Action of Red Light on Solid (+)-10-Bromo-2-chloro-2-nitrosocamphane: (i) Nuclear and Electron Paramagnetic Resonance Studies; (ii) Reaction Products; (iii) Solid-state Photolysis Reaction Mechanisms

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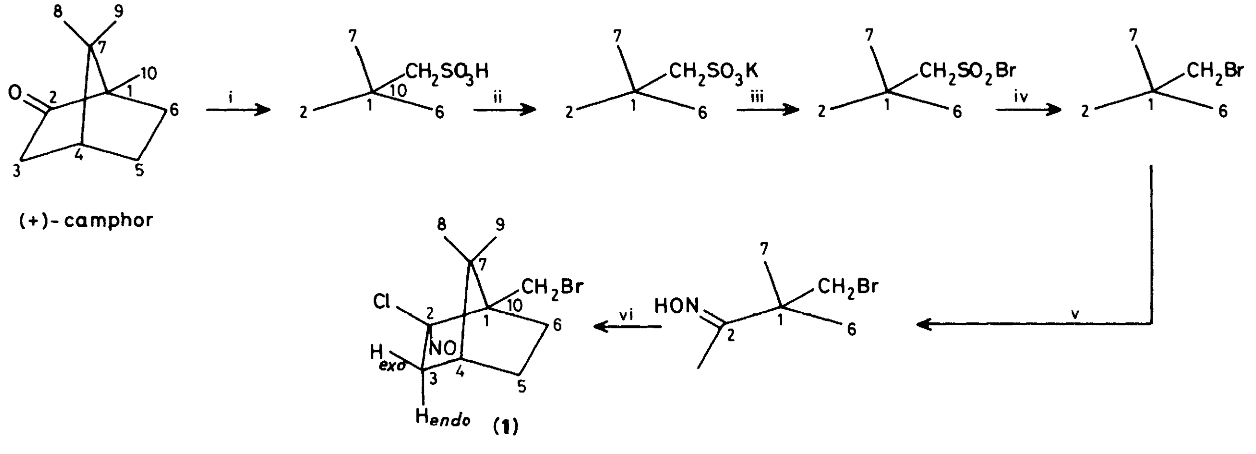
Photolysis of blue, solid (+)-10-bromo-2-chloro-2-nitrosocamphane (**1**) with red light produces two nitroxide radicals (**2**) and (**3**), 10-bromocamphor (**4**), a 10-bromo-2-chloro-2-nitrocamphane (**5**), a 2-chloro-5,5-dimethyl-1,2-dinitrobicyclo[2.2.2]octane (**6a**), and a corresponding 1-nitrato-analogue (**6b**). E.p.r. spectra of (**2**) and (**3**) are described and interpreted. Analyses of the ^{1}H n.m.r. spectra of compounds (**1**) and (**5**) show that n.m.r. methods can be used to determine configurations at active XCCl (X = NO or NO_2) centres of *gem*-chloronitroso and *gem*-chloronitro derivatives of the terpenes. The combination of chemical and spectroscopic evidence enables some of the steps involved in the solid-state red photolysis reactions of (**1**) to be unravelled.

(+)-10-Bromo-2-chloro-2-nitrosocamphane can be prepared by means of the six-stage synthesis shown in Scheme 1.[1–5] It was one of the earliest chloronitroso derivatives of the alkanes to be reported, and its o.r.d. and c.d. spectra were examined by Mitchell and his co-workers during the course of their early classical Cotton effect and asymmetric photolyses studies.[2,3,6] *X*-Ray single-crystal analysis shows that its molecular structure is (1), with the chlorine atom at position 2 *cis* to the >CMe$_2$ bridge.[7] The renewal of interest in the photochemical reactions of the geminal chloronitroso derivatives of the alkanes,[8–10] coupled with the fact that its crystal and molecular structures are known, caused us to believe that it would be well worth extending our interest in the photochemical reactions of *C*-nitroso solids[11,12] to include this compound. We have therefore carried out detailed spectroscopic examinations of the starting material and its irradiation products. The results enable some of the sequence of solid-state reactions that take place when (+)-10-bromo-2-chloro-2-nitrosocamphane is irradiated with red light to be unravelled.



Scheme 1. *Reagents:* i, H_2SO_4–$(CH_3CO)_2O$; ii, KOH; iii, PBr_5; iv, xylene at reflux; v, NH_2OH–HCl; vi, Cl_2–ether

Results and Discussion

(i) *The* ^{1}H *and* ^{13}C *N.m.r. Spectra of* (+)-10-*Bromo-2-chloro-2-nitrosocamphane.*—A 360 MHz ^{1}H n.m.r. spectrum, and corresponding homonuclear double resonance spectra, of (1) are shown in Figures 1A and 1B—E, respectively. The n.m.r. double-resonance experiments and the coupling constants, $J_{H\text{-}H}$, enable the different regions to be unambiguously assigned to the individual protons in the molecule. ^{1}H Chemical shifts and H–H coupling constants obtained from such analyses are listed in Table 1. ^{13}C Chemical shifts extracted from fully, and partially, decoupled ^{13}C-{^{1}H} spectra are also listed in Table 1. The data obtained in this way show that in this compound 3-H$_{exo}$, *i.e.* the neighbouring hydrogen atom on the same side of the molecule as the *chlorine* atom, resonates at lower magnetic field than 3-H$_{endo}$. This is an important result for it now follows that the coupling constants associated with the ring proton whose signals appear at lowest field enable the configuration at the ONCCl residue to be determined in other chloronitrosoterpenes.

