 10), and this, combined with the effect of the source temperatures (ca. 200°), immediately raises the question of the magnitude of the thermal processes - isomerisation and dehydrochlorination - which could occur prior to ion impact. Also these thermal processes could be subject to metal catalysis within the instrument. Aplin and Frearson[6] have shown that transition metals can catalyse the isomerisation of t-α-hydroxy ketones above 130° and this accounts for the skeletal isomerisation of these compounds during mass spectrometric analysis.

a) Fragmentation Routes Common to all Three Ring Systems.

The cracking patterns of 1,2-dichloro-1,2-divinylcyclobutane, 1- and/or 2-chloro-4-(α-chlorovinyl)-cyclohexene-1 and 1,6-dichloro-1,5-cyclo-octadiene are shown in Table 10 (to facilitate comparison all intensities in the Table are corrected to values corresponding to a value of 100 for m/e 88; in fact the true base peak for the cyclobutane compound was m/e 105 for the spectra obtained with the M.S.9 spectrometer). It can be seen from Table 10 that the fragmentation patterns are very similar, although the cyclobutane isomer shows important differences which will be discussed later. Possible fragmentation routes of the isomers (involving ions of relative intensity greater than or equal to 10% of the base peak = 100%) are shown in Figures 38, 39 and 40. Where possible, these assignments are made on the basis of observation of metastable ions. It can be seen that the isomers have certain metastable transitions in common viz., m* = 90.5, 78.2, 75.05, 59.4 and 56.5. These correspond respectively to the transitions indicated in the equations 1 to 4.

$$C_8H_{10}Cl_2\ m/e\ 176 \xrightarrow{-Cl^{\cdot}} m/e\ 141 \xrightarrow{-C_2H_4\ m^*\ 90.5} m/e\ 113 \qquad (1)$$

$$m/e\ 141 \xrightarrow{-HCl\ m^*\ 78.2} m/e\ 105 \qquad (2)$$

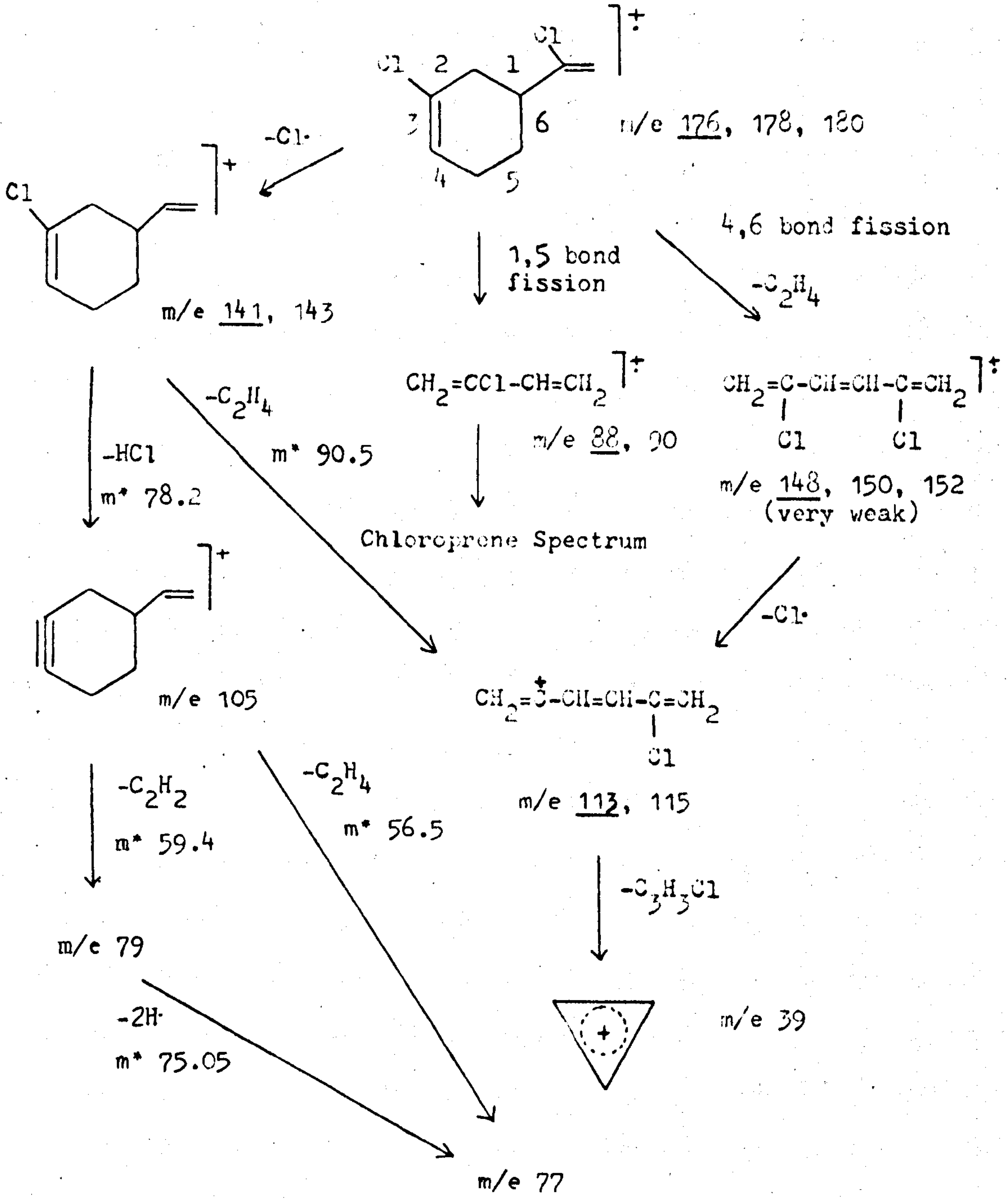
$$m/e\ 105 \xrightarrow{-C_2H_4\ m^*\ 56.5} m/e\ 77 \qquad (3)$$

