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Reaction of Dinitrogen Trioxide with 2-Methylpropene and Other Alkenes. Evidence for Electrophilic Nitrosation

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The solid dimer product from the reaction of dinitrogen trioxide and 2-methylpropene was converted to the corresponding oxime by heating with or without a solvent for *ca.* 2 days. This establishes the orientation of the dinitrogen trioxide addition product as the 1-nitroso- rather than the 2-nitroso-compound as previously thought. A number of other alkene–dinitrogen trioxide adducts have been prepared; most were shown by i.r. spectroscopy to exist partially in the oxime form, the fraction of oxime increasing on warming or on standing for a long time. Hydrolysis of two of the adducts gave products which were in accord with the suggested orientation. There was a striking analogy between these results and those obtained by other workers who examined the products of addition of dinitrogen tetraoxide (acting as nitrosonium nitrate) with alkenes, and their hydrolysis products.

IT is known that dinitrogen trioxide reacts with alkenes to give N_2O_3 adducts. However the situation regarding the orientation of addition and hence the mechanism of the reaction is far from clear, since both modes of addition have been reported for the same alkenes on a number of occasions. It has, however, been shown [1] that the same product, believed to be a β-nitronitrosoalkane (a nitrosite) is obtained from the reaction of an alkene with dinitrogen trioxide in a suitable solvent, as it is from the reaction of nitrous acid in water, as expected since nitrous acid solutions are known to contain dinitrogen trioxide. The structure of dinitrogen dioxide has been established from u.v.,[2] i.r.,[3] and n.m.r.[4] spectroscopic studies, and shows the presence of a weak N–N bond formed by a π–π overlap. Because of the uncertainty regarding the orientation of the addition, various mechanistic possibilities have been suggested for the addition. Many workers [5–7] believed that the molecule was polarised in the $NO_2^+NO^-$ sense and so reacted by electrophilic nitration, whereas others [8] considered the polarity to be $NO^+NO_2^-$. Schechter and Ley [1] have suggested that the reaction were best accounted for by a free radical mechanism, since apparently the orientation of addition to alkenes did not conform to that expected on polar grounds for a heterolytic mechanism, although it is perhaps pertinent to note here that in all probability the orientation of addition has not, in many cases, been properly assigned. The work of Ridd [9] and others in the area of *N*-nitrosation and diazotisation of aromatic amines has shown that electrophilic nitrosation can occur *via* dinitrogen trioxide (N_2O_3), the nitrous acidium ion ($H_2NO_2^+$), the nitrosonium ion (NO^+) or nitrosyl halides (NOX) depending upon the reaction conditions. An earlier paper by us [10] reports the results of a kinetic study for the reaction of nitrous acid in water with a number of alkenes. At low acidity for both 2,3-dimethyl- and 2-methyl-but-2-ene, the reaction was second order in nitrous acid and so was consistent with reaction *via* dinitrogen trioxide. 2,3-Dimethylbut-2-ene was more reactive than 2-methylbut-2-ene towards dinitrogen trioxide by a factor of seven, confirming that the reaction is one of electrophilic nitrosation, under these conditions.

The purpose of the present work is to attempt to clear up the uncertainty in the literature regarding the orientation of addition of dinitrogen trioxide to alkenes, and so to establish whether the mechanism of such reactions is better represented by one involving electrophilic nitrosation, rather than by free radical addition.

EXPERIMENTAL

The alkenes were all obtained commercially and purified by g.l.c. where necessary.

Reactions with Nitrous Acid.—A solution of sodium nitrite was added slowly to a stirred mixture of a sulphuric acid (2N) and the olefin at 0°. In the case of 2-methylpropene, the solution was kept saturated with the gas. The product blue or green liquids together in some cases with a white solid, formed fairly quickly and were easily separated, washed, and dried. In one instance (2-methylprop-2-enol) the nitrosyl bromide adduct was isolated by carrying out the reaction in the presence of a large excess of sodium bromide.

Reactions with Dinitrogen Trioxide.—Liquid dinitrogen trioxide (prepared from concentrated sulphuric acid and sodium nitrite [11]) was condensed on a cold-finger and allowed to drop into an ethereal solution of the olefin cooled in an ice–salt mixture. Excess of dinitrogen trioxide and the solvent were removed under vacuum. In some cases the addition was reversed, and in others no solvent used; the products were the same in all cases.

The products were examined by i.r. and in some cases n.m.r. spectroscopy. The elemental analyses of the solid dimeric products are given in the Table.

