Reduction of 6-Hydroxyimino-1,3,3-trimethyl-2-oxabicyclo[2.2.2]octane and Nitrosation of the Resulting Amines. New Rearrangement Products of the Monoterpenoid 1,3,3-Trimethyl-2-oxabicyclo[2.2.2]octane

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Reduction of 6-hydroxyimino-1,3,3-trimethyl-2-oxabicyclo[2.2.2]octane (1) with lithium aluminium hydride in diethyl (or better di-isopropyl) ether and nitrosation of the reaction mixture gave in fair yield *N*-nitroso-5,7,7-trimethyl-6-oxa-3-azabicyclo[3.2.2]nonane (5), which in turn afforded in good yield 5,7,7-trimethyl-6-oxa-3-azabicyclo[3.2.2]nonane (4) by treatment with copper(I) chloride in conc. hydrochloric acid. Reduction of (1) with lithium aluminium hydride in tetrahydrofuran, or better with sodium bis-(2-methoxyethoxy)aluminium hydride in benzene, gave 5,7,7-trimethyl-6-oxa-3-azatricyclo[3.2.2.$0^{2,4}$]nonane (6), which afforded, *via* nitrosation, 1,3,3-trimethyl-2-oxabicyclo[2.2.2]oct-5-ene (7) in excellent yield. Catalytic reduction of (1) gave in high yield an 80 : 20 mixture of *cis*- and *trans*-6-amino-1,3,3-trimethyl-2-oxabicyclo[2.2.2]octane (2) and (3), respectively. Nitrosation of (2) gave a near quantitative yield of 1-[3-(1-hydroxy-1-methylethyl)cyclopentyl]ethanone (9), whereas (3) afforded the known *cis*-4-hydroxy-4,7,7-trimethyl-6-oxabicyclo[3.2.1]octane (11). The structures of the new compounds reported were determined from i.r., n.m.r., and mass spectral data.

We have previously [1] described a synthesis of 1,3,3-trimethyl-2-oxabicyclo[2.2.2]oct-5-ene (2,3-didehydro-1,8-cineole) (7) starting from *trans*-6-bromo-1,3,3-trimethyl-2-oxabicyclo[2.2.2]octane † (*trans*-2-bromo-1,8-cineole). As a consequence of our interest in compound (7), we sought a better method for its preparation, starting from 6-hydroxyimino-1,3,3-trimethyl-2-oxabicyclo[2.2.2]-octane (2-hydroxyimino-1,8-cineole) (1).

In the synthesis of 1,8-cineole derivatives, the oxime (1) is the parent compound [2] from which the corresponding ketone and then *trans*-2-bromo-1,8-cineole are prepared. Therefore we studied the nitrosation procedure on *cis*- and *trans*-2-amino-1,8-cineole (2) and (3), respectively, which were available by reduction of (1) with lithium aluminium hydride or sodium–ethanol,[3] in the hope of obtaining alkenes [*e.g.* (7)] as elimination products.

Treatment with sodium nitrite in aqueous acetic acid at 0 °C of the reaction mixture obtained by reduction with lithium aluminium hydride of (1) in diethyl ether gave unexpected results, however. A yellow oily mixture was obtained, one component of which (70% by g.l.c.) was identified as the nitroso compound (5) on the following basis. The presence of an *N*-nitroso-group was indicated by u.v. and i.r. absorptions at 238 nm (ε 7 300) and 1 450 cm^{-1}, respectively. The n.m.r. spectrum in benzene showed a series of doublets, typical of two N(NO)-methylene protons (2-CH_2 and 4-CH_2), one of which is vicinal to a methine proton (1-CH) (*cf.* *N*-nitrosocamphidine [4]). A molecular model indicated that the axial C-2 proton formed a dihedral angle of *ca.* 90° with the C-1 bridgehead proton, thus leading to $J_{1,2}$ close to zero (doublet at δ 2.76, $J_{a,e}$ 14.5 Hz), whereas the equatorial C-2 proton formed a dihedral angle of *ca.* 25°, giving rise to the observed value of $J_{1,2}$ which is in agreement with the value calculated from the Karplus equation (d of d at δ 4.65, $J_{a,e}$ 14.5 Hz, $J_{1,2}$ 6 Hz; calc. *ca.* 7 Hz). The equatorial C-2 proton signal showed a further splitting of 1.6 Hz due to W long-range coupling with the corresponding equatorial C-4 proton. The mass spectrum showed a weak molecular ion at *m/e* 198 and an intense (*M* — NO) peak at *m/e* 168.

