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The reaction of nitrogen dioxide with conjugated dienes (2,5-dimethylhexa-2,4-diene, hexa-2,4-diene and 2,3-dimethylbuta-1,3-diene) in organic solvents (mainly hexane, benzene and diethyl ether) results mainly in 1,4-addition giving, with the first two substrates, a mixture of 1,4-dinitro compounds and 1,4-nitro alcohols. The latter are presumably formed from hydrolysis of the intermediate nitronitrites. With 2,3-dimethylbuta-1,3-diene, only the *cis* and *trans* 1,4-dinitro compounds were isolated. The reactions effectively stop after the addition of two nitrogen dioxide radicals, only traces of tetrasubstituted products being obtained. With the unconjugated hepta-1,6-diene, addition can be made to occur to both double bonds but, when two equivalents of nitrogen dioxide are added very slowly, the main products derive from addition to one double bond and cyclisation to form *cis* and *trans* 1,2-bis(nitromethyl)cyclopentane. All the above reactions give a very complex mixture of products and the product composition depends markedly on the reaction conditions; however, with the conjugated dienes, the 1,4-dinitro compounds can be obtained in yields of *ca.* 50%. The crystal structure of *trans*-1,4-dinitro-2,3-dimethylbut-2-ene was determined.

Introduction

Some work^{1,2} has been done on the reaction of a number of conjugated alkenes with nitrogen dioxide in the gas phase and the reactivity of conjugated dienes has been shown to be greater than that of mono alkenes by factors of 10³–10⁴. Under the conditions used, the rate determining step was considered to be the reaction of the alkene or diene with molecular nitrogen dioxide;‡ the FTIR analysis of the reaction mixture indicated that this was followed by the trapping of the organic radical formed by oxygen leading to the final formation of nitroperoxynitrates. The rate of reaction of one diene (2,5-dimethylhexa-2,4-diene) with nitrogen dioxide has also been studied with carbon tetrachloride as solvent.³ These studies did not include the isolation of the products formed but the reaction of dienes with a mixture of nitrogen dioxide and iodine has been shown to give some dinitro compounds as side-products, the major products being iodonitro compounds.⁴ Dinitro compounds are also formed in the reaction of 2,5-dimethylhexa-2,4-diene with nitric oxide.⁵

Most of the above work was carried out with very low concentrations of nitrogen dioxide because of the interest in the reactions of nitrogen dioxide when present as a pollutant in the atmosphere. Our own interest derived from the possible use of these reactions in the synthesis of polynitro compounds. Many studies have shown that the reactions of nitrogen dioxide with organic compounds normally give a large number of products⁶ but there is evidence that the reaction of nitrogen dioxide with alkenes can give significant yields of dinitro compounds under carefully controlled conditions.^{6b}

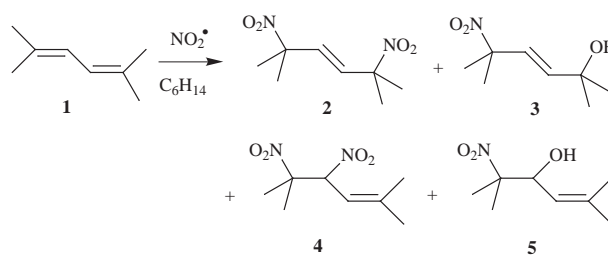
Results and discussion

Our normal procedure involved small scale experiments in which a solution of nitrogen dioxide in an organic solvent was

added slowly to a stirred solution of the organic substrate in the same solvent at room temperature. In some experiments, the order of addition was reversed. The solvent was then removed under reduced pressure and the products were separated by HPLC. The identification of the products was carried out by ¹H NMR spectroscopy, ¹³C NMR spectroscopy and by CI mass spectrometry. Where sufficient material was available, these procedures were supplemented by elemental analysis and, with two of the products, by X-ray crystallography. The NMR and CI MS results are discussed below and the elemental analyses are given in the Experimental section.