The product from excess of dinitrogen trioxide and 1,1-diphenylethylene in ether after removal of the solvent was a yellow oil which solidified on standing. Recrystallisation from pentane containing a little methylene dichloride afforded a white solid, m.p. 108°. It was identified as 1,1-diphenyl-2-nitroethanol, lit.,[12] m.p. 107—108° (Found: C, 69.0; H, 5.0; N, 5.75. Calc. for $C_{14}H_{13}NO_3$: C, 69.1; H, 5.4; N, 5.76%), $\nu_{max.}$ 3 500 (OH) and 1 560 (NO_2) cm^{-1}, *m*/*e* 243 (M^+), 182 (Ph_2CO), 105 (PhCO), and 77 (Ph), δ 7.38 (10 H), 5.05 (2 H), and 4.53 (1 H). The OH proton was not split and so is tertiary (*cf.* spectrum of 2-methyl-2-

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[1] H. Schechter and D. E. Ley, *Chem. and Ind.*, 1955, 535.

[2] J. Mason, *J. Chem. Soc.*, 1959, 1288.

[3] L. D'Or and P. Tarte, *Bull. Soc. roy. Sci. Liège*, 1953, **22**, 276.

[4] L. O. Anderson and J. Mason, *Chem. Comm.*, 1968, 99.

[5] N. Levy, C. W. Scaife, and A. E. Wilder-Smith, *J. Chem. Soc.*, 1948, 54.

[6] C. K. Ingold and E. H. Ingold, *Nature*, 1947, **159**, 743; T. R. Govindachari and B. R. Pai, *J. Org. Chem.*, 1953, **18**, 1253.

[7] E. C. Kooyman, E. Farenhorst, and E. G. G. Werner, *Rec. Trav. chim.*, 1951, **70**, 689.

[8] A. Michael and G. H. Carlson, *J. Org. Chem.*, 1939, **4**, 169.

[9] J. H. Ridd, *Quart. Rev.*, 1961, **15**, 418.

[10] J. R. Park and D. L. H. Williams, *J.C.S. Perkin II*, 1972, 2158.

[11] P. I. Protsenko and V. B. Stradomsky, *Zhur. obshchei Khim.*, 1955, **25**, 1043.

[12] M. Konowalow and G. Jatzewitsch, *Chem. Z.*, 1905, **II**, 825.

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Elemental analyses of dimer adducts

Alkene	Found (%) C	H	N	Cl	Adduct formula	Calc. (%) C	H	N	Cl	M.p. (°C)
Propene	30.3	5.1	23.6		$C_3H_6N_2O_3$	30.5	5.1	23.7		108
2-Methylpropene	36.6	6.3	21.3		$C_4H_8N_2O_3$	36.4	6.1	21.2		82
3-Chloropropene	23.7	3.3	20.6	23.3	$C_3H_5ClN_2O_3$	23.6	3.3	18.4	23.3	97
2,3-Dimethyl-but-2-ene	44.2	7.1	17.3		$C_6H_{12}N_2O_3$	45.0	7.5	17.5		208

nitropropan-1-ol,[13] where the OH proton is split and appears at δ 3.89).

Hydrolysis Experiments.—The products of the reactions of dinitrogen trioxide with 3-chloro-2-methylpropene and 2-methylbut-2-ene were treated with sulphuric acid (2M) at 65° for two days. The solutions were extracted with ether, dried, and the solvent removed. From 3-chloro-2-methylpropene there was obtained by distillation a white solid, b.p. 96° at 10 mmHg, which when recrystallised from benzene had m.p. 106°. It was identified as 3-chloro-2-hydroxy-2-methylpropionic acid (lit., m.p. 106—107°) by elemental analysis of the acid and also of its *S*-benzylthiouronium salt. It had identical physical properties with an authentic sample prepared from hypochlorous acid and methacrylic acid.[14] Similarly from 2-methylbut-2-ene was obtained a brown oil which on oxidation with periodic acid gave both acetone and acetic acid, characterised by the 2,4-dinitrophenylhydrazone and *S*-benzylthiouronium salt respectively.