$$m/e\ 105 \xrightarrow{-C_2H_2\ m^*\ 59.4} m/e\ 79 \xrightarrow[m^*\ 75.05]{-2H^{\cdot}} m/e\ 77 \qquad (4)$$

The cyclobutane derivative exhibited a greater number of metastable ions (p.194) in keeping with its more complex cracking pattern.

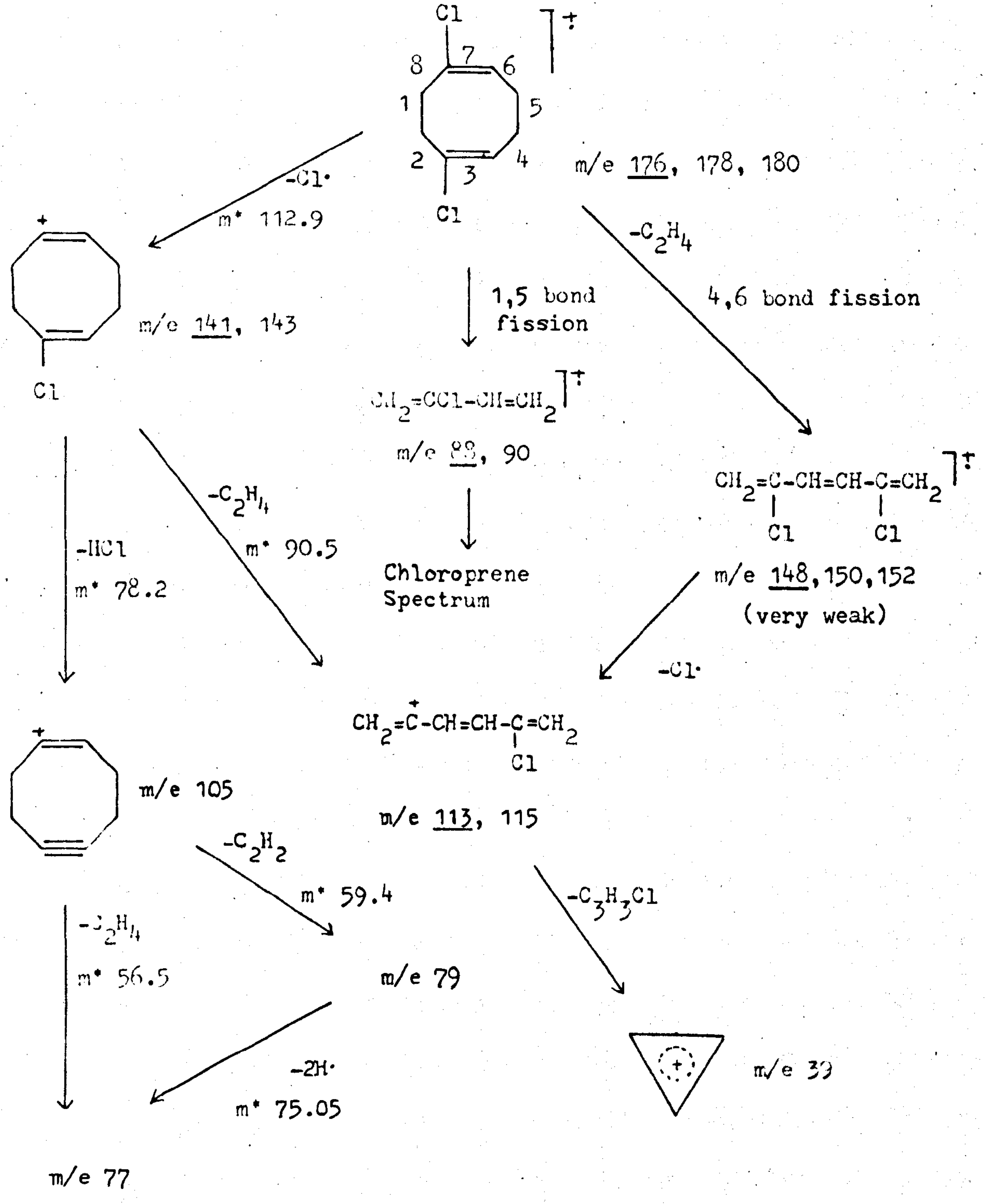
The molecular ions were very weak (1-4%) and this indicates their comparable instability. A secondary process of importance is the

