# The Action of Light on Solid Humulene Nitrosite, $C_{15}H_{24}N_2O_3$. Characterization of Reaction Products, E.P.R. Studies and Reaction Mechanisms

By **Derek K. MacAlpine, Andrew L. Porte,*** and **George A. Sim,** Department of Chemistry, The University of Glasgow, Glasgow G12 8QQ

Humulene nitrosite (1) exhibits needle and platelet crystalline forms. Photolysis of compound (1) with red light generates N_2, NO, NO_2, dinitrohumulene (2), 1,4,4-trimethyl-8-methylene-9-nitrocycloundeca-1,5-diene (3), isomers (4) and (5) of compound (3) and, in the case of the *platelets*, caryophyllene derivatives. Several nitroxide radicals are also generated, and changes in their e.p.r. spectra have been monitored as a function of irradiation time. These spectra have been analysed to yield spin-Hamiltonian parameters, and they give information about the molecular structures of the nitroxides and about their formation and decay in the solid. The combination of chemical and spectroscopic evidence enables some of the steps involved in the solid photolysis reaction to be unravelled.

HUMULENE NITROSITE (1),[1] was first prepared by Chapman.[2,3] It was used by Mitchell in his early work on the Cotton effect [4] and in his early studies of asymmetrical photochemical reactions involving circularly polarized light.[5] The compound exists in two crystalline forms. Needles are obtained when it is rapidly recrystallized out of an ethanolic solution, but if the crystallization from this same solvent is allowed to take place slowly then platelets are also formed. The two forms are deep blue, the colour arising from the intense $\pi^* \leftarrow n$ transition of the nitroso-group at *ca.* 670 nm. The deep blue colour noticeably bleaches when the solids are left exposed to visible light, and when either form of solid humulene nitrosite is irradiated with red light photochemical reaction takes place, nitrogen, nitric oxide and nitrogen dioxide are evolved,[6] the blue colours fade, and eventually white solids and a viscous yellow liquid are obtained. Similar changes are also observed when solid nitrosites of other sesquiterpenes are exposed to red light. The reactions that take place in solid humulene nitrosite are discussed below.

(1) (2) (3)
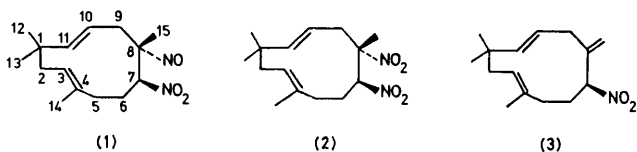
The non-gaseous photolysis products obtained from red irradiation of the *needles* separate into two fractions, the first of which dissolves in ether–light petroleum (1 : 1 v/v) and contains only diamagnetic species: this fraction contains the more abundant photolysis products. The second fraction is paramagnetic, though it is magnetically dilute, and it is not soluble in this mixed solvent. Two crystalline derivatives, dinitrohumulene (2),[1] and 1,4,4-trimethyl-8-methylene-9-nitrocycloundeca-1,5-diene (3),[1] have been isolated from the soluble fraction, and the isomers of (3), compounds (4) and (5), can also be detected spectroscopically although we have not managed to isolate them in pure form from the reaction mixture. We have not detected nitronitratohumulene (6) [1] or caryophyllene derivatives in the products obtained in the red photolysis of the *needles*. The component insoluble

in ether–light petroleum (1 : 1) is a yellow solid that contains several nitroxide radicals.

Similar results were obtained when the *platelets* were irradiated with red light, although much smaller yields of dinitrohumulene were generated, and again no nitronitratohumulene was detected. In this case the major diamagnetic species obtained are compounds (3), (4),

(4) (5) (6)
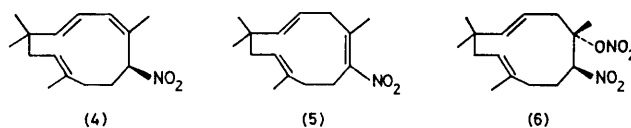
and (5), and several substances we have not been able to purify, but which nevertheless can be shown from i.r. and ^1H n.m.r. spectra to consist of dinitrated humulene and caryophyllene derivatives.