E.p.r. Spectra of Radicals obtained on irradiating Solid (+)-10-*Bromo-2-chloro-2-nitrosocamphane with Red Light.*—A polycrystalline sample of (1) in an evacuated, sealed, quartz tube slowly decomposes to produce a yellow viscous oil when it is irradiated with red light from a filtered 150 W quartz–halogen lamp. Monitoring the irradiation in the cavity of an e.p.r. spectrometer shows that two radicals are formed. A polycrystal-

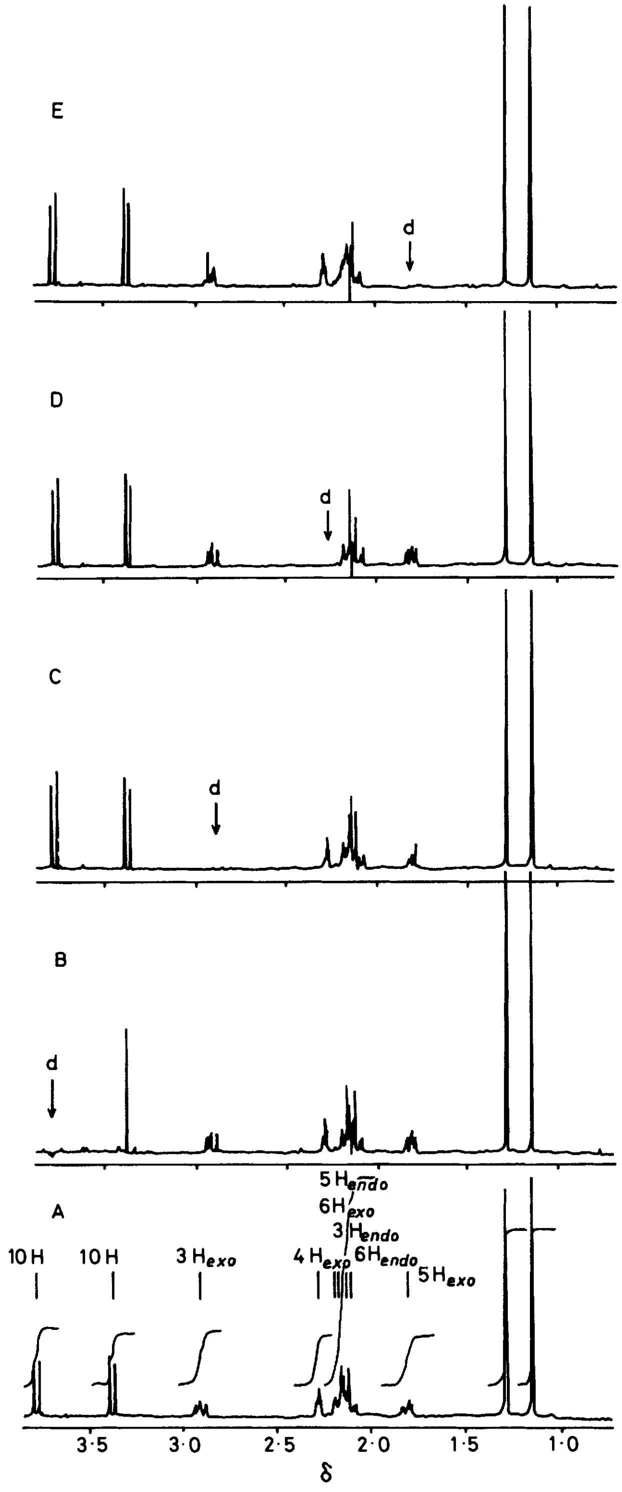


Figure 1. The 360 MHz ^{1}H n.m.r. spectrum of (+)-10-bromo-2-chloro-2-nitrosocamphane (**1**) (A) in CDCl$_3$, and the effect of double irradiation at the 10-H (B), 3-H$_{exo}$ (C), 4-H$_{exo}$ (D), and 5-H$_{exo}$ (E), resonance frequencies

Table 1. ^{1}H and ^{13}C chemical shifts and coupling constants $J_{\text{H-H}}$ in (+)-10-bromo-2-chloro-2-nitrosocamphane (**1**) and 10-bromo-2-chloro-2-nitrocamphane (**5**)

^{1}H Chemical shifts (δ) in CDCl$_3$ solution

Compd.	3-H$_{exo}$	3-H$_{endo}$	4-H$_{exo}$	5-H$_{exo}$	5-H$_{endo}$
(**1**)	2.91(m)	2.14(d)	2.28(t)	1.80(m)	2.17(m)
(**5**)	2.61(m)	3.26(d)	1.96(t)	1.88(m)	1.40(m)
	6-H$_{exo}$	6-H$_{endo}$	8-H$_3$	9-H$_3$	10-H$_2$
(**1**)	2.17(m)	2.12(m)	1.29(s)	1.14(s)	3.78(d), 3.38(d)
(**5**)	2.36(m)	1.12(m)	1.25(s)	1.16(s)	4.16(d), 3.80(d)

^{13}C Chemical shifts [δ (p.p.m.)] in CDCl$_3$ solution

	C-1	C-2	C-3	C-4	C-5
(**1**)	61.47	145.71	42.56	48.03	26.63
(**5**)	57.24	112.10	44.64	45.90	25.23
	C-6	C-7	C-8	C-9	C-10
(**1**)	30.05	53.72	20.93	20.29	32.85
(**5**)	28.81	52.57	23.32	20.53	29.41