RESULTS AND DISCUSSION

We have confirmed (for 3-chloropropene) the earlier observation [1] that the same products of reaction are obtained using (a) dinitrogen trioxide in ether, or in the absence of a solvent, and (b) nitrous acid in water. The reactions of 2-methylbut-2-ene, 3-chloro-2-methylpropene, 3-hydroxy-2-methylpropene, 2-methyl-1-chloropropene, and 2,4,4-trimethylpent-2-ene all gave only the monomer product as blue or green liquids, whereas both monomer and dimer products were obtained from propene, 2-methylpropene, 3-chloropropene, and 2,3-dimethylbut-2-ene. The solid dimer gradually precipitated from the monomer products of propene and 2-methylpropene on standing. Most of the products showed signs of decomposition when kept at room temperature for some days. The products from 2-methylpropene were examined in more detail. The dimer melted at 82° to a blue liquid and it also dissolved in both acetone and carbon tetrachloride to give an initially colourless solution which gradually developed, over some minutes, a blue colour, suggesting the rapid but not instantaneous dissociation to the monomer in solution. This was confirmed by an examination of the ^1H n.m.r. spectrum of the solution at different times. Figure 1 shows the spectrum taken as near as possible after dissolving the solid in deuterioacetone, and Figure 2 is the spectrum taken 30 min later. The two signals at δ 1.71 and 5.37 (in the ratio 3 : 1) give way fairly rapidly to two signals at δ 1.23 and 5.64 (also in the ratio 3 : 1). The former pair can readily be ascribed to the CH_3 and CH_2 protons in the dimer molecule and the latter to the corresponding protons in the monomer. Clearly the monomer is the stable form of the nitrosite in solution, although the energy barrier for the dissociation appears to be small. Recent work by Snyder *et al.*[15] has shown that, as expected, entropy changes associated with the dissociation of bisnitrosoalkanes are important. In our case the reaction is too fast to allow the observation of the spectrum of the pure dimer. When the solid dimer is heated to *ca.* 90° for two days, a yellow liquid is formed with strong peaks in the i.r. spectrum at 3 580 and 1 650 cm^{-1} characteristic of the OH and CN stretching frequencies. The OH frequency is shifted to 2 650 cm^{-1} after exchange with dueterioethanol. The ^1H n.m.r.

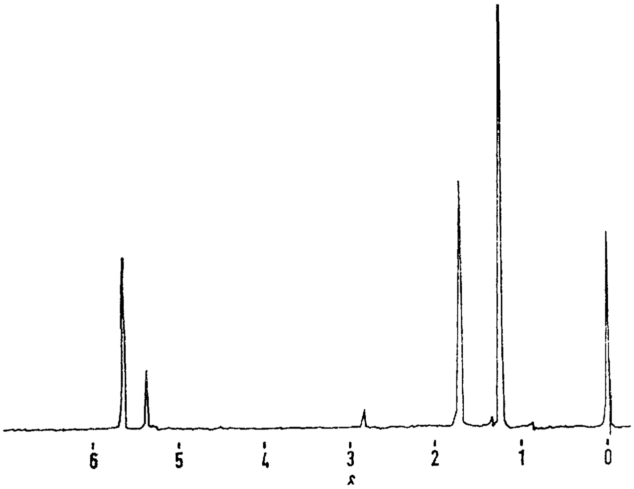

FIGURE 1 N.m.r. spectrum [in $(CD_3)_2CO$] of nitroso-dimer of 2-methylpropene immediately on dissolution

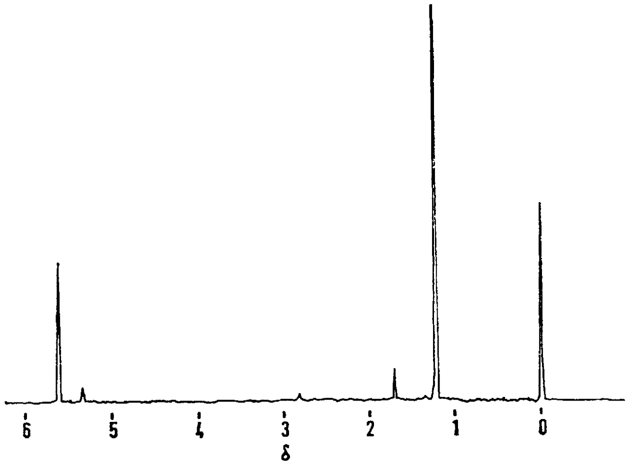

FIGURE 2 N.m.r. spectrum [in $(CD_3)_2CO$] of nitroso-dimer of 2-methylpropene after 30 min in solution

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[13] N. S. Bhacca, D. P. Hollis, L. F. Johnson, and E. A. Pier, 'N.M.R. Spectra Catalog, II, Spectrum 422,' Varian Associates, Palo Alto, 1963.

