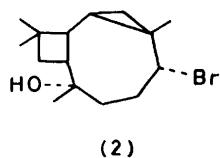
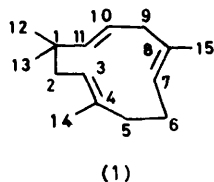


The Action of Nitrogen Dioxide and Nitric Oxide on Humulene, $C_{15}H_{24}$, and Humulene Nitrosite, $C_{15}H_{24}N_2O_3$. Reaction Mechanisms and Isolation and Characterization of Reaction Products

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Humulene nitrosite (3), dinitrohumulene (5), and nitronitratohumulene (4) are obtained as crystalline products when nitrogen dioxide and nitric oxide react with humulene. 1H N.m.r., ^{13}C n.m.r., i.r., and mass spectroscopy enable the molecular structures for each of these compounds to be deduced. The yellow oil, obtained when humulene nitrosite reacts with nitric oxide and nitrogen dioxide, contains dinitrohumulene (5), nitronitratohumulene (4), 1,1,4-trimethyl-8-methylene-7-nitrocycloundeca-3,10-diene (9), isomers (11) and (12) of compound (9), the caryophyllene derivative 4,11,11-trimethyl-8-methylene-2,5-dinitrobicyclo[7.2.0]undec-3-ene (10), three nitroxide radicals, and several olefinic compounds derived from further reaction at position C(10)=C(11) of the humulene structure with oxides of nitrogen. These compounds originate from reactions in which a 'master' aliphatic radical (15) takes part, and their characterization enables details of the mechanisms of reaction of N_2O_3 with humulene nitrosite to be unravelled.

THE structure of humulene (1) has been established through a combination of chemical degradation studies on the sesquiterpene,¹⁻¹³ and X-ray analyses¹⁴⁻¹⁶ of its silver nitrate adduct. The X-ray analyses revealed the stereochemistry of the adduct and also suggested that although liquid humulene is conformationally mobile it nevertheless does have a preferred conformation. Humulene readily undergoes interesting transannular reactions in which the eleven-membered ring yields tricyclic compounds. Thus, α -caryophyllene alcohol is obtained when humulene is treated with sulphuric acid,¹⁷⁻¹⁹ and, when the hydrocarbon is treated with *N*-bromosuccinimide, the attack of the bromonium ion triggers a double cyclization to humulene bromohydrin (2).^{20,21}



Sesquiterpenes used to be characterized by allowing them to react with N_2O_3 to produce crystalline nitrosite derivatives. Chapman first prepared humulene nitrosite almost a hundred years ago,^{22,23} and this same nitrosite was used by Mitchell in his early work on the Cotton effect²⁴ and in his studies on asymmetrical photochemical reactions involving circularly polarized light.²⁵ Aliphatic nitroso-groups exhibit intense $\pi^* \leftarrow n$ transitions at *ca.* 670 nm and as a result humulene nitrosite is a brilliant blue solid that is photochemically decomposed when irradiated with red light: if solid humulene nitrosite is left exposed to daylight its blue colour fades, and eventually white solids and a viscous yellow liquid are obtained.

A small sample of humulene nitrosite (kindly donated by Dr. S. T. R. S. Mitchell for the purposes of carrying out pilot studies of its photochemical reactions) was, because of some unexpected observations, chromato-

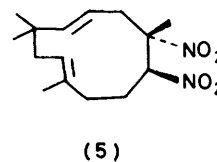
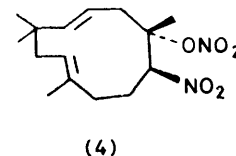
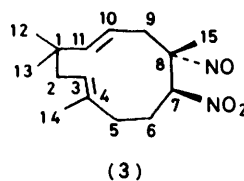
graphed, when small amounts of two colourless crystalline impurities were obtained. As our photochemical studies progressed we several times synthesized more humulene nitrosite; each time care was taken to follow as closely as possible the procedures described by Chapman and Mitchell²²⁻²⁵ in which humulene is allowed to react in the dark with an equivalent amount of N_2O_3 generated by dropwise addition of glacial acetic acid to saturated aqueous sodium nitrite. Blue crystals and a yellow oil are obtained from this reaction.

The blue crystals were recrystallized from ethanol and then chromatographed on silica plates using ether-light petroleum (1:1) as solvent. Every time the reaction was carried out the chromatogram of these crystals revealed the presence of the same three components that were obtained from Mitchell's sample, and whose characteristics are listed in Table I.

