Rearrangements involving a *C*-Nitroso Group: Formation of Dialkylhydroxylamines and Nitroxides

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Photoaddition of a nitrosamine to α-pinene and 5-methylenebicyclo[2.2.1]heptene in acidified methanol solution gave the tertiary nitrosoalkanes derived from 1,2-addition across the double bonds in the latter case and from addition involving cyclobutane ring opening in the former case. Under the reaction conditions, these tertiary nitrosoalkanes underwent a rearrangement involving the *C*-nitroso-group and a labile pair of proximate π or σ electrons to form bridged bicyclic hydroxylamines. These hydroxylamines are easily oxidized by air to the corresponding nitroxide radicals; one of them is stable enough to be purified. Using bromotrichloromethane as solvent, the intermediate carbon radical in the photoaddition to 5-methylenebicyclo[2.2.1]heptene can be trapped to give a good yield of bromotricyclane derivatives.

THE chemistry of *C*-nitroso-compounds is well known and has been summarized in several reviews.[1-4] Among these reactions there is good evidence that a *C*-nitroso-function is a highly polarized group that provides a strongly electrophilic nitrogen centre such as in (1). Protonation of a *C*-nitroso-group has been proposed to generate a nitrenium cation intermediate[4] (2). Reactions with a simple olefin, however, have only been discovered recently: the 'ene' type mechanism has been

[1] P. A. S. Smith, 'The Chemistry of Open-chain Organic Nitrogen Compounds,' Benjamin, New York, 1966, vol. 2, p. 355.

[2] (*a*) H. Boyer in 'The Chemistry of the Nitro and Nitroso Groups,' ed. H. Feuer, Interscience, New York, 1969, Part 1, p. 15; (*b*) H. A. Morrison, *ibid.*, p. 165.

[3] B. G. Gowenlock and W. Luttke, *Quart. Rev.*, 1958, **12**, 321.

[4] H. Metzger and H. Meier in 'Methoden der Organischen Chemie,' Thieme Verlag, Stuttgart, 1969, vol. 10–1, p. 891.

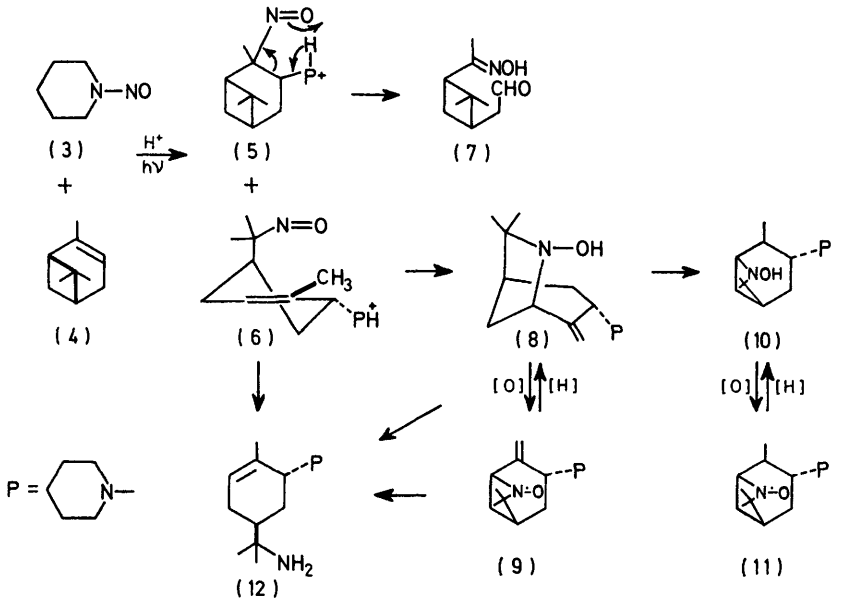
suggested for this reaction.[5] In this paper we report a skeletal rearrangement involving a labile π or σ electron attack on a *C*-nitroso-group.

$$[R-\ddot{N}=O \longleftrightarrow R-\overset{+}{N}-O^{-}] \xrightarrow{H^{+}} R-\overset{+}{N}-OH$$
(1) (2)

RESULTS

Photoaddition of *N*-nitrosopiperidine (3) to α-pinene (4) in acidified methanol solution gave *C*-nitroso-compounds (5) and (6) as the primary products as judged by the subsequent reaction patterns (Scheme 1).[6] *C*-Nitroso-compound (5) was formed from straightforward 1,2-addition and underwent the ammonium assisted cleavage reaction followed by other transformations to give biscarbonyl derivatives, such as (7). The formation of (6) involved scission of the cyclobutane ring following the attack of the piperidinium radical from the less hindered α-side of the pinene; the resulting *C*-nitroso-compound had to have the configuration as indicated in (6) which would have a great relevance to its subsequent reactions. The presence of (6) as an intermediate in the photoaddition was proven by reduction[6] of the crude product to give the corresponding amine (12) among others. Such a tertiary nitrosoalkane might undergo light-catalysed reactions, *e.g.*, homolytic dissociation [7-10] and/or HNO elimination to form olefin; [11] it is doubtful that substitution (*e.g.*, S_N1 or S_N2 type) reaction or elimination (*E*1 or *E*2 type) can occur to account for some of the products observed [6] in the photoaddition. The persistent blue colour of (6) disappeared quickly on termination of photolysis and a white crystalline product,[12] m.p. 135—136°, was isolated from the basic fraction of the photolysate.

