Action of Red Light on Solid (−)-2-Chloro-2-nitrosocamphane: Nuclear and Electron Paramagnetic Resonance Studies, Reaction Products, and Solid-state Photolysis Reaction Mechanisms

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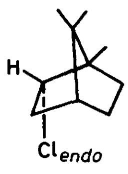
Analysis of the ^1H n.m.r. spectrum of (−)-2-chloro-2-nitrosocamphane (**3**) defines its molecular structure. Irradiation of the blue solid rapidly inverts the configuration at C(2) and causes a photochemically initiated Beckmann rearrangement to the nitroxide radical (**7**). Extended irradiation generates two additional nitroxide radicals (**8**) and (**9**), camphor oxime (**10**), camphor (**11**), 2-chloro-2-nitrocamphane (**12**), and 2-chloro-2-nitratocamphane (**13**). N.m.r. methods show that in (**12**) the configuration at C(2) is inverted relative to that in the parent chloro-nitroso compound (**3**). The combination of chemical and spectroscopic evidence enables some of the steps in the solid-state red photolysis reactions of (**3**) to be unravelled.

(−)-2-Chloro-2-nitrosocamphane, *i.e.* (−)-2-chloro-2-nitroso-1,7,7-trimethylbicyclo[2.2.1]heptane, is obtained when chlorine reacts with the oxime of natural (+)-camphor. It is a deep blue monomeric solid. Some years ago Mitchell and his co-workers[1–3] discovered that when a blue solution of this substance in alcohol is exposed to red light, for short periods, its absorption band at 670 nm is displaced by 6 nm towards longer wavelengths, and its optical rotatory dispersion curve in this same region of the spectrum is inverted, 'without appreciable photolysis'. The inversion of the Cotton effect was interpreted in terms of a 2,2′-mutarotation in which the NO and Cl groups on C(2) are interchanged, and the configuration at C(2) is thereby inverted. These results, when the period of red irradiation was extended for longer periods, furthermore indicated that two processes were taking place simultaneously, the first involving a rapid mutarotation, and the second involving slow photolysis.

Hope and Mitchell also examined[2] the u.v. absorption spectra of solutions of the un-irradiated [(−)-] and irradiated, [(+)-] isomers; they found that the differences in their spectra are closely analogous to those between bornyl chloride (1) and isobornyl chloride (2). They accordingly suggested that the (−)- and (+)-isomers of 2-chloro-2-nitrosocamphane have structures (3) and (4), respectively.

Davidson found[3] that the quantum efficiency for the red photomutarotation of (3), in ethanol, is 0.97, and postulated that this reaction takes place by the mechanism shown in Scheme 1.

Detailed analyses of n.m.r. spectra can discriminate between the possible configurations of geminal chloro-nitroso and chloro-nitro derivatives of bicyclo[2.2.1]heptane.[4] We have therefore extended the work of the earlier investigators and used a mixture of n.m.r., e.p.r., and other spectroscopic methods to determine the structures of (−)-2-chloro-2-nitrosocamphane and some of its reaction products, to identify some of the unstable intermediates that are formed, and to unravel some of the complex sequence of solid-state reactions that takes place when the parent blue solid is irradiated with red light.



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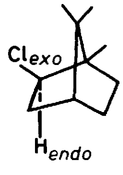

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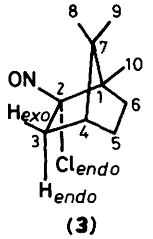

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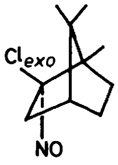

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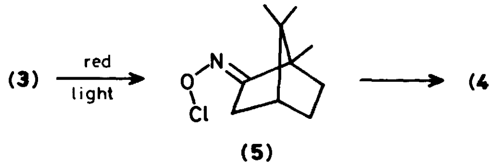

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Scheme 1.

Results and Discussion

The ^1H *and* ^{13}C *N.m.r. Spectra of* (−)-*2-Chloro-2-nitrosocamphane.*—A 360 MHz ^1H n.m.r. spectrum, and corresponding homonuclear double-resonance spectra of (−)-2-chloro-2-nitrosocamphane in $CDCl_3$ are shown in Figures 1(A) and 1(B)—(H), respectively, and ^1H chemical shifts and H,H coupling constants obtained from a detailed analysis of these spectra are listed in Table 1. ^{13}C Chemical shifts extracted from fully and partially decoupled 25.2 MHz ^{13}C-{^1H} spectra are also listed in this Table. The analysis shows that nitroso-dimers are absent, that only one monomer is present in $CDCl_3$ solution, that the 3-H_{endo} signals appear at highest δ values, and that the chlorine atom in this molecule is therefore in the *endo*-position.[4] The structure (3) assigned by Mitchell and his co-workers is correct. The configuration at C(2) in this compound is opposite to that at the corresponding position of (+)-10-bromo-2-chloro-2-nitrosocamphane.[4,5]

E.p.r. Spectra of Radicals obtained on Irradiating Solid (−)-*2-Chloro-2-nitrosocamphane with Red Light.*—A polycrystalline sample of (3) slowly decomposes and eventually yields a yellow viscous liquid when irradiated in an evacuated, sealed quartz tube 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 three radicals are formed.