Figure 38 Major Fragmentation Routes of 2-Chloro-4-(α-chlorovinyl) -cyclohexene-1.



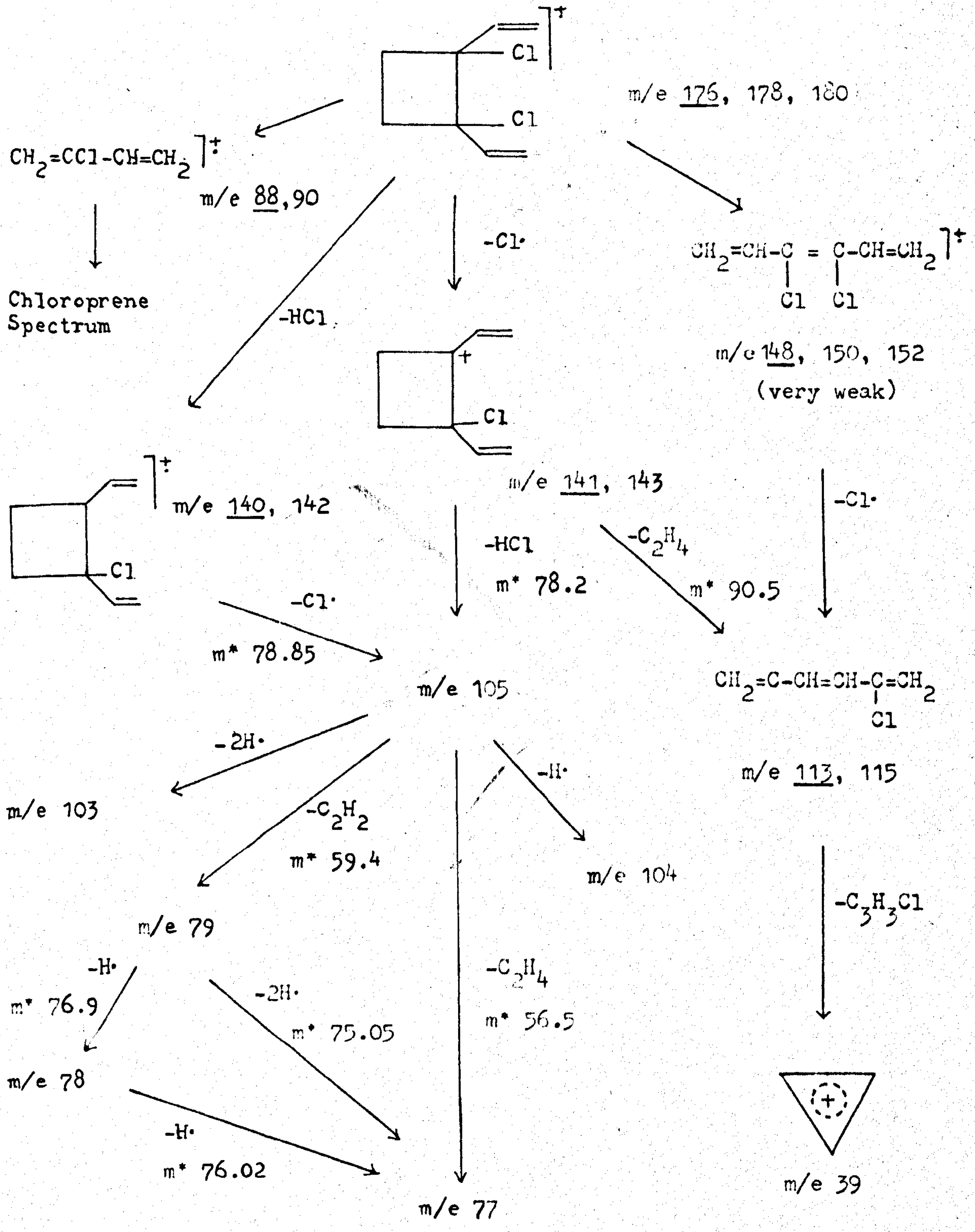
(m/e for major chlorine isotope underlined; assigned metastable peaks are indicated with an asterisk).

