Reactions of nitrogen dioxide with hexenes. The mechanistic and structural factors controlling the product composition

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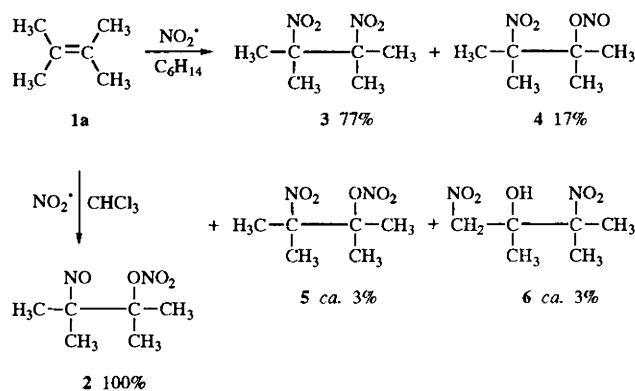
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The reaction of nitrogen dioxide with a number of hexenes has been investigated using several solvents and the major products have been identified. The heterolytic reaction path has been effectively eliminated by the use of hexane as solvent. The mechanism of the heterolytic reaction path is discussed with the aid of *ab initio* molecular orbital calculations on possible nitrosating agents with particular reference to the *syn* and *anti* forms of nitrosyl nitrate. A new mechanism is proposed for the formation of certain trisubstituted derivatives.
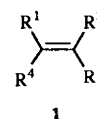
This study of the reactions of nitrogen dioxide † with a number of hexenes was carried out partly to determine how the product composition varies with the substrate structure and reaction conditions and partly to establish the best conditions for the detection of possible examples of ^{15}N nuclear polarisation in the reaction. An account of the resulting CIDNP effects has already been published [1,2] but the studies now reported provide some more general evidence on the factors that determine the product composition.

The early literature on the reactions of nitrogen dioxide with alkenes is extensive and confused but the subject was clarified by the detailed product analyses of Levy, Scaife and their co-workers [3] and by the mechanistic studies of Brand and Stevens.[4] By 1964, when the subject was reviewed,[5] the principal features of the homolytic reaction path appeared well established. The first stage of the reaction was considered to involve the reversible addition of molecular nitrogen dioxide to the double bond followed by the reaction of the resulting organic radical with a second nitrogen dioxide molecule to form either the dinitro compound or the nitronitrite. The nitronitrite can then react further to give either the nitroalcohol or the nitronitrate. With some substrates, the reversibility of the first stage is clear from the *cis–trans* isomerisation [6,7] of the substrate that sometimes accompanies the overall reaction. More recently, kinetic evidence has been provided to show that, with relatively high concentrations of nitrogen dioxide, the double bond can also be attacked by molecular dinitrogen tetroxide [8,9] and that, when present in very low concentrations, molecular nitrogen dioxide can act predominantly by abstraction of an allylic hydrogen atom.[10] With some substrates, there is also evidence of an important 'heterolytic' pathway leading to nitrosocompounds [11–13] and this has been considered to occur through nitrosation by nitrosonium ions.[12,13]

The substrates used in the present work were the hexenes (1a–e). These were chosen to provide evidence on how the types of product formed vary with the degree of alkyl substitution about the double bond. The products formed from 2,3-dimethylbut-2-ene (1a) have already been studied.[11,12,14] For reactions in chloroform solution, this compound is reported to react with nitrogen dioxide by the heterolytic route to give the nitrosonitrate 2 as the only product.[12]

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† The term 'nitrogen dioxide' without the qualification 'molecular' is used to refer both to this species and to the various forms of the dimer in equilibrium with it.

Scheme 1

a R[1] = Me; R[2] = Me; R[3] = Me; R[4] = Me (2,3-dimethylbut-2-ene)
b R[1] = Me; R[2] = Et; R[3] = H; R[4] = Me (2-methylpent-2-ene)
c R[1] = Et; R[2] = H; R[3] = Et; R[4] = H [(E)-hex-3-ene]
d R[1] = H; R[2] = Et; R[3] = Et; R[4] = H (2-ethylbut-1-ene)
e R[1] = H; R[2] = H; R[3] = butyl; R[4] = H (hex-1-ene)

Results

The standard procedure involved the slow addition of nitrogen dioxide in a given solvent to an equal volume of a stirred solution of the alkene in the same solvent, both solutions being initially at room temperature. The solvent was then removed and the reaction products were analysed by HPLC followed by ^{1}H and ^{13}C NMR spectroscopy and CI mass spectrometry.

As a check on the identification, the chemical shifts in the ^{13}C spectra were compared with those expected from the additivity of the substituent effects of the –OH and –NO₂ groups. Good agreement was obtained after using slightly lower substituent constants for these groups at the α-position than those given in the literature [15] (see Experimental). All of the products have two or more electronegative substituents and, in such compounds, the combined effect of the electronegative substituents appears somewhat less than true additivity would suggest.