$J_{\text{H-H}}$/Hz

	3-H$_{exo}$–3-H$_{endo}$	3-H$_{exo}$–4-H$_{exo}$	3-H$_{exo}$–5-H$_{exo}$	4-H$_{exo}$–5-H$_{exo}$
(**1**)	13.5	5.5	2.0	5.5
(**5**)	15.6	4.5	3.1	4.5
	5-H$_{exo}$–5-H$_{endo}$	5-H$_{exo}$–6-H$_{exo}$	5-H$_{exo}$–6-H$_{endo}$	5-H$_{endo}$–6-H$_{endo}$
(**1**)	*	*	4.5	*
(**5**)	12.3	11.8	5.3	9.2
	5-H$_{endo}$–6-H$_{exo}$	6-H$_{exo}$–6-H$_{endo}$	10-H$_A$–10-H$_B$	
(**1**)	4.5	*	10.4	
(**5**)	5.3	14.7	11.7	

* Because of very small relative chemical shifts between 5-H$_{exo}$, 6-H$_{exo}$, and 6-H$_{endo}$, and tight coupling between these nuclei, accurate estimates of these coupling constants cannot be obtained from the 360 MHz n.m.r. spectrum of compound (**1**).

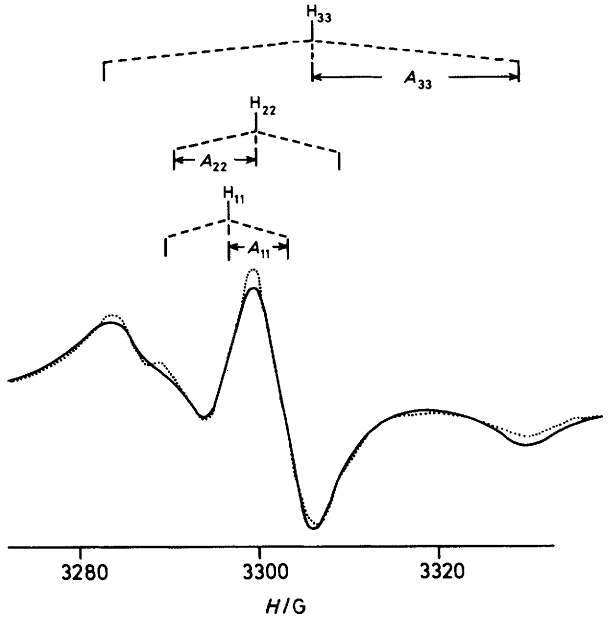


Figure 2. The 77 K e.p.r. spectrum of the nitroxide radical (**2**), obtained by irradiating a solid sample of (+)-10-bromo-2-chloro-2-nitrosocamphane with red light. The dotted line is the spectrum calculated from the spin Hamiltonian parameters in Table 2

line e.p.r. spectrum of the first is shown in Figure 2: its signal-to-noise ratio is relatively poor and irradiation for *ca.* 5 h is needed to produce this spectrum. Figure 2 shows that any tumbling motions of the radical in the solid must be of such a low frequency that they do not average out the magnetic anisotropies in the g and hyperfine coupling tensors, and it suggests that the radical is of fairly high molecular weight. The spectrum is

Table 2. Spin Hamiltonian parameters for radicals (**2**) and (**3**). Hyperfine coupling components are in G (10 G = 1 mT). Limits of error for g and A tensor components are ± 0.0003 and ± 0.4 G, respectively. Broadening functions are assumed to have the Gaussian form $(2\pi)^{-\frac{1}{2}}\ \beta^{-1} \exp[-(H'-H)^2(2\beta^2)^{-1}]$.

Radical	g_{11}	g_{22}	g_{33}	β(G)
(**2**)	2.0093	2.0075	2.0035	3.5
(**3**)	2.0075	2.0069	2.0038	3.5
	$A_{11}(^{14}N)$	$A_{22}(^{14}N)$	$A_{33}(^{14}N)$	
(**2**)	7.0	9.5	23.5	
(**3**)	7.0	8.5	19.6	
Isotropic, solution, parameters				
	$\langle g \rangle$	$a(^{14}N)$	a(Cl)	$a(^1H)$
(**2**)	2.0069 ± 0.0002	13.4 ± 0.2	1.2 ± 0.2	
(**3**)	2.0058 ± 0.0002	11.8 ± 0.2		3.2 ± 0.2

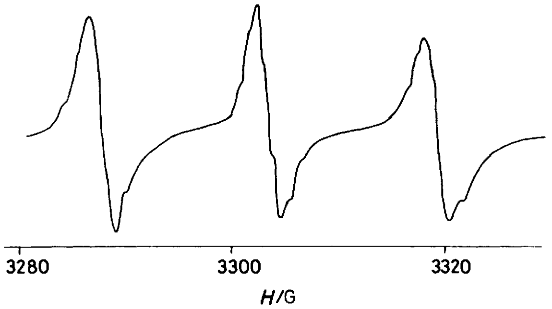


Figure 3. The 295 K e.p.r. spectrum of a dilute degassed solution, in $CHCl_3$, of the nitroxide radical (**2**), obtained by irradiating a solid sample of (+)-10-bromo-2-chloro-2-nitrosocamphane with red light

characteristic of a nitroxide radical, and if the spin Hamiltonian is written in the form (1) then Figure 2 can be analysed in terms

$$\mathcal{H} = \beta_e H\cdot g\cdot S + S\cdot A(^{14}N)\cdot I \qquad (1)$$

of a superposition of three Kneubühl-type curves[13] to give the principal components of the g and $A(^{14}N)$ tensors listed in Table 2. The irradiated polycrystalline solid at this stage, when dissolved in chloroform (*ca.* 10^{-3}M), and the solution out-gassed, yields the e.p.r. spectrum shown in Figure 3. This consists of a 1:1:1 triplet in which the wings are relatively broadened but the central component is just resolved to reveal a 1:2:3:4:3:2:1 pattern, and it shows that the unpaired electron interacts with one ^{14}N nucleus and with two other equivalent nuclei whose spin quantum numbers I are 3/2: the isotropic parameters obtained from Figure 2 are also listed in Table 2. Figures 2 and 3 and the data in Table 2 are consistent with the assignment of structure (**2**) to this nitroxide.