[14] G. F. Bloomfield, E. H. Farmer, and C. G. B. Hose, *J. Chem. Soc.*, 1933, 800.

[15] J. P. Snyder, M. L. Heyman, and E. N. Suciu, *J. Org. Chem.*, 1975, **40**, 1395.

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spectrum (Figure 3) consists of two signals at δ2.00 and 2.26 and one at 7.16 in the ratio 3 : 3 : 1. Both the signals in the CH_3 region are doublets and the one in the CH region is made up of seven lines with a coupling constant of about 1.3 Hz. This spectrum together with the i.r. spectrum is consistent with the oxime form (I).

$$(CH_3)_2C(NO_2)CH{=}NOH$$

(I)

It is not clear at first why there are two methyl proton peaks, but there must be some rotational isomerism, possibly resulting from hydrogen bonding between the hydroxy-proton and the oxygen atom of the NO_2 group. The methine proton falls in the range δ 6.8—7.9 quoted by Jackman and Sternhell.[16] The OH proton does not appear to be present in our spectrum, but appears only as an extremely broad and hardly discernible absorption in the spectrum of acetaldoxime.[17] Scheinbaum[18] has recently converted a number of dimeric nitrosites to the oxime form by refluxing in ethanol with zinc chloride.

The conclusion is that, since the nitroso-dimer from 2-methylpropene can be completely converted to the oxime form, the nitroso-group must have been initially attached to C-1, since it is difficult to see how a tertiary nitroso-compound is capable of forming the oxime. This contrasts with the earlier assignment by Levy *et al.*[5] of a 1-nitro-2-nitroso-structure, but is more compatible with the product expected from an electrophilic nitrosation.

The blue liquid monomer product from 2-methylpropene (which gradually precipitated some dimer on standing) whilst showing the presence of the monomer form of the nitrosite also contained some of the oxime form and also a significant quantity of another unidentified product. Further conversion to the oxime form could be affected by heating with or without a solvent for two days.

We find upon examination of the i.r. spectra of the blue-green liquid products from the other alkenes studied in the present work, that there is evidence of partial isomerisation to the oxime form (as indicated also by the n.m.r. spectrum of the 2-methylpropene adduct), from the characteristic OH and CN group frequencies. The extent of oxime formation varied from one alkene to another and also with each preparation, but was increased significantly upon heating or upon standing at room temperature for a longer period of time. This applied to all the alkene products studied except that from 2,3-dimethylbut-2-ene, where no oxime formation is possible. In this case the solid product was found to be particularly stable and readily sublimed to give needle shape crystals. In common with all the other dimeric products it melted (208°) to give a blue liquid; in benzene it gave a blue solution which gave a single signal at δ1.3 in the n.m.r. spectrum. Partial conversion to the oxime form was observed also for the nitrosyl bromide adduct of 2-methylprop-2-enol which appeared to exist in the monomeric form and which slowly was converted, on standing, to the oxime form as shown by the growth of the OH and CN absorption in the i.r. spectrum.

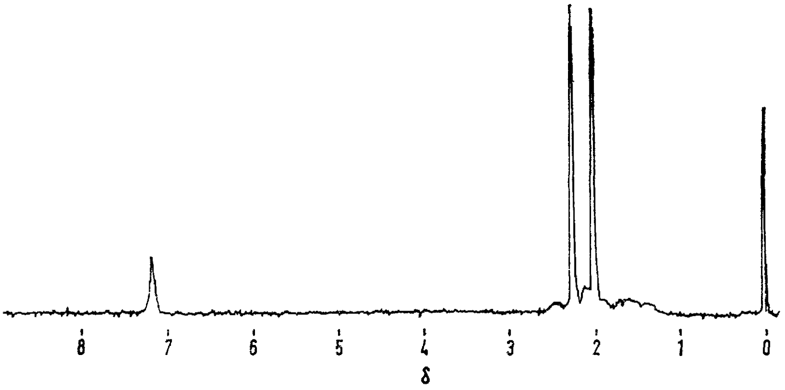

FIGURE 3 N.m.r. spectrum [in $(CD_3)_2CO$] of nitroso-dimer of 2-methylpropene after heating solid for two days at *ca.* 90°

Our results on the orientation of addition are wholly consistent with a mechanism in which dinitrogen trioxide acts as an electrophilic nitrosating agent rather than as a nitrating agent on a free-radical carrier for a homolytic mechanism. Studies with aromatic amines[9] and with alkenes in water with dilute nitrous acid solution[10] have shown that at least at low acidities in water dinitrogen trioxide does act as a carrier of NO^+. This work does not distinguish between a carbonium ion mechanism or one where the addition is concerted through a four-centred transition state.