The stated yields are based on the products obtained after HPLC separation. For several reasons, including handling
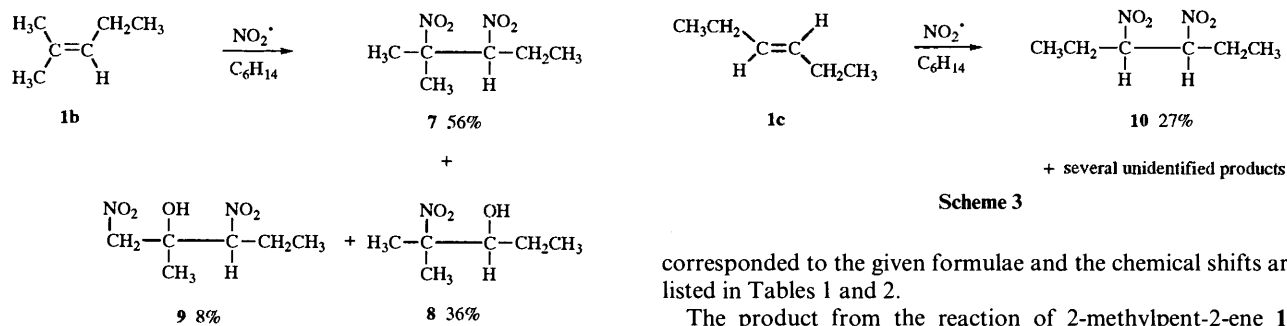
Table 1 ^{1}H NMR chemical shifts for the products formed by the reaction of nitrogen dioxide with 2,3-dimethylbut-2-ene (**1a**, Scheme 1) and 2-methylpent-2-ene (**1b**, Scheme 2). Compounds **9a** and **9b** are diastereoisomers

| | δ_H(CHCl$_3$) | | | | | |
Compound	1-H	3-H	4-H	5-H	2-CH$_3$	3-CH$_3$
2	2.12 (s)^a	—	0.86 (s)^a	—	2.12 (s)^a	0.86 (s)^a
3	1.74 (s)	—	1.74 (s)	—	1.74 (s)	1.74 (s)
4	1.63 (s)	—	1.25 (s)	—	1.63 (s)	1.25 (s)
5	1.75 (s)^a	—	1.71 (s)^a	—	1.75 (s)^a	1.71 (s)^a
6	4.61 (d)^b 4.71 (d)^b	—	1.69 (s)	—	1.42 (s)	1.71 (s)
7	1.69 (s)	5.03 (q)	1.70 (m)^b 2.10 (m)^b	1.01 (t)	1.69 (s)	—
8	1.28 (s)	4.34 (q)	1.85 (m)^b 2.15 (m)^b	0.97 (t)	1.30 (s)	—
9a	4.72 (d)^b 4.54 (d)^b	4.61 (q)	1.95 (m)^b 2.10 (m)^b	1.02 (t)	1.43 (s)	—
9b	4.61 (d)^b 4.52 (d)^b	4.59 (q)	1.95 (m)^b 2.10 (m)^b	1.05 (t)	1.44 (s)	—

^{a} These values are in close agreement with those in the literature (ref. 12). ^{b} Diastereotopic hydrogens.

Table 2 ^{13}C NMR chemical shifts for the products formed by the reaction of nitrogen dioxide with 2,3-dimethylbut-2-ene (**1a**, Scheme 1) and 2-methylpent-2-ene (**1b**, Scheme 2). Compounds **9a** and **9b** are diastereoisomers. The calculated values are in parentheses

| | δ_C(CHCl$_3$) | | | | | | |
Compound	1-C	2-C	3-C	4-C	5-C	2-CH$_3$	3-CH$_3$
3	23.0	91.5	91.5	23.0	—	23.0	23.0
	(21.7)	(90.6)	(90.6)	(21.7)	—	(21.7)	(21.7
4	25.2	95.0	73.8	22.4	—	25.2	22.4
5	22.4	92.8	91.6	20.8	—	22.4	20.8
7	22.8	88.5	94.3	22.4	10.7	23.0	—
	(19.6)	(84.0)	(97.8)	(17.7)	(8.4)	(19.6)	—
8	25.5	71.1	98.6	21.9	10.7	27.4	—
	(25.6)	(68.0)	(103.8)	(19.7)	(8.4)	(25.6)	—
9a	80.3	71.9	95.3	21.6	10.7	22.5	—
9b	81.1	71.9	94.9	21.8	10.7	22.0	—
	(80.6)	(71.0)	(98.8)	(19.7)	(8.40)	(20.6)	—

Scheme 2

Scheme 3

losses and some loss of nitrogen dioxide, the percentages given are greater than the yields in terms of the initial alkene and so the values should be taken as illustrating the proportions in which the products are formed.