Figure 1 shows e.p.r. spectra obtained at different times from the radicals formed when a polycrystalline sample of humulene nitrosite is irradiated in a source of red light. The paramagnetic species obtained by irradiating the *needles* or the *platelets* with red light appear to be the same. The nature, and the concentrations of the radicals present in the sample obviously change with irradiation dosage and, with our light source radical formation is essentially stabilized after irradiating for 13 h, and the spectrum then obtained is shown in (E) of Figure 1. This is characteristic of magnetically dilute, polycrystalline samples of nitroxide radicals that contain the structural unit (7).

(7) (8)
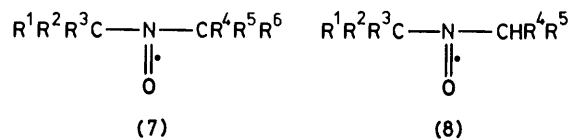
The e.p.r. spectrum obtained from a dilute chloroform solution of the viscous oil obtained when humulene nitrosite is irradiated with red light is shown in Figure 2. It shows that nitroxide radicals containing structures (7) and (8) are present. As expected, the part of this spectrum that originates from (8) decays if the degassed solution is allowed to stand, and eventually the spectrum

shown in Figure 3 results. This same spectrum is also obtained when the yellow solid that is insoluble in the ether–light petroleum (1 : 1 v/v) mixture is dissolved in chloroform. It shows that two nitroxide radicals containing the structural unit (7) must be present: their isotropic spin-Hamiltonian parameters are

$\langle g \rangle = 2.0058 \pm 0.0002$, $a(^{14}N) = 1.46 \pm 0.02$ mT and

$\langle g \rangle = 2.0062 \pm 0.0002$, $a(^{14}N) = 1.49 \pm 0.02$ mT respectively.

Figure 4 is the e.p.r. spectrum obtained from solid

FIGURE 2 E.p.r. spectrum, at 290 K, of a dilute ethanol-free CHCl₃ solution of the viscous yellow solid obtained when humulene nitrosite is irradiated with red light

taining structures (8), and the relative amounts of the species (7) and (8) present at any time during the red irradiation of the parent humulene nitrosite, can now

TABLE 1

$g_{11} = 2.0089 \pm 0.0003$, $g_{22} = 2.0065 \pm 0.0003$,
$g_{33} = 2.0019 \pm 0.0002$, $\langle g \rangle = 2.0058 \pm 0.0003$
$A_{11}(^{14}N) = 0.80 \pm 0.05$ mT, $A_{22}(^{14}N) = 0.45 \pm 0.05$ mT,
$A_{33}(^{14}N) = 3.31 \pm 0.02$ mT, $a(^{14}N) = 1.52 \pm 0.05$ mT,
$\beta = 0.25$ mT, and broadening functions are assumed to have the Gaussian form $(2\pi)^{-\frac{1}{2}}\beta^{-1}\exp[-(h^1 - h)^2(2\beta^2)^{-1}]$.

be obtained by subtracting a suitably scaled version of the spectrum in Figure 4 from the spectra shown in Figure 1. The difference spectrum thus obtained after irradiation for 1.5 h is shown in Figure 5: it can be
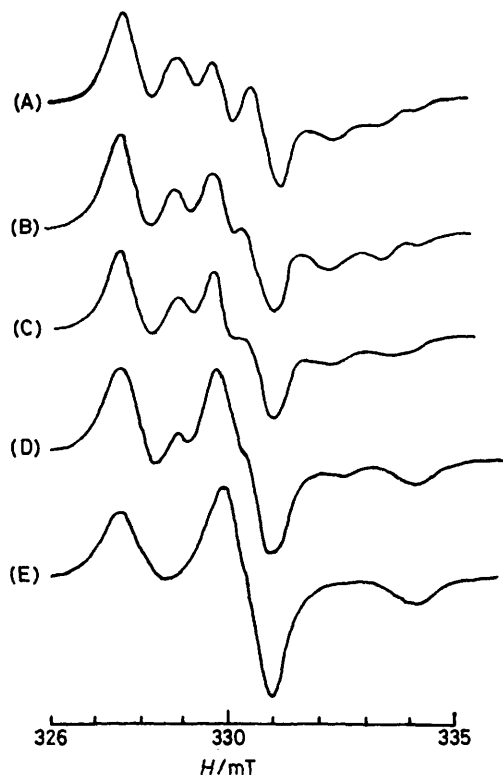