Figure 39 Major Fragmentation Routes of 1,6-Dichloro-1,5-cyclooctadiene.



(m/e for major chlorine isotope underlined; assigned metastable peaks are indicated with an asterisk)

Figure 40 Major Fragmentation Routes of 1,2-Dichloro-1,2-divinylcyclobutane[a].



(m/e for major chlorine isotope underlined; assigned metastable peaks are indicated with an asterisk).

[a] Additional routes are indicated in the text e.g. p.199, 200.

ready fission of the rings to give the ion of m/e 88 and its associated ^{37}Cl isotope peak at m/e 90, attributed to chloroprene. In most cases this is the base peak.

$$C_8H_{10}Cl_2 \xrightarrow{-C_4H_5Cl} m/e\ 88 \qquad (5)$$

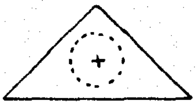
In agreement with the analogous findings of Brittain et al, there is no metastable ion corresponding to this transition, indicating that this is a fast process, and there is a similar, small loss of ethylene to give the peak at m/e 148 (^{35}Cl) - again there is no corresponding metastable ion.

$$C_8H_{10}Cl_2 \xrightarrow{-C_2H_4} m/e\ 148 \qquad (6)$$

This could occur by ring cleavage although hydrogen transfer and the loss of a side chain could apply in the case of the four and six membered ring compounds. Loss of atomic chlorine from m/e 148 follows to give the ion of m/e 113 (^{35}Cl).

$$m/e\ 148 \xrightarrow{-Cl^{\cdot}} m/e\ 113 \qquad (7)$$

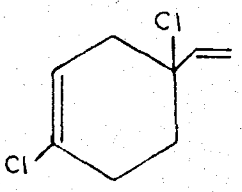
It can be seen from Table 10 that, with a few exceptions, the spectra below m/e 88 are similar to that of chloroprene. One of the differences is the fragment of m/e 39. This could be derived from any of a number of ions, one of which is m/e 113 (see Figures 38-40) which could lose C_3H_3Cl giving the ion in question. The structure of this ion may be that of the doubly charged $C_6H_6\rceil^{++}$ ion or more probably that of a cyclopropenium ion. The latter is considered reasonable since Breslow et al[7] have prepared 3-chlorocyclopropene and have isolated from it a stable salt of the cyclopropenium ion. Also these workers have recorded the mass spectrum of the parent olefin (molecular ion m/e 74, ^{35}Cl) and found a strong peak at m/e 39 (85%) which they attribute to the structure,



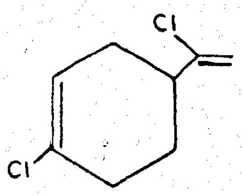
pointing out that this can be considered as aromatic and therefore stable. There was also an ion (intensity not recorded) of m/e 73 (^{35}Cl) corresponding to the chlorocyclopropenium ion. It can be seen that weak ions of m/e 74 and 73 are found in the spectra of chloroprene dimers (Table 10) which suggests that some formation of 3-chlorocyclopropene occurs in the mass spectrometer.

b) Fragments with Significant Intensity Differences.