When the solid is further red-irradiated, the spectrum of this first radical gradually disappears, and on irradiating further for *ca.* 5 h it is finally replaced by the spectrum shown in Figure 4. This solid, in its turn, gives the e.p.r. spectrum shown in Figure 5 when it is dissolved in chloroform (*ca.* 10^{-3}M) and the solution out-gassed. Analyses of Figures 4 and 5 shows that this second radical is also a nitroxide radical, but in it the electron interacts with one ^{14}N nucleus and with two equivalent protons, and its spin Hamiltonian parameters, listed in Table 2, are consistent with the assignment of structure (**3**). Extended irradiation of the solid at this stage eventually causes the spectra in Figures 4 and 5 to disappear and only e.p.r.-silent products are then obtained.

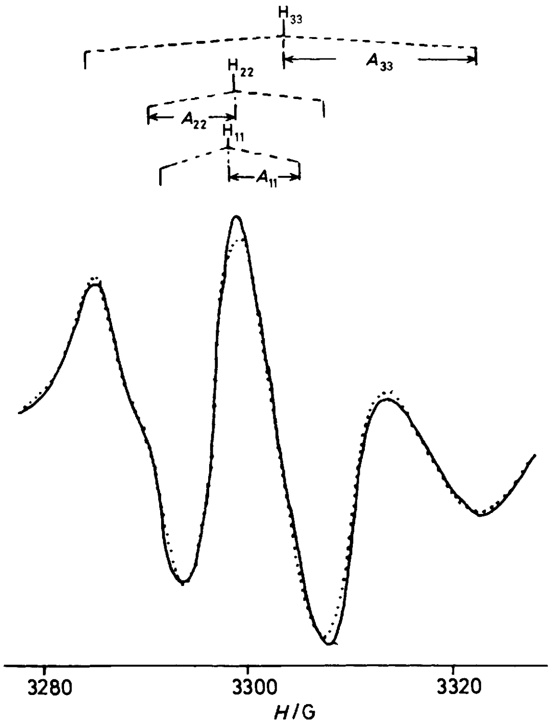


Figure 4. The 77 K e.p.r. spectrum of the nitroxide radical (**3**), obtained by irradiating a solid sample of (+)-10-bromo-2-chloro-2-nitrosocamphane with red light. The dotted line is the spectrum calculated from the spin Hamiltonian parameters in Table 2

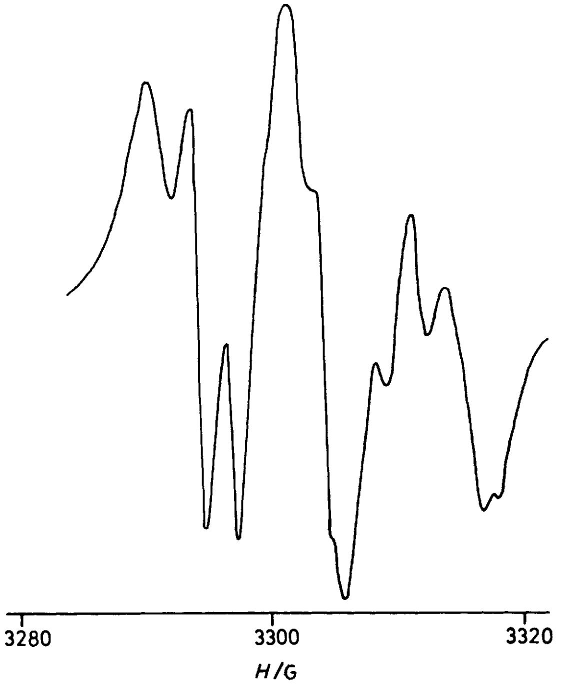
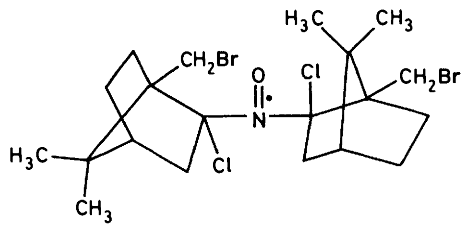
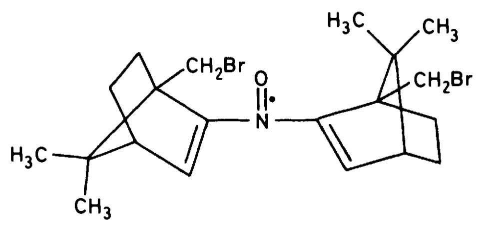


Figure 5. The 295 K e.p.r. spectrum of a dilute degassed solution, in $CHCl_3$, of the nitroxide radical (**3**), obtained by irradiating a solid sample of (+)-10-bromo-2-chloro-2-nitrosocamphane with red light

Radicals (**2**) and (**3**) are also formed when solutions of compound (**1**) in chloroform or toluene are red-irradiated: intense spectra of (**2**) and (**3**) are observed after 30 and 50 min irradiation, respectively, of the solutions.