TABLE I

Band	R_F Value	Appearance	M.p./°C (from ethanol)	% by weight
(A)	0.66	Blue needles	117—119	80
(B)	0.57	Colourless needles	136.3—137.3	9
(C)	0.37	Colourless needles	168—169	10

Elemental analysis, and n.m.r., i.r., and mass spectroscopy showed substance (A) to be humulene nitrosite (3), substance (B) to be nitronitratohumulene (4), and



substance (C) to be dinitrohumulene (5). The ^1H n.m.r. spectra are shown in Figure 1. The spectroscopic data show quite clearly that in each of these compounds

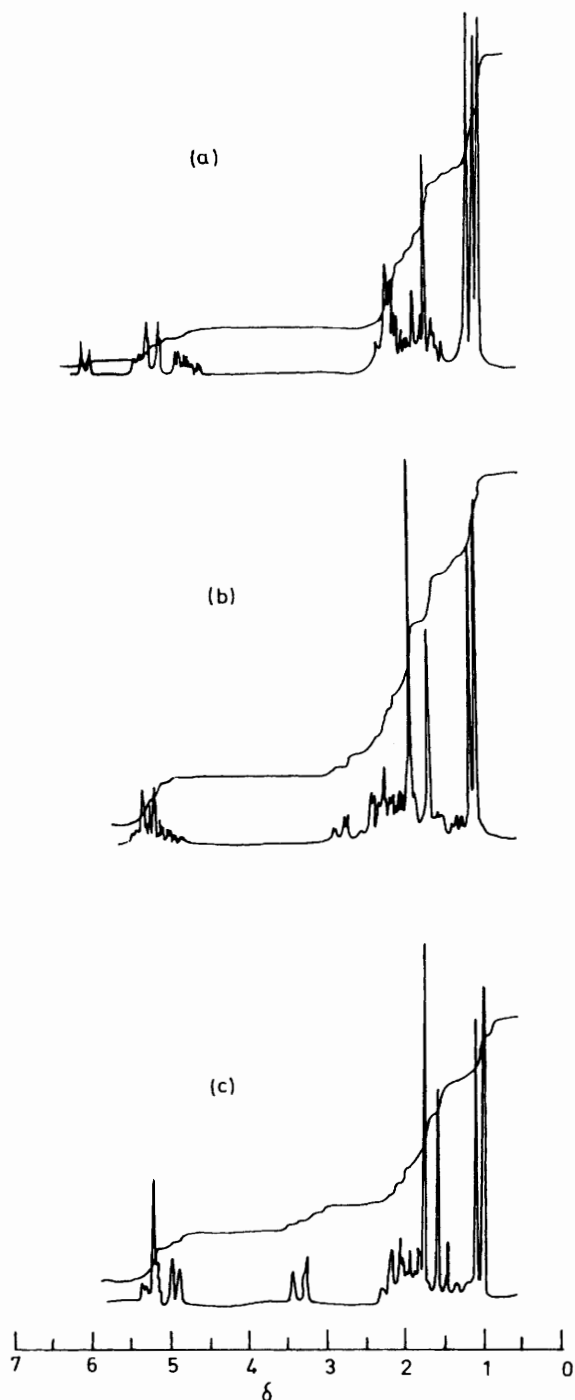


FIGURE 1 100 MHz ^1H N.m.r. spectra of dilute solutions of (a) humulene nitrosite, (b) dinitrohumulene, and (c) nitronitratohumulene in CDCl_3

cyclization of the eleven-membered ring has not taken place, and each of them is formed by appropriate addition across the $\text{C}(7)=\text{C}(8)$ double bond of humulene.

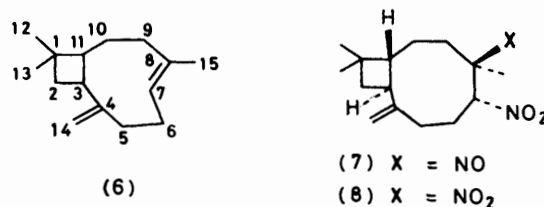
The three compounds appear to be isostructural; their n.m.r. and i.r. spectra are very similar, and both dinitro- and nitronitratohumulene form solid solutions with humulene nitrosite.

The early studies of Mitchell²⁵ showed that humulene nitrosite (3) exists as a racemic mixture. In the ^1H n.m.r. spectrum of this compound no signals originating from protons attached to the chiral carbon atoms or from protons attached to adjacent carbon atoms are duplicated. The spectrum shows no evidence for the existence of diastereoisomers and it appears that addition of N_2O_3 to humulene is stereospecific.

The similarities in the ^1H n.m.r. data show that the configurations and conformations of dinitrohumulene and nitronitratohumulene must be similar to the configuration and conformation of humulene nitrosite.

We were not surprised to find dinitrohumulene, since NO_2 is present in the reaction mixture, but the presence of the nitronitratohumulene was unexpected. This nitronitratohumulene, at least some of the dinitro-compound, and the compounds present in the yellow oil, originate from further reactions that involve humulene nitrosite and nitric oxide.

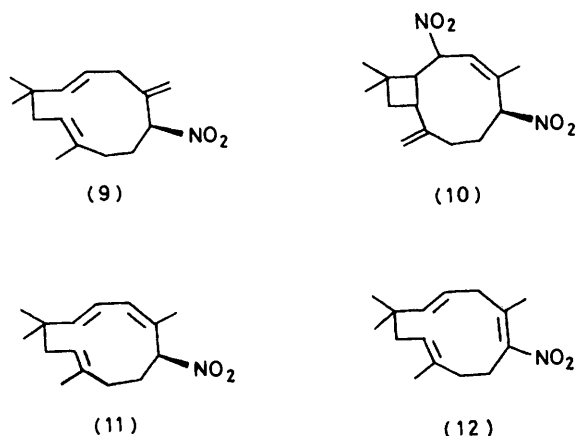
The isomeric sesquiterpene caryophyllene (6) reacts with N_2O_3 in a similar manner, and the corresponding



nitrosite (7) and dinitro (8) derivatives of caryophyllene have also been isolated and characterized.²⁶ Every peak in the ^1H n.m.r., i.r., and mass spectra of the seven compounds (1) and (3)—(8) has been assigned, and a master catalogue of compounds and spectra has been compiled in order to facilitate the understanding of reactions in which humulene and caryophyllene, or their derivatives, are involved. The catalogue enables the sites of reaction to be identified and the reaction products to be characterized.