The ions of m/e 140 and 141 (for ^{35}Cl) are readily explained by loss of hydrogen chloride and atomic chlorine respectively from the molecular ions. The point of interest here is the significant differences in relative intensity of these ions as exhibited by the three isomers. Considering the ion of m/e 140 (loss of HCl) it can be seen that this occurs most readily from the cyclobutane - the higher the temperature the greater is the loss - and least readily from the cyclo-octadiene. The loss from the cyclohexene isomer is only just greater than the latter. This overall order can be explained by the fact that the chlorines are allylic in 1,2-dichloro-1,2-divinylcyclobutane and therefore hydrogen chloride is more easily eliminated from it, or from an intermediate derived from it - in fact for this compound the loss of hydrogen chloride is preferred to the alternative loss of atomic chlorine as shown by the relative intensities of the peaks at m/e 140 and m/e 141. The other two dimers contain only vinylic chlorine which is not readily lost as hydrogen chloride. This point is illustrated by the chloroprene dimers,

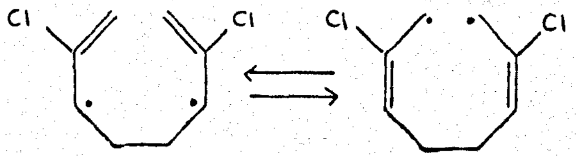


(IV)



(V)

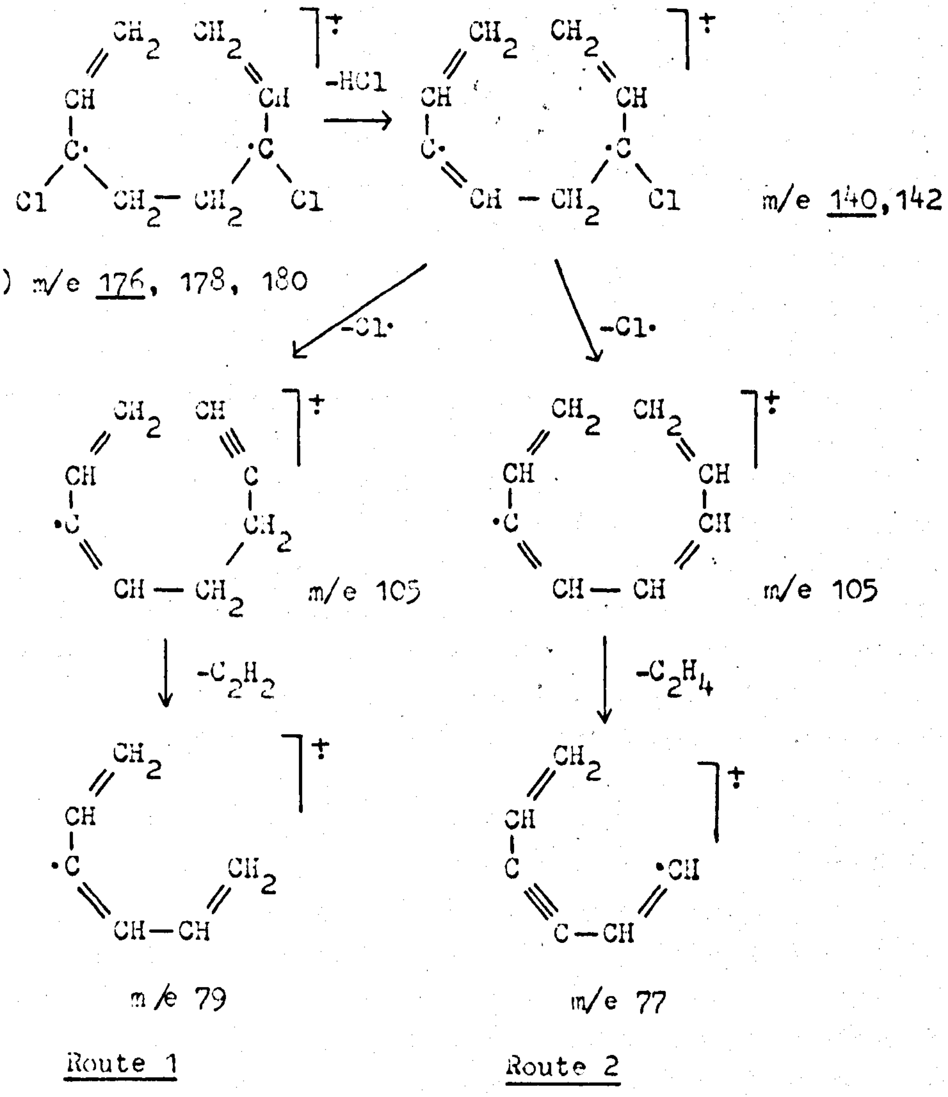
which differ only in the position of the chlorines-(IV) containing an allylic chlorine. In fact this dimer (IV) so readily loses hydrogen chloride that it is normally isolated only as its dehydrochlorination product 1-chloro-4-vinylcyclohexa-1,3-diene[1]. The observation that 1-chloro-4-(α-chlorovinyl)-cyclohexene-1 (V) does lose hydrogen chloride in the mass spectrometer may indicate that under these conditions it undergoes bond fission to give an intermediate that contains an allylic chlorine. Such an intermediate can be represented by the diradical intermediate (II) (p. 138). This proposal of bond fission can be extended to the other isomers. The intermediate (I), from the cyclobutane, contains two allylic chlorines therefore explaining the more facile loss of hydrogen chloride noted above. If the corresponding intermediate from the cyclo-octadiene is,