(2)



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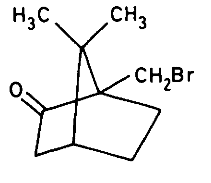

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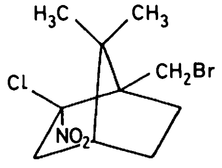

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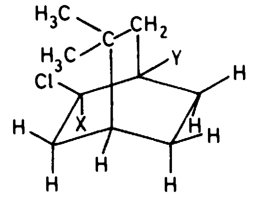


(6)

a; X = Y = NO_2

b; X = NO_2 ; Y = ONO_2

(ii) *Diamagnetic Products of Photochemical Reactions.*—The following changes are observed when (+)-10-bromo-2-chloro-2-nitrosocamphane is incorporated into a KBr disc and its i.r. spectrum then monitored when the disc is irradiated with red light. (a) The nitroso N–O stretching vibration at 1 576 cm^{-1} slowly disappears; (b) the appearance of a very strong absorption at 1 747 cm^{-1} shows that a carbonyl residue is formed in the photochemical reactions; (c) broad absorptions at 1 570, 1 340, and 850 cm^{-1} reveal the formation of NO_2 residues; (d) absorptions at 1 650, 1 320, 850, 760, and 670 cm^{-1} show that organic nitrato residues are produced.

The yellow viscous residue obtained when solid (+)-10-bromo-2-chloro-2-nitrosocamphane is exhaustively irradiated with red light in the absence of air can be separated into four fractions by t.l.c. on silica plates using hexane–ethyl acetate (1:1) as developer. These constitute *ca.* 20, 40, 25, and 10% of the photolysis products, and appear at R_F 0, 0.51, 0.60, and 0.66, respectively.

The component at R_F 0 is an inseparable mixture. The component at R_F 0.51 is 10-bromocamphor (**4**) and that at R_F 0.60 is the 10-bromo-2-chloro-2-nitrocamphane (**5**).

The fraction R_F 0.66 is an inseparable oil containing several compounds. Its i.r. spectrum shows that it contains roughly equal amounts of a bisnitro and a nitro nitrato derivative. Furthermore, in its ^1H n.m.r. spectrum, the sharp AB quartet at δ *ca.* 4, characteristic of the $-C(10)H_2Br$ residue of a 10-bromocamphor skeleton, disappears and is replaced by absorptions at $1.2 \leqslant \delta \leqslant 1.7$, whilst the *gem*-dimethyl doublet at $1.1 \leqslant \delta \leqslant 1.3$ characteristic of the bridging CH_3 residues of 2-substituted camphanes moves downfield. The remaining ^1H chemical shifts in this fraction are very similar to the shifts observed in 10-bromo-2-chloro-2-nitrocamphane (**5**). The spectroscopic evidence shows that this fraction contains skeletal rearrangement products and is consistent with the formation of roughly equal amounts of the bisnitro compound (**6a**) and its corresponding nitrato nitro analogue (**6b**).

We have used the ^1H homonuclear double-resonance spectra shown in Figures 6A—D to unravel the complex ^1H n.m.r. spectrum (Table 1) of 10-bromo-2-chloro-2-nitrocamphane (**5**). Replacing the nitroso residue of the parent compound with the NO_2 group only slightly influences the magnetic properties of the *exo* ring protons but it has a marked effect on the *endo* ring proton chemical shifts, 3-H_{endo} moving downfield by 1.12 p.p.m. whilst 5-H_{endo} and 6-H_{endo} move upfield by 0.77 and 1.00 p.p.m., respectively. In (**5**), the ring proton at lowest applied field is 3-H_{endo}, *i.e.*, in this case it is the neighbouring hydrogen atom on the same side of the molecule as the NO_2 group that resonates at lower magnetic field. The coupling constants for the ring proton whose signals appear at lowest field enable the configuration at the $ClCNO_2$ residue to be determined in other terpene derivatives.

(iii) *Solid-state Photolysis Reaction Mechanisms.*—The sequence of photochemical reactions when solid (+)-10-bromo-2-chloro-2-nitrosocamphane is irradiated with red light can now be unravelled [Schemes 2—8 (2—6 are very similar to schemes already proposed to account for photolysis reactions of other *C*-nitroso compounds[8-12])].

In Scheme 2, irradiation, with red light, of the nitroso group causes a $\pi^* \longleftarrow n$ transition to take place, and this results in homolysis of the C(2)–N bond to form a master radical intermediate (**7**) and nitric oxide. The liberated nitric oxide then reacts with neighbouring molecules of the parent nitroso compound (**1**) and provides an additional source of radical (**7**), an $NO_3^{\bullet}$ radical, and nitrogen, as in Scheme 3.

Radical (**7**) is scavenged by neighbouring parent (+)-10-bromo-2-chloro-2-nitrosocamphane molecules in the solid to produce nitroxide radicals (**2**) and (**3**), as in Scheme 5. Radical (**7**) is also scavenged by $NO_3^{\bullet}$ or NO_2 radicals, these latter being formed as in Schemes 3 and 4, to give 10-bromo-2-chloro-2-nitratocamphane (**8**), or the corresponding nitritocamphane derivative (**9**), or 10-bromo-2-chloro-2-nitrocamphane (**5**), respectively, as in Scheme 6. The large amount of 10-bromocamphor (**4**) can be accounted for if compounds (**8**) and (**9**) are unstable and decompose with loss of nitryl chloride, $ClNO_2$, or nitrosyl chloride, ClNO, respectively, as in Scheme 7.