2,5-Dimethylhexa-2,4-diene 1

The products obtained from this substrate are shown in Scheme 1: the relevant ¹H NMR chemical shifts and coupling constants



Scheme 1

are listed in Table 1 and the corresponding ¹³C chemical shifts are included in Table 2. The assignments of the ¹³C chemical shifts are based on the comparison with calculated values.⁷ Plots of these and other NMR spectra described below are available elsewhere.⁸ The products 2, 4 and 5 gave peaks at M·NH₄⁺ for the parent ions in the CI MS spectra with ammonia as the carrier gas and the nitro alcohol 3 gave peaks at 362 (2M·NH₂⁺) and 172 (M⁺ – 1). The dinitro compounds 2 and 4 together with the nitro alcohol 3 have been isolated previously from the reaction of the diene 1 with nitric oxide.^{5,9}

The four products obtained are those expected from the initial addition of nitrogen dioxide to give either dinitro compounds or nitro nitrites at the 1:2 and 1:4 positions. The

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‡ The term 'nitrogen dioxide' without the qualification 'molecular' will be used to refer to the mixture of this species and the various forms of the dimer in equilibrium with it.

Table 1 ^1H NMR chemical shifts and coupling constants for the products formed from the reaction of nitrogen dioxide with 2,5-dimethylhexa-2,4-diene **1**, hexa-2,4-diene **6** and 2,3-dimethylbuta-1,3-diene **9**. The numbering refers to the structures in Schemes 1–3

Compound	$\delta_{\text{H}}(\text{CDCl}_3)$ and J/Hz								
	1-H	2-H	3-H	4-H	5-H	6-H	2-Me	3-Me	5-Me
2	1.72s		6.14s	6.14s		1.72s	1.72s		1.72s
3	1.69s		5.90d 3J 16.2	5.89d 3J 16.2		1.27s	1.69s		1.27s
4	1.72s		5.90d 3J 10.4	5.36dm 3J 10.4 4J 1.4		1.82d 4J 1.4	1.57s		1.85d 4J 1.4
5	1.56s		4.81dd 3J 9.3 3J 5.0 ^a	5.09dh 3J 9.3 4J 1.3		1.74d 4J 1.3	1.48s		1.76d 4J 1.3
7a^b	1.70d 3J 6.8	5.09m 3J 6.8 3J 4.4 4J 2.1	6.10dd 3J 4.4 4J 2.1	6.10dd 3J 4.4 4J 2.1	5.09m 3J 6.8 3J 4.4 4J 2.1	1.70d 3J 6.8			
7b^b	1.66d 3J 6.9	5.05m 3J 6.9 3J 4.9 4J 2.4	6.07dd 3J 4.9 4J 2.4	6.07dd 3J 4.9 4J 2.4	5.05m 3J 6.9 3J 4.9 4J 2.4	1.66d 3J 6.9			
8a^{b,c,d}	1.62d 3J 6.8	5.02m	5.9m	5.9m	4.28m	1.28d 3J 6.6			
10	5.08s			5.08s			1.99s	1.99s	
11	5.12s			5.12s			1.95s	1.95s	

^a Coupling with the OH proton at δ 2.08. ^b Compounds **7** and **8** exist as a pair of diastereoisomers distinguished by the letters **a** and **b**. ^c The hydroxy group gives rise to a broad singlet at δ 1.6. ^d The results for **8b** have been omitted since there is some uncertainty over the correct values.

Table 2 ^{13}C NMR chemical shifts for the products formed from the reaction of nitrogen dioxide with 2,5-dimethylhexa-2,4-diene **1**, hexa-2,4-diene **6** and 2,3-dimethylbuta-1,3-diene **9**. The numbering refers to the structures in Schemes 1–3

Compound	$\delta_{\text{C}}(\text{CDCl}_3)$								
	1-C	2-C	3-C	4-C	5-C	6-C	2-Me	3-Me	5-Me
2	25.79	87.17	132.41	132.41	87.17	25.79	25.79		25.79
3	25.94	87.55	137.24	129.23	79.75	24.82	25.94		24.82
4	26.26	88.57	88.49	113.40	146.61	18.77	24.45		21.43
5	26.18	91.87	72.76	121.09	140.16	18.83	23.82		19.83
7a^a	19.20	83.25	131.19	131.19	83.25	19.20			
7b^a	18.89	82.92	130.82	130.82	82.92	18.89			
8a^a	17.82	87.12	132.20	127.61	74.67	13.11			
8b^a	16.18	86.21	131.21	127.28	73.38	13.11			
10	78.2	129.5	129.5	78.2			18.10	18.10	
11	78.0	129.9	129.9	78.0			18.40	18.40	

^a Compounds **7** and **8** exist as a pair of diastereoisomers distinguished by the letters **a** and **b**.

nitro nitrites would undergo rapid conversion to the corresponding nitro alcohols during separation and purification. The NMR and mass spectra are, in general, sufficient to identify the compounds but, since the ^1H NMR spectra of the dinitro compound **2** gives only two singlets, this could be either the *cis* or the *trans* isomer. It was shown to be the *trans* isomer by X-ray crystallography⁸ but since the crystal structure of this compound has recently been published by other workers⁵ the details of our own work are not given here.