(VI)

which contains no allylic chlorine, then this would explain the almost negligible loss of hydrogen chloride observed from this isomer.

The formation of the ions of m/e 105, 77 and 79 can also be explained on the basis of the intermediates discussed above. Thus, in the Figure 41, which represents the appropriate eliminations from the intermediate (I) derived from the cyclobutane, route 1 leads to the ion of m/e 79 and route 2 leads to the ion of m/e 77. Both paths pass through the ion of m/e 105 and are accompanied by the corresponding metastable ions.



(m/e for major chlorine isotope underlined)

Figure 41 Possible Fragmentation Routes of 1,2-Dichloro-1,2-divinyl-cyclobutane leading to Ions of m/e 140, 105, 79 and 77.

Analogous routes can be drawn for the two remaining dimers.

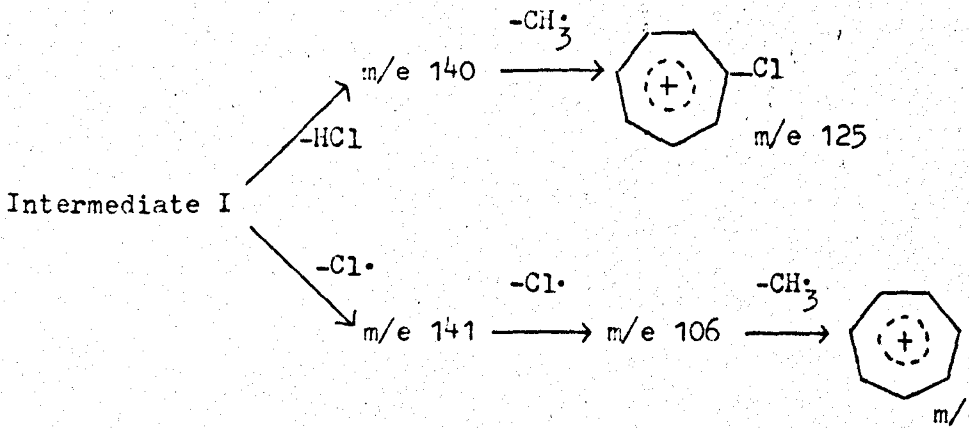
c) Fragmentation of 1,2-Dichloro-1,2-divinylcyclobutane.

This isomer, under electron impact, shows certain significant differences from the other dimers (Table 10). Using a M.S.2 spectrometer the base peak is that of the monomer. However, using the same accelerating potential (70 ev) as before, the base peak of each of the spectra obtained for this compound using a M.S.9 spectrometer at varying inlet temperatures, is not that of the monomer, but rather that of the ion m/e 105 which suggests a more ready loss of atomic chlorine and hydrogen chloride in these cases.

It has been postulated earlier (Equation 4) that the ions of m/e 77 and 79 are formed from the fragment of m/e 105 by loss of ethylene and acetylene respectively. Except for the highest temperature employed, in the case of the cyclobutane isomer, the ratio of the ions of m/e 77:105 has values in the range 0.5-0.7, depending on the inlet temperature, and the ratio of the ions of m/e 79:105 has values lying between 0.3 and 0.5, again depending on the inlet temperature. The values of the corresponding ratios for the cyclohexene and cyclooctadiene isomers are lower (in the ranges 0.1-0.2 and 0.1-0.4 respectively). This suggests that the losses of ethylene and acetylene may be more facile from the cyclobutane than from the other two derivatives. One possible explanation for this could be the release of ring strain.

