Studies on the Reactions between Nitric Oxide and Conjugated Dienes

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Chlorine-substituted dienes interact with nitric oxide to form low molecular weight polymers. Initiation is by addition of nitric oxide. The short chain polymerisation is terminated by a cage reaction with nitrogen trioxide or by addition of nitric oxide, the nitroso-end group reacting further to form oximes and nitriles. Less reactive dienes gave similar products, there being a tendency for the chain reaction to give monomeric nitromono-olefins and mono-olefinic nitrates.

EARLY work on the interaction of olefins with oxides of nitrogen is difficult to interpret owing to the lability of the oxides and uncertainty as to their purity. Of the oxides NO, NO_2, N_2O_4, N_2O_3, the first two are free radicals and the last two readily dissociate into the former. Although there is ambiguity in the literature as to whether homolytic or heterolytic reactions are involved, it is becoming increasingly evident that, in non-polar solvents, homolytic reactions [1] result in the formation of the nitroso-compounds (RNO), nitro-compounds (RNO_2), nitrites (RONO), and nitrates ($RONO_2$) from nitrogen dioxide [2-4] or nitrogen trioxide.[5] Nitric oxide is a very stable free radical and it is only in recent years that its ability to interact with olefins has been appreciated. Our own studies on the stabilisation of readily polymerised olefins has involved us in a consideration of the products formed when nitric oxide reacted with conjugated olefins. Using carefully purified reagents, isoprene, 1- and 2-chlorobuta-1,3-diene, and 2,3-dichlorobuta-1,3-diene could be made to react with nitric oxide at 6° to yield polymeric oils. In order to understand the nature of the reactions involved, investigations were extended to include dienes of greater stability and in certain circumstances nitro-, nitroso-, nitrato-, and hydroxyimino-derivatives of olefins were isolated.

In the gas phase nitric oxide can give rise to initiation steps as a result of hydrogen abstractions [6,7] followed by termination involving isomerism to oxime.[8] Alternatively, at high temperature, Batt and Gowenlock [9] have suggested that an intermediate *N*-nitrito-*N*-nitrosomethylamine is involved [reaction (1)]. The reaction between ethoxyl radicals and nitric oxide at 181°

$$CH_3NO + 2NO \longrightarrow [CH_3N(NO)ONO] \longrightarrow N_2 + CH_3ONO_2 \quad (1)$$

gave ethyl nitrite, ethanol, and acetaldehyde [reaction (2)].[10] Arden and Phillips [11] detected the presence of

$$EtONO \rightleftharpoons EtO\cdot + NO \longrightarrow HNO + CH_3CHO \quad (2)$$

$$EtO\cdot + HNO \longrightarrow EtOH + NO \quad (3)$$

nitrogen and nitrogen dioxide while studying the same reaction at 95°.

The liquid phase reaction of olefins with nitric oxide has also been investigated. Cyclohexene yielded 1-nitrocyclohexene and dimeric nitro(nitroso)cyclohexane.[12] Brown [13] using liquid isobutene and nitric oxide at 28° obtained an unstable, viscous oil (66%) that underwent 'fume-off' on attempted distillation. Partial separation of the oil followed by an examination of the i.r. spectra indicated 1- and 3-nitro-2-methylpropene (74%), nitro-t-butyl nitrite (9%), dimeric nitroso(nitro)-2-methylpropane (3%), and other minor components. Phillips and Coyne [14] isolated an important intermediate, tris(nitro-t-butyl)hydroxylamine (45%), under similar circumstances and the reaction sequence (4) was suggested. This compound was unstable at moderate temperatures and gave rise to the nitroisobutenes and many of the other minor products.

$$R\cdot + NO \longrightarrow RNO \xrightarrow{2R\cdot} R_2NOR \quad (4)$$

More recent work [15-17] suggests that the hydroxyl-

[1] H. Shechter, *Record Chem. Progr., Kresge-Hooker Science Library*, 1964, **25**, 55.

[2] (*a*) F. Conrad and H. Shechter, *J. Amer. Chem. Soc.*, 1953, **75**, 5610; (*b*) T. S. Cautrell, J. T. Gardikes, H. Shechter, and G. V. D. Tiers, *ibid.*, 1967, **89**, 3005; (*c*) J. C. D. Brand and I. D. R. Stevens, *Chem. and Ind.*, 1956, 469; *J. Chem. Soc.*, 1958, 629; (*d*) W. D. Emmons and T. E. Stevens, *J. Amer. Chem. Soc.*, 1958, **80**, 338.

[3] M. Braid, D. M. Gardner, M. Hauptschein, R. E. Oesterling, and E. A. Tyczkowski, *J. Org. Chem.*, 1963, **28**, 1281.

[4] A. A. Petrov and K. B. Rall, *Zhur. obshchei. Khim.*, 1964, **34**(11), 3621.