The absolute and relative yields of these products depend very much on the conditions of reaction. In *n*-hexane as solvent, the dinitro compound **2** was precipitated as white crystals during the addition of the nitrogen dioxide to the alkene. When relatively low concentrations of nitrogen dioxide§ were used (<1 mol dm⁻³), the yields of **2** exceeded 70% but the use of greater concentrations of nitrogen dioxide gave lower yields of **2** and significant yields (*ca.* 15%) of the 1:2 adducts **4** and **5** (see Experimental section). This could arise from the greater proportion of reaction through molecular dinitrogen tetroxide under these conditions.³ Changing the mode of addition

(adding the alkene solution to the solution of nitrogen dioxide) had little effect on the final product composition but the precipitation of the dinitro compound **2** then occurred more slowly.

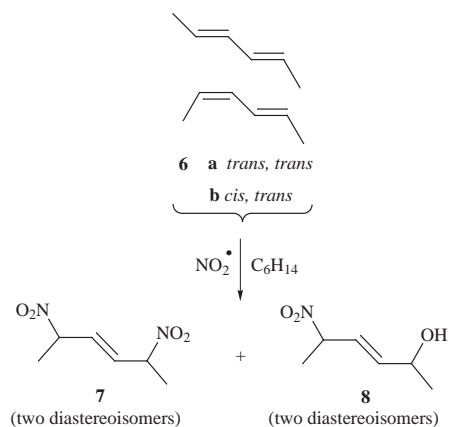
In benzene and in diethyl ether as solvents, no initial precipitation of the dinitro compound **2** occurred. Experiments were therefore carried out using solutions of **2** in these solvents to see whether any further reaction between **2** and nitrogen dioxide could be observed. No evidence for any such reaction was found.

Hexa-2,4-diene **6**

The reactions of nitrogen dioxide with both the *trans,trans* and *cis,trans* forms of this diene were studied (Scheme 2). In hexane as solvent, both gave a complex mixture of reaction products and, with both substrates, only the 1,4-dinitro compound **7** and the 1,4-nitro alcohol **8** could be isolated. The yields varied with the conditions but usually about 50% of **7** and about 18% of **8** were obtained; the other products were not identified. In diethyl ether as solvent, the yield of **7** was similar but the yield of **8** rose to *ca.* 40%.

Both the dinitro compound **7** and the nitro alcohol **8** are formed as a mixture of diastereoisomers with slightly different NMR spectra (Tables 1 and 2). For both **7** and **8**, the two dia-

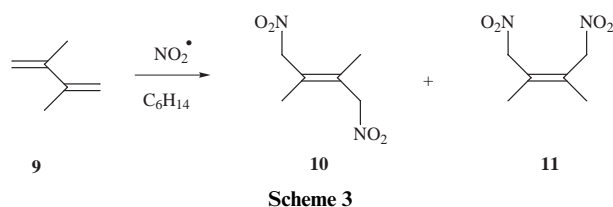
§ These concentrations have been calculated with respect to molecular nitrogen dioxide.



stereoisomers were formed in similar amounts. The symmetry of compound **7** and the complexity of the ^1H NMR spectrum of compound **8** prevented the determination of the constant for coupling across the double bond: the stereochemistry has been assumed to be *trans* by analogy with compounds **2** and **3**. Both of the diastereoisomers of **7** gave the expected peak at 192 m/z ($\text{M}\cdot\text{NH}_4^+$) in the CI MS spectrum but one of the diastereoisomers of **8** gave a peak at 162 m/z ($\text{M}\cdot\text{NH}_3^+$) and the other at 163 m/z ($\text{M}\cdot\text{NH}_4^+$).

2,3-Dimethylbuta-1,3-diene 9

The reactions of this compound with nitrogen dioxide were studied in a number of solvents but the only two products that were identified were the *trans* and *cis* forms of the dinitro compound (**10** and **11**, Scheme 3). There are several references



to the formation of these compounds in the literature, mostly without a clear indication of the stereochemistry^{4,10} although the ring opening of a dimethylsilacyclopent-3-ene with nitrogen dioxide¹¹ should yield the *cis*-dinitro compound **11**. Unfortunately, the dinitro compounds formed under different conditions^{10,11} appear to have the same mp. Since the symmetry of the molecules prevents the determination of the stereochemistry from the ^1H NMR spectrum (Table 1), one of our products was studied by X-ray crystallography and proved to be the *trans* form (Fig. 1). The bond lengths and bond angles are given in Table 3 and details of the structure determination in Table 4.¶ As expected, the mp ($71.8\text{--}72.3\text{ }^\circ\text{C}$) is very similar to that reported for the *cis* compound ($70\text{--}71\text{ }^\circ\text{C}$).¹¹ Both isomers gave the expected peak at 192 m/z ($\text{M}\cdot\text{NH}_4^+$) in the CI MS spectrum.