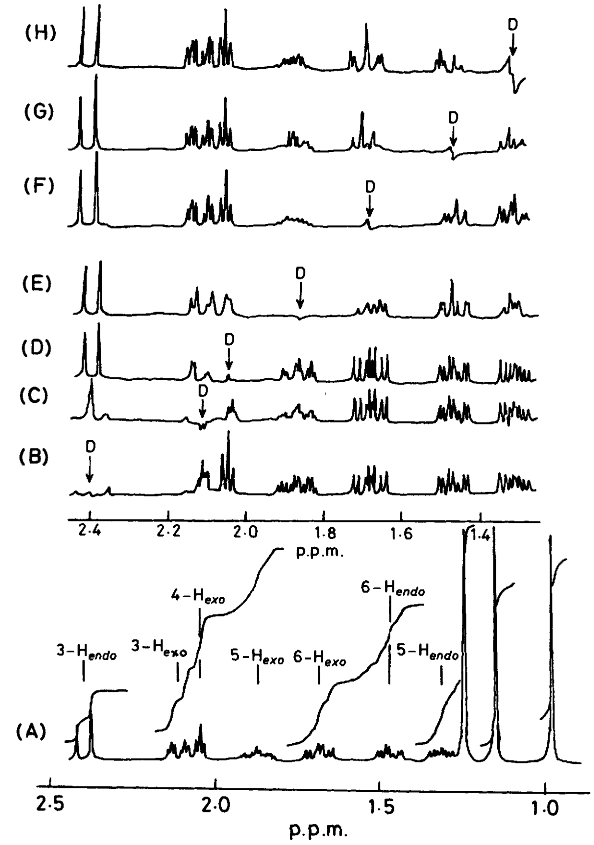


Figure 1. The 360 MHz ^{1}H n.m.r. spectrum of (−)-2-chloro-2-nitrosocamphane (**3**): (A) in CDCl$_3$; the effects of double irradiation at 3-H$_{endo}$ (B), 3-H$_{exo}$ (C), 4-H$_{exo}$ (D), 5-H$_{exo}$ (E), 6-H$_{exo}$ (F), 6-H$_{endo}$ (G), and 5-H$_{endo}$ (H) resonance frequencies

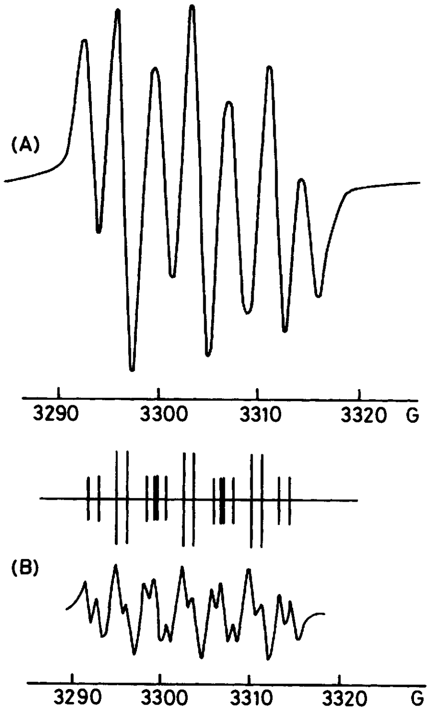


Figure 2. The 295 K e.p.r. spectrum of the nitroxide radical (**7**) obtained by irradiating solid (−)-2-chloro-2-nitrosocamphane with red light (A), and the corresponding spectrum (B) at 295 K of the same irradiated solid dissolved in CHCl$_3$ (*ca.* 10^{-3}M)

Table 1. Chemical shifts (^{1}H and ^{13}C) and coupling constants ($J_{H,H}$) in (−)-2-chloro-2-nitrosocamphane (**3**) and 2-chloro-2-nitrocamphane (**12**)

δ_H(CDCl$_3$)					
Compd.	3-H$_{endo}$	3-H$_{exo}$	4-H$_{exo}$	5-H$_{exo}$	5-H$_{endo}$
(**3**)	2.40	2.11	2.05	1.87	1.31
(**12**)	3.20	2.58	1.94	1.76	1.29[a]
	6-H$_{exo}$	6-H$_{endo}$	8-H$_3$	9-H$_3$	10-H$_3$
(**3**)	1.68	1.46	1.15	0.98	1.25
(**12**)	1.68[a]	1.05[a]	1.14	0.93	1.23
δ_C(CDCl$_3$)					
	C-1	C-2	C-3	C-4	C-5/C-6
(**3**)	55.47	145.04	40.31	46.75	26.45
(**12**)	56.28	112.65	44.57	45.06	25.52
	C-6/C-5	C-7	C-8/C-9	C-9/C-8	C-10
(**3**)	29.46	51.47	20.73	19.40	12.68
(**12**)	31.52	50.92	21.02	20.45	11.79
$J_{H,H}$/Hz					
	3-H$_{exo}$, 3-H$_{endo}$	3-H$_{exo}$, 4-H$_{exo}$	3-H$_{exo}$, 5-H$_{exo}$	4-H$_{exo}$, 5-H$_{exo}$	
(**3**)	14.4	4.1	3.9	4.7	
(**12**)	15.6	4.5	3.0	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$_{endo}$	
(**3**)	13.0	12.0	3.5	9.0	
(**12**)	*b*	*b*	*b*	*b*	
	5-H$_{endo}$, 6-H$_{exo}$	6-H$_{exo}$, 6-H$_{endo}$			
(**3**)	5.0	14.0			
(**12**)	*b*	*b*			

[a] These three shifts are assigned on the basis that changes in substitution pattern at C-2 should noticeably affect 6-H$_{endo}$ and have little effect at 6-H$_{exo}$. [b] Unambiguous values for these coupling constants cannot be obtained from the spectra on Figure 6.