Identification of products

In preliminary experiments (see below), we established that the so-called 'heterolytic' reaction ^{12} of **1a** to give the nitrosonitrate **2** could be almost completely eliminated by working in hexane as solvent. Since our interest lay in the products of the radical reactions, the initial studies on the identification of the products were carried out in hexane.

After HPLC separation, the product from the reaction of 2,3-dimethylbut-2-ene gave four fractions (Scheme 1): the first was a small amount of the nitronitrate **5**; the second was the main product **3**, the third was the nitronitrite **4** and the last contained a small amount of the dinitroalcohol **6**. The mass spectra

corresponded to the given formulae and the chemical shifts are listed in Tables 1 and 2.

The product from the reaction of 2-methylpent-2-ene **1b** (Scheme 2) also gave four fractions: the first was the main product **7** and the second was the nitroalcohol **8**. The products from fractions three and four gave molecular ions of the same mass and had very similar NMR spectra; these were identified as the two diastereoisomers of the dinitroalcohol **9**. In all these molecules, the hydrogens at C^4 are diastereotopic and, for compounds **7** and **8**, this is also true for the methyl groups at C^2; this property is seen in the ^{1}H NMR absorption of the hydrogens at C^4 (Table 1) and in the ^{13}C NMR absorption of the relevant methyl groups (Table 2). Diastereotopic hydrogens and methyl groups are also present in a number of the other products described below.

The product from the reaction of (E)-hex-3-ene **1c** (Scheme 3) gave six fractions but only one appeared to correspond to a pure compound; this was the dinitrohexane **10** formed in a yield of ca. 30%. Unfortunately, it proved impossible to separate the components in the other fractions. The ^{1}H and ^{13}C NMR spectra of **10** are listed in Tables 3 and 4.

The corresponding reaction of 2-ethylbut-1-ene **1d** (Scheme

Table 3 ^{1}H NMR chemical shifts for the products formed by the reaction of nitrogen dioxide with (E)-hex-3-ene (1c, Scheme 3) and hex-1-ene (1e, Scheme 5)

|	δ_H(CHCl$_3$)					
Compound	1-H	2-H	3-H	4-H	5-H	6-H
10	1.0 (t)	1.90 (m)^a 2.10 (m)^a	5.0 (q)	5.0 (q)	1.90 (m)^a 2.10 (m)^a	1.0 (t)
14	5.1 (d)^a 4.6 (d)^a	5.2 (m)	1.92 (m)^a 2.05 (m)^a	1.37 (m)	1.37 (m)	0.92 (t)
15	4.35 (m)	4.35 (m)	1.50 (m)	1.30 (m)	1.30 (m)	0.95 (t)

^{a} Diastereotopic hydrogens.

Table 4 ^{13}C NMR chemical shifts for the products formed by the reaction of nitrogen dioxide with (E)-hex-3-ene (1c, Scheme 3) and hex-1-ene (1e, Scheme 5). The calculated values are in parentheses

	δ_C(CHCl$_3$)					
Compound	1-C	2-C	3-C	4-C	5-C	6-C
10	9.2 (8.4)	23.6 (20.4)	88.0 (88.1)	88.0 (88.1)	23.6 (20.4)	9.2 (8.4)
14	74.0 (71.4)	82.7 (78.4)	30.8 (30.1)	27.2 (27.1)	21.9 (22.4)	13.6 (13.4)
15	80.7 (77.4)	68.7 (67.4)	33.4 (36.1)	27.3 (29.1)	22.4 (22.4)	13.9 (13.4)

Table 5 ^{1}H NMR chemical shifts for the products formed by the reaction of nitrogen dioxide with 2-ethylbut-1-ene (1d, Scheme 4). Compounds 13a and 13b are diastereoisomers

	δ_H(CHCl$_3$)				
Compound	1-H	3-H	4-H	2-CH_2CH$_3$	2-CH$_2$CH_3
11	4.98 (s)	2.06 (q)	0.95 (t)	2.06 (q)	0.95 (t)
12	4.45 (s)	1.59 (q)	0.94 (t)	1.59 (q)	0.94 (t)
13a	4.68 (d)^a 4.12 (d)^a	4.88 (q)	1.67 (d)	1.75 (q)	1.05 (t)
13b	4.75 (d)^a 4.55 (d)^a	4.90 (q)	1.65 (d)	1.71 (q)	1.06 (t)

^{a} Diastereotopic hydrogens.