FIGURE 1 E.p.r. spectra of a polycrystalline sample of humulene nitrosite irradiated, at 290 K, with red light for, respectively, . (A) 1.5 h, (B) 3.0 h, (C) 4.5 h, (D) 8 h, (E) 13.0 h. Relative intensities of spectra (A)—(E) can be obtained from Figure 6

FIGURE 3 E.p.r. spectrum, at 290 K, of an out-gassed ethanol-free CHCl₃ solution of the viscous yellow oil, obtained when humulene nitrosite is irradiated with red light and then allowed to stand until radicals (8) have disproportionated

material enriched in these two nitroxide radicals: the differences in the magnetic parameters of the two radicals (7) are not sufficiently different for their spectra to be resolved in the solid. If the spin-Hamiltonian for these radicals is written in the form (1) then Figure 4 can

$$\mathcal{H} = \beta_e H.g.S + S.A.I \qquad (1)$$

be essentially analysed in terms of a superposition of three curves of the type described by Kneubühl[7] and the principal components of the g-tensor and the hyperfine interaction tensor A, along with the line-broadening parameter β, can be obtained from it. The parameters thus obtained are listed in Table 1. These parameters are those expected for nitroxide radicals containing structures (7).

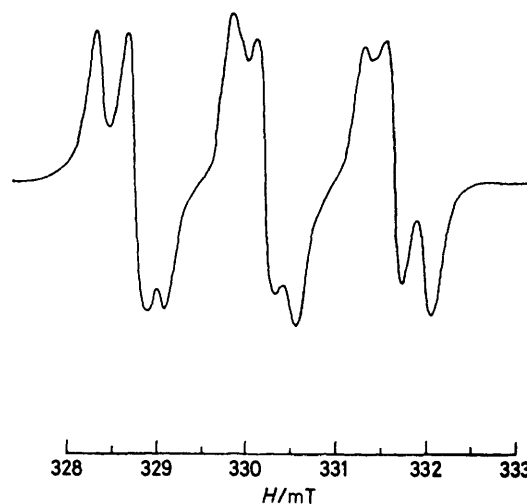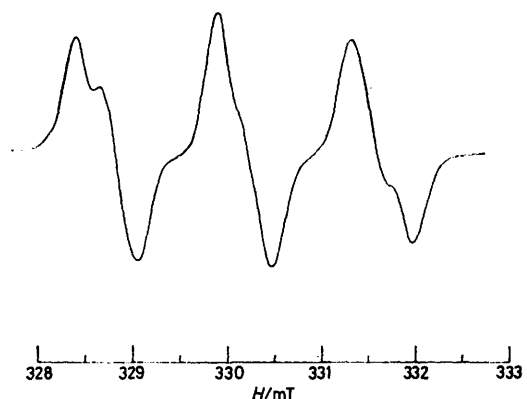Spin-Hamiltonian parameters of the radicals con-

analysed in terms of a superposition of six Kneubühl-type curves to yield the spin-Hamiltonian parameters listed in Table 2. These are the parameters expected for nitroxide radicals containing structures (8).

The relative concentrations of the radicals (7) and (8), obtained using our light source, are plotted as a function of irradiation time in Figure 6. The figure shows that
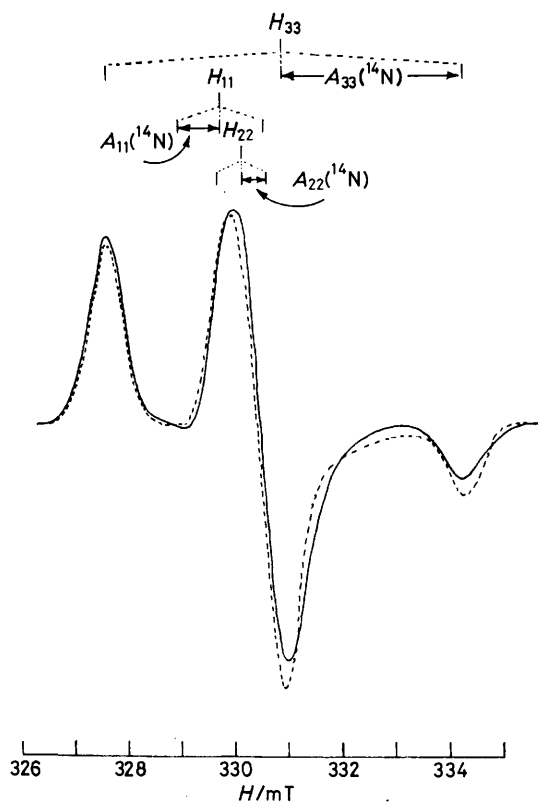
FIGURE 4 E.p.r. spectrum of a polycrystalline sample of the solid, enriched in nitroxide radicals (7), isolated from the products obtained by irradiating humulene nitrosite with red light. The dotted line is the spectrum calculated from the spin-Hamiltonian parameters in Table 1