[5] (*a*) P. E. Ley and H. Shechter, *Chem. and Ind.*, 1955, 535; (*b*) M. L. Scheinbaum, *J. Org. Chem.*, 1968, **33**, 2586.

[6] K. J. Laidler and B. W. Wojciechowski, *Canad. J. Chem.*, 1960, **38**, 1027; *Trans. Faraday Soc.*, 1963, **59**, 369.

[7] O. L. Poly and F. O. Rice, *J. Chem. Phys.*, 1938, **6**, 273.

[8] M. H. Back and K. J. Laidler, *Canad. J. Chem.*, 1966, **44**, 215.

[9] L. Batt and B. G. Gowenlock, *Trans. Faraday Soc.*, 1960, **56**, 682; M. I. Christie, *Proc. Roy. Soc.*, 1959, **A249**, 258.

[10] J. B. Levy, *J. Amer. Chem. Soc.*, 1953, **75**, 1801; 1956, **78**, 1780.

[11] E. A. Arden and L. Phillips, *Proc. Chem. Soc.*, 1962, 354.

[12] G. F. Bloomfield and G. A. Jeffrey, *J. Chem. Soc.*, 1944, 120.

[13] J. F. Brown, *J. Amer. Chem. Soc.*, 1957, **79**, 2480; *J. Org. Chem.*, 1964, **29**, 2235.

[14] L. V. Phillips and D. M. Coyne, *J. Org. Chem.*, 1964, **29**, 1937.

[15] S. F. Nelsen and P. D. Bartlett, *J. Amer. Chem. Soc.*, 1966, **88**, 143.

[16] (*a*) V. A. Ginsburg, L. L. Martynova, and M. N. Vasileva, *Zhur. obshchei Khim.*, 1967, **37**, 1026; (*b*) G. R. Chalfont and M. J. Perkins, *J. Amer. Chem. Soc.*, 1967, **89**, 3054; 1968, **90**, 7141.

[17] (*a*) I. T. Brownlie and K. U. Ingold, *Canad. J. Chem.*, 1967, **45**, 2427; (*b*) K. Adamic, D. F. Bowman, T. Gillan, and K. U. Ingold, *J. Amer. Chem. Soc.*, 1971, **93**, 902; (*c*) A. R. Forrester, J. M. Hay, and R. H. Thomson, 'Organic Chemistry of Stable Free Radicals,' Academic Press, London, 1968, pp. 222—224.

amine could result from a nitroxide intermediate [reaction (5)]. The first step in the liquid phase reaction

$$RNO + R\cdot \longrightarrow R_2NO\cdot \xrightarrow{R\cdot} R_2NOR \qquad (5)$$

was believed to be an initial attack by nitrogen dioxide on the olefin to form a nitroalkyl radical. Brown observed that there was an induction period if purified nitric oxide was used and the induction period could be eliminated if a trace of air was added. By analogy with Bamberger's [18] benzenediazonium compound, formed when nitrosobenzene was treated with nitric oxide, Brown [13] explained the evolution of nitrogen and initiation by nitrogen dioxide by postulating rearrangement to an unstable diazonium nitrate [reactions (6) and (7)]. Haszeldine [19] considered that the interaction of

$$RN_2ONO_2 \longrightarrow R\cdot + H_2 + \cdot ONO_2 \qquad (6)$$

$$\cdot ONO_2 + NO \longrightarrow 2NO_2 \qquad (7)$$

nitric oxide with tetrafluoroethylene was initiated by nitrogen dioxide impurity present in the nitric oxide.

RESULTS AND DISCUSSION

Our investigations with readily polymerised dienes and nitric oxide were designed to see where they fitted the above schemes. We also sought to identify the compounds formed, to measure their stabilities, and to attempt a clarification of the reaction mechanism.

High speed stirring was essential for smooth reaction at temperatures below ambient. The reaction was characterised by a slight evolution of heat, the rapid formation of a blue-green colour, attributed essentially to a nitroso-compound, followed after a few minutes by a steady evolution of nitrogen with a subsequent change of colour to amber. By measuring the time for the blue-green colour to appear and monitoring the rate of nitrogen evolution, the following order of reactivity was obtained: chloroprene, 2,3-dichlorobutadiene, 1-chlorobutadiene > isoprene > 2,5-dimethylhexa-2,4-diene > *trans,trans*-1,4-diphenylbutadiene > 1,4-diphenylcyclopentadiene > hexachlorocyclopentadiene. The chlorinated open chain dienes reacted readily at 6°, the phenyl-substituted olefins reacted at 15°, and hexachlorocyclopentadiene did not react at 130° (Table).