Scheme 4

Scheme 5
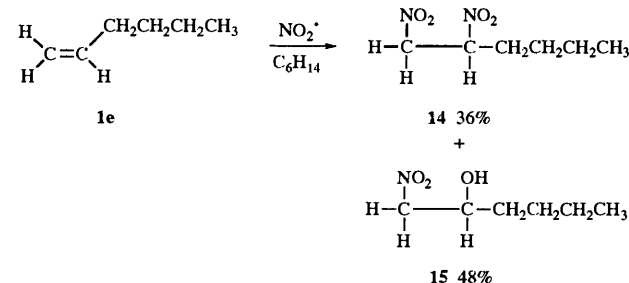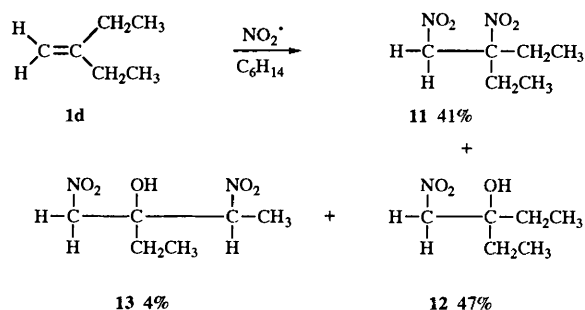
4) gave rise to 5 fractions but one, amounting to 8% of the whole, did not yield an identifiable compound. One fraction gave the dinitrohexane 11 and another fraction held a mixture of this and the nitroalcohol 12. The other fractions contained the two diastereoisomers of the dinitroalcohol 13. The NMR spectra of these compounds are listed in Tables 5 and 6.

The reaction of hex-1-ene 1e (Scheme 5) gave three fractions, one of which, amounting to ca. 10% of the whole, did not give rise to an identifiable compound. The main product was the nitrohexanol 15; the other product was the dinitro compound 14. Details of the NMR spectra of these compounds are included in Tables 3 and 4.

The balance between the heterolytic and homolytic pathways

In chloroform solution, the reaction of 1a with nitrogen dioxide has been reported[12] to give only the nitrosonitrate 2; this compound was found to decompose on standing to give the nitronitrate 3 and other unidentified products.[12] Earlier studies of the corresponding reaction in ether solution gave ca. 20% of the dinitrocompound together with other products apparently derived for the subsequent reactions of the nitrosonitrate. The formation of 2 is clearly indicated by the strong blue colour of the solutions and by the marked separation of the two methyl singlets in the ^{1}H NMR spectrum (Table 1); a consequence of the magnetic anisotropy of the nitroso group.

Our own studies of the reaction of 1a with nitrogen dioxide in those solvents accorded well with the results in the literature although, in chloroform, one further complication came from

the formation of ethyl nitrite by the reaction of nitrogen dioxide with the small amount of ethanol present as a stabiliser. The other substrates (except 1c) also gave blue or green solutions after reaction with nitrogen dioxide in diethyl ether.

Since this work was directed towards the radical processes present, it was clearly desirable to reduce or eliminate the heterolytic reaction path and the work was therefore extended to non-polar solvents. A non-polar solvent (2,2,4-trimethyl-pentane) has been used before[16] for such reactions of nitrogen dioxide but only on alk-1-enes, where the contribution of the heterolytic pathway is small. The ^{1}H NMR spectrum of the reaction mixture obtained from treating 1a with nitrogen dioxide in benzene indicated that the initial reaction gave only the nitrosonitrate 2; on standing, decomposition occurred together with the formation of the dinitrocompound 3, the nitronitrite 4 and the nitronitrate 5. The formation of 3 and 4 is particularly interesting since it implies that the initial formation of the nitrosonitrate may be reversible. The corresponding reaction in [^{2}H$_{12}$]cyclohexane gave some 2 but also a white precipitate of the dinitro compound 3.

Finally, the heterolytic reaction path was essentially eliminated by allowing nitrogen dioxide to react with 1a in hexane: none of the nitrosonitrate was apparent in the solution and the only remaining evidence of the heterolytic pathway was a trace of the nitronitrate 5 among the reaction products. However, this elimination of the heterolytic pathway does require the use of a freshly prepared solution of nitrogen dioxide in hexane; a solution that is 24 h old gives extensive

Table 6 ^{13}C NMR chemical shifts for the products formed by the reaction of nitrogen dioxide with 2-ethylbut-1-ene (**1d**, Scheme 4). Compounds **13a** and **13b** are diastereoisomers. The calculated values are in parentheses

Compound	$\delta_C(CHCl_3)$					
	1-C	2-C	3-C	4-C	2-CH_2CH_3	2-CH_2CH_3
11	75.9	91.9	27.0	7.9	27.0	7.9
	(76.7)	(92.7)	(27.4)	(5.4)	(27.4)	(5.4)
12	82.3	74.2	29.1	7.7	29.1	7.7
	(82.7)	(76.7)	(33.4)	(7.4)	(33.4)	(7.4)
13a	73.8	78.5	86.0	13.9	27.2	7.3
13b	73.7	77.8	86.3	13.9	27.6	7.0
	(77.7)	(79.7)	(86.4)	(10.4)	(28.4)	(7.4)