in the early stages of the red photolysis reaction the concentration of radicals (8) builds up first, reaches a maximum, and then these radicals decay to diamagnetic
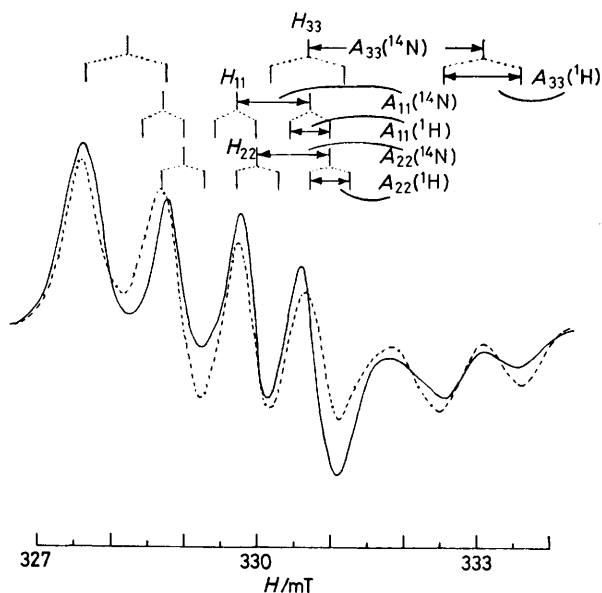

FIGURE 5 E.p.r. spectrum of radicals (8) present in a polycrystalline sample of humulene nitrosite irradiated with red light for 1.5 h. The dotted line is the spectrum calculated from the spin-Hamiltonian parameters in Table 2

TABLE 2

$g_{11} = 2.0091 \pm 0.0003$, $g_{22} = 2.0073 \pm 0.0003$,
$g_{33} = 2.0034 \pm 0.0002$,
$A_{11}(^{14}N) = 1.00 \pm 0.05$ mT, $A_{22}(^{14}N) = 1.00 \pm 0.05$ mT,
$A_{33}(^{14}N) = 2.46 \pm 0.01$ mT,
$A_{11}(^{1}H) = 0.54 \pm 0.05$ mT, $A_{22}(^{1}H) = 0.54 \pm 0.05$ mT,
$A_{33}(^{1}H) = 1.05 \pm 0.01$ mT,
$\langle g \rangle = 2.0066 \pm 0.0003$, $a(^{14}N) = 1.49 \pm 0.05$ mT,
$a(^{1}H) = 0.71 \pm 0.05$ mT, $\beta = 0.40$ mT.

products on further irradiation. On the other hand, the concentration of radicals (7) steadily builds up as the radiation dosage increases.
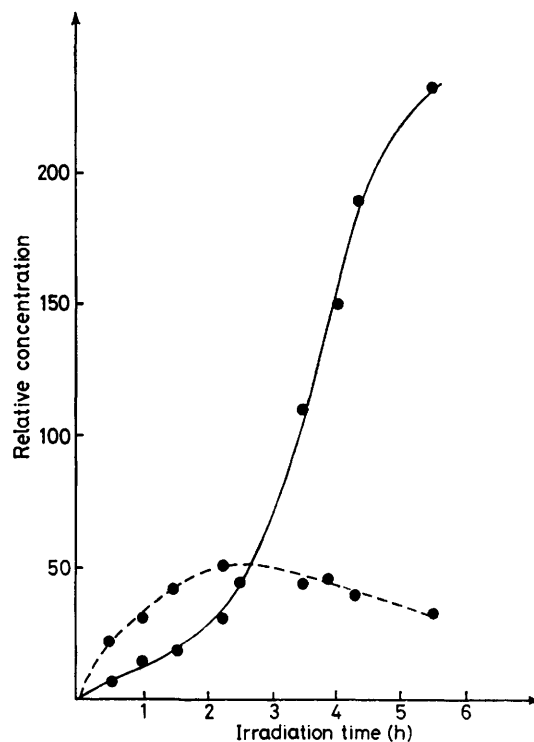