The compound was obtained as crystals in a 20% yield if the photolysate was worked up quickly under conditions avoiding contact with the air. Prolonged purification of the substance increased the amount of a yellow oil caused by oxidation by air as also indicated by t.l.c. examinations of crude or purified products which always showed the presence of a faster moving compound. The n.m.r. spectra of the crystals was diffused but showed two olefinic protons and a broad six proton signal due to two methyl groups; the broadened n.m.r. spectra suggested the presence of a radical species in the solution. Prolonged exposure to the air or deliberate oxidation by air in a basic ethanol solution gave the second compound as yellow needles which exhibited an e.s.r. signal of doublet of triplets with *G* 2.006 4, a_N 14, and a_H 8 G. The e.s.r. data suggested the yellow needles were a nitroxide radical [7,8] and, therefore, the precursor must be a hydroxylamine. In agreement, the yellow substance was reduced by lithium aluminium hydride to give the white crystals which could be acetylated. In the n.m.r. spectra of the acetate, while the small coupling of the olefinic protons (*J* 2.3 Hz) at τ 5.18 and 5.21 indicated the presence of an exocyclic vinyl group, the i.r. absorption at 1 765 cm^{-1} corresponded to that of a hydroxylamine acetate group. These data and the subsequent reaction patterns led us to assign structure (8) to the hydroxylamine and (9) to the nitroxide radical.



SCHEME 1

Catalytic hydrogenation of nitroxide (9) or a mixture of (8) and (9) over platinum oxide gave the dihydro-derivative (10) which was readily oxidized by air to nitroxide (11) as shown by t.l.c. examination during work-up. Nitroxide (11) was a yellow oil possessing an e.s.r. signal pattern very similar to that of (9). Catalytic hydrogenation of a mixture of hydroxylamine (8) and nitroxide (9) over platinum oxide in an acidified methanol solution gave the *p*-menthene de-

[5] W. B. Motherwell and J. S. Roberts, *J.C.S. Chem. Comm.*, 1972, 329.

[6] H. H. Quon and Y. L. Chow, *Tetrahedron*, 1975, **31**, 2349.

[7] Th. A. J. W. Wajer, A. Mackor, Th. J. de Boer, and J. D. W. Van Voorst, *Tetrahedron*, 1967, **23**, 4021.

[8] A. Mackor, Th. A. J. W. Wajer, Th. J. de Boer, and J. D. W. Van Voorst, *Tetrahedron Letters*, 1966, 2115; *Tetrahedron*, 1968, **24**, 1623; A. Mackor, Th. A. J. W. Wajer, and Th. J. de Boer, *Tetrahedron Letters*, 1967, 2757.

[9] J. A. Massen, H. Hittenhausen, and Th. J. de Boer, *Tetrahedron Letters*, 1971, 3213.

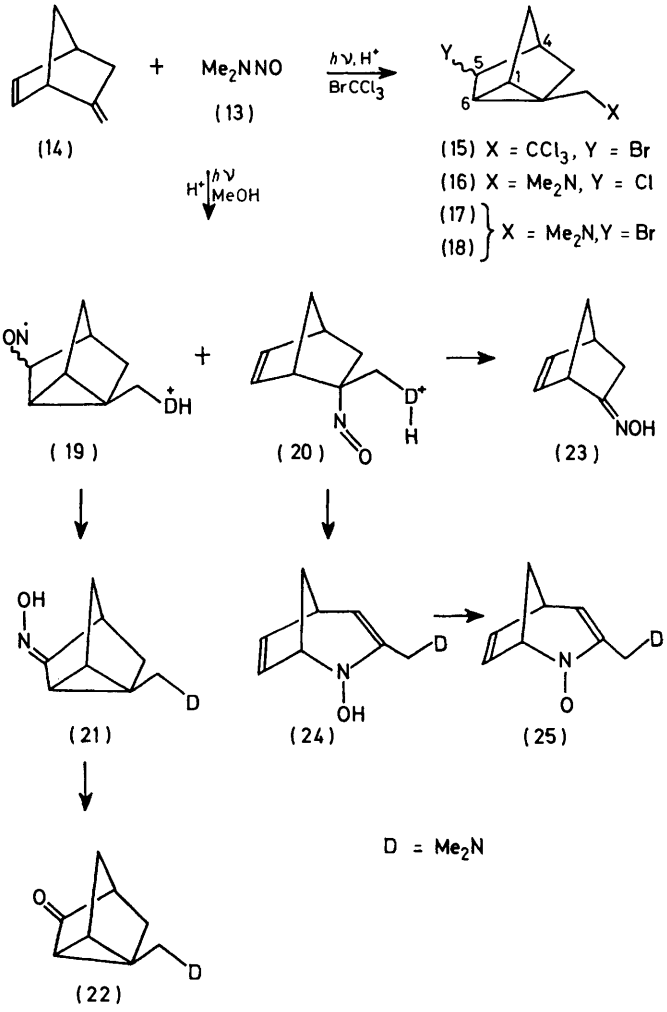
[10] Y. L. Chow, J. N. S. Tam, and K. S. Pillay, *Canad. J. Chem.*, 1973, **53**, 2477.

[11] K. Anderson, C. Crumpler, and D. Hammick, *J. Chem. Soc.*, 1935, 1679.

[12] This compound has been discussed in the preliminary communication, H. H. Quon, T. Tezuka, and Y. L. Chow, *J.C.S. Chem. Comm.*, 1974, 428.

rivative [6] (12). Hydrogenolysis of the C(1)–N bond was presumably facilitated by its allylic disposition to the exocyclic double bond.

Photoaddition of *N*-nitrosodimethylamine (13) to 5-methylenebicyclo[2.2.1]hept-2-ene (14) was first carried out in bromotrichloromethane * in the presence of hydrochloric acid [13] (Scheme 2). During the photolysis the absorption



SCHEME 2

due to trichloronitrosomethane at 315 nm steadily increased as the nitrosamino absorption at 345 nm decreased. Among the four compounds (15)—(18) obtained, trichlorobromo adduct (15) (3%) was a mixture of the *exo*- and *endo*-bromo-isomers and precipitated during the photolysis; dimethylaminochloro-adduct (16) was detected in g.l.c.–m.s. analysis as a very minor component. On the basis of the observed physical constants, structures (15) and (16) were tentatively assigned.