Formation of compounds (**6a** and **b**) can be explained by Scheme 8, which provides an alternative to the photolysis route leading to Schemes 2—7. In it, at some point during irradiation, for example during the reactions shown in Schemes 2 or 3, both the nitroso group and the bromine atom on C(10) are lost, and the biradical (**10**) is formed. Molecular rearrangement then

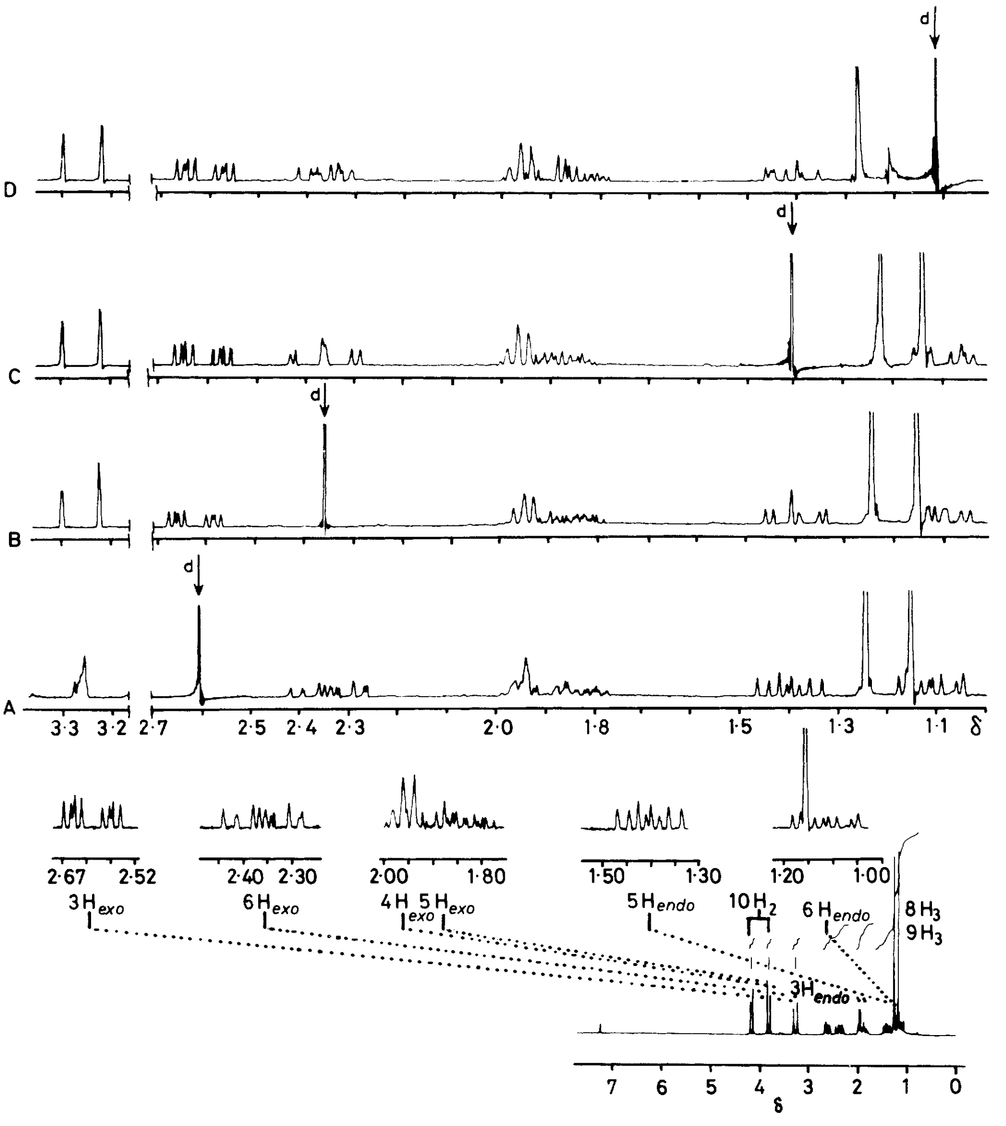
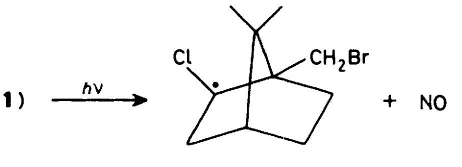


Figure 6. The 200 MHz ^1H n.m.r. spectrum of component R_F 0.60, 10-bromo-2-chloro-2-nitrocamphane (**5**), recorded in $CDCl_3$, and the effects of double irradiation at 3-H_{exo} (A), 6-H_{exo} (B), 5-H_{endo} (C), and 6-H_{endo} (D), resonance frequencies



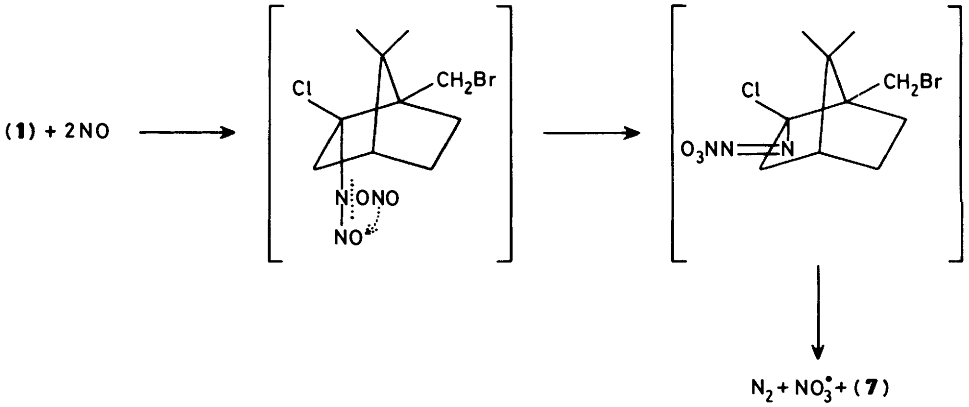
(**7**)

Scheme 2.

takes place and the bridge at C(7) migrates to produce biradical (**11**), which reacts further with NO_2 and/or $NO_3^{\bullet}$ radicals to form the rearrangement products (**6a** and **b**), respectively.