FIGURE 6 Relative concentrations of nitroxide radicals (7), (———), and (8) (– – – –), obtained by red irradiating a polycrystalline sample of humulene nitrosite, plotted vs. irradiation time

Once formed these nitroxide radicals all appear to be indefinitely stable in the solid state as long as the humulene nitrosite is kept in darkness. Furthermore, no changes can be detected in their e.p.r. spectra when the solids or solutions are further irradiated with red light, but when the out-gassed solution that gives rise to the spectrum shown in Figure 2 is further irradiated with white light from a tungsten lamp then the spectrum slowly changes to that shown in Figure 7. This consists of a 1 : 1 : 1 triplet, as a result of coupling with one ^{14}N nucleus, each component of which is further split into a 1 : 1 doublet through additional coupling to one proton:

$$\langle g \rangle = 2.0064 \pm 0.0003, \quad a(^{14}N) = 0.68 \pm 0.02 \text{ mT},$$
$$a(^{1}H) = 0.29 \pm 0.02 \text{ mT}$$

It is the spectrum expected for a conjugated nitroxide radical containing the structure (9).

The large number of products that are generated when humulene nitrosite is photolysed have a common origin, and they are all accounted for by the sequence of

$$R^1R^2R^3C-\overset{\overset{\displaystyle O}{\|}\cdot}{N}-CR^4=CHR^5$$

(9)
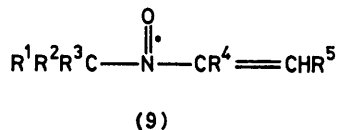