Intense signals from the first of these, shown in Figure 2(A), are readily observed on irradiating for short periods of about 10 min, the same period during which changes in circular dichroism and optical rotatory dispersion in solutions of this compound are observed. If the solid is then left in darkness at this point the spectrum slowly decays in intensity and eventually disappears after about 48 h. At this stage the crystals are not visibly altered by the red light and continuous red irradiation of the solid sample for 15 h causes this spectrum steadily to increase in intensity without changing its form. Figure 2(A) is the e.p.r. spectrum of a rapidly reorienting nitroxide radical in which the unpaired electron is nearly isotropically coupled to one ^{14}N nucleus and to two protons. The absence of anisotropic direct dipolar contributions to hyperfine coupling implies that this radical is globular, and that like other globular camphane derivatives it rapidly and isotropically rotates in the solid, the correlation time for molecular reorientation being of the order of 10^{-9} s.[6–8] The e.p.r. spectrum shown in Figure 2(B) is obtained from a degassed solution of the solid at this stage, in chloroform (*ca.* 10^{-3}M). It is very similar to spectrum 2(A), but it is better resolved and reveals a weaker coupling to a third proton. Substituting ^{15}N for ^{14}N spreads out the components of nitroxide radical spectra and overlapping between hyperfine lines in the middle of the spectrum is then avoided. In order to remove the possibility of ambiguities in the analysis of the spectrum in Figure 2, the naturally occurring ^{14}N in (−)-2-chloro-2-nitrosocamphane was replaced by ^{15}N to give the e.p.r. spectrum shown in Figure 3(A); when this red-irradiated

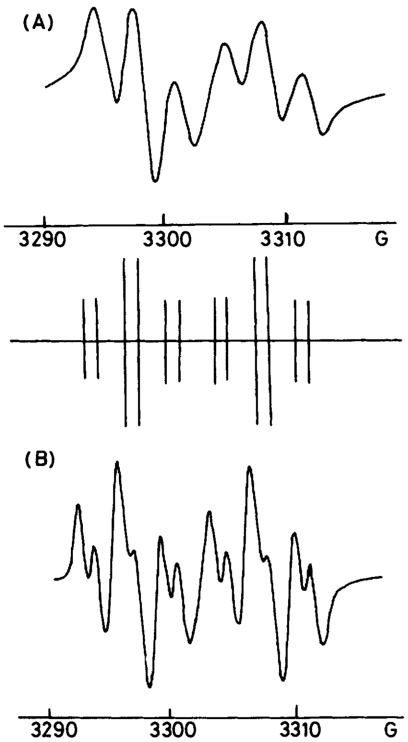
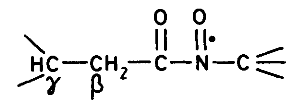


Figure 3. The 295 K e.p.r. spectrum of the [^{15}N]nitroxide radical (7) obtained by irradiating solid (−)-2-chloro-2-[^{15}N]nitrosocamphane with red light (A), and the corresponding spectrum (B) at 295 K of the same irradiated solid dissolved in $CHCl_3$ (*ca.* 10^{-3}M)



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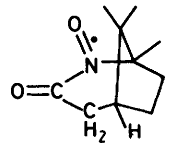


(7)

solid is dissolved in $CDCl_3$ (10^{-3}M-solution), the spectrum shown in Figure 3(B) is obtained.

Analysis of Figures 2 and 3 gave the spin-Hamiltonian parameters listed in Table 2. These show unambiguously the presence of a nitroxide radical in which one unpaired electron interacts with one nitrogen nucleus and with three protons, two of which are equivalent. The small nitrogen hyperfine coupling interaction indicates that a significant amount of delocalization of the unpaired electron away from the π* orbital of the N$\doteq$O fragment has occurred, and a review of the literature[9–16] for nitroxide radicals shows that the observed nitrogen hyperfine coupling in this case falls within the range expected for compounds in which a carbonyl group is conjugated to the N$\doteq$O residue.

The e.p.r. results reveal the presence of the structure (6) in the radical, and the relationships[17–21] $a(^{14}N) \approx 33.1\ \rho_N$ G and $a(C_\beta{}^1H) \approx (3.2 + 43.5\ \cos^2\theta)\rho_{C(\alpha)}$ show that the spin-densities on N and C_α are about 0.22 and 0.19, respectively. These results show that the formation of this first nitroxide radical involves a skeletal rearrangement of (3). The e.p.r. spectra and spin-Hamiltonian parameters are those expected for the acylnitroxide radical (7).

Table 2. Isotropic spin-Hamiltonian parameters for the radical (7)[a]

Naturally occurring radical	$\langle g\rangle$ = 2.006 6(2) $a[^1HC(3)]$ = 3.3(1) G	$a(^{14}N)$ = 7.4(1) G $a[^1HC(4)]$ = 1.1(1) G
[^{15}N]-Radical	$\langle g\rangle$ = 2.006 6(2) $a[^1HC(3)]$ = 3.3(1) G	$[a(^{15}N)]$ = 10.6(1) G $a[^1HC(4)]$ = 1.1(1) G

[a] 1 G = 10^{-4} T.

Table 3. Isotropic spin-Hamiltonian parameters for the radicals (8) and (9)

Radical	$\langle g\rangle$	$a(^{14}N)$/G	a(Cl)/G	$a(CH)$/G
(8)	2.006 9(2)	13.0(2)	1.5(2)	
(9)	2.005 7(2)	11.9(2)		3.0(2)

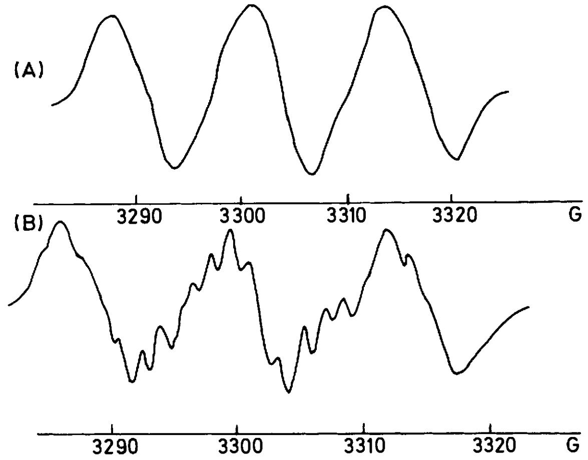
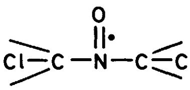


Figure 4. The 295 K e.p.r. spectra of the nitroxide radical (8): (A) is the spectrum obtained from the solid; (B) is the corresponding spectrum of the same solid dissolved in $CHCl_3$



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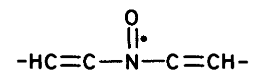


$-HC{=}C{-}\overset{\overset{\displaystyle O}{\|\bullet}}{N}{-}C{=}CH-$

(9)

A second radical is detected when the solid sample containing the first radical is further irradiated with red light for more than 18 h. On continuing to irradiate, the initial deep blue colour of the solid turns pale blue, the crystal structure starts to break down, and the spectrum shown in Figure 2(A) slowly disappears and is replaced by that of a relatively unstable radical with the spectrum shown in Figure 4(A). The e.p.r. spectrum shown in Figure 4(B) is obtained from a degassed solution of the solid at this stage in $CHCl_3$. It consists of a 1:1:1 triplet in which the central component shows further splitting to produce a 1:2:3:4:3:2:1 pattern. The spectra and the spin-Hamiltonian parameters in Table 3 show that this second radical contains structure (8).