The two major products were dimethylamino-bromo-adducts (17) and (18) (57%) and were isomeric at C(5). Both i.r. and mass spectra of (17) and (18) were strikingly similar † showing the presence of one bromine atom, *m/e* 231 and 229 (M^+), and a cyclopropyl ring, 3 060, 830, and 800 cm^{-1}. Although the n.m.r. spectra of (17) and (18) revealed many structural details, they did not allow a clear distinction between the two configurations. The observed coupling constants $J_{4,5}$ and $J_{5,6}$ were nearly the same (*ca.* 1.5 Hz) for both compounds regardless of the *exo*- or *endo*-orientations of the bromo-group as in other reported cases.[15,16] In both cases, the cyclopropyl protons at C(1) and C(6) exhibited an AB quartet, each line of which was further split by the coupling with other protons.

When photoaddition of nitrosamine (13) to (14) was carried out in acidified methanol solution under nitrogen, the new absorption at 295 nm due to the dimer of a *C*-nitroso-compound steadily built up to a maximum then decreased gradually on further irradiation. On termination of irradiation at the maximum intensity of the 295 nm absorption and subsequent chromatographic separation, it gave a light blue oil (23%), 2-dimethylaminomethyltricyclo[2.2.1.$0^{2,6}$]-heptan-5-one oxime (21) (18%) and bicyclo[2.2.1]hept-5-en-2-one oxime (23) (*ca.* 4%); a small amount of ketone (22) corresponding to oxime (21) was also detected in chromatographic fractions (Scheme 2). The same photoaddition, when run until complete disappearance of the nitrosamino absorption at 342 nm, gave the same oil and (21) and (22) in 14, 15, and 10% respectively; oxime (23) was also detected in the chromatographic fraction of the basic material.

Crystalline oxime (21) exhibited typical i.r. absorptions for a cyclopropyl ring (880, 860, and 840 cm^{-1}) and a hydroxyimino-group (920 cm^{-1}). For this single oxime, the geometrical isomerism as shown in (21) was assigned on the basis of the chemical shift of 4-H [17] at τ 6.84. Hydrolysis of a crude chromatographic fraction of oxime (21) gave ketone (22). Oxime (23)‡ could not be extracted into an organic solvent from an aqueous solution and appeared to be fairly soluble in water. The compound could not be obtained in a pure state but the structure was suggested on the basis of the n.m.r. signal at τ 4.02 and the hydroxyimino-absorptions at 1 000 and 940 cm^{-1}.

The light blue oily fraction obtained immediately after chromatographic separation exhibited the u.v. absorption at 292 nm typical for the dimer of a *C*-nitroso-compound in addition to the 242 nm absorption. The i.r. spectra exhibited strong absorptions at 1 265 and 1 100 cm^{-1}, also typical for this type of dimer.[19] While the blue colour persisted when kept in a freezing compartment, it disappeared on standing at room temperature or on attempted distillation, giving an oil which displayed a u.v. absorption at 242 nm. This oil remained unchanged for several months in a freezing compartment or on brief treatment with 1N-HCl solution at room temperature. However on heating the acidic solution of the oil it turned into a black tarry mixture. The oil was identified as *N*-hydroxy-3-dimethylaminomethyl-2-azabicyclo[3.2.1]octa-3,6-diene (24).

The ^1H n.m.r. spectra of hydroxylamine (24) showed the presence of $\Delta^{6,7}$-olefinic proton signals at the expected position (τ 3.95 and 4.21) as well as the 4-H signal at a considerably

* An application of bromotrichloromethane as a radical trap in this photoaddition has been described.[13]

† I.r. and mass spectra for (17) and (18) are recorded in ref. 14.

‡ This compound has been reported but no details are given.[18]

[13] R. A. Perry, Ph.D. Thesis, Simon Fraser University, 1975.

[14] K. S. Pillay, Ph.D. Thesis, Simon Fraser University, 1975.

[15] R. S. Neale and E. Whipple, *J. Amer. Chem. Soc.*, 1964, **86**, 3130.

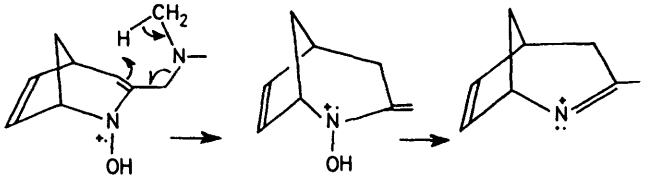
[16] W. H. Urry, Z. F. L. Gaibel, J. C. Dugan, and S. S. Tseng, *J. Amer. Chem. Soc.*, 1973, **95**, 4338.

[17] K. S. Pillay, S. C. Chen, T. Mojelsky and Y. L. Chow, *Canad. J. Chem.*, 1975, **53**, 3014.

[18] S. Ranganathan, D. Ranganathan, and A. K. Mehotra, *J. Amer. Chem. Soc.*, 1974, **96**, 5261.

[19] C. N. R. Rao and K. R. Bhaskar, in ref. 2, p. 137.

high field (τ 5.15) in agreement with a β-proton of an enamine system.[20] The CH_2N signal was shifted downfield by 0.6 p.p.m. relative to the normally observed chemical shift indicating that the methylene group was also attached to a double bond.[20] The presence of the enamine system is further substantiated by the ^{13}C n.m.r. spectrum which was obtained by off-centre resonance decoupling experiments. The olefinic C-3 signal shifted downfield to 169.8 p.p.m. (from Me_4Si) while the C-4 signal appeared at considerably higher field at 83.7 p.p.m. in accord with the expected ^{13}C chemical shifts for an enamine system.[21] The mass spectra exhibited intense peaks at *m/e* 137 and 120 which were confirmed to be those for $C_8H_{11}NO^{+\cdot}$ and $C_8H_{10}N^{+\cdot}$ fragments by high resolution technique; a fragmentation pattern is proposed in Scheme 3.



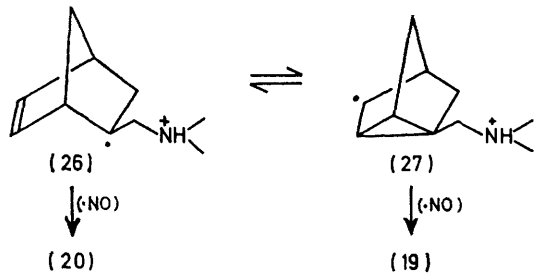
SCHEME 3

Further confirmation of the structure was derived from the observation that the hydroxylamine (24) turns to a brownish solid on storage at room temperature. This solid showed an e.s.r. signal at *g* 2.006 7 (triplet of equal intensity) with a_N 14.25 G (linewidth *ca.* 4.5 G) typical for a nitroxide.[7,8] Prolonged storage turned the solid into a dark tar but the e.s.r. signal could be observed even after one year: nitroxide (25) could not be isolated pure.