In the case of chloroprene and 2,3-dichlorobutadiene white crystalline solids precipitated during the reactions. Subsequent isolation and examination showed them to be air-sensitive, dimeric nitroso-compounds. They were insoluble in most organic solvents but could be recrystallised from sulpholan–water. The compounds were the dimers of 2-chloro-1-nitro-4-nitrosobut-2-ene (15%) and 2,3-dichloro-1-nitro-4-nitrosobut-2-ene (40%). The dimers were inert to nitric oxide and melted with decomposition at 110 and 107° respectively. The 2,3-dichlorobutadiene derivative isomerised slowly at 50° in nitromethane to form 2,3-dichloro-4-nitrobut-2-enal oxime.

Since these nitroso-dimers in benzene were inert to nitric oxide it is concluded that dimerisation and precipitation prevented redissociation and so prevented their further reaction to give the polymeric oils which were the major products.

The brown viscous oils were a mixture of thermally unstable, low molecular weight polymers. Examination showed the presence of primary nitro (CH_2NO_2), and nitrate ester groups. Molecular distillation of the oil from chloroprene gave a slow decomposition and this could be related to the loss of a broad OH i.r. band in the original oil and to the appearance of nitrile [reaction

Interaction of nitric oxide (50 ml min^{-1}) with conjugated dienes in benzene solvent (50 ml)

10.8mM-Diene (g)	Reaction temp. (°) [h]	Time (min) for appearance of: Maximum N_2	Solution colour	Precipitate	Product (g, % w/w)
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, 10	None	Oil (0.93, 100)
1-CB [a,d,e] (0.96)	6 [1.5]	14.5	Blue, 0.5 Green,[c] 3	None	Oil (2.01, 100)
DCB [a,d,e] (1.33)	6 [1]	13	Green, 0.5	2	Oil (1.94, 69) Solid (0.86, 31)
DPB [d] (2.22)	15 [g] [1.5]	18	Green, 6	None	Oil (3.27, 100)
TMB [a,d,e] (1.19)	6 [3] [f]	28	Blue,[c] 1	None	Oil (2.44, 100)
DPCP [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
Cyclohexene (0.81)	6 [51]	Very small	Blue, 23	Trace	Blue oil (1.4)
Mixed chloroprene dimers [j] (1.1)	6 [8]	Very small	Green	Trace	Green oil

[a] G.l.c. at end of reaction showed only benzene present. [b] Benzene (100 ml, 5.0mM). [c] Colour remained until degassing started, when solution became amber. [d] 1-CB = 1-Chlorobuta-1,3-diene; DCB = 2,3-dichlorobuta-1,3-diene; DPB = *trans,trans*-1,4-diphenylbuta-1,3-diene; TMB = 1,1,4,4-tetramethylbuta-1,3-diene; DPCP = 1,4-diphenylcyclopentadiene. [e] After reaction a bright blue solid was observed in the 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 h. [h] Diene (1.08 g) recovered, contaminated with a brown oil, little N_2 evolved. [i] No reaction at 20 or 81°; chlorobenzene (50 ml) as solvent. [j] Contained *ca.* 1% monomer.

[18] E. Bamberger, *Ber.*, 1897, **30**, 506.

[19] J. M. Birchall, A. J. Bloom, R. N. Haszeldine, and C. J. Willis, *J. Chem. Soc.*, 1962, 3021.

(8)]. The oil from 2,3-dichlorobutadiene formed the nitrile even more readily.

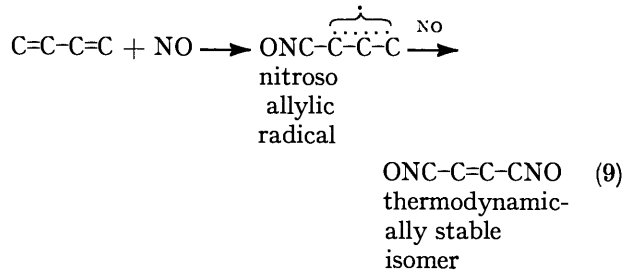
$$RCH_2NO \rightleftharpoons RCH{=}NOH \longrightarrow RC{\equiv}N + H_2O \quad (8)$$

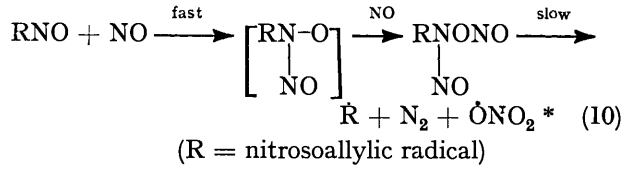
From a consideration of the number average molecular weights, the elemental analyses, and the results of fractionation by gel permeation chromatography, it is concluded that the oils from chloroprene and 2,3-dichlorobutadiene were low molecular weight polymers ranging from the dimer up to the decamer. The major component was a trimer probably with nitro- and nitrato-end groups. The other dienes gave oils which were essentially similar in that they were nitro-compounds or nitrates, 1,4-addition predominating. Likewise the number of linked diene units was small.