The formation of a third nitroxide radical can be detected when solid (−)-2-chloro-2-nitrosocamphane is red-irradiated for more than 25 h, and it persists for further extended periods of irradiation until eventually it too decays and diamagnetic products are finally formed. Its spectrum (Figure 5) consists of a 1:1:1 triplet, each component of which is further split into a 1:2:1 triplet through additional coupling to two equivalent protons. When the solid sample containing this third radical is dissolved in $CHCl_3$ (*ca.* 10^{-3}M), no further hyperfine splitting of this spectrum is detected, even when the solution is further diluted and thoroughly degassed. Spin-Hamiltonian parameters

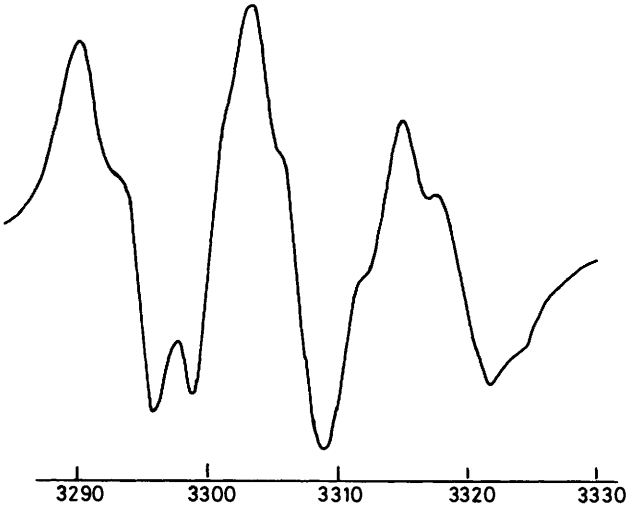


Figure 5. The e.p.r. spectrum of the nitroxide radical (**9**)

extracted from Figure 5 are also listed in Table 3, and show[16] that this third species is a nitroxide radical that contains the structure (**9**).

We have not managed to detect e.p.r. signals of triplets or of biradicals during this work.

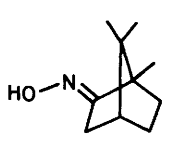
The Diamagnetic Products of the Photochemical Reactions.—When (−)-2-chloro-2-nitrosocamphane is incorporated into a KBr disc and its i.r. absorption spectrum periodically examined as the disc is irradiated with red light, the 760 cm^{-1} absorption due to the C–Cl stretching vibration disappears during the early stages of irradiation and is replaced by another C–Cl absorption, at 780 cm^{-1}. At the same time the nitroso absorption at 1 580 cm^{-1} slowly decreases in intensity, and over about 1 h is gradually replaced by a weaker absorption at 1 565 cm^{-1}.

Solid polycrystalline (−)-2-chloro-2-nitrosocamphane on exhaustive irradiation with red light at 290 K in an evacuated, sealed glass tube eventually decomposes to a yellow viscous oil. Comparison of the i.r. spectrum of the oil with that of (**3**) reveals the following differences. The nitroso absorption at 1 580 cm^{-1} in (**3**) is absent in the yellow oil; new absorption bands at 1 555, 1 350, and 690 cm^{-1} in the oil reveal the formation of one nitro derivative; weak absorption at 1 650 cm^{-1} shows that a trisubstituted ethylenic residue has been formed; additional absorption at 1 270 and 875 cm^{-1} indicates the formation of one nitrato residue; the presence of a broad band at 3 300 cm^{-1} and two weak bands at 1 688 and 925 cm^{-1} in the oil indicates that an oxime has been formed, and broad absorption at 1 740 cm^{-1} shows that a carbonyl residue has been produced on irradiation.

The yellow viscous oil can be separated into five fractions by t.l.c. on silica plates using ether–light petroleum (1:1) as eluant. These constitute roughly 15, 15, 40, 15, and under 10% of the photolysis products and appear at R_F 0, 0.40, 0.52, 0.60, and 0.65, respectively.

The component at R_F 0 is an inseparable mixture. The component at R_F 0.40 is the camphor oxime (**10**) in which the hydroxy group is *syn* to C(3)H$_2$. The component at R_F 0.52 is camphor (**11**). The component at R_F 0.60 is the 2-chloro-2-nitrocamphane (**12**), and the component at R_F 0.65 is the 2-chloro-2-nitratocamphane (**13**).

The assignment of structure (**10**) to the oxime follows from the differential chemical shifts of its ^{13}C n.m.r. spectrum relative to the corresponding shifts of (**11**).[22] Inversion of the configuration at C(2) in the 2-chloro-2-nitro derivative (**12**) relative to that in (**3**) follows from detailed analyses of the 360 MHz ^{1}H n.m.r. spectrum in Figure 6(A) and the homonuclear double resonance spectra in Figure 6(B)—(F), respectively. ^{1}H Chemical shifts and H,H coupling constants obtained from these spectra are also listed in Table 1, along with the corresponding ^{13}C chemical shifts extracted from fully and partially decoupled 25.2 MHz ^{13}C–{^{1}H} spectra, and the data show that the 3-H$_{endo}$ signals are at highest δ values in the spectra of this compound. The NO$_2$ group is therefore in the *endo*-position.[4] The 2-chloro-2-nitrocamphane obtained from the photolysis reaction is (**12**). The configuration at C(2) in the parent 2-chloro-2-nitrosocamphane has inverted during red irradiation.