DISCUSSION

The results touch upon two major aspects associated with photochemical addition of nitrosamines to olefins. The first aspect is an aminium radical-initiated radical addition to a carbon–carbon double bond,[22] which may also involve skeletal rearrangements [6] and is terminated by the formation of *C*-nitroso-compounds (5), (6), (19), and (20). The second aspect is subsequent reactions of these *C*-nitroso-compounds which exhibit characteristics of an ionic pathway and might involve a deep-seated rearrangement.

We have reported the cyclobutane ring scission during the piperidinium radical-initiated addition to α-pinene (4) wherein the long-lived transient, *C*-nitroso-compound (6) is obtained.[6] This ring-scission pathway progressively increases as the photolysis temperature is raised from −40° to the room temperature as indicated by the successive decreases in the unrearranged 1,2-addition product (5) which has been obtained as the cleavage products. In the photoaddition of *N*-nitrosodimethylamine (13) to (14), the initial attack of the bulky dimethylaminium radical at the least substituted carbon of the exocyclic double bond [see (26)] is expected to be followed by the ready ring closure to generate new carbon-radical



SCHEME 4

(27) by analogy with a number of radical additions [23-25] to (14). Steric crowding appears to severely hinder the approach of the dimethylaminium radical to the endocyclic double bond.[25] The transformations of the two carbon radicals (26) and (27) are probably reversible since cyclopropylcarbinyl–homoallyl radical rearrangement is known,[26,27] although the rates of the two processes may differ considerably. The yields of *C*-nitroso-compounds (19) and (20) are dependent on the rates of competing processes among the reversible ring closure [(26) ⟶ (27)] and nitrosyl group scavenging steps as in Scheme 4. The configuration of *C*-nitroso-compound (19) cannot be proven but the *endo*-approach of a nitroso group (or its donor) is expected to be favoured on steric grounds.

The same photolysis in bromotrichloromethane, instead of in methanol, is instructive in substantiating that the photoaddition is indeed a radical process in which the solvent acts as a radical scavenger.[23,24,28,29] The product pattern (15)—(18) indicates that both the aminium radical as well as the trichloromethyl radical are chain carrying species that result in formation of trichloronitrosomethane as a by-product. Since side products other than (17) and (18) are only a small amount, as detected by g.l.c. and t.l.c., the attacks of both chain carriers appear to be fairly specific as shown in Scheme 5. Pre-

$$MeNH^{+\cdot} + R_2C{=}CR_2 \longrightarrow Me_2\overset{+}{N}HCR_2\dot{C}R_2$$
$$Me_2\overset{+}{N}HCR_2\dot{C}R_2 + CBrCl_3 \longrightarrow Me_2\overset{+}{N}HCR_2CR_2Br + \cdot CCl_3$$
$$\cdot CCl_3 + Me_2NNO + H^+ \longrightarrow Cl_3CNO + Me_2NH^{+\cdot}$$

SCHEME 5

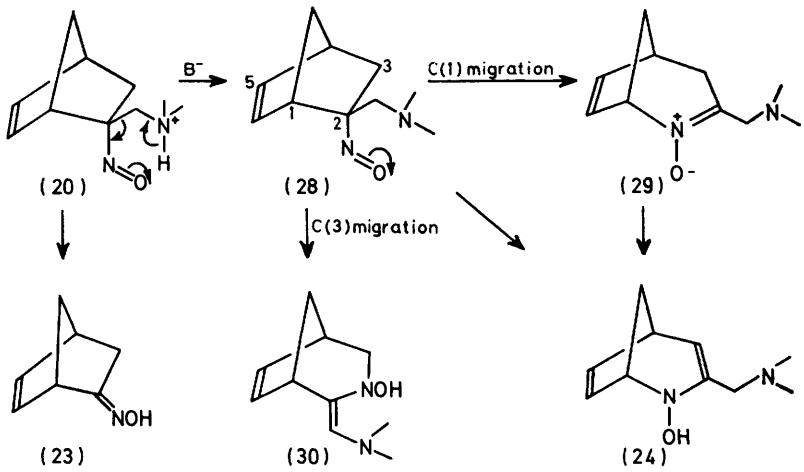
dominant formation of the cyclopropyl derivatives indicates that the rate of the chain transfer process from trichlorobromomethane to (26) is slower than the rate of the cyclization process (26) ⟶ (27) as is true with radical addition of bromotrichloromethane to (14).[23,24,28,29]

Both tertiary nitrosoalkanes (6) and (20) should possess, in theory, a relatively long life-time. For (6), since the

[20] P. Laszlo and P. J. Stang, ' Organic Spectroscopy,' Harper and Row, New York, 1971, p. 65.
[21] G. C. Levy and G. L. Nelson, ' Carbon-13 NMR for Organic Chemists,' Wiley–Interscience, New York, 1972.
[22] Y. L. Chow, *Accounts Chem. Res.*, 1973, **6**, 354.
[23] E. S. Huyser and G. Echegaray, *J. Org. Chem.*, 1962, **27**, 429.
[24] M. C. Lasna and A. Thuillier, *Compt. rend.*, 1971, vol. 273, p. 1258.
[25] S. J. Cristol, T. W. Russel, and D. I. Davies, *J. Org. Chem.*, 1965, **30**, 207.
[26] D. I. Davies, J. N. Done, and D. H. Hey, *Chem. Comm.*, 1966, 725.
[27] C. R. Warner, R. J. Strunk, and H. G. Kuivila, *J. Org. Chem.*, 1966, **31**, 3381.
[28] N. O. Brace, *J. Org. Chem.*, 1962, **27**, 3027.
[29] D. I. Davies and L. T. Parfitt, *J. Chem. Soc.* (*C*), 1967, 2691.

steric constraints of the bulky piperidine group will preferentially place the nitrosodimethylcarbinyl side chain in the axial orientation, the electrophilic nitroso-group can be located right above the π-electron cloud of the double bond. This electrophilic interaction might be accompanied by a proton migration from the allylic methyl to the nitroso oxygen atom to form hydroxylamine by a mechanism similar to an 'ene' reaction.[30] It is pertinent to add that the similar *C*-nitroso-compound obtained during photoaddition of (3) to β-pinene [6] cannot bring the electrophilic nitroso-group to within the striking distance of the π-electron cloud, owing to preferential equatorial orientation of the nitrosodimethylcarbinyl side chain. As a result, a similar hydroxylamine corresponding to (8) is not obtained in photoaddition to β-pinene.