The absolute and relative yields of the two products proved curiously sensitive to the solvent used (Table 5), with the more polar solvents giving relatively more of the *trans* isomer. However, these product compositions refer to reactions carried out without a significant excess of nitrogen dioxide and analysed

¶ Full crystallographic details, excluding structure factor tables, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details of the deposition scheme, see 'Instructions for Authors', *J. Chem. Soc., Perkin Trans. 1*, available via the RSC Web page (<http://www.rsc.org/authors>). Any request to the CCDC for this material should quote the full literature citation and the reference number 207/263.

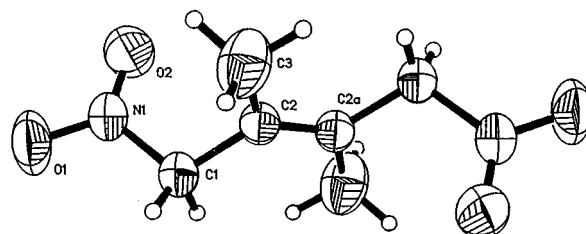


Fig. 1 The structure of *trans*-2,3-dimethyl-1,4-dinitrobut-2-ene.

Table 3 Bond lengths and bond angles for compound **10** as determined by X-ray crystallography. The specification of the atoms is based on the numbering in Fig. 1

Bond lengths/Å		Bond angles ($^\circ$)	
C(1)–C(2)	1.493(3)	C(2)–C(1)–N(1)	112.5(2)
C(2)–C(2a)	1.323(4)	C(1)–C(2)–C(2a)	121.0(3)
C(2)–C(3)	1.495(5)	C(1)–N(1)–O(1)	117.0(2)
C(1)–N(1)	1.500(4)	O(1)–N(1)–O(2)	123.3(3)
N(1)–O(1)	1.213(3)	C(1)–C(2)–C(3)	113.8(2)
N(1)–O(2)	1.209(3)	C(3)–C(2)–C(2a)	125.2(3)
		C(1)–N(1)–O(2)	119.7(2)

Table 4 Details of structure determination for **10**

Formula	$\text{C}_6\text{H}_{10}\text{N}_2\text{O}_4$
Space group	$P2_1/c$
$a/\text{Å}$	7.029(2)
$b/\text{Å}$	8.586(2)
$c/\text{Å}$	7.773(4)
$\alpha/^\circ$	90.0
$\beta/^\circ$	114.34(3)
$\gamma/^\circ$	90.0
$V/\text{Å}^3$	427.4
Z	2
$F(000)$	184
$D_s/g\text{ cm}^{-3}$	1.35
Cryst. size/mm	$0.44 \times 0.38 \times 0.24$
$\mu(\text{Mo-K}\alpha)/\text{cm}^{-1}$	1.07
Data collection instrument	Nicolet R3mV
Radiation	$\text{Mo-K}\alpha$ ($\lambda = 0.71073\text{ Å}$)
Orientation reflections: no.;	22
range ($2\theta/\text{degrees}$)	$15 \leq 2\theta \leq 25$
Temp./K	293
Data measured	881
Unique data	755
No. of unique with $I \geq 3.0\sigma(I)$	591
No. of parameters	55
R^a	0.0547
R_w^b	0.0630
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.00365F^2$
Largest shift/esd, final cycle	0.04
Largest peak/ $e\text{ Å}^{-3}$	0.21

$$^a R = \Sigma [|F_o| - |F_c|] / \Sigma |F_o|, \quad ^b R_w = \Sigma w^{\frac{1}{2}} [|F_o| - |F_c|] / \Sigma w^{\frac{1}{2}} |F_o|.$$

Table 5 The yields (%) of *cis*- and *trans*-2,3-dimethyl-1,4-dinitrobut-2-ene formed by the addition of a solution of nitrogen dioxide to an equivalent amount of 2,3-dimethylbuta-1,3-diene in the same solvent