In ethanol-free chloroform, pure humulene nitrosite reacts with N_2O_3 to yield the same yellow oil that is obtained in the corresponding reaction involving humulene. The components of this oil separate into two main fractions. The first fraction dissolves in ether-light petroleum (1 : 1); the second fraction, amounting to *ca.* 8% of the original oil, consists of yellow solids that are insoluble in this mixed solvent. Analysis of these main fractions gives the following results.

Three crystalline derivatives have been isolated from the soluble fraction and have been characterized as 1,1,4-trimethyl-8-methylene-7-nitrocycloundeca-3,10-diene (9), dinitrohumulene (5), and the caryophyllene derivative 4,11,11-trimethyl-8-methylene-2,5-dinitrobicyclo[7.2.0]undec-3-ene (10). Smaller amounts of the



isomeric humulene derivatives (11) and (12) have also been identified. The ^1H n.m.r. spectra of (9) and (10) are shown in Figures 2 and 3.

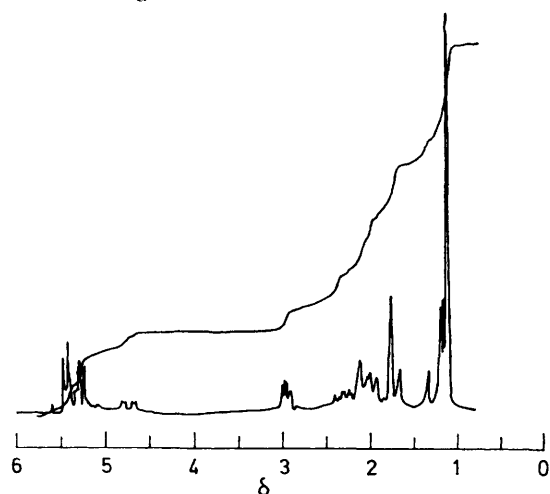


FIGURE 2 100 MHz ^1H N.m.r. spectrum, in CDCl_3 solution, of compound (9)

The insoluble fraction is paramagnetic, and the e.s.r. spectrum shown in Figure 4 is obtained from a dilute,

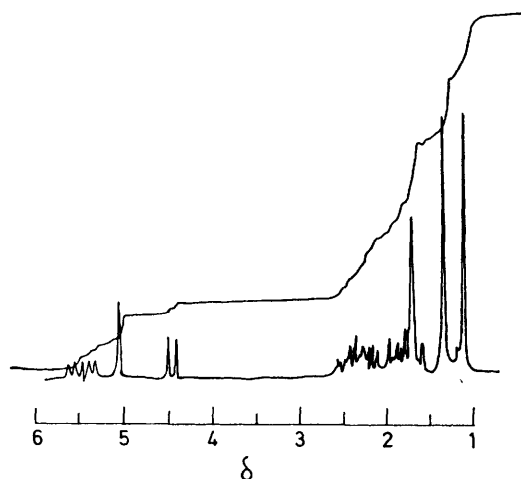


FIGURE 3 100 MHz ^1H N.m.r. spectrum, in CDCl_3 solution, of compound (10)

freshly-prepared and degassed solution of the yellow solid dissolved in chloroform. When this solution is allowed to stand for some time, its e.s.r. spectrum changes

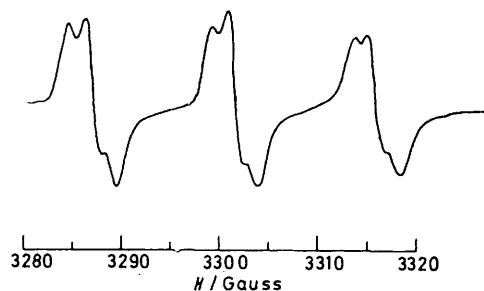


FIGURE 4 E.s.r. spectrum of a dilute degassed solution, in CHCl_3 , of the yellow oil formed on reaction of humulene nitrosite with N_2O_3 ; spectrum recorded at 295 K

to that shown in Figure 5, thereby showing that the paramagnetism originates from three nitroxide radicals, two of which are stable and contain the molecular fragment $\text{R}^1\text{R}^2\text{R}^3\text{C}-\dot{\text{N}}\text{O}-\text{CR}^4\text{R}^5\text{R}^6$ and the other, an unstable species, which contains the molecular fragment