There is thus a parallel between the reactions of dinitrogen trioxide and dinitrogen tetroxide. The latter, whilst capable of forming nitro-compounds *via* a free-radical mechanism, can also in the absence of weakly basic solvents, react as nitrosonium nitrate, and effect an electrophilic nitrosation.[19-21] The dimeric

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[21] L. Parts and J. T. Miller, *J. Phys. Chem.*, 1969, **73**, 3088.

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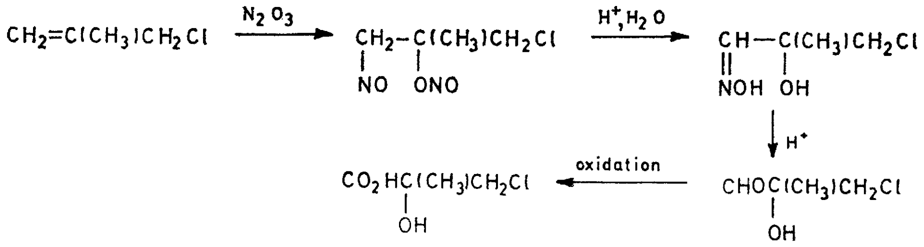
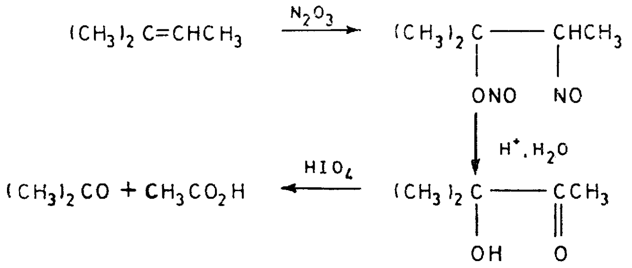
nitroso-nitrate adduct from 2-methylpropene had an n.m.r. spectrum very similar to that found for the dimer from 2-methylpropene and nitrogen trioxide in the present work.

Hydrolysis of Nitrosites.—Additional evidence as to the regioisomerism of the nitrosites can be obtained from the characterisation of the products of acid-catalysed hydrolysis in aqueous solution. A preliminary account of some of this work has already been published.[22] The hydrolysis in acid solution of the product from dinitrogen trioxide and 3-chloro-2-methylpropene gave in good yield 3-chloro-2-hydroxy-2-methylpropionic acid. A reasonable reaction sequence for the formation of this acid is given in Scheme 1. It is much easier to account for the product in terms of a 2-nitro-1-nitroso-formulation of the nitrosite, rather than the 1-nitro-2-nitroso-form given by Kooyman *et al.*[7] Similarly we have obtained a hydrolysis product from the monomer adduct from dinitrogen trioxide and 2-methylbut-2-ene. This product gave, upon reaction with periodic acid, acetone, and acetic acid (identified as the 2,4-dinitrophenylhydrazone and *S*-benzylthiouronium salt respectively) as expected from 3-hydroxy-3-methylbutan-2-one. A probable reaction sequence is given in Scheme 2. This result again is more in accord with a formulation where the nitroso-group in the adduct is attached to a carbon atom bearing a hydrogen atom, so that isomerisation to the oxime can occur, followed by hydrolysis to the carbonyl compound. The orientation of addition conflicts with that proposed by other workers,[23] but agrees with the early work of Michael and Carlson,[8] and also with the orientation found for the addition of nitrosyl chloride to 2-methylbut-2-ene.[24]



SCHEME 1



SCHEME 2

Exactly the same hydrolysis procedure was applied by other workers[19,20] to establish the orientation of addition of dinitrogen tetroxide (acting as nitrosonium nitrate) to alkenes. Indeed, the same hydroxy-acid was obtained[19] from the hydrolysis product of the dinitrogen tetroxide adduct with 3-chloro-2-methylpropene as we have isolated from the dinitrogen trioxide reaction. This is to be expected if the two products are the nitroso-nitrate and nitroso-nitrite respectively, and is taken as strong supporting evidence for our formulation. The hydrolysis of the nitrosyl chloride adducts with alkenes similarly leads to the formation of chlorocarbonyl compounds.[25]