Solvent	<i>cis</i> -product	<i>trans</i> -product	$[\textit{trans}]/[\textit{cis}]$
Hexane	22	26	1.2
Carbon tetrachloride			1 ^a
Dichloromethane			2.4 ^a
Diethyl ether	10	58	5.8
Acetonitrile	2 (6) ^b	7.6 (18) ^b	3.8 (3) ^b

^a The product ratio was measured from the ^1H NMR spectrum of the reaction mixture. ^b Carried out by the reverse mode of addition.

within about an hour of the initial reaction. When a marked excess of nitrogen dioxide is present, the *cis*:*trans* ratio in the more polar solvents changes with time and, over a period of 24 hours, closely approaches unity. After further time, the ratio

Table 6 ^1H NMR chemical shifts and coupling constants for the products formed from the reaction of nitrogen dioxide with hepta-1,6-diene **12**. The numbering of the cyclic structures accords with that of the linear structures. Where the signals of diastereotopic atoms are clearly separate, they are distinguished by the letters a and b

Compound	$\delta_{\text{H}}(\text{CDCl}_3)$ and J/Hz						
	1-H	2-H	3-H	4-H	5-H	6-H	7-H
13	a 4.56dd b 4.9–5.2m 2J 14.4	4.9–5.2m	a 1.87m b 1.98m	1.48m	2.05m	5.75m 3J 10.6 3J 17.0 3J 6.8	4.9–5.2m
14^a	4.2–4.4m	4.2–4.4m	1.4–1.6m	1.4–1.6m	2.07q 3J 6.6	5.75m 3J 10.3 3J 17.1 3J 6.7	4.9–5.0m
15^b	a 4.64dd b 4.41dd	4.3m	1.58m	1.58m	1.58m	4.3m	a 4.64dd b 4.41dd
16	a 4.27dd b 4.43dd 2J 12.4 3J 8.2 3J 6.7	2.93m	1.4–2.0m	1.4–2.0m	1.4–2.0m	2.93m	a 4.27dd b 4.43dd 2J 12.4 3J 8.2 3J 6.7
17	a 4.34dd b 4.42dd 2J 12.6 3J 7.7 3J 6.2	2.47m	1.5–2.0m	1.5–2.0m	1.5–2.0m	2.47m	a 4.34dd b 4.42dd 2J 12.6 3J 7.7 3J 6.2

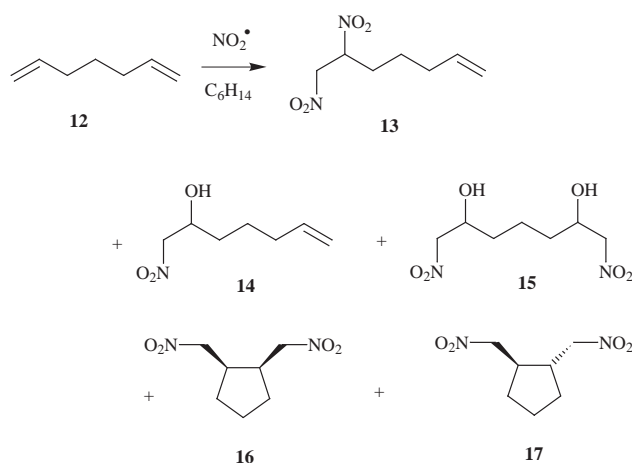
^a The OH signal is at δ 2.66. ^b The OH signal is at δ 2.93.

then remains constant. Separate experiments starting with the *cis* compound confirmed the isomerisation of this substrate in the presence of nitrogen dioxide. These isomerisations presumably follow the conventional mechanism¹² involving the initial addition of one nitrogen dioxide radical to the double bond.

There is also some evidence for a subsequent reaction of the *cis* compound with nitrogen dioxide since the isomerisation of this substrate in hexane was accompanied by the precipitation of a small amount of a white crystalline solid. This was impure but the ^1H NMR spectrum was consistent with a mixture of the diastereoisomers of the expected tetranitrocompound and included a doublet of doublets at δ 5.22 suggesting that the methylene protons had become diastereotopic as a result of addition to the double bond. The amount of this compound formed was unfortunately too small for more complete characterisation.

Hepta-1,6-diene **12**

This product differs from the other substrates in that the double bonds are not conjugated and so the 1,4-addition characteristic of the other substrates is not observed. The products obtained are shown in Scheme 4.