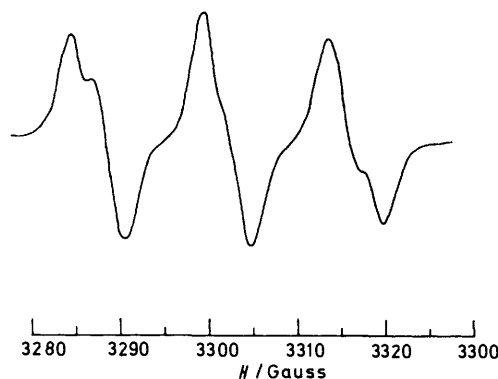


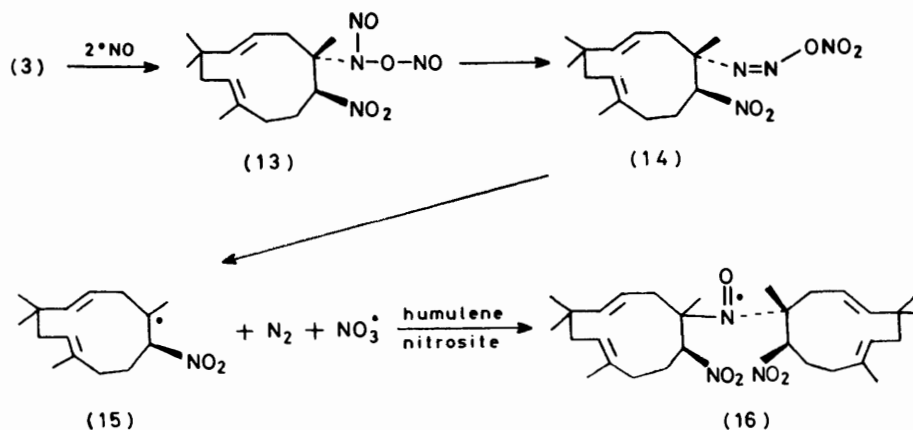
FIGURE 5 E.s.r. spectrum of nitroxide radicals A^1 and A^2 in CHCl_3 solution. Spectrum recorded at 295 K

$\text{OR}^1\text{R}^2\text{R}^3\text{C}-\dot{\text{N}}-\text{CHR}^4\text{R}^5$. The isotropic spin-Hamiltonian parameters of these radicals are shown in Table 2. The formation of radicals A^1 and A^2 can be accounted for by the sequence of reactions in Scheme 1, based on the well documented reaction of C-nitroso-compounds,²⁷⁻³¹ in which humulene nitrosite reacts with two molecules of nitric oxide, forming the complex (13). This rearranges to the diazonium nitrate (14) which decomposes, with

TABLE 2

Radical	$\langle g \rangle$	a (^{14}N) (Gauss)	a (^1H) (Gauss)
A^1	2.0059 ± 0.0002	14.6 ± 0.2	
A^2	2.0062 ± 0.0002	15.0 ± 0.2	
B	2.0062 ± 0.0002	14.8 ± 0.2	3.5 ± 0.5

loss of N_2 and NO_3 ; to produce the radical (15). This radical, in turn, is then scavenged by humulene nitrosite to yield the two diastereoisomeric forms of the nitroxide radical (16): radicals A^1 and A^2 are believed to be these diastereoisomers. A possible structural assignment for radical B will be considered later.

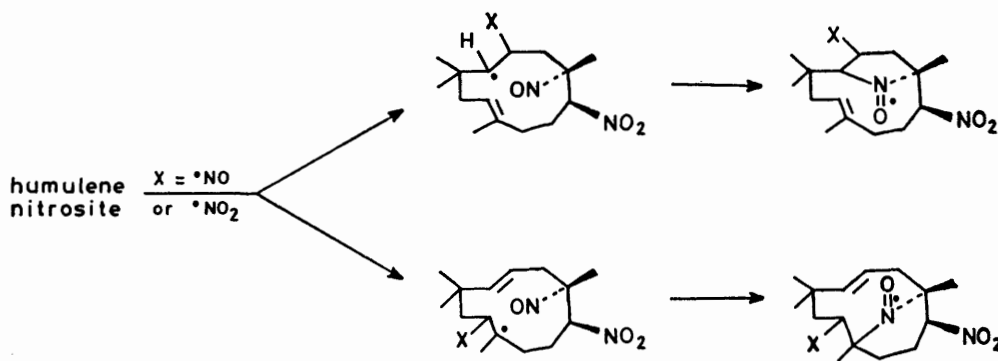


SCHEME 1

The *intra*-molecular reaction sequences (Scheme 2) that could also explain the e.s.r. spectra can be discounted on three grounds. First, nitric oxide does not initiate addition reactions across double bonds. Secondly, we have carried out separate experiments in which NO_2 is allowed to react with humulene nitrosite. These experi-

but they all have a common origin that can be traced to the reaction sequence (3) \longrightarrow (13) \longrightarrow (14) \longrightarrow (15) followed by one or other of several subsequent reactions that involve the 'master' radical (15), as shown in Scheme 3.

The following reactions are open to radical (15).