Table 7 The ratio R of the concentration of the dinitroproduct (**3, 7, 11, 14**) to the concentration of the nitronitrite (**4**) or the nitroalcohol (**8, 12, 15**)

Substrate	Solvent		
	Hexane	Benzene	Diethyl ether
1a	4.5	4.8	2.0
1b	1.5	2.0	1.5
1d	0.87	0.94	1.0
1e	0.75	0.78	0.78

formation of the nitrosonitrate presumably because of some oxidation of the solvent by nitrogen dioxide. The results with an 'aged' solution of nitrogen dioxide can also be obtained by adding a trace of acetic acid to the freshly prepared solution.

The balance between the dinitro and nitronitrite products

In what follows, we have followed the common assumption that the nitroalcohols are formed by the hydrolysis of the nitronitrites during the separation procedures.

The variation of the ratio of the concentration of the dinitro compound to that of the corresponding nitronitrite and nitroalcohol is shown in Table 7 for a range of substrates and solvents. For the reactions of **1a** and **1b** in diethyl ether and benzene, the results come in part from the decomposition of the nitrosonitrate. However, the fact that, for **1a**, the ratio R is very similar in hexane and in benzene suggests that, in benzene, the decomposition of the nitrosonitrate occurs, at least in part, by dissociation into dinitrogen tetroxide and the original alkene.

For all solvents, the results in Table 7 indicate that there is a clear increase in R with the extent of alkylation about the double bond. The only other clear conclusion is that, with the exception of the reaction of **1a** in diethyl ether, there is no significant variation of the ratio R with the solvent used.

Discussion

The present discussion is restricted to the mechanism of the heterolytic pathway and to the several reaction paths available to the radical **17** (Scheme 6) formed by homolytic attack on the alkene **16**. The earlier discussions of nuclear polarisation in these reactions[1,2] concerned a different problem: the consequences for CIDNP effects of the proposed first-order and second-order (with respect to NO_2) reactions for forming the radical **17**. For simplicity, the second-order reaction is not included in Scheme 6: it has been represented[8] as an alkene catalysed homolysis of dinitrogen tetroxide and hence also leads to the radical **17**.

One unexpected feature of the experimental results is the strong preference of the tetrasubstituted alkene **1a** for the heterolytic path under almost all conditions. The persistence of this reaction path in benzene and cyclohexane solvents makes the suggested involvement of nitrosonium ions[12,13] unlikely

Scheme 6
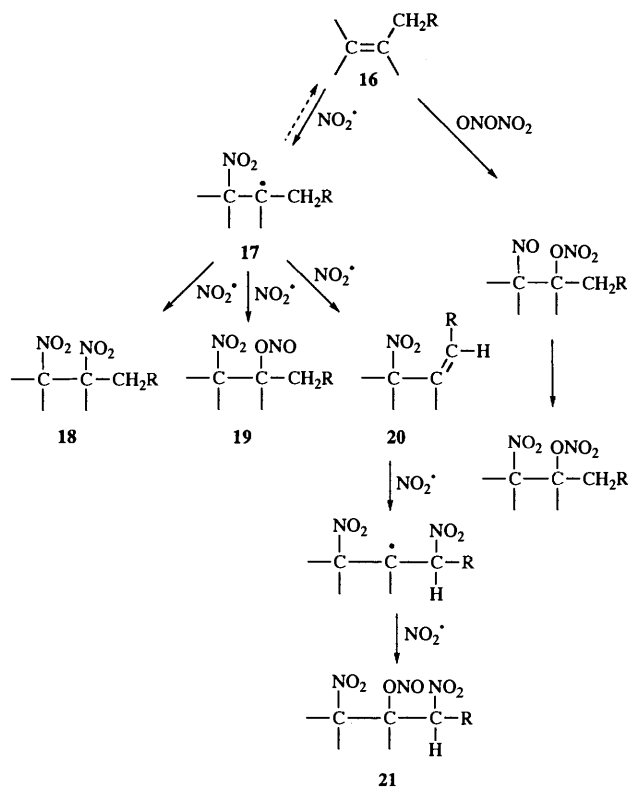
and we have therefore considered what other mechanisms could be involved. N-Nitrosation by nitrogen dioxide in alkaline solution has been considered[17] to occur through reaction with covalent nitrosyl nitrate and there is spectroscopic evidence[18] from matrix isolation and thin film studies for two forms of this molecule. Nitrosyl peroxynitrite **22** has also been considered as a potential intermediate in the past[19] but there appears to be no physical evidence for this species. Studies with nitrosyl chloride have suggested that the addition of NOX to alkenes can sometimes occur in a one step process.[20]

The structures of these nitrosating agents have been optimised at the MP2/6-31G* level and the energy calculated at the MP4SDQ/6-31G* level. The structures and charge distribution for the two conformations of nitrosyl nitrate are given in Fig. 1. Neither structure is planar, as shown by the dihedral angles listed in the legend. The energies have been corrected to apply to 25 °C and the resulting energy terms relative to planar dinitrogen tetraoxide **23** are included in Table 8.