The identification of these substrates by ^1H NMR spectroscopy is complicated by the extra hydrogen atoms present and by the fact that a number of these atoms are diastereotopic. As a result, the ^1H NMR spectra showed a number of complex multiplets not all of which were analysed (Table 6). The ^{13}C NMR spectra are therefore more important in the identification of the compounds and a comparison of the results with those calculated from an empirical program⁷ are shown in Table 7. The nitro alcohol **14** is a known compound¹³ and our ^1H NMR spectrum accords with that in the literature.

The fractions corresponding to the cyclic compounds **16** and **17** were easily recognised from the absence of the ^{13}C NMR signals for the double bond combined with the peak for $\text{M}\cdot\text{NH}_4^+$ in the CI MS spectrum; the nitro alcohol **14** gave a corresponding peak at 177 ($\text{M}\cdot\text{NH}_3^+$). The dinitro compound **13** appeared unstable and no CI MS spectrum could be obtained.

The stereochemistry of the *cis* and *trans* bis(nitromethyl)cyclopentanes was deduced from the difference in the ^1H NMR spectra of these molecules. The cyclopentane ring is non planar and exists as a number of rapidly interconverting puckered forms. In the *trans* compound, the interconversion of the puckered forms causes the 4-H atoms to become chemically equivalent on the NMR timescale and this leads to a significant simplification of the spectra. This assignment accords with the conclusions of other authors^{14,15} that, in related derivatives of tetrahydrofuran and pyrrolidine, the ^{13}C signals of the *trans* isomer are shifted a few ppm downfield relative to those of the *cis* isomer.

The relative yields of the products shown in Scheme 4 are very dependent on the experimental conditions. Full details of the experiments carried out are given elsewhere⁸ but the main features are illustrated by the results listed in Table 8. When the solution of nitrogen dioxide is added to the diene over a period of a few minutes, neither of the cyclopentane derivatives (**16** and **17**) was detected in the products and even the very slow addition of the reagents gave these products in only a small yield. Some of the tetrasubstituted nitrodiol **15** is formed during the normal addition of nitrogen dioxide to the diene but the yield is significantly greater when the solution of the diene is slowly added to the solution of nitrogen dioxide. One of the other fractions obtained during these experiments gave ^1H and ^{13}C NMR spectra consistent with the corresponding

Table 7 ^{13}C NMR chemical shifts of the products formed from the reaction of nitrogen dioxide with hepta-1,6-diene **12**. The numbering follows that of Table 6. Calculated chemical shifts⁷ are given in parentheses

Compound	$\delta_{\text{C}}(\text{CDCl}_3)$						
	1-C	2-C	3-C	4-C	5-C	6-C	7-C
13	73.9 (79.3)	82.4 (84.3)	30.2 (31.9)	24.3 (24.4)	32.5 (32.9)	136.5 (138.7)	116.3 (114.6)
14	80.6 (80.9)	68.5 (68.9)	33.2 (33.8)	24.3 (24.4)	33.0 (33.6)	137.9 (138.7)	115.2 (114.6)
15	82.2 (80.9)	69.2 (68.9)	34.6 (33.8)	21.8 (27.8)	34.6 (33.8)	69.2 (68.9)	82.15 (80.9)
16	75.7 (76.6)	40.0 (43.7)	28.6 (33.0)	21.9 (23.5)	28.6 (33.0)	40.0 (43.7)	75.7 (76.6)
17	78.8 (76.6)	41.0 (43.7)	30.3 (33.0)	23.7 (23.5)	30.3 (33.0)	41.0 (43.7)	78.8 (76.6)

Table 8 The variation of the product composition with the time of mixing and the relative concentrations in the reaction of a solution of hepta-1,6-diene with an equal volume of a solution of nitrogen dioxide

[NO ₂]	[Alkene]	Time	Product composition (%)				
			13	14	15	16	17
0.45 ^a	0.20 ^a	1.5 min	27	24	15		
0.69 ^a	0.12 ^a	6.3 h	21	19		5	5
0.19 ^a	0.10 ^a	25 h	18	17		10	9
0.44 ^b	0.11 ^b	35 min	10	11	29		

^a In hexane as solvent and with the addition of the nitrogen dioxide to the alkene. ^b In dichloromethane as solvent and with the addition of the alkene to the solution of nitrogen dioxide.

trinitro alcohol (with one OH group of **15** replaced by a nitro group) but this proved too unstable for more complete characterisation.