In an acid solution, *tertiary* *C*-nitroso-compound (20) is expected to undergo the cleavage pathway *via* the cyclic transition state to give oxime (23) (Scheme 6) in analogy to the cleavage reaction observed during a similar photoaddition to camphene and norbornene.[17,31] While the extent of this cleavage reaction cannot be judged, this pathway obviously can be halted by making the photolysate basic as soon as the photolysis is over since the cleavage occurs only [17] from the protonated species (20). The observed clean rearrangement of the unprotonated species (28) to (24) provides further support for the requirement of protonation in the reaction (20) ⟶ (23).



SCHEME 6

In principle, two ring expansion pathways of (28) (Scheme 6) are possible involving either the σ-electrons of C(1)–(C2) or those of C(3)–C(2) to shift into the electron deficient centre of the nitroso-group. The formation of hydroxylamine (24), and lack of that of (30), indicates that the former allylic σ-electron's shift is favoured over that of the latter. The electron shifts may be followed by the prototropy to hydroxylamine (24) or reorganization of the electron distribution to form nitrone (29). Whether nitrone (29) is a significant intermediate during this skeletal rearrangement (28) ⟶ (24) and, also, in the subsequent oxidation of hydroxylamine (24) to (25) is unclear at this stage. However it is pertinent to point out that as far as we are aware no nitrone–enehydroxylamine tautomerization has ever been recorded.[32]

Oxidation by air of hydroxylamines to nitroxides is a known reaction.[33-36] Some bridged bicyclic nitroxides have been known to be fairly persistent radicals.[36] The isotropic *g* factors as well as isotropic hyperfine coupling constants for (9), (11), and (25) are in good agreement with those of bicyclic nitroxides reported.[36] Decomposition of these nitroxides appears to be complex and has not been traced to a particular reaction; some reactions of bridged bicyclic nitroxide have been reported recently.[36,37]

EXPERIMENTAL

General Conditions.—Unless specified otherwise the following conditions prevailed. N.m.r. spectra were measured with a Varian A-56/60 or an XL-100 (with or without a Fourier transform attachment) spectrometer in $CDCl_3$ and were expressed in τ values. Other instruments included Hitachi–Perkin-Elmer model RMU-6E, Cary 14, Varian E-4, and Perkin-Elmer 457 spectrophotometers and a Varian 1200 g.l.c. apparatus with a flame ionization detector. The g.l.c.–m.s. measurements used Varian 1 400 (20% SE-30 column) coupled with the mass spectrometer. M.p.s were reported as determined with a Fisher-Johns hot stage or a Gallenkamp heating block. Elemental analyses were performed by Mr. M. K. Yang with a Perkin-Elmer microanalyser. α-Pinene and 5-methylenebicyclo[2.2.1]hept-2-ene (Aldrich) and *N*-nitrosodimethylamine (NND) and *N*-nitrosopiperidine

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[33] F. Klages, R. Heinle, H. Sitz, and E. Specht, *Chem. Ber.*, 1963, **96**, 2387.
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[37] J. A. Cella, J. A. Kelley, and E. F. Kenehan, *Tetrahedron Letters*, 1975, 2869.

(NNP) (Eastman Kodak) were distilled before use and stored in a refrigerator.

Preparation and Reaction of 7-Hydroxy-6,6-dimethyl-2-methylene-3-piperidin-1-yl-7-azabicyclo[3.2.1]*octane* (8) *and the Nitroxide* (9).—Typical conditions for preparation of hydroxylamine (8) and nitroxide (9) are as follows. A solution containing NNP (3.47 g), α-pinene (6.51 g), concentrated hydrochloric acid (4 ml), and methanol (320 ml) was irradiated with a Hanovia medium pressure mercury lamp through a Pyrex filter under nitrogen for 3 h. During irradiation, the solution was cooled externally with an ice–salt bath and exhibited a blue colour which disappeared slowly. The solution was quickly neutralized with a saturated sodium carbonate solution and evaporated. The residue was diluted with water and extracted with light petroleum to afford an oil (7.02 g). A light petroleum solution of this fraction was cooled in dry ice–acetone to afford crystals, m.p. 125—132°, which were recrystallized from light petroleum inside a nitrogen filled chamber to give hydroxylamine (8),[6] m.p. 130—133°. If precautions were taken to minimize contact of the solutions and air, (8) can be obtained in 17—20% yield.

When the photolysate was worked up over a prolonged period without such precautions, a yellow solution was obtained from which (8) could not be crystallized directly from light petroleum. The oil (5 g) was chromatographed on a silicic acid column. Elution with chloroform gave unchanged NNP (200 mg). The next ten fractions were evaporated to give the oxime derived from the cleavage reaction [compound (12) of ref. 12]. Elution with 1% methanol in chloroform gave a light yellow oil which was sublimed twice to give nitroxide (9), m.p. 122—123°, $\nu_{max.}$ (Nujol) 3 100, 1 650, 1 310, 1 210, 1 170, 1 115, 1 045, 915, 895, and 865 cm^{-1}; *m/e* 249 (M^+), 234 (7%), 233 (11), 176 (38), 174 (50), 150 (100), 91 (25), and 84 (43); e.s.r., (CCl_4) *g* 2.0063, doublet of triplets, a_N 14, a_H 8 G; $\lambda_{max.}$ (MeOH) 275 and 420 nm (Found: C, 72.1; H, 10.25; N, 11.2. $C_{15}H_{25}N_2O$ requires C, 72.25; H, 10.25; N, 11.25%).