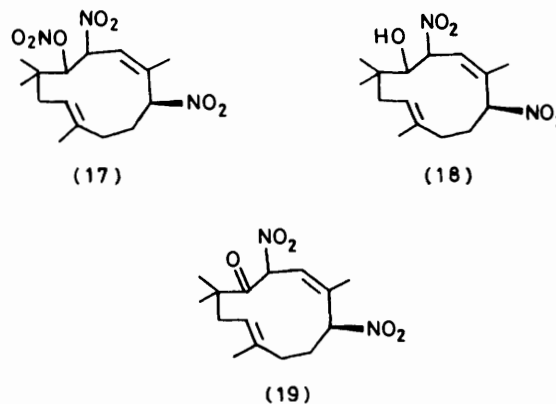
SCHEME 2

ments show that in this reaction NO_2 slowly replaces the nitroso-group, giving dinitrohumulene in both the *cis*- and *trans*-isomeric forms, but radicals are not produced. Thirdly, i.r. spectra show that the olefinic residues of humulene nitrosite are not destroyed when nitroxide radicals are formed.

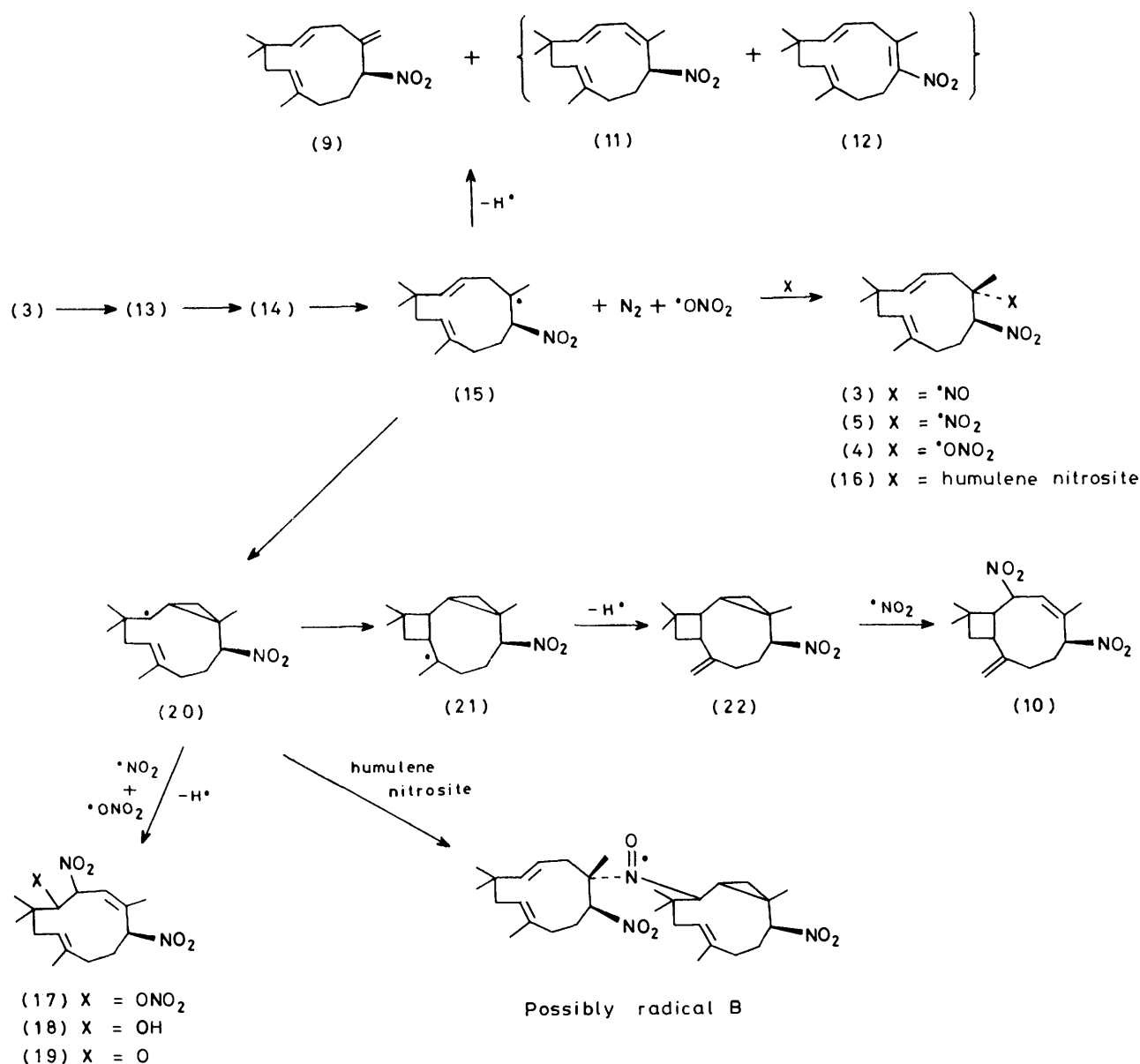
The polycrystalline e.s.r. spectra of the yellow insoluble components are standard, classical e.s.r. spectra of magnetically dilute nitroxide radicals. No more than about 1% of the yellow solid can consist of nitroxide radicals. The major components are diamagnetic and we have attempted, without success, to separate them, but nevertheless ^1H n.m.r., i.r., and mass spectra all clearly show that in these major components the C(10)=C(11) double bond of compound (11) has disappeared, and compounds (17), (18), and (19) can be detected in the mixture.