reactions shown in Scheme 1. This is based on the Gowenlock–Kresze–Pfab mechanism that accounts for the products obtained when other nitroso-alkanes are photolysed.[8-12] Absorption of a quantum of red light by the nitroso-group causes an $\pi^*\leftarrow$n transition to take place. The π^* electron weakens the C(8)–N bond which ruptures, and a ' master ' radical (10) is produced and nitric oxide is liberated. In the solid the nitric oxide then reacts with a neighbouring molecule of the parent humulene nitrosite to produce the complex (11). The latter, (11), now rearranges to the diazonium nitrate (12) which decomposes with loss of nitrogen and $NO_3\cdot$ to produce more of the ' master ' radical (10). Subsequent
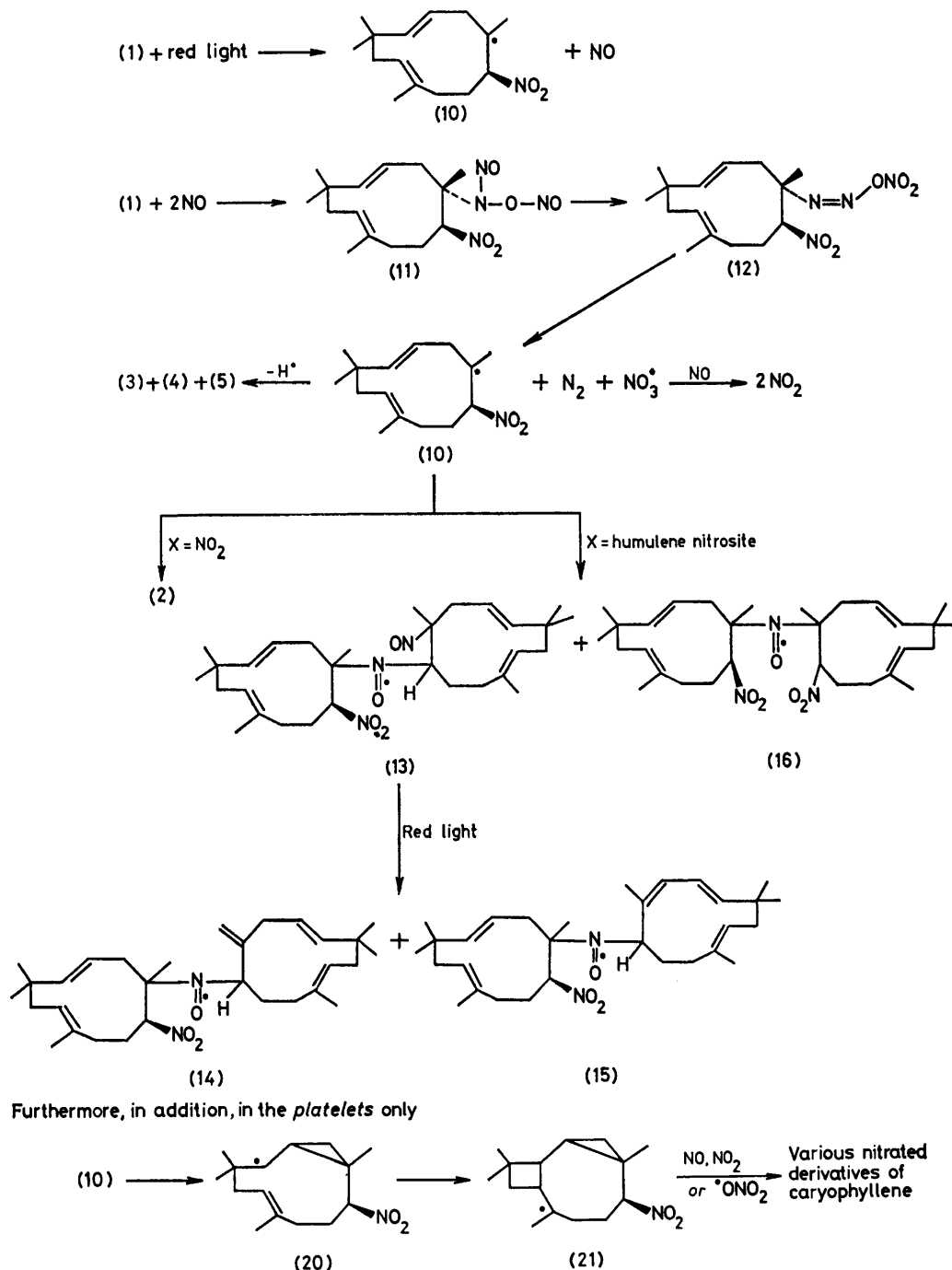
Scheme 1

reaction of ·NO₃ with nitric oxide then generates nitrogen dioxide.

The following reactions are then open to the 'master' radical (10).

(a) It can lose a hydrogen atom, possibly to ·NO₃, to generate the olefins (3), (4), or (5).

(b) ·NO₂ can add to (10) to generate dinitrohumulene (2). Compounds (2), (3), (4), and (5) are the major products generated by the photolysis reaction.
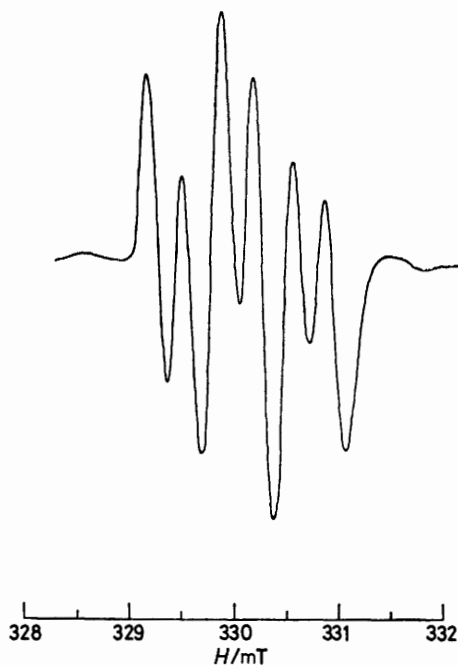

FIGURE 7 E.p.r. spectrum, obtained at 295 K, when the solution whose spectrum is shown in Figure 2 is further irradiated with white light.