While this work was in progress, calculations using an identical optimisation procedure but different energy approximations were published for the anti form of nitrosyl nitrate **24b**[21] and for nitrosyl peroxynitrite **22**;[21] some details of these are included in Table 8. Calculations were also carried out on a planar structure for the syn form of nitrosyl nitrate but this was
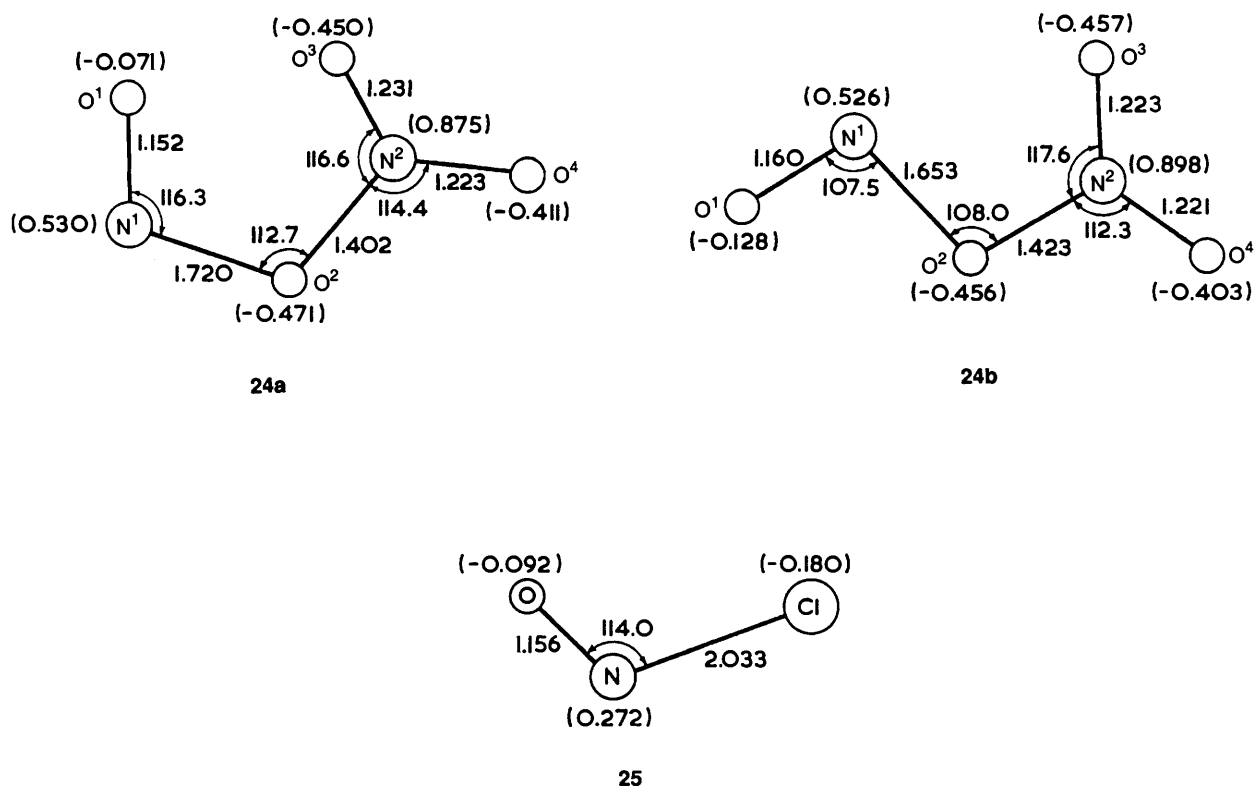
24a

(-0.071) O¹
1.152
116.3
(0.530) N¹
1.720
112.7
(-0.471) O²
1.402
(-0.450) O³
1.231
116.6
(0.875) N²
1.223
114.4
(-0.411) O⁴

24b

(0.526) N¹
1.160
107.5
(-0.128) O¹
1.653
108.0
(-0.456) O²
1.423
112.3
(-0.457) O³
1.223
117.6
(0.898) N²
1.221
(-0.403) O⁴

25

(-0.092) O
1.156
114.0
(0.272) N
2.033
(-0.180) Cl

Fig. 1 The calculated bond lengths (Å) bond angles (°) and atomic charges (in parentheses) for the *syn* nitroso nitrate **24a**, the *anti* nitroso nitrate **24b** and nitrosyl chloride **25**. The dihedral angles are: **24a**, a($N_2O_2N_1O_1$), 2.3°, a($O_3N_2O_2N_1$), 35.7°, a($O_4N_2O_2N_1$), 215.1°; **24b**, a($N_2O_2N_1O_1$), 184.4°, a($O_3N_2O_2N_1$), 16.6°, a($O_4N_2O_2N_1$), 195.6°; for details, see Experimental section. The bond angles and bond lengths for **24b** are almost identical to those given in ref. 21.