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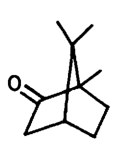

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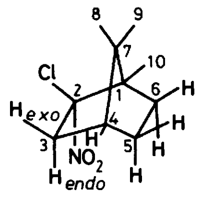

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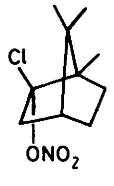

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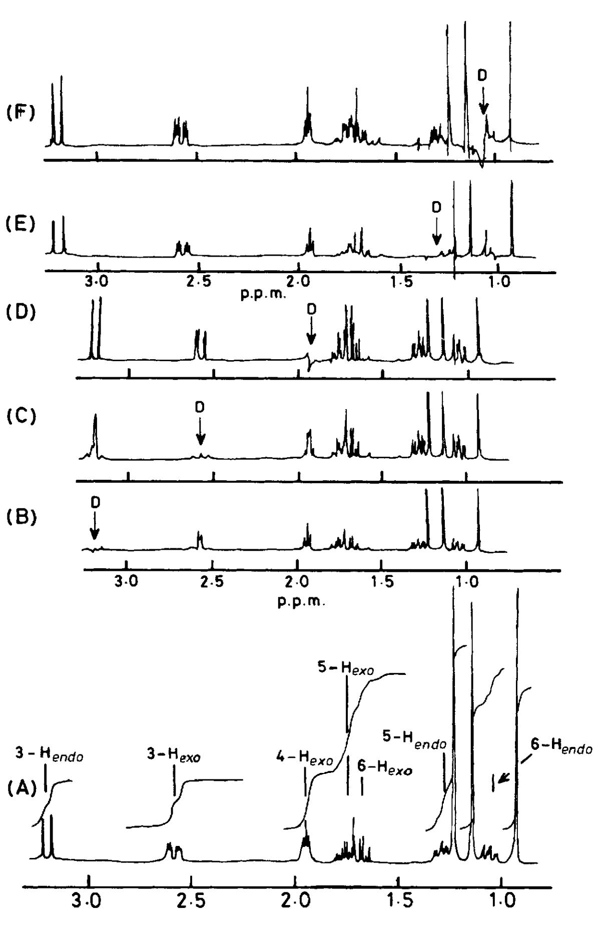
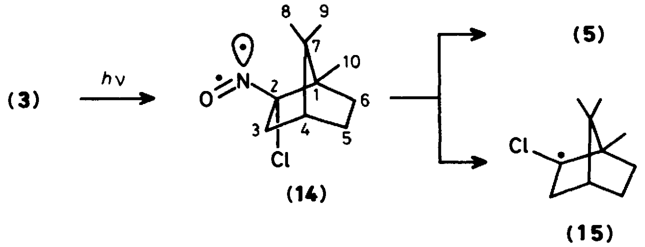
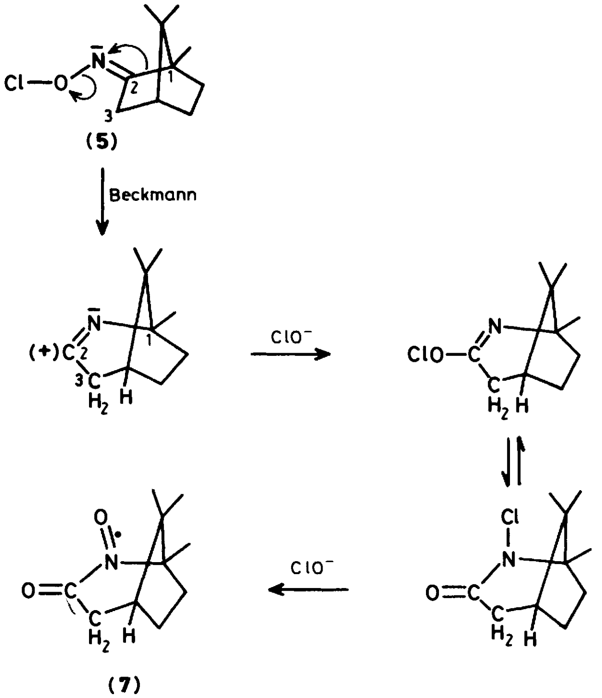


Figure 6. The 360 MHz ^{1}H n.m.r. spectrum of 2-chloro-2-nitrocamphane (**12**): (A) in CDCl$_3$; the effects of double irradiation at the 3-H$_{endo}$ (B), 3-H$_{exo}$ (C), 4-H$_{exo}$ (D), 5-H$_{endo}$ (E), and 6-H$_{endo}$ (F) resonance frequencies

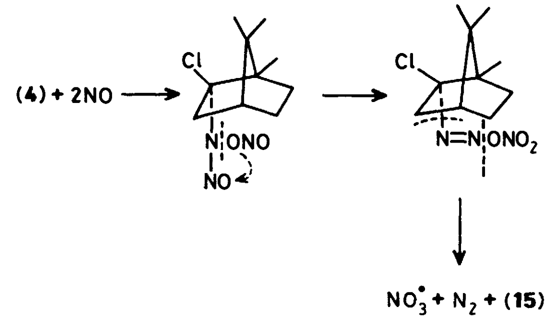
Solid-state Photolysis Reaction Mechanisms.—All the information obtained from the solution Cotton-effect studies,[1–3] and from the analyses of the paramagnetic and diamagnetic products obtained from the irradiated solid, can now be pieced together to construct mechanisms for the photochemical reactions that take place when solid (−)-2-chloro-2-nitrosocamphane is irradiated with red light. The sequence of reactions is summarized in Schemes 2—8. In Scheme 2 irradiating the nitroso group in (3) with red light causes an $\pi^* \longleftarrow n$ transition and the intermediate biradical (**14**) is formed. This either rearranges, as in Davidson's Scheme 1, to the chloro oxime (**5**), or undergoes homolysis of its C(2)–N bond to give a radical intermediate (**15**) and nitric oxide. Formation of (**5**), rather than (**15**), strongly predominates at this stage, and the chloro oxime (**5**) can then undergo reversible rearrangement back to the original (−)-2-chloro-2-nitrosocamphane (**3**) or its (+)-isomer (**4**).