A series of experiments was carried out to see if the products obtained resulted from free radical reactions and clarification was sought on postulates made by earlier workers. Certainly the large yields of nitro-compounds from the dienes is in agreement with some initiation by nitrogen dioxide. Rigorous efforts to purify nitric oxide, including numerous trap to trap distillations under high vacuum to produce a colourless liquid oxide, did not result in any induction period.[13,19] When nitrogen dioxide was injected into a solution of chloroprene in benzene at 20°, the chloroprene consumption and nitrogen evolution were affected in a non-reproducible manner. Brown's suggestion that nitrato-radicals [equations (6) and (7)] can account for the nitrogen dioxide is in keeping with our own yields of nitrate esters.

An alternative type of initiation involving peroxides and nitric oxide, analogous to reaction of t-butyl hydroperoxide and nitric oxide [20] which forms t-butyl nitrate, does not apply, because a sample of partially oxidised chloroprene had no effect on the reaction. Bailey [21] has shown that chloroprene forms involatile dialkyl polyperoxides rather than hydroperoxides and this would explain the lack of reaction, although at higher temperatures reactions (2) and (3) could become more important. Conversion of nitric oxide to nitrogen dioxide and nitrogen is a slow process [19] but becomes appreciably more rapid under ion impact or under u.v. light. In our experiments the time for the rate of nitrogen evolution to reach a maximum was independent of any added nitrogen dioxide suggesting that there was an intermediate which slowly released nitrogen. Burrell suggests that in an excess of nitric oxide, chloronitrosocyclohexane is in equilibrium with a *N*-nitrito-*N*-nitrosoamine RN(NO)ONO which then undergoes a rate-controlling decomposition similar to equation (6).[22] He reported that absorption of nitric oxide to the nitrosocyclohexane was rapid at −80°. Using pure nitric oxide and dienes the initiation sequence would seem to be (9) and (10) the reaction continuing as a result of nitrogen dioxide formation [equation (7)].

Unlike the mono-olefins nitric oxide can initiate in this case without induction periods, the driving force resulting from formation of the nitrosoallylic radical. Brown's





(R = nitrosoallylic radical)

diazonium nitrate intermediate has never been identified. Tedder [24] detected an unstable, conjugated diazonium nitrate of hex-1-yne only at −78°. Our unsuccessful attempts to trap a diazonium nitrate, ONC-C=C-C-$\overset{+}{N}$=N·NO^-_3, with reagents such as 2-naphthol, *m*-dimethoxybenzene, or methanol is in agreement with Zollinger's [25] observation that diazonium salts are incapable of existence unless resonance stabilised. The nature of the rearrangement leading to the formation of N_2 remains uncertain.

It has been demonstrated that 2,2,6,6-tetramethyl-4-piperidone nitroxide reacts specifically with alkyl radicals.[17a] We found that the nitroxide formed an unstable solid with nitrogen dioxide, presumably analogous to the compound formed from diphenyl nitroxide,[17c] and found no detectable reaction with nitric oxide. The nitroxide was added to the diene–nitric oxide mixture in anticipation that nitrogen dioxide would be diverted or that the nitroallylic radical would be trapped. Nitroxide was consumed during the course of reaction and at high concentrations of nitroxide little nitrogen was evolved but isolation of the nitroxide adducts was not possible. Similar effects were observed when iodine was added. This could indicate interruption of the initiation sequence.

Conclusions.—The available evidence favours a free radical process when conjugated dienes react with nitric oxide. 1,4-dinitrosoalk-2-ene [equation (9)] rapidly reacts to generate nitrogen dioxide according to equations (10) and (7). Nitrogen dioxide builds up in the recycle

* The alternative initiation by nitrogen trioxide cannot be ruled out since it has been reported to be a more reactive radical than nitrogen dioxide.[23]

[20] R. F. Kopczewki and J. R. Shelton, *J. Org. Chem.*, 1967, **32**, 2909.

[21] H. C. Bailey, *Adv. Chem.*, 1968, **75**, 138.

[22] (*a*) E. J. Burrell, *J. Phys. Chem.*, 1962, **66**, 401; (*b*) V. A. Ginsburg, L. L. Martynova, and M. N. Vasileva, *Zhur. obshchei Khim.*, 1967, **37**, 1026.

[23] G. Sosnovsky, 'Free Radicals in Preparative Organic Chemistry,' MacMillan, New York, 1964, p. 225.