† Throughout this paper, *cis* and *trans* refer to the relative positions of the substituent and the ether bridge in the 2-oxabicyclo[2.2.2]octane derivatives.

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Treatment of (5) with copper(I) chloride in concentrated hydrochloric acid gave 5,7,7-trimethyl-6-oxa-3-azabicyclo[3.2.2]nonane (4) in 83% yield. Structure (4) was confirmed by spectral data (NH i.r. stretching and bending bands; AB and ABC overlapping systems due to 2-CH_2, 4-CH_2, and 1-CH protons in the n.m.r. spectrum; M^+, *m/e* 169). A slightly higher overall yield of (4) was obtained by carrying out the reduction in di-isopropyl ether. The major product formed from reduction of (1) with lithium aluminium hydride is thus the bicyclic secondary amine (4), where expansion of the C_6 ring has taken place with incorporation of nitrogen.

At present, this seems to be the only way to obtain (4) starting from 1,8-cineole derivatives, because neither the Beckmann rearrangement of (1) [5] nor the reaction of ammonia with cineolic anhydride [6] gave 6-oxa-3-azabicyclo[3.2.2]nonane derivatives.

The reduction of (1) with lithium aluminium hydride in tetrahydrofuran was then examined; 5,7,7-trimethyl-6-oxa-3-azatricyclo[3.2.2.$0^{2,4}$]nonane (6) was obtained (33% yield), which showed aziridine i.r. absorptions at 3 275, 3 015, and 1 635 cm^{-1}, an AB system for the 2- and 4-CH protons in its n.m.r. spectrum, the B part being split by coupling with the C-1 bridgehead proton, and the molecular ion at *m/e* 167 in its mass spectrum.

Compound (6) was not unexpected, because it is known that aziridines are formed by reduction of ketoximes (particularly hindered ketoximes) with lithium aluminium hydride, by using solvents such as tetrahydrofuran.[7] Reduction of (1) with sodium bis-(2-methoxyethoxy)aluminium hydride (70% solution in benzene, Red-Al®) indeed gave a better yield (50%) of (6) (*cf.* ref. 8). Nitrosation of the aziridine (6), as in similar cases,[9] gave rise to elimination of nitrous oxide and formation of an alkene, namely (7), in 89% yield. Since only two steps are required starting from (1), this appears at present to be the best method to obtain (7).

In order to obtain the pure primary amines (2) and (3), we resorted to the catalytic hydrogenation of (1) (PtO_2; AcOH), which gave an 80 : 20 (by g.l.c.) mixture of (2) and (3), respectively, in 83% overall yield, which was separated by chromatography on acid alumina. The *cis*- and *trans*-position of the amino group in (2) and (3), respectively, was determined by n.m.r. spectroscopy, the i.r. spectra being quite similar. The *cis*-isomer (2) exhibited the 6-CH proton signal at δ 2.65 as a doublet of doublets (X part of an ABX system), whereas the *trans*-isomer (3) showed the same proton at lower field (δ 3.00) as a doublet of doublets further split by W long-range coupling.

Nitrosation of (2) and (3) gave rise to two interesting stereospecific rearrangements, instead of the formation of alkenes. In the case of (2), the intermediate *cis*-diazonium ion (8) underwent, during elimination of nitrogen, attack by C-7 from the rear, followed by opening of the oxygenated ring and formation of compound (9) in 95% yield (by g.l.c.). Compound (9) showed carbonyl and hydroxy group i.r. absorptions, and n.m.r. singlets due to the *gem*-dimethyl and MeCO groups; moreover, in the presence of sulphuric acid it gave the 2,4-dinitrophenylhydrazone of 1-(3-isopropylidenecyclopentyl)ethanone, whereas the normal 2,4-dinitrophenylhydrazone was obtained in the presence of hydrochloric acid. The *trans*-diazonium ion intermediate (10) derived from (3) gave the known [10] bicyclic compound (11) (80% by g.l.c.), resulting from attack from the rear of the oxygen atom [11] (*cf.* Scheme), the ketone (9) being completely absent.