22 O–N··O–O–N–O

23 O₂N–NO₂ (drawn as N–N with O₂ on each)
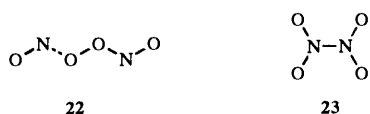
shown to be an energy maximum.[21] The *anti* form of nitrosyl nitrate was also included in a review of the properties of nitrogen oxides as calculated by density functional theory.[22]

The values for the energies of **22** and **24** relative to that of planar dinitrogen tetraoxide **23** depend very much on the level of calculation and especially on the treatment of the electron correlation; calculations at the RHF/3-21G level predict **22** and **24** to be more stable than **23**. However, the reasonable agreement between the MP4 and CI calculations in Table 8 is encouraging and the small energy terms suggest that nitrosyl nitrate is a plausible intermediate in these reactions; nitrosyl peroxynitrite appears far too unstable to be an effective intermediate.

The relatively low energy difference between **23** and **24** is supported by experimental studies. From high pressure studies[23] at 0.4 GPa, ΔH for the isomerisation of **23** to **24** has been given as 19.1 kJ mol⁻¹. Arguments based on the additivity of thermochemical data[24] have given 40.9 kJ mol⁻¹ for the heat of formation of nitrosyl nitrate and this yields a value of 21.3 kJ mol⁻¹ for the isomerisation of **23** to **24**. These results presumably refer to the more stable, *anti*, isomer of **24**.

The entropy terms in Table 8 show that the formation of both conformations of nitrosyl nitrate is favoured by an increase in temperature and the high dipole moments of these compounds relative to that of planar dinitrogen tetraoxide ($\mu = 0$) would favour the formation of nitrosyl nitrate in polar solvents. The very high charge on the nitroso nitrogen atom in **24a** and **24b** relative to that for nitrosyl chloride **25** and the long ON–ONO₂ bonds (Fig. 1) accord with the view that nitrosyl nitrate is a powerful nitrosating agent. In non-polar solvents, the *syn* isomer could also add to the alkene in a less polar one-step

Table 8 Properties of the *syn* **24a** and *anti* **24b** forms of the nitrosyl nitrate and of nitrosyl peroxynitrite **22** calculated at the MP4SDQ/6-31G*//MP2/6-31G* level (unless specified otherwise). Energy terms (kJ mol⁻¹) and entropy terms (J K⁻¹ mol⁻¹) are given relative to those for planar dinitrogen tetroxide **23** at the same temperature. The dipole moments (μ) are in Debyes

	Compound		
Property (T/K)	**24a**	**24b**	**22**
$\Delta E\,(0)^a$	29.8	18.4	106.0
$\Delta E\,(0)^{a,b}$	—	22.2	106.3
$\Delta E\,(0)^{a,c}$	—	44.4	145.2
$\Delta E\,(298.15)$	26.3	14.6	95.9
$\Delta S\,(298.15)$	18.8	25.9	28.6
$\Delta G\,(298.15)$	20.7	6.8	87.4
$\mu\,(0)$	4.17	3.42	1.21

a Excluding corrections for zeropoint energies. *b* Calculated at the QCISD(T)/6-31G*//MP2/6-31G* level (ref. 21). *c* Calculated using density-functional theory at the DFT/6-31G* level (ref. 21).

process (by analogy with nitrosyl chloride)[20] and this may explain the persistence of nitrosation in solvents of low polarity.

The results in Table 7 show that alkylation at the double bond favours the formation of the dinitrocompound rather than the nitronitrite. Although this could derive from the greater electrophilicity of the NO₂ radical when attacking *via* a nitrogen atom, the changes are small and there is also evidence for significant steric interactions that destabilise the *syn* conformations of alkyl nitrites.[25] The presence of CIDNP effects in these reactions[1,2] indicates that the combination of the two radicals must occur essentially on encounter.

The final point concerns the trisubstituted compounds. Here, the most significant observation is that only one trisubstituted compound has been detected in each reaction and that this compound is not necessarily the one that would be expected from the abstraction of the most reactive allylic hydrogen atom

in the substrate: thus, consider the formation of **9** from **1b** in Scheme 2. It also seems unlikely that these products can be explained by the subsequent reactions of the nitronitrite or nitroalcohol formed, for again there is no reason why the abstraction of the allylic hydrogen should be restricted to a single centre. We propose, therefore, the reaction path outlined in Scheme 6, where the abstraction of the allylic hydrogen atom to form the alkene **20** competes with the formation of the dinitro compound **18** and the nitronitrite **19**. There are many examples in the literature where hydrogen abstraction competes with the recombination of radicals.[26] This mechanism predicts the right trisubstituted compound for all of the reactions reported here.