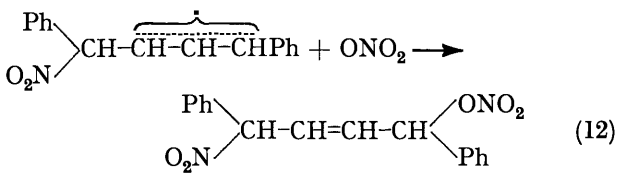
[24] E. Robson and J. M. Tedder, *Proc. Chem. Soc.*, 1963, 344.

gases and hence can enter into competition as an initiator.

When R is $ONCH_2$–C(Cl)=C(X)–CH and X is Cl or H,

$$R^{\bullet} + NO_2 \longrightarrow RNO_2 \longrightarrow$$
1,4-hydroxyimino(nitro)-alkene or nitroso-dimer (11)

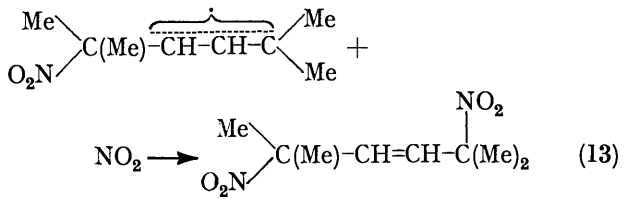
nitronitroso-compounds result from 1,4 radical additions [reaction (11)]. Competition for the allylic radical R• results in low molecular weight polymer and in the case of certain other dienes, 1,4-nitro(nitrato) and



(12)

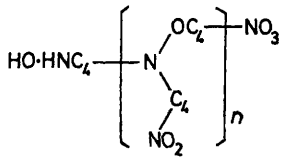
-dinitroalkenes result. The competition probably reflects the relative reactivities of the allylic radicals.

Thus 1,4-diphenyl-1-nitrobutenyl radical could trap the nitrato radical before it escapes from its solvent cage [reaction (12)] while a similar process (13) takes



(13)

place for nitro radical. In agreement with other workers, analysis of the oily product strongly suggests [14,26] (A) as a structural unit for the trimer and pentamer.



(A)

EXPERIMENTAL

Liquid dienes were trap-to-trap distilled under high vacuum immediately before use. Transferences were made under purified nitrogen. In some experiments the nitric oxide was, after purification, distilled six times under high vacuum using liquid nitrogen and isopentane–slush baths as refrigerants; greaseless stop cocks were used. In these cases, reaction was followed by observing manometers attached to the vacuum line.

2,5-Dimethylhexa-2,4-diene was prepared by isomerisation of 2,5-dimethylhexa-1,5-diene.[27] 1,4-Diphenylcyclopentadiene was prepared from ethyl 2-benzoylpropionate.[28] 2,3-Dichlorobutadiene was prepared by dehydrochlorination of 2,3,4-trichlorobut-1-ene with aqueous sodium hydroxide.

Analysis.—Ratios of nitrogen to the oxides of nitrogen were analysed by gas–solid chromatography (g.s.c.) using a 2 m Porapak Q copolymer column (Waters Associates Inc.) at 20°. Mass spectrometry of the gases resulted in their disproportionation before analysis.

Procedure.—The glass apparatus (capacity *ca.* 100 ml) was designed to allow argon or nitric oxide to be passed at a measured flow rate through the apparatus. The stirrer (6 000 r.p.m.) allowed the gases to be recycled through the liquid. The exit gases after passing through a trap at −80° were passed to the g.s.c. column using a sampling valve, samples being taken every few minutes. The benzene or hexane solvent was flushed for a number of hours with argon at low stirrer speeds and then the gas was changed to nitric oxide at 50 ml min^{-1}. When g.s.c. showed that all the argon had been displaced, the diene was injected below the surface of the solvent using syringes, the needle tips being protected by argon filled capsules having serum caps at both ends. The bottom serum cap was placed in close contact with the serum cap on the reaction flask and the needle passed through both serum caps. At the conclusion of the experiment the apparatus was reflushed with argon.

Stability Tests.—In view of the known instability of the reaction products hammer tests and examination by differential scanning calorimetry (d.s.c.) were carried out on all products. Distillations were carried out behind safety screens. The isoprene reaction product liberated oxides of nitrogen violently at 80°. D.s.c. was carried out on 1—2 mg samples in sealed pans at a nitrogen flow of 15 mol min^{-1} and a heating rate of 8° min^{-1} using an indium standard.

Molecular Weights M.—Cryoscopic measurements were carried out under nitrogen [29] the thermistor being calibrated using naphthalene and benzil standards.

2-*Chlorobutadiene.*—To benzene (*ca.* 50 ml) at 6° was added the freshly distilled chloroprene (*ca.* 1 ml). There was an observable adsorption of gas, a slight increase in temperature above the bath temperature of 6°, and the solution became blue-green. After a few minutes the colour turned to amber and there was a white solid precipitate accompanied by a gradually increasing evolution of nitrogen. After thorough argon flushing at the end of nitrogen evolution the solid was filtered off and the solvent was removed at 20° and 0.02 mmHg and analysed by g.l.c. for unchanged diene.