Crude hydroxylamine obtained from crystallization showed two spots on a t.l.c. plate, the faint spot at R_F 0.62 corresponding to nitroxide (9) and the strong spot at R_F 0.15 corresponding to hydroxylamine (8). When the t.l.c. solution was left exposed to the air, the former spot became stronger and the latter became weaker and eventually disappeared. This solution exhibited very strong e.s.r. signal for nitroxide (9). The oxidation process could be achieved by bubbling an air stream through an ethanol solution of hydroxylamine (8) (50 mg) containing 1 drop of 2N-NaOH solution. Upon the usual work-up, nitroxide (9) (35 mg) was obtained as yellow crystals. Both hydroxylamine (8) and nitroxide (9) were stable for several months when stored in an evacuated desiccator and for an even longer time if the desiccator is kept in a refrigerator.

To a nitroxide (9) (261 mg) solution in tetrahydrofuran (15 ml), a suspension of lithium aluminium hydride (271 mg) in tetrahydrofuran was added. The mixture was stirred for 15 h under nitrogen and then decomposed with water and extracted with ether. The ether solution was dried and evaporated to give hydroxylamine (8), m.p. 130—133°; the i.r. spectrum was superimposable on that of an authentic sample. The work-up operations were carried out in an isolated chamber under nitrogen except the evaporation step which was done with a rotary evaporator.

Hydroxylamine (8) (145 mg) obtained from the above reduction was acetylated in a mixture of pyridine (1 ml) and acetic anhydride (0.5 ml) overnight under a nitrogen atmosphere. The solution was worked up by the usual method and the crude product was chromatographed on a silicic acid column. The major fraction (120 mg) was further chromatographed on preparative t.l.c. (6 plates). Extraction of the major band with methylene chloride afforded an oil (88 mg) which was distilled at 90—100° and 0.01 mmHg to give a clear oil, $\nu_{max.}$ (neat) 3 095, 1 765, 1 645, 1 385, 1 365, and 910 cm^{-1}; τ 5.10br and 5.21br (each 1 H, 2 × t, *J* 2—3 Hz), 5.93 (1 H, d, *J* 2.5 Hz), 6.33 (1H, t, *J* 9.0 Hz, each line further split by small couplings), 8.02 (3 H, s), 8.67 (6 H, s).

A methanol (40 ml) solution of nitroxide (9) (98 mg) containing PtO_2 (10 mg) was agitated under a hydrogen pressure of 53 lb in^{-2}. The filtered solution was rapidly evaporated under a reduced pressure to give an oil which showed the major spot at R_F 0.18 and a very faint spot at R_F 0.65 on a silicic acid t.l.c. plate (10% MeOH–CH_2Cl_2). On leaving the t.l.c. solution in contact with the air, the high R_F spot rapidly increased in intensity as the lower R_F spot became weaker. The n.m.r. spectrum was diffused and showed a broad doublet at τ *ca.* 9.00 but no signal in the olefinic proton region (τ 3—6). On keeping overnight in a refrigerator, the oil showed the high R_F spot on a t.l.c. plate and in the e.s.r. spectrum (CCl_4) a double triplet a_N 14, a_H 8 G, *m/e* 251 (2%), 235 (5), 219 (3), 180 (7), 166 (7), 152 (9), 137 (13), 124 (20), 111 (31), 95 (33), and 58 (100), $\nu_{max.}$ 2 930, 1 450, 1 370, 1 230, 1 110, and 1 000 cm^{-1}.

Nitroxide (9) (800 mg) dissolved in methanol (40 ml) containing one drop of concentrated hydrochloric acid and Pt–C (125 mg) was hydrogenated at 53 lb in^{-2} pressure for 45 h. The solution was filtered and the crude product was separated to acidic (47 mg) and basic (493 mg) fraction. Alumina chromatography of the basic fraction gave amine (12) (380 mg) as an oil; the i.r., n.m.r., and mass spectra were superimposable with those of an authentic sample.[6]

Addition of NND to 5-Methylenebicyclo[2.2.1]*hept-2-ene.*—A solution of NND (3.55 g, 0.048 mol), 5-methylenebicyclo-[2.2.1]hept-2-ene (4.24 g, 0.04 mol), and concentrated hydrochloric acid (4.8 ml) in methanol (320 ml) was cooled to 0° and was irradiated with a 200 W Hanovia lamp through a Nonex filter under nitrogen. During the irradiation the u.v. absorption at 295 nm for a *C*-nitroso-dimer built up gradually and reached its maximum intensity after 5 h at which time the irradiation was stopped and sodium carbonate was added with stirring. The solution was evaporated at 10° under vacuum to 150 ml and was cooled. The precipitated inorganic salts were filtered. Evaporation of the solvent at 10° gave a dark brown oil (6.5 g), $\nu_{max.}$ 3 240br (s), 3 060 (m), 1 265 (s), 1 030 (s), and 930 (s) cm^{-1}; τ 3.40 (m, D_2O exch.), 3.73—4.32 (m), 4.83—5.35 (m), 6.88br (s), 7.67 (s), and 7.70 (s).