The large number of compounds generated in the reaction of humulene nitrosite with nitric oxide and nitrogen dioxide at first sight appear to be very different,

(a) The $\cdot\text{ONO}_2$ radical can abstract a proton to generate the olefins (9), (11), and (12). The concentrations of



these compounds show that loss of a proton from the C-15 Me group to generate (9) is preferred. (b) $\cdot\text{NO}_2$



SCHEME 3

can add to (15) to generate dinitrohumulene (5). (c) •ONO₂ can add to (15) to generate nitronitrohumulene (4). (d) Humulene nitrosite can scavenge (15) to generate the diastereoisomeric nitroxide radicals A¹ and A² (16). (e) (15) can undergo transannular cyclization to produce in succession, radicals (20) and (21), and compound (22). These can not be detected since their cyclopropane rings immediately react with •NO₂ and •ONO₂ to produce compounds (10), (17), (18), and (19). Humulene nitrosite can scavenge radical (20) to generate an unstable nitroxide radical that may be precursor of radical B.

EXPERIMENTAL

Light petroleum refers to the fraction of b.p. 40–60 °C.
Humulene.—A sample of the higher boiling fractions of hop

oil (obtained from White Stevenson Ltd., North Albert Road, Reigate, Surrey) was distilled, and the fraction of b.p. 90–100 °C (at 1 mmHg) collected. The ¹H n.m.r. spectrum showed that this fraction consisted mainly of humulene and a small amount of caryophyllene and other hydrocarbons. The relative amounts of the sesquiterpenes were conveniently monitored by ¹H n.m.r. spectroscopy: the spectrum of the *gem*-dimethyl group of humulene consists of a single intense peak at δ 1.10, while that of the same group in caryophyllene is made up of two peaks at δ 1.03 and 1.01. Humulene was separated from the mixture by means of the technique of Hildebrand and Sutherland,³² in which use is made of the differential solubilities of the adducts (humulene : 2 AgNO₃) and (caryophyllene : AgNO₃) in water and ethanol as solvents.

Reaction of Humulene with the Oxides of Nitrogen.—The following reactions were carried out in total darkness in

order to avoid complications from photolytic reactions. A solution of humulene (3 g) in light petroleum (7.5 ml) was cooled to 10 °C. Saturated aqueous NaNO₂ (2 g) was also cooled to 10 °C and the two solutions were then mixed. Glacial acetic acid (1.2 ml) was then added dropwise, with continual stirring during 1 h. The light petroleum layer turned blue-green, and when left for 30 min at 0 °C an oily blue solid precipitated out. This solid was filtered off and washed with light petroleum to remove the oil which was characterized (¹H n.m.r.) as unchanged humulene. This humulene was recycled and treated with an excess of N₂O₃ to obtain more blue crystals. Repetition of these procedures several times increased the yield of crystalline material to ca. 45% of the theoretical weight of humulene nitrosite. Each cycle produced a crude product that became greener, and eventually a yellow oil was the sole reaction product.

Recrystallization of the blue solid from ethanol yielded blue needles (m.p. 112 ± 2 °C). T.l.c. on silica [ether-light petroleum (1 : 1 v/v) as eluant] showed the presence of three components of *R_F* 0.37, 0.57, and 0.66. A sample (400 mg) was chromatographed on silica [1.5 m column; ether-light petroleum (1 : 1 v/v) as eluant] and 25 10-ml fractions were collected. Fractions 1—6, *R_F* 0.66, 80% by weight of the original 400 mg, contained humulene nitrosite (1, 1, 4, 8-tetramethyl-7-nitro-8-nitrosocycloundeca-3,10-diene) (3) (Found: C, 64.3; H, 8.35; N, 10.45; O, 16.85. C₁₅H₂₄N₂O₃ requires C, 64.28; H, 8.57; N, 10.0; O, 17.15%), m.p. 117—119 °C; ¹H n.m.r. spectrum: 3-H, δ 5.44 (1 H, X of ABX, *J*_{2,3} 9, *J*_{2',3} 3.5 Hz); 2-, 5-, 6-, and 9-H₂, (8 H, m), 1.6 ≤ δ ≤ 2.6; 7-H, δ 6.08 (1 H, d, only one of the 6-H₂ couples with this proton, *J* 8 Hz); 10-H, δ 4.8 (1 H, octet, X of ABXY, *J*_{10,11} 16, *J*_{10,9} 9, *J*_{10,9'} 4 Hz); 11-H, δ 5.21 (1 H, d, Y of XY, *J*_{11,10} 16 Hz); 12-H₃, δ 1.11 (3 H, s); 13-H₃, δ 1.16 (3 H, s); 14-H₃, δ 1.78 (3 H, d, *J*_{3,14} < 1 Hz); and 15-H₃, δ 1.25 (3 H, s); ¹³C-{¹H} decoupled spectrum chemical shifts (p.p.m.) (multiplicity of corresponding region of partially decoupled ¹³C-{¹H} spectrum in brackets): C-1 38.3 (s); C-2 40.6 (t with additional structure); C-3 145.8 (d); C-4 135.3 (s); C-5 35.4 (t); C-6 25.2 (t); C-7 88.9 (d); C-8 102.1 (s); C-9 41.4 (t); C-10 117.6 (d with additional structure); C-11 125.1 (d with additional structure); C-12, C-13 17.6, 15.5 (each q); and C-14, C-15 29.9, 28.7 (each q); *v*_{max}. cm⁻¹ (KBr disc) 3 015, 3 010, 2 965, 2 960, 2 865, and 2 860 (C-H); 1 665, 1 660, 980, 840 [*trans*-HR¹C(10)=C(11)HR² and HR¹C(3)=C(4)R²R³ systems]; 1 570 (N=O); 1 560, 1 360, and 872 (RNO₂); and 1 380, 1 365, 1 170, and 810 (>CMe₂); *m/e* 250, 220, 203, 189, 175, 177, 161, 147, 133, 135, 121, 105, 107, 93, 91, 77, 79, 65, 53, 41 [the parent peak for C₁₅H₂₄N₂O₃, expected at 280, was not observed since the NO group is cleaved inside the mass spectrometer; the peak at 250 originates from an ion of the 'master' aliphatic radical (15)].