In the cyclobutane case the fragment of m/e 78 can be produced by at least two routes viz., loss of hydrogen from the ion of m/e 79 (observed metastable 76.9) and by the elimination of ethylene (observed metastable 57.4) from the fragment of m/e 106. This latter ion arises by loss of $^{35}Cl\cdot$ from the species of m/e 141.

The ions of m/e 125 and 91 derived from the cyclobutane isomer are much more intense than the other two ring systems. This can be rationalised in terms of a chlorotropylium ion and tropylium ion respectively.



(9)

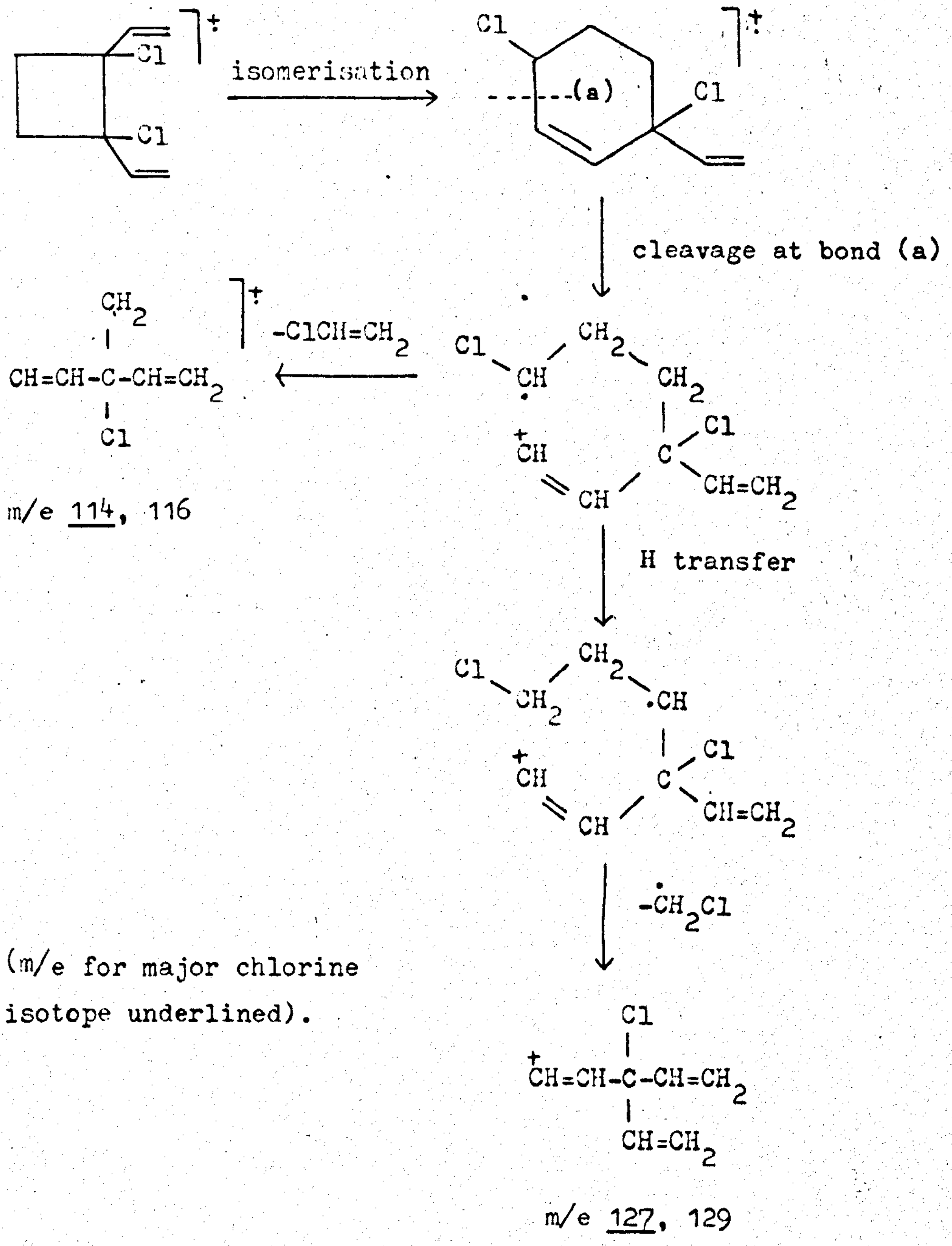
(10)