Scheme 2.



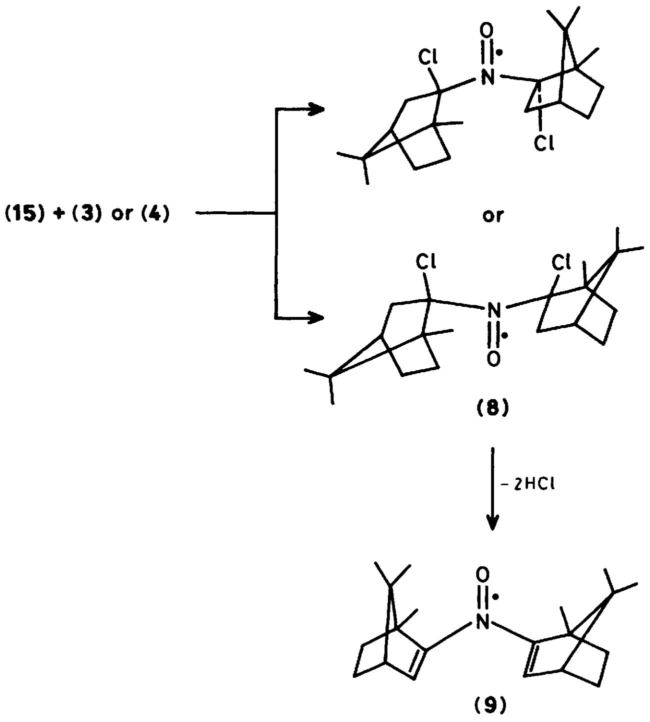
Scheme 3.



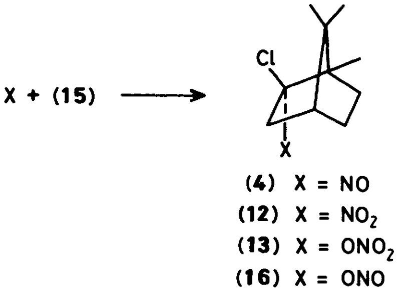
Scheme 4.

$$NO + NO_3^{\bullet} \rightleftharpoons 2NO_2$$

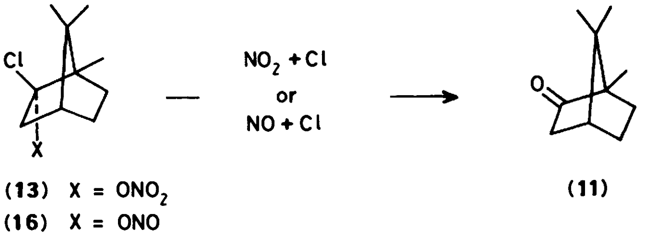
Scheme 5.



Scheme 6.



Scheme 7.



Scheme 8.

The chloro oxime (**5**), and possibly also the photochemically excited intermediate (**14**), can also undergo Beckmann-like rearrangement as shown in Scheme 3, the reaction, in the case of

(**5**), being triggered by the inductive effect of the chlorine atom. Molecular models show that the Cl–O residue in (**5**) is in the *anti*-position relative to C(1), and rearrangement essentially as in Scheme 3, followed by oxidation with hypochlorite ion, or with $ClO^{\bullet}$ radical, produces the required acylnitroxide radical (**7**). Although the scheme is speculative it should be noted that the radical (**7**) has also been obtained by de Boer *et al.* by oxidation of the corresponding hydroxamic acid formed in similar Beckmann-like rearrangements that take place when (**3**) reacts with aluminium chloride, or with Me_2AlCl or Me_3Al.[23,24] Schemes 1—3 require the presence of the chloro oxime (**5**) and they explain why photomutarotation and formation of the acylnitroxide radical (**7**) take place almost simultaneously, and in the early stages of the red irradiation.[2,3] In these early stages, epimerisation at C(2) and the formation of (**7**) appear to take place without disruption of the crystal structure, and the intense e.p.r. signals obtained from (**7**), even after only a few minutes of red irradiation of the parent material, imply a highly efficient C(2)–Cl cleavage in Scheme 2 to give (**5**), thereby substantiating Davidson's high quantum efficiency measurement.[3] The intense e.p.r. signals also imply that Scheme 3 involves a series of rapid and efficient reactions.

The radicals (**8**) and (**9**) are not observed until much later on in the irradiation when the crystal structure is starting to show signs of breaking down, and we therefore believe that they are formed by subsequent red irradiation of the mutarotated product (+)-2-chloro-2-nitrosocamphane (**4**) formed in Scheme 1. $\pi^* \longleftarrow n$ Excitation of (**4**) causes homolysis of its C(2)–N bond, forming more of radical (**15**) and nitric oxide, which then reacts with neighbouring molecules of the parent nitroso compounds, providing a third source of the radical (**15**), an $NO_3^{\bullet}$ radical, and nitrogen as shown in Scheme 4.[25–29] The radical (**15**) is scavenged by neighbouring parent 2-chloro-2-nitrosocamphane molecules in the solid to give the radicals (**8**) and (**9**), which are therefore assigned to the structures shown in Scheme 6. The radical (**15**) is also scavenged by $NO_3^{\bullet}$ or NO_2 radicals, in the sterically less-hindered *endo*-position to give the 2-chloro-2-nitro- (**12**), 2-chloro-2-nitrato- (**13**), and 2-chloro-2-nitrito (**16**) derivatives of camphane shown in Scheme 7.