Experimental

(+)-10-*Bromo-2-chloro-2-nitrosocamphane*.—Reychler's method[1] was used to sulphonate natural camphor, and the resultant camphor-10-sulphonic acid was then converted into its potassium salt.[3] The method described by Dallacker *et al.*[4,5] was then used to convert this into 10-bromocamphor which, using standard methods, was in its turn converted into the corresponding oxime, m.p. 155—156 °C. All subsequent procedures were based on the method described by Davidson,[3] and were carried out in a darkened fume cupboard. A solution of 10-bromocamphor oxime (5 g) in anydrous diethyl ether (300 ml) was cooled to 0 °C, and dry chlorine gas was passed through until the mixture became dark green in colour. Excess of chlorine and ether were then removed by passing dry nitrogen through the mixture. This left a deep-blue viscous oil which was extracted with ethanol, yielding a blue solution and an insoluble green gum. The blue solution was then quickly passed through a column (15in × ½in) of acid alumina, using ethanol as eluant, to give a product which on concentrating and recrystallizing from ethanol gave pure (+)-10-*bromo-2-chloro-2-nitrosocamphane* (**1**) (Found: C, 43.4; H, 5.8; N, 4.9; Br, 28.3. $C_{10}H_{15}BrClNO$ requires C, 42.7; H, 5.7; N, 5.0; Br, 28.3%); m.p. 130—131 °C; ^1H and ^{13}C n.m.r. data in Table 1; $\nu_{max.}$ (KBr disc) 3 000, 2 960, 2 930, 2 888 (CMe_2, CH_2, CH_2Br), 1 576 (N=O), 1 395, 1 375, 1 205, 1 140, 1 045, 805 (CMe_2), 1 450, 780 (CH_2), 1 430, 1 240 (CH_2Br), 1 305 (C–H), 875 (C–N), 750 (C–Cl), and 636 cm^{-1} (C–Br); *m/z* 251, 195, 171, 169, 135, 134, 133, 129, 127, 125, 119, 115, 113, 109, 108, 107, 105, 95, 93, 91, 82, 81, 79, 77, 69, 67, 55, 53, 44, 41, 39, and 32 [the parent peak for



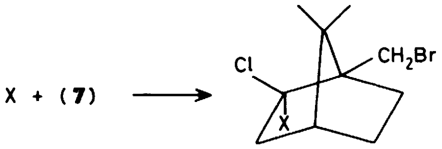
Scheme 3.

$$NO + NO_3 \rightleftharpoons 2NO_2$$

Scheme 4.

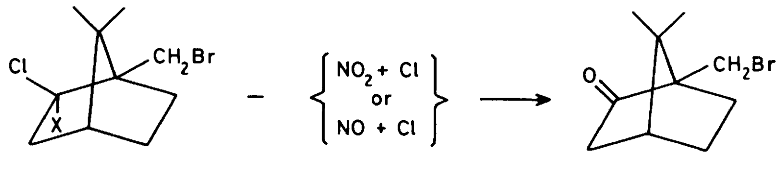
$$(1) + (7) \longrightarrow (2) \xrightarrow{-2HCl} (3)$$

Scheme 5.



(5) X = NO_2
(8) X = ONO_2
(9) X = ONO

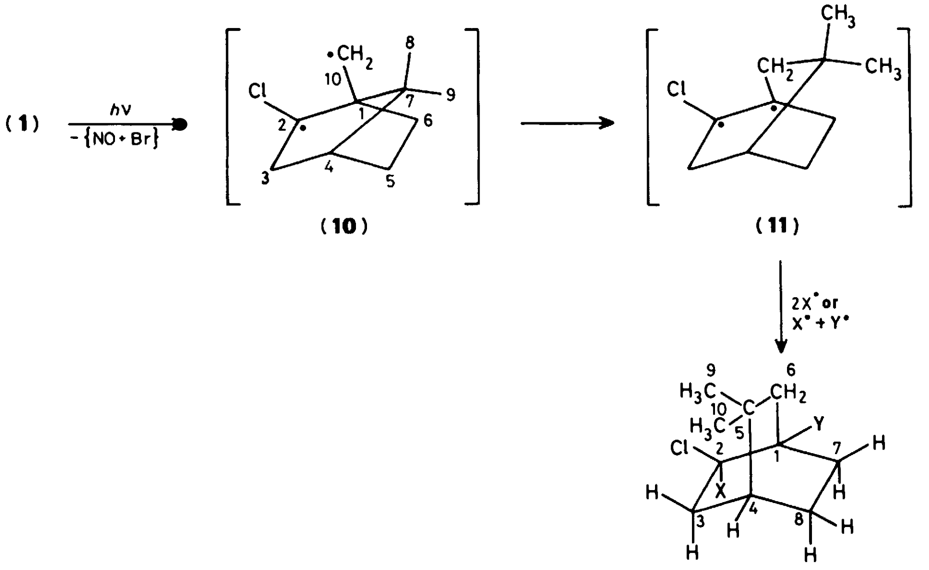
Scheme 6.