The yield of precipitated solid was at an optimum at *ca.* 2% chloroprene in benzene and fell to zero with increasing dilution. The rate of nitrogen evolution could not be correlated with other reaction parameters and was partly a function of the apparatus (Table). The *dimer* of 2-chloro-1-nitro-4-nitrosobut-2-ene was recrystallised from sulpholan–water to give white crystals, m.p. 110° (decomp.) [Found C, 29.2; H, 3.0; Cl, 20.9; N, 17.0%; *M*, 280 (sulpholan). $C_4H_5ClN_2O_3$ requires C, 29.2; H, 3.0; Cl, 21.3; N, 17.1%; *M*, 164]. The i.r. spectrum had strong bands corresponding to nitro-groups [30] at 1 550 (asym. str.) and 1 375 (sym. str.) cm^{-1}, a band at 1 672 (C=C str.) corresponding to trisubstituted ethylene, but there were no bands corresponding to conjugated olefins, nitrite groups,

[25] H. Zollinger, ' Diazo and Azo Chemistry,' Interscience, New York, 1961, pp. 14, 42.
[26] I. Kende, L. Sumegi, and F. Tüdos, I.U.P.A.C. Internat. Symposium on Macromol. Chem., 1969, vol. III, p. 5/23.
[27] S. H. Harper, H. W. B. Reed, and R. A. Thompson, *J. Sci. Food Agric.*, 1951, **2**, 94.
[28] J. R. Adams and N. L. Drake, *J. Amer. Chem. Soc.*, 1939, **61**, 1326.
[29] A. Finch, P. J. Gardner, R. D. G. Lane, and B. Smethurst, *Lab. Practice*, April 1965.
[30] J. F. Brown, *J. Amer. Chem. Soc.*, 1955, **77**, 6341.

nitrate esters, *gem*-dinitro-, tertiary nitro-, or secondary nitro-compounds. The bands at 1 425 (C–H deform, of CH_2NO_2) and 828 (C–H deform.) are in agreement with a primary nitro-compound corresponding to 1,4-addition. The weak bands at 1 640 (N=N str.), 1 235, and 1 205 cm^{-1} agree with a dimeric nitroso-compound, *m/e* (20 eV), (no M^+) 164, τ [$(CD_3)_2SO$] 3.32 1 H, t, (*J* 6 Hz), 4.27 (2 H, s), and 4.85 (2 H, d, *J* 6 Hz).

The dimer was 15% dissociated in sulpholan at 28° and gave a pale green solution. Treatment with alkali and excess of sodium nitrite solution gave a red colour due to the sodium salt of the nitrolic acid which became yellow on acidification; this conforms to the presence of a primary nitro-group. The compound was stable under nitrogen but became semi-solid after standing for one year in air. D.s.c. exotherm started at 58° with a maximum at 110° (1.6 ± 0.3 cal mg^{-1}). Hydrogen chloride and oxides of nitrogen were identified as products.

Polymeric Oil.—The major product after removal of the benzene solvent was a viscous brown oil which gave the red nitrolic acid characteristic of a primary nitro-group, which was also confirmed by the i.r. spectrum. There were also i.r. bands at 1 645, 1 280, 840, 758, and 705 cm^{-1} indicative of nitrate esters.[30] Nitrite bands were absent but there was a broad band at *ca.* 3 300 cm^{-1} (H bonded OH). There was little sign of bands attributable to unsaturation. Attempted molecular distillation resulted in evolution of water and formation of nitrile. The i.r. spectrum of the distillate showed that the original OH band had been replaced by a sharp band at 2 150 cm^{-1} (C≡N or C≡C str.) Attempts to separate the constituents of the oil by thin layer and column chromatography were unsuccessful but resolution was obtained using gel permeation chromatography (g.p.c.) of a 1% solution in tetrahydrofuran at 35°. Using an apparent length for the chloroprene molecule of 0.43 nm (and assuming that the refractive indices of the components were similar and that there was ideal behaviour of nitro-compounds and nitrates) there were peaks corresponding to dimer through to the decamer, the trimer and pentamer predominating, $\bar{M}_n$ 240 (Hewlett-Packard 301A) (Found: C, 33.7; H, 2.9; Cl, 18.9; N, 12.7%), excluding major contribution from compounds of the type R(RO)N–N(OR)R suggested by Brown.[13]