The large amount of camphor (**11**) can be accounted for if compounds (**13**) and (**16**) are unstable and decompose with loss of $ClNO_2$ or ClNO as in Scheme 8. The smaller amount of camphor oxime (**10**) detected in the red photolysis reaction may come directly from the geometrically similar chloro oxime (**5**), or from the photoexcited intermediate (**14**), when the photolysis has built up to produce a reasonable concentration of hydrogen atoms *via* the reactions shown in Scheme 6.

Experimental

(–)-2-*Chloro*-2-*nitrosocamphane*.—Camphor oxime (10 g), prepared as described by Davidson,[3] in anhydrous diethyl ether (500 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 of ether were removed by passing dry nitrogen through the mixture, the blue solid was extracted into the minimum volume of light petroleum (b.p. 40—60 °C), and the unchanged oxime hydrochloride was filtered off. An ethanolic solution of the blue solid was then quickly passed through a column ($15 \times \frac{1}{2}$ in) of acid alumina (activity grade 1), using ethanol as eluant, to give a product which on concentration and recrystallization from ethanol gave pure (–)-2-*chloro*-2-*nitrosocamphane* (**3**) (Found: C, 59.6; H, 7.8; Cl, 17.8; N, 6.4. $C_{10}H_{16}ClNO$ requires C, 59.6; H, 7.9, Cl, 17.6; N, 6.9%); m.p. 145—146 °C; yield 10%; ^1H and ^{13}C n.m.r. data in Table 1; $\nu_{max.}$(KBr) 2 960, 2 880 (CMe_2, CMe, CH_2), 1 580 (N=O), 1 390, 1 380, 1 190, 1 140, 1 055, 870 (CMe_2, CMe), 1 455, 750 (CH_2), 1 310 ($\geqslant$C–H), 810 (C–N), and 760 cm^{-1} (C–Cl); *m*/*z* 171, 166, 152, 135, 127, 124, 109, 108, 95, 93, 81, 79, 69, 67, and 55 [the parent peak for $C_{10}H_{16}ClNO$ was not observed since the NO group is cleaved inside the mass spectrometer; the peak at 171 originates from an ion of the 'master radical' (**15**)].

(–)-2-*Chloro*-2-[^{15}N]*nitrosocamphane*.—This compound was similarly prepared from camphor [^{15}N]oxime, obtained by allowing [^{15}N]hydroxylamine hydrochloride (Amersham International; 98.8% ^{15}N) to react with natural camphor.

Photolysis of (–)-2-*Chloro*-2-*nitrosocamphane* (**3**) *with Red Light*.—A pure sample of solid (**3**) was placed in a glass tube 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. The components were separated by preparative t.l.c. on 20 × 20 cm silica plates, using ether–light petroleum (1:1, v/v) as eluant, into five main bands at R_F 0, 0.40, 0.52, 0.60, and 0.65.

The component at R_F 0 (15%) is an oil which we have not been able to separate further.

The component at R_F 0.40 (15%) forms clear needles when recrystallized from ethanol. Elemental analysis and ^1H and ^{13}C n.m.r., i.r., and mass spectra showed it to be *camphor oxime* (**10**), in which the OH group is *syn* to C-3 (Found: C, 71.8; H, 10.3; N, 8.5. $C_{10}H_{17}NO$ requires C, 71.8; H, 10.2; N, 8.4%); m.p. 118—119 °C; $\delta_H(CDCl_3)$ 9.23 (1 H, s, OH), 2.55 (1 H, m, 3-H_{exo}), 1.98 (1 H, d, 3-H_{endo}), 0.72 (3 H, s, 8-H_3), 0.84 (3 H, s, 9-H_3), and 0.95 (3 H, s, 10-H_3): *J* (3-H_{exo}, 3-H_{endo}) 18, *J* (3-H_{exo}, 4-H_{exo}) 4.3, *J* (3-H_{exo}, 5-H_{exo}) 2.3 Hz; ^{13}C–{^1H} decoupled spectrum $\delta_C(CDCl_3)$ 51.65 (s, C-1), 169.25 (s, C-2), 33.08 (t, C-3), 43.64 (d, C-4), 27.23 (t, C-5), 32.58 (t, C-6), 48.17 (s, C-7), 19.42 (q, C-8), 18.51 (q, C-9), and 11.06 p.p.m. (q, C-10); $\nu_{max.}$(KBr) 3 300 (OH), 2 960, 2 885 (CMe_2, CMe, CH_2), 1 688 (C=N), 1 390, 1 370, 1 275, 1 200, 1 080, 830 (CMe_2, CMe), 925 (=N–O–), 1 440, 725 (CH_2), and 1 325 cm^{-1} ($\geqslant$CH); *m*/*z* 167, 152, 134, 124, 109, 108, 93, 91, 83, 79, 77, 67, and 65.

The component at R_F 0.52 (40%) forms white crystals when recrystallized from ethanol. Elemental analysis and ^1H and ^{13}C n.m.r., i.r., and mass spectra showed it to be camphor; m.p. 176—177 °C.

The component at R_F 0.60 (15%) on recrystallizing from ethanol yields white crystals. Elemental analysis and ^1H and ^{13}C n.m.r., i.r., and mass spectra showed that this is the 2-*chloro*-2-*nitrocamphane* (**12**) (Found: C, 54.7; H, 7.0; Cl, 16.5; N, 6.4. $C_{10}H_{16}ClNO_2$ requires C, 55.2; H, 7.3; Cl, 16.3; N, 6.4%); m.p. 218—219 °C; ^1H and ^{13}C n.m.r. data are listed in Table 1; $\nu_{max.}$(KBr) 2 980, 2 885 (CMe_2, CMe, CH_2), 1 550, 1 350, 693 (NO_2), 1 397, 1 383, 1 194, 1 143, 1 052, 880 (CMe_2, CMe), 1 460, 720 (CH_2), 1 312 ($\geqslant$C–H), 820 (>C–N), and 765 cm^{-1} (C–Cl); *m*/*z* 171, 135, 134, 115, 108, 107, 95, 94, 93, 91, 81, 79, 77, 69, 67, 53, 41, 32, and 28.