(8) X = ONO_2
(9) X = ONO

(4)

Scheme 7.



(10)

(11)

(6)

a; X = Y = NO_2
b; X = NO_2 , Y = ONO_2

Scheme 8.

$C_{10}H_{15}BrClNO$ was not observed since the NO group is cleaved inside the mass spectrometer: the peak at 251 originates from an ion of the master radical (**7**)].

Photolysis of(+)-10-*Bromo*-2-*chloro*-2-*nitrosocamphane with Red Light*.—A pure sample of solid (**1**) was placed in a flask that was evacuated, sealed, and then irradiated at 20 °C with red light from a filtered 150 W quartz–halogen lamp for several weeks, until the blue crystals were converted into a yellow viscous oil, whose components were separated, by preparative t.l.c. on 20 × 20 cm silica plates, using hexane–ethyl acetate (1:1 v/v) as developer, into four main bands at R_F 0, 0.51, 0.60, and 0.66.

The component at R_F 0 (20%) is an inseparable oil.

The component at R_F 0.51 (40%) when recrystallized from ethanol formed white crystals. Elemental analysis, ^1H and ^{13}C n.m.r., i.r., and mass spectra showed it to be 10-*bromocamphor* (**4**) (Found: C, 52.2; H, 6.4; Br, 35.1. $C_{10}H_{15}BrO$ requires C, 52.2; H, 6.5; Br, 34.6%); m.p. 76—77 °C; $\delta_H(CDCl_3)$ 2.60 (1 H, m, 3-H_{exo}), 2.05 (1 H, d, 3-H_{endo}), 2.25 (1 H, t, 4-H_{exo}), 1.07 (3 H, s, 8-H_3), 1.25 (3 H, s, 9-H_3), and 3.80, 3.59 (2 H, AB, J_{AB} 11.1 Hz, 10-H_2); J (3-H_{exo}–3-H_{endo}) 17.9, J (3-H_{exo}–4-H_{exo}) 4.5, J (3-H_{exo}–5-H_{exo}) 2.4, J (4-H_{exo}–5-H_{exo}) 4.5 Hz; ^{13}C-{^1H} decoupled spectrum $\delta_C(CDCl_3)$ 61.47 (s, C-1), 217.0 (s, C-2), 47.38 (t, C-3), 48.22 (d, C-4), 27.56 (t, C-5), 29.04 (t, C-6), 50.77 (s, C-7), 20.73 (q, C-8), 20.31 (q, C-9), and 29.00 p.p.m. (t, C-10); $\nu_{max.}$(KBr) 2 990, 2 970 2 940, 2 930 (CMe_2, CH_2, CH_2Br), 1 747 (C=O), 1 393, 1 377, 1 200, 1 170, 1 045, 853 (CMe_2), 1 460, 776 (CH_2), 1 430, 1 236 (CH_2Br), 1 330 (C–H), and 635 cm^{-1} (C–Br); *m*/*z* 230, 152, 151, 150, 133, 123, 109, 108, 107, 95, 93, 91, 82, 81, 79, 77, 69, 67, 55, 53, 43, and 41.

The component at R_F 0.60 (25%) when recrystallized from ethanol formed white crystals. Elemental analysis, ^1H and ^{13}C n.m.r., i.r., and mass spectra showed it to be the 10-*bromo*-2-*chloro*-2-*nitrocamphane* (**5**) (Found: C, 40.6; H, 5.1; Br, 26.2; N, 4.5. $C_{10}H_{15}BrClNO_2$ requires C, 40.6; H, 5.1; Br, 26.9; N, 4.7%); m.p. 182—183 °C; ^1H and ^{13}C n.m.r. data are listed in Table 1; $\nu_{max.}$(KBr) 3 000, 2 965, 2 930, 2 890 (CMe_2, CH_2, CH_2Br), 1 560, 1 340, 838 (NO_2), 1 395, 1 375, 1 205, 1 135, 1 040, 830 (CMe_2), 1 455, 820 (CH_2), 1 430, 1 255 (CH_2Br), 1 305 (CH), 855 (C–N), 750 (C–Cl), and 620 cm^{-1} (C–Br); *m*/*z* 251, 171, 151, 133, 127, 109, 108, 107, 105, 95, 94, 93, 91, 82, 81, 79, 77, 69, 67, 65, 57, 55, 53, 51, 44, 43, 41, 39, 38, 36, and 28 [the parent peak for $C_{10}H_{15}BrClNO_2$ was not observed since the NO_2 group is cleaved inside the mass spectrometer: the peak at 251 originates from an ion of the master radical (**7**)].

The component at R_F 0.66 (10%) was an inseparable oil with several components. ^1H N.m.r. and i.r. spectra indicate that this fraction contains roughly equal amounts of compounds (**6a** and **b**), $\delta_H(CDCl_3)$ 3.0 (1 H, d, 3-H_{endo}), 2.8 (1 H, br d, 3-H_{exo}), 2.24 (1 H, br m, 7-H_{exo}), 1.95 (2 H, br m, 4-H_{exo} and 8-H_{exo}), 1.5 (br m, 7-H_{endo} and 8-H_{endo}), 1.55, 1.60 (6 H, s, 9-H_3 and 10-H_3), and 1.64 and 1.47 (2 H, 6-H_2); $\nu_{max.}$ (thin film) 2 965, 2 930, 2 890, 2 880, 2 855 (CMe_2, CH_2, C–H), 1 648, 1 310, 857, 760, 675 (ONO_2), 1 560—1 580, 1 295—1 340, and 830—860 cm^{-1} (several NO_2).

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