Most workers[1,5,7,23] have regarded nitrosites as nitro-nitrosoalkanes, although some authors[8,26,27] have considered the structure in terms of a nitroso-nitrite. Ornishchenko[26] obtained an amino-alcohol, rather than a diamine from the reduction of the product of reaction of dinitrogen trioxide with santene; this would support the nitrite structure. However Boer and Turley[28] in a crystal structure determination of the product from ethylene and dinitrogen trioxide, established the product as the *trans*-dimer of 1-nitro-2-nitrosoethane, with N–N bonding of the nitroso-groups. On the other hand the results of our hydrolysis experiments are more in accord with the nitrite formulation, particularly when the results are compared with those obtained for the hydrolysis of the nitroso-nitrates.[19,20] It may well be that the various views could be reconciled in terms of a nitro-nitrite isomerisation at some stage; a further detailed study in this area would be appropriate.

C-Nitroso-compounds are generally thought of as being unstable as the monomer,[29] rapid dimerisation or oxime formation occurring. This suggests that the monomeric form of the nitrosites obtained in this and earlier work, is stabilised in some way, so that its conversion to the oxime is a relatively slow process, as is observed experimentally. This stabilisation could arise by the formation of a cyclic structure as (II), involving a five-membered ring as shown, with some N–N interaction, or possibly involving some partial bonding between nitrogen and oxygen. A fully developed

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[22] J. R. Park and D. L. H. Williams, *Chem. Comm.*, 1969, 332.

[23] C. A. Burkhard and J. F. Brown, *J. Org. Chem.*, 1964, **29**, 2235.

[24] N. Thorne, *J. Chem. Soc.*, 1956, 2587.

[25] B. W. Ponder and D. R. Walker, *J. Org. Chem.*, 1967, **32**, 4136.

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[27] T. Kametani and Y. Masuda, *J. Pharm. Soc. Japan*, 1952, **72**, 81 (*Chem. Abs.*, 1952, **46**, 11,208).

[28] F. P. Boer and J. W. Turley, *J. Amer. Chem. Soc.*, 1969, **90**, 1371.

[29] B. G. Gowenlock and W. Lüttke, *Quart. Rev.*, 1958, **12**, 321.

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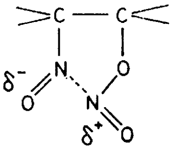
cyclic structure of this type has recently been suggested [30] for the dinitrogen trioxide adduct with tetracyclone, which subsequently underwent rapid hydrolysis to give the *cis*-dihydroxy-compound. It is not so unusual for the nitroso-oxime isomerisation to be a relatively slow process, there are a number of instances [31] where the rates of such reactions have been measured.


(II)

In establishing the orientation of addition of dinitrogen trioxide to 2-methylpropene, by conversion of the product completely to the oxime form, it is of course assumed that no interchange of an oxygen atom occurs between the NO and NO_2 groups in the adduct, by the action of heat. This seems a reasonable assumption, but such a reaction has been proposed [23] to account for the fact that the nitrosite from 2-methylbut-2-ene was converted to its oxime form by treatment with alkali; a cyclic intermediate was suggested. If such a reaction occurs in alkaline solution, it seems unlikely to take place merely by heating. It appears more likely to us that the orientation of addition in the nitrosite has been incorrectly assigned, so that these workers merely observed the normal base-catalysed isomerisation to the oxime.

The product obtained from 1,1-diphenylethylene and excess of dinitrogen trioxide in ether was not a nitrosite, as for all the other alkenes studied, but rather 1,1-diphenyl-2-nitroethanol. Its structure was established quite unambigously by elemental analysis, i.r., n.m.r., and mass spectroscopy. It may well be here that nitrosation by dinitrogen trioxide does not occur because of steric hindrance by the phenyl groups. This would particularly be so if the addition was a concerted process, as has been argued [32] for nitrosyl chloride addition. If this reaction is suppressed, it is conceivable that another reaction involving free radical attack occurs, though it is not clear what the detailed mechanism is, particularly with regard to the OH group formation. On the other hand the product could conceivably have been formed from the nitrosite by oxidation of the nitroso-group and hydrolysis of the nitrite group by traces of water.

We thank the S.R.C. for a research studentship (to J. R. P.)

[5/1900 *Received*, 1*st October*, 1975]

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