A portion of this residue (2.0 g) was chromatographed on a silicic acid column (60 g) and eluted with methylene chloride containing increasing amounts of methanol. Elution with 1% methanol in methylene chloride gave a bluish oil (400 mg) which exhibited u.v. absorptions at 207 nm (shoulder), 242 (ε 1 530) and 292 (ε 113) nm and the strong i.r. absorptions at 1 265, 1 100, 1 020, and 800 cm^{-1}; the oil was decolourized rapidly. Distillation of this fraction at 20° and 3.5 mmHg afforded *N-hydroxy-3-dimethylaminomethyl-2-azabicyclo*[3.2.1]*octa-3,6-diene* (24), $\lambda_{max.}$ (MeOH) 208 (shoulder) and 243 (ε 1 620); $\nu_{max.}$ ($CHCl_3$) 3 380, 3 060, 2 830, 2 785, 1 620, 1 268, 1 038, 1 018, 988, 930, 905, 845, 825, and 695 cm^{-1}; τ 3.95 (d of dt, *J* 5.6, 2.0 and 1.0 Hz), 4.21 (d of q, *J* 5.6 and 2.0 Hz), 5.15 (m, 4-H), 6.93 (2 H, s), 7.70 (6 H, s), and 7.0—8.12 (5 H, m); ^{13}C n.m.r. (p.p.m. from Me_4Si)

169.8(C-3), 136.3(C-7), 128.8(C-6), 83.7(C-4), 62.5(N-CH_2), 45.2(N-CH_3), 39.3(C-1), 35.5(C-8), and 26.4(C-5); *m/e* 180.1244 (M^+, 1%; calc. 180.1263), 163 (1), 138 (11), 137.0822 (100; calc. 137.0840), 120.0798 (62; calc. 120.0813), 79 (31), 58 (100), 44 (30), and 42 (33) (Found: C 66.75; H, 9.0; N, 15.45. $C_{10}H_{16}N_2O$ requires C, 66.65; H, 8.95; N, 15.55%).

Elution with 5% methanol in methylene chloride gave several fractions (100 mg) containing mostly (24) contaminated with a small amount of a compound with a lower R_F value. The major component present in the fraction (60 mg) eluted with 10% methanol in methylene chloride was tentatively assigned as bicyclo[2.2.1]hept-5-en-2-one oxime (23), $\nu_{max.}$ 3 240, 3 060, 1 650, 1 080, 1 035, 1 000, and 940 cm^{-1}; τ 4.02 (m).

Elution with 20—50% methanol in methylene chloride gave a mixture (325 mg) of 2-dimethylaminomethyltricyclo-[2.2.1.$0^{2,6}$]heptan-5-one (22) and the corresponding oxime (21). The remaining material (120 mg), eluted with 50—100% methanol in methylene chloride, was mainly one compound (by t.l.c.) which, after two sublimations, gave 2-dimethylaminomethyltricyclo[2.2.1.$0^{2,6}$]heptan-5-one oxime (21) as a crystalline solid, m.p. 67—68°; $\nu_{max.}$ 3 240, 2 820, 2 780, 1 265, 1 020, 1 040, 920, 880, 860, and 840 cm^{-1}; τ 1.85 (1 H, m, D_2O exch.), 6.84 (1 H, m), 7.38 (2 H, m), 7.55 (1 H, m), 7.77 (6 H, s), 7.78 (1 H, m), and 8.27 (4 H, m); *m/e* 180.126 6 (M^+, calc. for $C_{10}H_{16}N_2O$: 180.126 3; 23%), 163.123 3 (calc. for $C_{10}H_{15}N_2$: 163.123 5), 91 (25), 85 (21), 84.091 4 (calc. for $C_5H_{10}N$: 84.088 13; 100), and 58 (100).

A methanol solution (320 ml) of NND (3.552 g, 0.048 mol), (14) (4.24 g, 0.04 mol), and concentrated hydrochloric acid (4.8 ml) was irradiated as described above. After the competition of photolysis (5 h), the yellow photolysate was concentrated to a small volume under vacuum at 10°. The residual solution was diluted with water to *ca.* 100 ml and extracted with ether (4 × 50 ml) to give an oil (95 mg) which showed several spots on a t.l.c. plate.

The aqueous acidic solution was made basic (pH 9—10) with saturated sodium carbonate solution, extracted with methylene chloride (8 × 50 ml) and worked up in the usual manner to give a brown coloured oil (4.21 g), $\nu_{max.}$ 3 200br (m), 3 060 (m), 1 755 (s), 1 265 (s), 1 030 (s), 1 095 (m), 1 060 (m), and 840 (m) cm^{-1}; τ 3.95 (m), 4.22 (m), 5.18 (m), 6.93br (s), 7.75 (s), and 7.0—9.2 (m). Chromatography of this oil (2.0 g) on neutral alumina (60 g) and elution with methylene chloride afforded the azabicyclic compound (24) (218 mg). The fractions (505 mg) eluted with 1% methanol in methylene chloride consisted of a mixture of (24) and the tricyclic ketone (22) and were rechromatographed on silicic acid (12 g) to afford pure (24) (148 mg) on elution with methylene chloride. Subsequent elution from the silicic acid column with 2—10% methanol in methylene chloride gave an oil (118 mg) which was distilled at 20° and 0.2 mmHg to give (22) as an oil, $\nu_{max.}$ 3 020, 2 820, 2 770, 1 755, 1 030, 840, 830, and 820 cm^{-1}; τ (CCl_4) 7.48br (2 H, s), 7.80 (6 H, s), 8.15 (6 H, m), and 8.92 (d, *J* 5.5 Hz, 6-H).

The fractions eluted from the alumina column with 2% methanol in methylene chloride were mixtures (331 mg) of the oximes (21) and (23) containing various amounts of ketone (22). Elution with 5% methanol in methylene chloride and up to 100% methanol gave fractions of oxime (21) contaminated with small amounts of oxime (23) (390 mg). A portion (110 mg) of this mixture was refluxed with sodium hydrogen sulphite (258 mg) in ethanol–water (1 : 1; 5 ml) for 4 h. The solution was diluted with water, acidified with excess of 0.1N-hydrochloric acid (15 ml), and extracted with methylene chloride; no residue remained after evaporation of the solvent. The aqueous solution was made basic with sodium carbonate solution and was extracted with methylene chloride (4 × 30 ml). The residue (26 mg) obtained after work-up of the extracts was distilled at 20° and 0.2 mmHg to give tricyclic ketone (22) (identified by i.r. and n.m.r.).