The last transition of equation 10 is supported by a weak metastable ion at m/e 78.2. Additionally, in agreement with the findings of Jennings _et al_,[8] who studied the fragmentation of some tropylium ions in the mass spectrometer, there is a weak metastable ion (46.5) that corresponds to the transition:-

$$\underset{m/e\ 91}{C_7H_7]^+} \longrightarrow \underset{m/e\ 65}{C_5H_5]^+} + \underset{m/e\ 26}{C_2H_2} \qquad (11)$$

The ions of m/e 125 and 91 are commonly found[9] to be in high abundance and their further fragmentation is in keeping with the ions at m/e 105, 77 and 51. Although these can reasonably be derived from the diradical (I) by ion impact, an alternative explanation must be considered, viz., does a thermal elimination and isomerisation to give 1-chloro-4-ethyl benzene as demonstrated earlier (p.188) play a part here? Indeed it is significant that results, comparable to the above fragmentation, have been reported[10] for 2-,3- and 4-chloro ethyl benzenes, which show base peaks at m/e 125, strong peaks at m/e 105 (48-88%) and a weaker ion of m/e 51 (ca. 13%). Also 4-chlorotoluene exhibits its strongest ion at m/e 91, while that of m/e 125 is of relative intensity 17. Thermal processes could also explain the fact that the base peak in the M.S.9 analyses of the cyclobutane derivative is at m/e 105. On the other hand none of the intensities for the ion of m/e 125 are very large (ca. 10% of base peak = 100%), which suggests that initial formation of aromatic compounds may not be of major significance. If one confines the question to the fragments of m/e 105 and 91 (the strongest of those under discussion), it is evident that these vary in intensity with the alteration of the temperature of the inlet system, although they do not vary in a like manner. On the information available it is not possible to ascertain whether this effect or the isomerations discussed above, are due to (a) metal catalysis within the instrument, (b) thermal rearrangement before electron impact or (c) electron impact itself. It is unlikely that the source temperature, which remained constant for all the analyses, was the cause. The fact that the spectra obtained on M.S.2 and M.S.9 spectrometers do differ with respect to the intensities of the ions of m/e 105 and 91 favours (a) or (b).

As recorded earlier, (p.188) Brittain et al have suggested isomerisation of cyclobutanes (also 1,5-cyclo-octadiene) under electron impact to their cyclohexene isomers. This was followed by ring cleavage to give linear structures from which losses of propene and an ethyl radical occurred (Fig. 37). Their postulate was supported by the observations of the appropriate metastable ions. In the cases examined by these authors the intensity of the fragments so formed varied between 11 and 22%. If 1,2-dichloro-1,2-divinylcyclobutane were to undergo an analogous rearrangement to the corresponding cyclohexene derivative, as suggested by Brittain et al, then the equivalent bond cleavages to those postulated by these workers, would lead, on the one hand, to loss of $ClCH=CH_2$ and on the other, to loss of $\dot{C}H_2Cl$. Such rearrangements would be as shown in the Figure 42.



(m/e for major chlorine isotope underlined).

Figure 42 Possible Rearrangement of 1,2-Dichloro-1,2-divinylcyclobutane leading to losses of $ClCH=CH_2$ and $\dot{C}H_2Cl$.

It is apparent from Table 10 that if these losses occur from chloroprene dimers then they are very small indeed. It appears therefore, the postulate of Brittain et al is not generally applicable.

Conclusions

The conclusions that can be drawn from the mass spectra of the chloroprene dimers examined is rather tenuous and would benefit from a knowledge of the appearance potentials of certain of the ions (eg. m/e 91, 105) and the effect of lowering the electron beam energy. The cracking patterns of the three isomers do show similarities as regards the major fragmentation routes and in the position of the metastable ions, and are characteristic of organo chlorine compounds in their ready loss of Cl and HCl. The differences observed in the case of 1,2-dichloro-1,2-divinylcyclobutane can be explained by release of ring strain and formation of an excited triplet state intermediate having allylic chlorines which readily eliminate hydrogen chloride from the molecular ion and subsequently form tropylium ions. Thermal and/or metal catalysed, induced rearrangement to aromatic like species are an alternative interpretation. There was no evidence for a Cope rearrangement of the cyclobutane to 1,6-dichloro-1,5-cyclo-octadiene since this latter compound does not readily lose hydrogen chloride - rather atomic chlorine. The rearrangements to cyclohexene intermediates as suggested by Brittain et al may not be applicable to those isomers containing hetero atoms similar to chlorine.

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