(c) Neighbouring humulene nitrosite molecules can scavenge (10) to produce nitroxide radicals. Scavenging can take place at NO or at NO₂ sites of neighbouring molecules but the e.p.r. evidence shows that the molecular packing in the solid is such that attack at an NO₂ site followed by generation of (13) is preferred. The nitroso-group of (13) can be further photolysed by red light to produce (14) and (15). Radicals (13), (14), and (15) all contain the structural unit (8), their spin-Hamiltonian parameters would be indistinguishable in the polycrystalline solid, and so spectrum 5, and its spin-Hamiltonian parameters listed in Table 2, are assigned to (13), (14), and (15).

(d) Scavenging can also take place at neighbouring NO sites, although less readily, thereby generating the nitroxide radicals (16). These contain the structural unit (7) and they exist in several diastereoisomeric forms: spectra 3 and 4 and their spin-Hamiltonian parameters, listed in Table 1, are assigned to the diastereoisomeric forms of (16).

(e) Radicals (13), (14), and (15) may be the precursors of the conjugated radical (9) and its spectrum (Figure 7). In solution, (13), (14), and (15) must disproportionate as shown in Scheme 2, to a mixture of the corresponding hydroxylamines (17) and nitrones (18) and then both the nitroxide radicals and the nitrones could be excited by white light to produce (19). Structure (9), spectrum 7 and its spin-Hamiltonian parameters are then assigned to compounds (19).
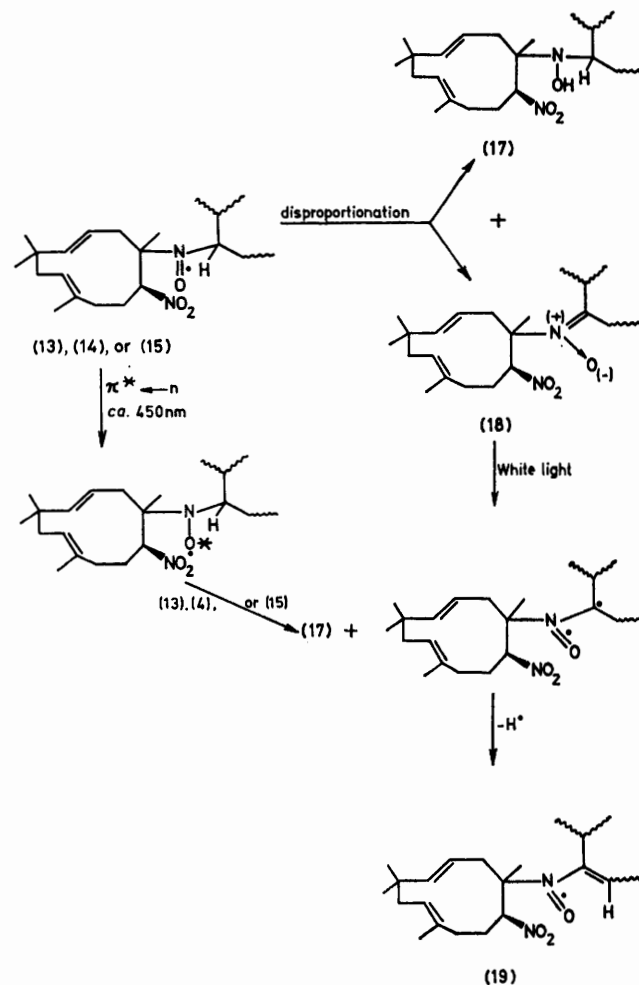
SCHEME 2

(f) In the *platelets* the radical (10) can undergo transannular cyclization to produce in succession, radicals (20) and (21). Radical (21) can then react with ·NO, ·NO₂, or ·ONO₂ to generate a mixture of caryophyllene derivatives. The differences in the nature of the diamagnetic products obtained on red irradiation, might signify that the conformation of the cycloundecadiene ring in the platelets is different from that encountered in the needles.