Fractions 7—12, *R_F* 0.57, 9%, contained nitronitrato-humulene (1,1,4,8-tetramethyl-8-nitrate-7-nitrocycloundeca-3,10-diene) (4) (Found: C, 57.85; H, 7.85; N, 9.0; O, 25.5. C₁₅H₂₄N₂O₅ requires C, 57.68; H, 7.68; N, 8.97; O, 25.65%), m.p. 136.3—137.3 °C, *M*⁺ 312; ¹H n.m.r. spectrum: 3-H, δ 5.17 (1 H, X of ABX, *J*_{2,3} 9.5, *J*_{2',3} 5 Hz, small additional couplings for which *J* < 1 Hz); 2-, 5-, and 6-H₂ (6 H, m), 1.4 ≤ δ ≤ 2.2; 7-H, δ 4.92 (1 H, d, couples with only one of the 6-H₂ protons, *J* 9.6 Hz); C(9)H₂-C(10)H=C(11)H (ABXY system), δ_A 3.38, δ_B 2.11, δ_X 5.17, δ_Y 5.21 (*J*_{AB} 17, *J*_{AX} 2, *J*_{AY} < 1, *J*_{BX} 9.5, *J*_{BY} < 1, *J*_{XY} 16 Hz); 12- and 13-H₃, δ 1.08 and 1.17 (each 3 H, s); 14-H₃,

δ 1.65 (3 H); and 15-H₃, δ 1.82 (3 H); *v*_{max}. cm⁻¹ (KBr disc) 3 015, 3 010, 2 965, 2 960, 2 865, 2 860 (C-H); 1 665, 1 660, 997, 830 [*trans*-HR¹C(10)=C(11)HR² and HR¹C(3)=C(4)R²R³ systems]; 1 632, 1 287, 852, 730, and 695 (R-ONO₂); 1 555, 1 362, and 870 (R-NO₂); and 1 387, 1 374, 1 160, and 800 (>CMe₂).

Fractions 15—20, *R_F* 0.37, 10%, contained dinitro-humulene (1,1,4,8-tetramethyl-7,8-dinitrocycloundeca-3,10-diene) (5) (Found: C, 61.4; H, 7.9; N, 10.0; O, 20.7. C₁₅H₂₄N₂O₄ requires C, 60.9; H, 8.1; N, 9.5; O, 21.5), m.p. 168—169 °C, *M*⁺ 296; ¹H n.m.r. spectrum: 3-H, δ 5.36 (1 H, X of ABX, *J*_{2,3} 9, *J*_{2',3} 5 Hz); 2-, 5-, and 6-H₂ (6 H, m), 1.4 ≤ δ ≤ 2.4; 7-H, δ 5.26 (1 H, d, couples with only one of the 6-H₂ protons, *J* 8.8 Hz); C(9)H₂-C(10)H=C(11)H (ABXY system); 9-H_A, δ 2.80 (1 H, *J*_{9A,9B} 15, *J*_{9A,10} 3, *J*_{9A,11} 1 Hz); 9-H_B, δ 2.28 (1 H, *J*_{9A,9B} 15, *J*_{9B,10} 8.8, *J*_{9B,11} ca. 2 Hz); 10-H, δ 4.96 (1 H, octet, *J*_{10,11} 15.9, *J*_{10,9A} 3, *J*_{10,9B} 8.8 Hz); 11-H, δ 5.22 (1 H, br d, *J*_{11,10} 15.9 Hz, small additional couplings of *J* ca. 1 Hz); 12- and 13-H₃, δ 1.11 and 1.16 (each 3 H, s); 14-H₃, δ 1.71 (3 H, small couplings < 1 Hz); 15-H₃, δ 1.92 (3 H, s), *v*_{max}. cm⁻¹ (KBr disc) 3 015, 3 010, 2 965, 2 960, and 2 860 (C-H); 1 665, 1 660, 980, and 840 [*trans*-HR¹C(10)=C(11)HR² and HR¹C(3)=C(4)R²R³ systems]; 1 550, 1 545, 1 360, 1 355, and 872 (RNO₂); and 1 390, 1 375, 1 165, and 805 (>CMe₂).