A fraction (50 mg) containing (23) as the major component contaminated with (21) and (22) was taken up in 0.5N-hydrochloric acid solution (10 ml). This solution was extracted with ether (3 × 20 ml). The ether solution after usual work up left no material behind. The aqueous solution was made basic and was extracted with methylene chloride (3 × 20 ml). The extracts were worked up to give an oil (35 mg) which showed a much weaker olefinic signal with respect to others in the n.m.r. spectra. A pure sample of hydroxylamine (24) turned into a brownish semisolid on storage at room temperature for several weeks. This sample in methylene chloride solution showed the e.s.r. signal of an equal triplet, *g* 2.006 7, a_N 14.25 G (line width *ca.* 4.5 G) which could be detected after keeping the sample for a year in a refrigerator.

Addition of NND to 5-Methylenebicyclo[2.2.1]*hept-2-ene in Bromotrichloromethane.*—A solution of NND (1.776 g, 0.024 mol), (14), and concentrated hydrochloric acid (2.4 ml) in bromotrichloromethane (100 ml) was photolysed as described above. During the irradiation a new peak emerged at 315 nm. After 2 h, the absorption at 345 nm disappeared and the bluish green photolysate was evaporated under vacuum. The resulting precipitate was filtered and washed with ether to give a white solid (197 mg, 3%) which showed two spots on a t.l.c. plate, $\nu_{max.}$ 3 070, 1 235, 890, 805, 790, and 660 cm^{-1}; *m/e* 308 (M^+, 1%), 306 (M^+, 3), 304 (M^+, 5), 302 (M^+, 3), 227 (9), 225 (27), 223 (28), 189 (19), 187 (56), 185 (32), 143 (14), 141 (36), 127 (38), 109 (37), 105 (72), 91 (69), 79 (100), 77 (43), and 66 (76). Since the molecular peak indicated that the compounds might contain one bromine and three chlorine atoms they were tentatively assigned as the two stereoisomers of 2-(2,2,2-trichloroethyl)-5-bromotricyclo[2.2.1.$0^{2,6}$]-heptane (15).

The filtrate was added with water (50 ml) and was extracted with ether to give the neutral fraction (619 mg) which exhibited several spots on a t.l.c. plate. The aqueous solution was made basic (pH 9.5) with saturated sodium carbonate solution and extracted with methylene chloride to give an oil (2.64 g), $\nu_{max.}$ 2 820, 2 770, 1 220, 1 030, 800, 730, and 640 cm^{-1}; τ (CCl_4) 6.07 (m), 7.82 (s), and 7.87 (s.) Analysis of this oil by g.l.c.–m.s. (6 ft × 1/8 in; 20% SE-30; 120°; programmed at 10° min^{-1}) showed two major and one minor component. The first major g.l.c. peak appeared to be due to a monobromo-compound on the basis of its g.l.c.–m.s. pattern *m/e* 231 (M^+, 26%), 230 (29), 229 (26), 228 (25), 150 (81), 105 (42), 84 (100), 79 (43), and 58 (75). The second major peak in g.l.c. appeared to be an isomer of the first compound, *m/e* 231 (5%), 230 (5), 229 (5), 228 (4), 150 (77), 105 (37), 84 (100), and 58 (44). The minor peak observed in the g.l.c. contained one chlorine atom and was tentatively assigned as 2-dimethylaminomethyl-5-chlorotricyclo-[2.2.1.$0^{2,6}$]heptane (16) on the basis of its m.s. pattern, *m/e* 187 (M^+, 4%) 186 (5), 185 (M^+, 11), 150 (45), 105 (20), 84 (30), 79 (25), and 58 (100).

The basic fraction was chromatographed on basic alumina (260 g). Elution with 1% methanol in methylene chloride and distillation of the oil (355 mg) at 20° and 0.5

mmHg gave 2-dimethylaminomethyl-5-bromotricyclo-[2.2.1.$0^{2,6}$]heptane (17) or (18); $\nu_{max.}$ 3 060, 2 820, 2 775, 1 220, 1 150, 1 030, 880, 830, 800, and 730 cm^{-1}; τ (CCl_4) 6.06 (t, J 1.5 Hz, 5-H), 7.63br (2 H, s), 7.85 (6 H, s), 7.9 (2 H, m), 8.6 (3 H, m), 8.68 (part A of AB q, J_{AB} 5.5 Hz, $\Delta\nu_{AB}$ 11.0 Hz, each line further split, J 1.5 Hz, H-6), and 8.83 (part B of AB q, each line further split, J 1.5 Hz, H-1); *m/e* (20°) 231 (M^+, 11%), 230 (7), 229 (M^+, 11), 228 (6), 150 (83), 105 (41), 91 (24), 84 (100), 79 (46), and 58 (66) (Found: C, 52.65; H, 7.05; N, 6.4. Calc. for $C_{10}H_{15}BrN$: C, 52.4; H, 6.6; N, 6.1%).

Continued elution with 1% methanol in methylene chloride afforded an epimeric mixture (812 mg) of bromonortricyclenes (17) and (18) as shown by the NMe singlets at τ 7.8 and 7.75. Further elution with the same solvent gave an oil (145 mg) which was distilled at 20° and 0.5 mmHg to give the other isomer of 2-dimethylaminomethyl-5-bromotricyclo[2.2.1.$0^{2,6}$]heptane (18) or (17) as an oil, $\nu_{max.}$ 3 060, 2 820, 2 775, 1 200. 1 030, 860, 830, 795, and 725 cm^{-1}; τ (CCl_4) 6.08br (s, $W_{1/2}$ 4 Hz, H-5), 7.57br (2 H, s), 7.82 (6 H, s), 7.88 (2 H, m), 8.53 (3 H, m), 8.68 (part A of AB q, J_{AB} 5.5 Hz, $\Delta\nu_{AB}$ 15.5 Hz, each line further split, J 1.5 Hz, H-6), and 8.94 (part B of AB q, each line further split, J 1.5 Hz, H-1); *m/e* (20°) 231 (M^+, 16%), 230 (16), 229 (M^+, 15), 228 (15), 150 (68), 105 (40), 91 (28), 84 (100), 79 (41), and 58 (68) (Found: C, 52.6; H, 6.85; N, 6.1%).

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