EXPERIMENTAL

Light petroleum refers to the fraction of b.p. 40—60 °C.
Humulene and Humulene Nitrosite.—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 b.p. 90—100 °C (at 1 mmHg) collected. Humulene was separated from this fraction [1] and then used to synthesize humulene nitrosite.[1] Slow recrystallization of the blue nitrosite from ethanol yielded a

mixture of blue needles and blue platelets that were separated manually. Elemental analysis, ^1H n.m.r., ^{13}C n.m.r., i.r., and mass spectra showed both forms to be humulene nitrosite (1).[1]

Irradiation of Needles of Humulene Nitrosite with Red Light.—Needles of humulene nitrosite were irradiated in evacuated, sealed quartz tubes, using light generated in a tungsten lamp and then passed through a red filter transmitting in the 625—675 nm range. The nitrosite slowly decomposed, gases were evolved and a viscous yellow oil eventually formed. Preparative t.l.c. on silica, using ether–light petroleum (1 : 1 v/v) as eluant enabled this oil to be separated into three components of R_F 0, 0.37, and 0.8.

The component R_F 0 is paramagnetic. It was separated from the silica by extraction with acetone. Removal of the solvent from the extract then yielded a yellow solid that accounted for 10%, by weight, of the products obtained from the photolysis reaction: its e.p.r. spectrum in chloroform is indistinguishable from that shown in Figure 3. We have not been able to isolate pure samples of the nitroxide radicals that are formed, but extended t.l.c., run over several hours on silica, produced a broadened yellow band that was divided into two parts. The products at the lower R_F side of the broad band are diamagnetic. Extraction of the higher R_F side with acetone and then removal of the solvent yielded a yellow solid enriched in nitroxide radicals containing structures (7). Its e.p.r. spectrum is shown in Figure 4; $\nu_{max.}$ cm^{-1} (KBr disc) broadened absorptions at 3 015, and 3 010 (CH); broadened absorptions 1 665—1 640 (C=C); 1 560, 1 550, 1 360, 1 355, 875, and 870 (two RNO$_2$ residues); broadened absorptions 1 380—1 385 (similar CNOC residues); 975 (*trans*-R^{1}CH=CHR^2); 850 (R^{1}R^{2}C=CHR^3). The spectroscopic data are all consistent with structures (16).

The component R_F 0.37 is diagmagnetic. It was separated from the silica by extraction with chloroform. Removal of the solvent gave an oil which on extended t.l.c. on silica plates, using ether–light petroleum (3 : 7 v/v) as eluant, produced a broad band. The lower R_F region of this was extracted and recrystallized from hot ethanol to yield needles, m.p. 167.5—168.5 °C. Elemental analysis, ^1H n.m.r. spectra and i.r. spectra showed that this compound is dinitrohumulene (2).[1]

The component R_F 0.8 is diamagnetic. It was separated from the silica by extraction with chloroform. Removal of the solvent produced an oil from which a white solid eventually crystallized out. ^1H N.m.r., i.r., and mass spectra showed that this solid is 1,4,4-trimethyl-8-methylene-9-nitrocycloundeca-1,5-diene, (3).[1] ^1H N.m.r. and

i.r. spectra showed that the original oil consisted of a mixture of (3) and its isomers, compounds (4) and (5).

Irradiation of Platelets of Humulene Nitrosite with Red Light.—Platelets of humulene nitrosite were irradiated with red light using the procedures described above, and the viscous yellow oil eventually produced was separated, by means of preparative t.l.c. on silica [ether–light petroleum (1 : 1 v/v) as eluant], into six components at R_F 0, 0.15, 0.2, 0.3, 0.37, and 0.8. The products at R_F 0, 0.37, and 0.8 proved to be identical with the corresponding products obtained by irradiation of the needles with red light, although their relative yields differed. The olefins, R_F 0.8, are the major products obtained by photolysis of the platelets and the amount of dinitrohumulene, R_F 0.37, is much reduced in comparison with that obtained by irradiating the needles. We have not been able to isolate pure compounds from the bands at R_F 0.15, 0.2, or 0.3, but their i.r. and ^1H n.m.r. spectra show that the compounds in them contain at least two RNO$_2$ residues per molecule, and the spectroscopic properties of the band at R_F 0.3 indicate the presence of a dinitrocaryophyllene.

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