Reaction of Humulene Nitrosite with the Oxides of Nitrogen.—Pure humulene nitrosite was dissolved in ethanol-free chloroform and the solution was cooled to 10 °C. A saturated solution of sodium nitrite was also cooled to 10 °C and the two solutions were then mixed. Glacial acetic acid was added dropwise to the mixture, with continual shaking, until the blue colour of humulene nitrosite was discharged and a yellow oil was obtained. The yellow oil was separated into two fractions, one of which dissolved in ether-light petroleum (1 : 1 v/v). The second fraction, a yellow solid, ca. 8% by weight of the original yellow oil, was insoluble in this solvent. The soluble fraction was diamagnetic; chromatography on silica plates, eluting with ether-light petroleum (1 : 1 v/v) revealed the presence of three main products of *R_F* 0.83, 0.39, and 0.29.

The component of *R_F* 0.83 was an oil that was then subjected to preparative t.l.c. on silica with carbon tetrachloride as eluant. Figure 2 shows the ¹H n.m.r. spectrum of the solid extracted from the region of *R_F* 0.29. This, and the mass spectra, showed the solid to be 1,1,4-trimethyl-8-methylene-7-nitrocycloundeca-3,10-diene (9) [during the chromatographic purification of this compound, the i.r. and ¹H n.m.r. spectra showed traces of additional allylic methyl groups, *trans* double bonds, and geminal dimethyl residues; in particular, i.r. absorptions were observed at 1 510 cm⁻¹ and 1 325 cm⁻¹, and may be assigned to the conjugated nitro-group in compound (12)]; ¹H n.m.r. spectrum: 3-H, δ 5.38 (1 H, t, *J*_{2,3} 4.5 Hz); 2-, 5-, and 6-H₂ (6 H, m) 2.4 ≤ δ ≤ 1.7; 7-H, δ 4.75 (1 H, X of ABX C(7)H-C(6)H₂); 9-H₂, [octet, forms part of an ABXY system C(9)H₂-C(10)H=C(11)H]; 9-H_A, δ 3.0 (1 H, *J*_{9A,9B} 14, *J*_{9A,10} 5.0, *J*_{9A,11} 1 Hz); 9-H_B, δ 2.82 (1 H, *J*_{9B,10} 7.5, *J*_{9B,11} ca. 1 Hz); 10-H, δ 5.17 (1 H, *J*_{10,11} 16.5 Hz); 11-H, δ 5.5 (1 H); 12- and 13-H₃, δ 1.12 (6 H); 14-H₃, δ 1.75 (3 H); 15-H₂, δ 5.23 (1 H) and 5.30 (1 H); *v*_{max}. cm⁻¹ (KBr disc) 3 015, 3 010, 2 960, and 2 860 (C-H); 1 665, 1 657, 975, and 845 [*trans*-HR¹C(10)=C(11)HR² and HR¹C(3)=C(4)R²R³ systems]; 3 082, 1 635, 915 [R¹R²C(8)=C(15)H₂]; 1 550, 1 360, and 865 (R-NO₂); and 1 445, 1 380, 1 365,

1 170, and 810 ($>CMe_2$); m/e 249 (M^+), 233, 217, 203, 189, 175, 159, 161, 147, 133, 135, 119, 121, 107, 93, 95, 78, 69, 55, and 43.

The component of R_F 0.39 was recrystallised from ethanol to give clear needles, m.p. 168–169 °C, identical with an authentic sample of dinitrohumulene.

The component of R_F 0.29 was an oil that was further chromatographed on silica, eluting with carbon tetrachloride. Figure 3 shows the 1H n.m.r. spectrum of a solid extracted from the region of R_F 0.12. This, and the mass spectra, showed the compound to be 4,11,11-trimethyl-8-methylene-2,5-dinitrobicyclo[7.2.0]undec-3-ene (10) [during the chromatographic purification of this compound small amounts of the isomeric compounds (11) and (12) were detected]; 1H n.m.r. spectrum: 6- and 10- H_2 , $1.52 \leq \delta \leq 2.04$ (4 H); 1-H, 7- H_2 , and 10-H, $2.06 \leq \delta \leq 2.64$ (4 H); 5-H, δ 5.61 [1 H, X of ABX C(6) H_2 C(5)H, $J_{5,6A}$ 7.5, $J_{5,6B}$ 4, $J_{3,5} < 1$ Hz]; 3-H, δ 4.45 (1 H, $J_{2,3}$ 9 Hz); 2-H, δ 5.41 (1 H, dd, $J_{1,2}$ 7 Hz); 11- and 11- CH_3 , δ 1.13 and 1.34 (3 H, each, s); 8- CH_2 , δ 5.06 (2 H, broadened s); and 4- CH_3 , δ 1.73 (3 H, s); ν_{max} cm^{-1} (KBr disc) 3 010, 1 665, and 840 [$HR^1C(3)=C(4)MeR^2$]; 3 080, 1 630, and 900 [$>C(8)=CH_2$]; 1 550, 1 550, 1 370, 1 360, 865, and 865 ($R-NO_2$); and 2 960, 2 865, 1 450, 1 390, 1 180, and 805 ($>CMe_2$).

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