These rearrangements are in agreement with those described by us in the case of other 1,8-cineole derivatives, namely the dehydrobromination of *trans*-2-bromo-1,8-cineole and dehydration of 2-hydroxy-1,8-cineoles.[1]

EXPERIMENTAL

U.v. spectra were measured for solutions in 95% ethanol with a Hitachi–Perkin-Elmer EPS-3T spectrophotometer, and i.r. spectra with a Perkin-Elmer 257 spectrometer. N.m.r. spectra were recorded with a Perkin-Elmer R12 instrument (60 MHz; tetramethylsilane as internal standard), and mass spectra with an A.E.I. MS902 spectrometer. G.l.c. was performed on a Fractovap GI instrument (C. Erba; 2 000 × 3 dual column differential system, packed with 3% SE 30 on silanized Gaschrom; linear temperature programming 100—200 °C, heating rate 7 °C min^{-1}; nitrogen flow rate 50 ml min^{-1}). M.p.s were determined with a Fisher–Johns apparatus.

cis- *and* trans-6-*Amino*-1,3,3-*trimethyl*-2-*oxabicyclo*[2.2.2]-*octane* (2) *and* (3).—The oxime (1) [2] (10.0 g, 55 mmol) in glacial acetic acid (100 ml) was hydrogenated at 3 atm. pressure and 30 °C for 5 h in the presence of platinum oxide (1.0 g). The solution was filtered, cooled, neutralized with 4M sodium hydroxide, and extracted with ether. The ether extracts were treated with 1M-hydrochloric acid, and the acid extracts were cooled, made alkaline with 4M-sodium hydroxide, and extracted with ether. The combined extracts were dried (Na_2SO_4), filtered, and evaporated; the residue was distilled *in vacuo* (b.p. 40—43 °C at 0.4 mmHg) to give a liquid (7.70 g, 83%). G.l.c. showed two peaks in the ratio 80 : 20. The mixture was chromatographed on acid alumina (grade II) to give, with pentane as eluant, the minor component (3) as a g.l.c.-pure liquid, $[\alpha]_D^{22}$ +40.3° (*c* 4 in EtOH), b.p. 50—53 °C at 0.4 mmHg; $\nu_{max.}$(neat) 3 365, 3 285, and 1 605 cm^{-1}; δ($CDCl_3$) 1.05 (3 H, s, Me), 1.18 (2 H, s, NH_2; disappears with D_2O), 1.25 (3 H, s, Me), 1.28 (3 H, s, Me), and 3.00 (1 H, dq, *J* 16 Hz, 6-H); its *hydrochloride* had m.p. 265—267 °C (decomp.) (from 95%

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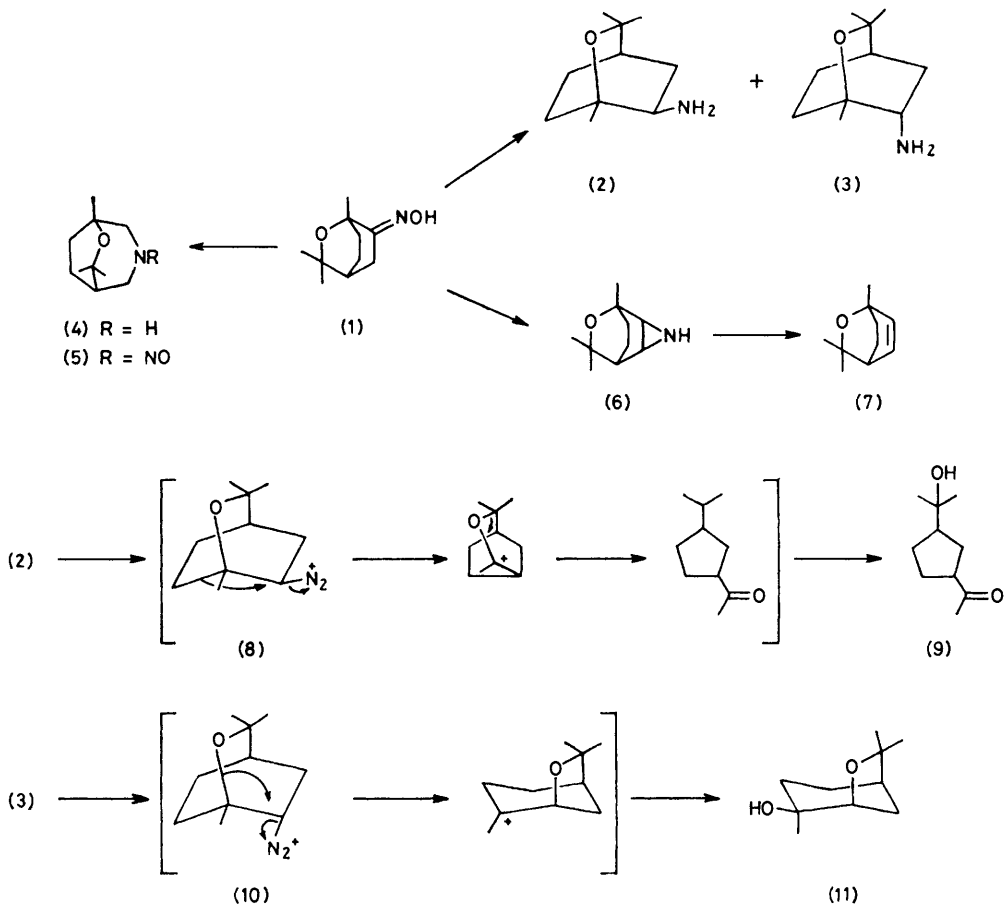
ethanol) (Found: C, 58.3; H, 9.7; N, 7.0. $C_{10}H_{20}ClNO$ requires C, 58.4; H, 9.8; N, 6.8%).