Experimental

Materials

The nitrogen dioxide was obtained from ARGO International. It was purified by distillation over phosphorus pentoxide in an all glass apparatus. The product collected as a white solid in a receiver cooled in liquid nitrogen. The alkenes were obtained from Aldrich in grades of the highest purity available; they gave the expected ^1H NMR spectra and were used without further purification. The solvents were obtained from BDH. Hexane, cyclohexane and benzene were purified by drying over either calcium sulfate or magnesium sulfate followed by filtration and further drying over phosphorus pentoxide. Diethyl ether was dried with sodium wire.

Reactions

The standard procedure involved the dropwise addition of a solution of nitrogen dioxide (10 cm^3, 0.5 mol dm^{-3}) in the required solvent at room temperature to a stirred solution of the alkane (10 cm^3, 0.5 mol dm^{-3}) in the same solvent at room temperature. For one of the alkenes (**1a**), a number of variations of this procedure were tried (*e. g.*, adding the alkene to the solution of nitrogen dioxide, or using excess nitrogen dioxide, or using higher or lower temperatures) but, in general, these methods proved less successful in terms of the yields obtained and the greater complexity of the products. Further details are available elsewhere.[27]

After at least five minutes, the solvent was removed under reduced pressure and the product passed down a 'flash' silica column, eluting with ethyl acetate. The products were then separated by HPLC using 2 × 25 cm × 1 cm Lichoprep 5-20 μm silica gel columns, refractive index detection and elution with light petroleum (bp 60–80 °C):ethyl acetate (90:10). The ^1H and ^{13}C NMR spectra of the separated products were carried out in deuteriochloroform using a 400 MHz Varian VXR400 spectrometer. In calculating the ^{13}C chemical shifts, the α-shift for –NO$_2$ was taken as 1°, 55; 2°, 53; 3°, 53 δ (lit.,[15] 1°, 62 δ) and the α-shift for –OH was taken as 1°, 47; 2° 42; 3°, 37 δ (lit.,[15] 1°, 50; 2°, 45; 3°, 40 δ). The standard β-shifts and γ-shifts[15] were used. After the products had been identified, some studies of the variation of the product composition with the solvent were based on the ^1H NMR spectra of the initial reaction product in deuterochloroform.

The CI MS measurements were carried out at the London University School of Pharmacy using ammonia as the carrier gas. In this technique, the mass observed for the parent peak is normally 18 units higher than the mass expected from the molecular formula because of the inclusion of one ammonium ion. However, with the nitrite **4**, the mass observed was only 16 units higher than that calculated from the molecular formula. Other nitrites have also been reported to show a peak in the CI MS spectrum that is two units less than expected.[28]

MO Calculations

Some of the calculations were carried out using GAUSSIAN 92/DFT[29] on the Convex computer at the London Computer

Table 9 Rotation constants (B/GHz) and vibration frequences (ω/cm^{-1}) calculated at the MP2/6-31G* level for structures **22–24**

	23	24a	24b	22
B_1	6.272	8.916	11.459	14.850
B_2	3.509	2.870	2.303	1.804
B_3	2.250	2.338	1.930	1.670
ω_1	105	52	43	80
ω_2	193	177	116	159
ω_3	252	221	215	200
ω_4	397	337	316	331
ω_5	474	604	497	358
ω_6	633	638	634	370
ω_7	730	729	745	390
ω_8	799	785	783	737
ω_9	1287	870	925	833
ω_{10}	1411	1298	1313	983
ω_{11}	1948	1832	1843	1711
ω_{12}	1979	1918	1869	1728

Centre and others using GAUSSIAN 92, revision E.1[30] on the Fujitsu VPX240/10 computer at the Manchester Computer Centre. Structures **22–25** were optimised at the MP2/6-31G* level and further energy calculations were carried out with this geometry at the MP4SDQ(FULL)/6-31G* level. The energies so obtained (in Hartrees) were **22**, −409.100 87; **23**, −409.141 25 **24a**, −409.129 90; **24b**, −409.134 25; **25**, −589.194 16. The frequences and rotation constants required to correct for the zero-point energies and bring the energy terms to room temperature were obtained from a calculation at the MP2/6-31G* level and are given in Table 9. As usual,[31] the frequences were reduced by a factor of 0.9 before substitution in the standard equations.[32] The set of 12 positive frequences for all compounds in Table 9 show that the optimisations have led to energy minima. The atomic charges in Fig. 1 come from the MP4SDQ(FULL)/6-31G* calculations.

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