2,3-*Dichlorobutadiene.*—Reaction conditions were as above (see Table). A white solid precipitated (40%), m.p. 107° (decomp.) [Found: C, 24.3; H, 2.0; Cl, 34.7; N, 13.6%, *M* (sulpholan), 196. $C_4H_4Cl_2N_2O_3$ requires C, 24.3; H, 2.0; Cl, 35.8; N, 14.1%, *M*, 198]. The i.r. and mass spectra were similar to those of the dimer from chloroprene and it was concluded that the compound was the *dimer* of 2,3-dichloro-1-nitro-4-nitrosobut-2-ene. The ^1H n.m.r. spectrum measured in $(CD_3)_2SO$ changed with time. Since the cryoscopic measurements in sulpholan had shown 100% dissociation of the dimer at 28° it is probable that the ^1H n.m.r. involved dissociation, isomerisation to oxime, and possibly nitro–aci-nitro-tautomerism. The d.s.c. exotherm had a maximum at 107° (0.2 cal mg^{-1}). The hammer test[31] was negative.

2,3-*Dichloro*-4-*nitrobut*-2-*enal oxime* was formed when the dimer (0.4 g) was dissolved in nitromethane (40 ml) at 50° to form a pale green solution. This became almost colourless after standing overnight and at −20° deposited white crystals (0.38 g, 95%) which were recrystallised from nitromethane, m.p. 120° [Found: C, 24.5; H, 2.0; Cl, 34.5; N, 14.4%; *M* (sulpholan), 194, $C_4H_4Cl_2N_2O_3$ requires C, 24.3; H, 2.0; Cl, 35.8; N, 14.1%; *M*, 198], $\nu_{max.}$ 3 250 (OH), 1 620 (C=N str.), τ ($CDCl_3$) 1.28 (1 H, s), 1.58 (1 H, s), and 4.5 (2 H, s). The mass spectrum was significantly different from that of the nitroso-dimer. The d.s.c. endotherm was at 121°.

The polymeric oil from the reaction decomposed slowly during removal of the solvent at 20° and 0.01 mmHg and small amounts of N_2O_3 and water were collected in low temperature traps. The oil had i.r. bands similar to those for the oil from chloroprene except that the nitrate ester bands were weaker and there was a band corresponding to a triple bonded carbon. Using a 1% solution in toluene at 25° it was shown by g.p.c. that there were at least six components present, $\bar{M}_n$ 314. It was concluded that major components in the oil were nitroso dimer and nitrile (elemental analysis corresponded to $C_4H_{2.8}Cl_{1.8}N_{1.8}O_{3.2}$).

1-*Chlorobutadiene.*—Details are summarised in the Table. The i.r. spectrum of the oily product was similar to that for chloroprene with characteristic nitro and nitrate bands. There was some i.r. evidence that there were nitro-groups in at least two environments, one being a primary nitro-group. The band at 980 cm^{-1} indicated *trans*-disubstituted ethylene, $\bar{M}_n$, 220 (elemental analysis corresponded to $C_4H_{4.6}Cl_{0.9}N_{2.1}O_{4.6}$).

Isoprene.—Details are in the Table. The product had characteristic nitro and nitrate bands in the i.r. (elemental analysis corresponded to $C_5H_{3.2}N_{1.2}O_{2.7}$).

2,5-*Dimethylhexa*-2,4-*diene.*—Details are in the Table. Distillation of the product (9.6 g) gave 2.5-*dimethyl*-2,5-*dinitrohex*-3-*ene* (0.4 g, 5%), b.p. 90° at 1 mmHg, m.p. 131—133° [Found: C, 47.5; H, 7.0; N, 13.6%; *M* (sulpholan), 198. $C_8H_{14}N_2O_4$ requires C, 47.5; H, 7.0; N, 13.9%; *M*, 202], τ ($CDCl_3$) 3.9 (2 H, s) and 8.28 (12 H, s). The i.r. spectrum showed bands characteristic of tertiary nitro-groups[30] and *trans*-disubstituted ethylene. The d.s.c. endotherm was at 133°. When the reaction with nitric oxide was carried out in more concentrated benzene solution a small amount of white solid was precipitated, which was insoluble in common organic solvents, but which could be recrystallised from nitromethane, m.p. 140° (decomp). The i.r. spectrum had bands corresponding to $(CH_3)_2$-C–NO_2,[30] no nitrate ester bands but bands at 1 640 (possibly N=N str.) and 1 660 cm^{-1}. The mass spectrum had a weak ion, *m/e* 368, and a major fragment, *m/e* 214, corresponding to $C_8H_{12}N_3O_4$. A furazan oxide structure[32] for the solid is not possible since there were no strong bands in the i.r. at 1 625—1 600 cm^{-1}. The most probable structure would seem to be the nitroso-dimer of 2,5-dimethyl-2-nitro-5-nitrosohex-3-ene. The d.s.c. exotherm maximum was at 141° (0.6 cal mg^{-1}).