In a number of respects, the pattern of products reported in all of the reactions above parallels that obtained in the reactions of nitrogen dioxide with alkenes⁶ and can be interpreted in the same way: that the initial addition of nitrogen dioxide is *via* nitrogen and occurs at the carbon atom that gives rise to the most stable radical; that the subsequent addition is at either the nitrogen or oxygen centre of nitrogen dioxide to give either dinitro compounds or nitro nitrites, and that these nitro nitrites readily hydrolyse during workup to yield nitro alcohols. The formation of the two cyclic compounds **16** and **17** does, however, provide additional evidence for the reaction of the substrate with two separate nitrogen dioxide radicals and accords with the earlier work of Brand and Stevens.¹⁶

Experimental

Materials

The nitrogen dioxide was obtained from ARGO International. It was purified by distillation over phosphorus pentoxide in a stream of dry oxygen using an all glass apparatus. The resulting white solid was kept over phosphorus pentoxide in a deep-freeze at -16°C . The dienes were obtained from Aldrich in purities of 98% or greater; they were used without further purification. The solvents were purified as described previously⁶ and were also degassed using ultrasound for 5 min before use.

Experimental procedure

The preparation of the solutions and the reactions were carried out under nitrogen. The normal procedure involved the dropwise addition of the solution of nitrogen dioxide (1–10 cm³) to the stirred solution of the diene (1–10 cm³) in the same solvent using a syringe pump. The reactions were carried out at room temperature unless otherwise specified. In some experiments,

the order of addition was reversed. The usual time of addition was 5 min but, with some experiments with hepta-1,6-diene, this was extended to 25 h.

After addition was complete, the reaction mixture was allowed to stand for up to 24 h and the solvent was then removed under reduced pressure. The reaction mixture was passed down a 'flash' silica column eluting with ethyl acetate and the products were then separated by HPLC using 2×25 cm \times 1 cm silica columns in series (particle size 0.005 mm) and refractive index detection. The best separations were obtained using a mobile phase of composition of ethyl acetate (10%)–hexane (90%) but, where this led to excessive retention times, an initial separation of the products was carried out using the composition 25:75 or 30:70 followed by separation of the faster moving components using the composition 10:90.

The ^1H and ^{13}C NMR spectra of the separated products were carried out in deuteriochloroform using a 400 MHz Varian VXR400 spectrometer. The CI MS measurements were carried out at the London University School of Pharmacy using ammonia as the carrier gas. The yields were estimated either from the weights of material isolated or from the analysis of the ^1H NMR spectra of the reaction mixture or from the relative areas of the HPLC peaks.

Reactions

Some typical experiments for each substrate are described below. A more detailed account is available elsewhere.⁸ The products **5**, **7**, **8**, **13**, **15**, **16** and **17** appear to be new but the small quantities isolated prevented a full characterisation; the ^1H and ^{13}C NMR spectra are given in Tables 1, 2, 6 and 7 and the CI MS spectra are described in the above text.

2,5-Dimethylhexa-2,4-diene. A solution of nitrogen dioxide (0.039 g, 0.85 mmol) in hexane (2 cm³) was added over a period of 5 min to a solution of the diene (0.06 g, 0.54 mmol) in hexane (2 cm³). During addition, the reaction mixture became cloudy and a white solid was precipitated. Filtration and recrystallisation of the solid from hot hexane gave *trans*-2,5-dimethyl-2,5-dinitrohex-3-ene **2**, yield 78% (Found: C, 47.6; H, 7.2; N, 13.7. Calc. for C₈H₁₄N₂O₄: C, 47.5; H, 7.0; N, 13.9%).

In another experiment with more concentrated reactants a solution of nitrogen dioxide (0.162 g, 3.52 mmol) in hexane (2 cm³) was added over a period of 5 min to a solution of the diene (0.064 g, 0.58 mmol) in hexane (2 cm³). During addition, the reaction mixture became cloudy and a solid was precipitated. The solvent was removed under reduced pressure and the products separated by HPLC to give *trans*-2,5-dimethyl-2,5-dinitrohex-3-ene **2** (35%), 2,5-dimethyl-2,3-dinitrohex-4-ene **4** (15%), *trans*-2-hydroxy-2,5-dimethyl-5-nitrohex-3-ene **3** (11%) and 3-hydroxy-2,5-dimethyl-2-nitrohex-4-ene **5** (15%).