The band at R_F 0.65 was removed from the t.l.c. plate by extracting with chloroform and then removing the solvent. Its ^1H n.m.r. and i.r. spectra showed that this component is the 2-*chloro*-2-*nitratocamphane* (**13**); $\delta_H(CDCl_3)$ 3.25 (1 H, d, 3-H_{endo}), 2.58 (1 H, m, 3-H_{exo}), 1.15 (3 H, s, 8-H_3), 0.93 (3 H, s, 9-H_3), 1.25 (3 H, s, 10-H_3); *J* (3-H_{exo}, 3-H_{endo}) 15.9, *J* (3-H_{exo}, 4-H_{exo}) 4.8, *J* (3-H_{exo}, 5-H_{exo}) 4.8 Hz; $\nu_{max.}$(KBr) 2 963, 2 930, 2 860 (CMe_2, CMe, CH_2), 1 600, 1 265, 870 (ONO_2), 1 015 (C–O), 1 370, 1 100 (CMe_2, $\geqslant$CMe), and 760 cm^{-1} (C–Cl).

Acknowledgements

We thank the University of Basrah for a study-leave scholarship (to N. N. M.), the S.E.R.C. for magnetic resonance facilities, and Dr. A. H. H. Al-Mowali for discussions.

References

1 S. Mitchell, J. S. Watson, and W. Dunlop, *J. Chem. Soc.*, 1950, 3440.

2 A. J. N. Hope and S. Mitchell, *J. Chem. Soc.*, 1953, 3483.

3 J. S. Davidson, Ph.D. Thesis, University of Glasgow, 1958, p. 50.

4 N. N. Majeed and A. L. Porte, *J. Chem. Soc.*, *Perkin Trans. 2*, 1987, 1139.

5 G. Ferguson, C. J. Fritchie, J. M. Robertson, and G. A. Sim, *J. Chem. Soc.*, 1961, 1976.

6 J. E. Anderson and W. P. Slichter, *J. Chem. Phys.*, 1964, **41**, 1922.

7 J. A. Medina, W. F. Sherman, A. A. Stadmuller, and G. R. Wilkinson, *Spectrochim. Acta*, *Part A*, 1982, **38**, 483.

8 C. A. Fyfe, 'Solid State N.M.R. for Chemists,' C.F.C. Press, Guelph, Ontario, 1983, p. 480 and references therein.

9 H. G. Aurich and F. Baer, *Tetrahedron Lett.*, 1965, 3879.

10 D. F. Minor, W. A. Waters, and J. V. Ramsbottom, *J. Chem. Soc. B*, 1967, 180.

11 A. Mackor, Th. A. J. W. Wajer, and Th. J. de Boer, *Tetrahedron*, 1968, **24**, 1623.

12 A. Caragheorgheopol, H. Caldararu, T. Constantinescu, and V. Em. Sahini, *J. Am. Chem. Soc.*, 1971, **93**, 6766.

13 C. M. Camaggi, R. J. Holman, and M. J. Perkins, *J. Chem. Soc.*, *Perkin Trans. 2*, 1972, 501.

14 M. J. Perkins and B. P. Roberts, *J. Chem. Soc.*, *Perkin Trans. 2*, 1974, 297.

15 P. F. Alewood, S. A. Hussain, T. C. Jenkins, M. J. Perkins, A. H. Sharma, N. P. Y. Siew, and P. Ward, *J. Chem. Soc.*, *Perkin Trans. 1*, 1978, 1066.

16 A. R. Forrester, Landolt-Börnstein Vol. 9, 'Magnetic Properties of Free Radicals, Part C1: Nitroxide Radicals,' Springer Verlag, Berlin, 1979, pp. 192–1066.

17 H. G. Aurich, K. Hahn, K. Stork, and W. Weiss, *Tetrahedron*, 1977, **33**, 969.

18 H. G. Aurich, I. Lotz, and W. Weiss, *Tetrahedron*, 1978, **34**, 879.

19 H. G. Aurich, K. Hahn, and K. Stork, *Chem. Ber.*, 1979, **112**, 2776.

20 H. G. Aurich and H. Czepluch, *Tetrahedron*, 1980, **36**, 3543.

21 H. G. Aurich, 'The Chemistry of Amino, Nitroso, and Nitro Compounds and their Derivatives,' ed. S. Patai, Interscience, New York, 1982, vol. 1, p. 565.

22 G. E. Hawkes, K. Herwig, and J. D. Roberts, *J. Org. Chem.*, 1974, **39**, 1017.

23 J. Lub and Th. J. de Boer, *Recl. Trav. Chim. Pays-Bas*, 1984, **103**, 328.

24 J. Lub, M. L. Beekes, and Th. J. de Boer, *Recl. Trav. Chim. Pays-Bas*, 1986, **105**, 22.

25 A. H. M. Kayen, L. R. Subramanian, and Th. J. de Boer, *Recl. Trav. Chim. Pays-Bas*, 1971, **90**, 866.

26 B. G. Gowenlock, J. Pfab, and G. Kresze, *J. Chem. Soc.*, *Perkin Trans. 2*, 1974, 511.

27 D. Forrest, B. G. Gowenlock, and J. Pfab, *J. Chem. Soc.*, *Perkin Trans. 2*, 1979, 576.

28 D. K. MacAlpine, A. L. Porte, and G. A. Sim, *J. Chem. Soc.*, *Perkin Trans. 1*, 1981, 2533.

29 A. A. Freer, D. K. MacAlpine, J. A. Peacock, and A. L. Porte, *J. Chem. Soc.*, *Perkin Trans. 2*, 1985, 971.

Received 28*th August* 1987; *Paper* 7/1586