The bulk of the reaction product was an oil, $\bar{M}_n$ 297 (elemental analysis corresponded to $C_8H_{13.2}N_{2.4}O_{5.9}$). The i.r. spectrum had bands corresponding to 1,4-addition, nitrate, and $(CH_3)_2C$–NO_2.

trans,trans-1,4-*Diphenylbutadiene.*—The oil from this reaction (3.2 g) (Table) on standing under nitrogen at −20° for a number of weeks deposited crystals of 1-*nitro*-4-*nitrato*-1,4-*diphenylbut*-2-*ene* (44%), m.p. 102° (decomp.), d.s.c. endotherm at 102°, exotherm at 108° [Found: C, 61.5; H, 4.5; N, 9.0%; *M* (benzene), 298. $C_{16}H_{14}N_2O_5$

[31] M. Fligge, D. Klamman, W. Roser, and P. Weyerstahl, *Ber.*, 1965, **98**, 1831.

[32] (*a*) N. Levy and C. W. Scaife, *J. Chem. Soc.*, 1946, 1093, 1100; (*b*) J. H. Boyer, U. Toggweiler, and G. A. Stoner, *J. Amer. Chem. Soc.*, 1957, **79**, 1748.

requires C, 61.3; H, 4.5; N, 8.9%; *M*, 314]. The i.r. spectrum had bands at 1 550, 1 370, 1 640, 1 270, and 840 cm^{-1} corresponding to secondary nitro-group and nitrate ester. Since there was no band at 1 625 cm^{-1} little 1,2-addition could have occurred. The remaining oil had an i.r. spectrum almost identical with that of the solid.

When the reaction was carried out on a high vacuum line using rigorously purified NO at 15° (2.5 h) 24% of diene was recovered but there was little evidence of any induction period. The more reactive diene, chloroprene, reacted similarly (6°). The blue-green nitroso colour was formed immediately and at the end of the reaction *ca.* 1/3 of the gas present was non-condensable at liquid nitrogen temperature.

Interaction of Chloroprene and Nitric Oxide in the Presence of Additives.—(i) *Nitrogen dioxide.* This was injected below the surface of the benzene at 20° immediately before the addition of chloroprene; analysis was by g.l.c. The speed of chloroprene consumption and the rate of nitrogen evolution was affected in a non-reproducible manner.

(ii) *Nitroso-intermediate trapping.* To chloroprene (4.8 ml) and nitric oxide in n-heptane (75 ml) at −40° was added diphenylacetylene (0.5 g). After 6.5 h the bulk of the diphenylacetylene (80%) was recovered; no oxadiazetidine could be identified.[33] To a similar experiment in dichloromethane at −5° was added a solution of methylene-*p*-chloroaniline (1 g) but again the bulk of the additive was recovered; no nitrone could be identified.

(iii) *Diazonium nitrate trapping.* Trapping with (a) methanol, (b) 2-naphthol, or (c) *m*-dimethoxybenzene did not produce the desired products.

(iv) *Iodine.* Iodine (0.6 g), when added to chloroprene (0.5 g) and nitric oxide (50 ml min^{-1}) in benzene (6°), suppressed the usual reaction. All the chloroprene reacted and *ca.* 70% of the iodine had been consumed. It had been shown previously that iodine and chloroprene did not react in the dark in the absence of nitric oxide.[34]

(v) *Nitroxides.* Similarly when 2,2,6,6-tetramethyl-4-piperidone nitroxide or the piperidine nitroxide was added, the usual reaction was suppressed. There was no residual chloroprene but traces of the dimer of 2-chloro-1-nitro-4-nitrosobut-2-ene were identified. An attempt made to follow the reaction by observing the absorption bands at 235—245 nm or at 225 nm was frustrated by either the reaction products forming films on the spectrometer cell walls or foaming. Previously, it had been shown that the nitroxides did not react with chloroprene in benzene and were unaffected by nitric oxide over 4 h. An oxygen free solution of 2,2,6,6-tetramethyl-4-piperidone nitroxide absorbed exactly 1 mol. equiv. of nitrogen dioxide gas and bright yellow crystals were precipitated. The crystals were stable at −20° under nitrogen but decomposed rapidly at room temperature.

We thank B.P. Chemicals International Ltd., for gifts of chemicals and for a maintenance grant for S. H. N. We also thank Mr. F. J. Bellringer for helpful discussions.

[5/147 *Received*, 22*nd January*, 1975]

[33] C. K. Ingold, *J. Chem. Soc.*, 1924, **125**, 87; W. J. Hickinbottom, 'The Chemistry of Carbon Compounds,' Elsevier, Amsterdam, 1954, vol. IIIA, p. 148.

[34] Nitrosyl iodide has been reported as being unstable, G. Porter, Z. G. Szabo, and M. G. Townsend, *Proc. Roy. Soc.*, 1962, **270**, 493.