***trans*-2,5-Dimethyl-2,5-dinitrohex-3-ene.** A solution of nitrogen dioxide (0.124 g, 2.70 mmol) in benzene (2 cm³) was added

over a period of 5 min to a solution of the olefin (0.072 g, 0.36 mmol) in benzene (2 cm³). After addition, the reaction mixture was stirred for 1 h at room temperature. There was no visible sign of reaction and the ¹H NMR spectrum of the isolated material was identical to that of the initial olefin.

trans,trans-Hexa-2,4-diene. A solution of nitrogen dioxide (0.096 g, 2.1 mmol) in hexane (2 cm³) was added over a period of 30 s to a solution of the diene (0.091 g, 0.11 mmol) in hexane (2 cm³). After stirring for 1 h, a pale yellow oil formed. The solvent was removed under reduced pressure and the products separated by HPLC to yield 2,5-dinitrohex-3-ene **7a** (first diastereoisomer) (28%) (Found: C, 40.7; H, 6.0; N, 15.2. C₆H₁₀N₂O₄ requires: C, 41.4; H, 5.8; N, 16.1%), 2,5-dinitrohex-3-ene **7b** (second diastereoisomer) (24%) (Found: C, 40.6; H, 5.8; N, 15.6. C₆H₁₀N₂O₄ requires: C, 41.4; H, 5.8; N, 16.1%), 2-hydroxy-5-nitrohex-3-ene **8a** (first diastereoisomer) (9%) (Found: C, 49.4; H, 7.6; N, 9.7. C₆H₁₁NO₃ requires: C, 49.7; H, 7.6; N, 9.7%) and 2-hydroxy-5-nitrohex-3-ene **8b** (second diastereoisomer) (9%) (Found: C, 49.9; H, 7.8; N, 9.3. C₆H₁₁NO₃ requires: C, 49.7; H, 7.6; N, 9.7%). The above products were assumed to be *trans* by analogy with the dinitro compound **2**.

2,3-Dimethylbuta-1,3-diene. A solution of nitrogen dioxide (0.092 g, 2.0 mmol) in hexane (2 cm³) was added over a period of 5 min to a solution of the diene (0.082 g, 1.0 mmol) in hexane (2 cm³). After the reaction mixture had been stirred for 1 h, the solvent was removed under reduced pressure and the products separated by HPLC to yield *trans*-2,3-dimethyl-1,4-dinitrobut-2-ene **10** (26%) (Found: C, 41.3; H, 5.7; N, 15.5. Calc. for C₆H₁₀N₂O₄: C, 41.4; H, 5.8; N, 16.1%) and *cis*-2,3-dimethyl-1,4-dinitrobut-2-ene **11** (22%) (Found: C, 40.9; H, 5.4; N, 16.0. Calc. for C₆H₁₀N₂O₄: C, 41.4; H, 5.8; N, 16.1%).

Hepta-1,6-diene. A solution of nitrogen dioxide (0.115 g, 2.5 mmol) in hexane (5 cm³) was added over a period of 1.5 h to a solution of the diene (0.094 g, 0.98 mmol) in hexane (5 cm³). The solvent was removed under reduced pressure and the products separated by HPLC to yield 1,2-dinitrohept-6-ene **13** (52%) and 2-hydroxy-1-nitrohept-6-ene **14** (37%) (Found: C, 52.2; H, 8.7; N, 8.3. Calc. for C₇H₁₃NO₃: C, 52.8; H, 8.2; N, 8.8%).

In an experiment involving the reverse mode of addition, a solution of hepta-1,6-diene (0.108 g, 1.12 mmol) in dichloromethane (10 cm³) was added over a period of 35 min to a solution of nitrogen dioxide (0.20 g, 4.35 mmol) in dichloromethane (10 cm³). Both solutions were maintained at 0 °C during reaction. The solvent was removed under reduced pressure

and the products separated by HPLC to yield 1,2-dinitrohept-6-ene **13** (10%), 2-hydroxy-1-nitrohept-6-ene **14** (11%) and 2,6-dihydroxy-1,7-dinitroheptane **15** (29%).

In an experiment involving the very slow mixing of the reagents, a solution of nitrogen dioxide (0.089 g, 1.93 mmol) in hexane (10 cm³) was added over a period of 25 h to a solution of the diene (0.098 g, 1.0 mmol) in hexane (10 cm³). The solvent was removed under reduced pressure and the products separated by HPLC to yield 1,2-dinitrohept-6-ene **13** (18%), 2-hydroxy-1-nitrohept-6-ene **14** (17%), *cis*-1,2-bis(nitromethyl)cyclopentane **16** (10%) and *trans*-1,2-bis(nitromethyl)cyclopentane **17** (9%).

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