Further elution with ether and dichloromethane gave in the last fractions a g.l.c.-pure sample of (2), $[\alpha]_D^{22}$ −47.6° (*c* 4 in EtOH), b.p. 53—55 °C at 0.4 mmHg; $\nu_{max.}$(neat) 3 355, 3 275, and 1 585 cm^{-1}; $\delta(CDCl_3)$ 1.05 (3 H, s, Me), 1.28 (6 H, s, 2Me), 1.50 (2 H, near s, NH_2; disappears with D_2O), 2.65 (1 H, dd, *J* 14 Hz, 6-H); its *hydrochloride* had m.p. 277—279 °C (decomp.) (from 95% ethanol) (Found: C, 58.5; H, 9.7; N, 6.9. $C_{10}H_{20}ClNO$ requires C, 58.4; H, 9.8; N, 6.8%).

petroleum–diethyl ether) (lit.,[10] m.p. 79.5 °C, $[\alpha]_D^{20}$ −92.3°); $\nu_{max.}$(KBr) 3 370 cm^{-1}; $\delta(CDCl_3)$ 1.13 (6 H, s, 2Me), 1.32 (3 H, s, Me), 2.21 (1 H, s, OH; disappears with D_2O), and 3.67 (1 H, d, *J* 6 Hz, CHO); *m/e* 170, 155, 152, 137, 126, 109, 97, 71, 69, and 43 (base peak). Further elution with ether gave in the last fractions a g.l.c.-pure sample of the main product, the *cyclopentyl ketone* (9), $[\alpha]_D^{22}$ −8.5° (*c* 4 in EtOH), b.p. 83—85 °C at 0.2 mmHg (Found: C, 70.4; H, 10.4. $C_{10}H_{18}O_2$ requires C, 70.5; H, 10.7%); $\nu_{max.}$(neat) 3 450 and 1 705 cm^{-1}; $\delta(CCl_4)$ 1.15 (6 H, s, 2Me), 1.4—2.0 (6 H, m, $3CH_2$), 2.12 (3 H, s, MeCO), 2.2—2.9br (2 H,



SCHEME

cis-4-*Hydroxy*-4,7,7-*trimethyl*-6-*oxabicyclo*[3.2.1]*octane* (11) *and* 1-[3-(1-*Hydroxy*-1-*methylethyl*)*cyclopentyl*]*ethanone* (9). —Nitrosation of the mixture of (2) and (3) (10.0 g, 59 mmol) in 10% aqueous acetic acid (100 ml) was carried out at 0—5 °C by adding in one portion a solution of sodium nitrite (10 g, 145 mmol) in water (20 ml); the resulting mixture was stirred for 1 h. The reaction was completed by heating for 10 min on a steam-bath, and the mixture was cooled, neutralized with 1M-sodium hydroxide, extracted with ether, dried (Na_2SO_4), and evaporated. The residue (9.90 g) showed three components on g.l.c. in the ratio 80 : 18 : 2. Chromatography on neutral alumina (grade I) gave, with light petroleum (b.p. 40—70 °C)–diethyl ether (3 : 1) as eluant, the second component as a white solid which was identified (g.l.c.) as the *cis*-alcohol (11), $[\alpha]_D^{20}$ −92° (*c* 4 in EtOH), m.p. 77—78 °C (from light m, 2CH), and 2.97br (1 H, s, OH; disappears with D_2O). Its yellow-orange 2,4-*dinitrophenylhydrazone*, prepared in the usual way with hydrochloric acid, had m.p. 109—110 °C (from 95% ethanol) (Found: C, 54.5; H, 6.3; N, 15.8. $C_{16}H_{22}N_4O_5$ requires C, 54.8; H, 6.3; N, 16.0%). If sulphuric acid was used in the preparation of the dinitrophenylhydrazone derivative, an orange-red compound, m.p. 136—137 °C (from 95% ethanol) was obtained instead, which was identical with the 2,4-dinitrophenylhydrazone of 1-(3-isopropylidenecyclopentyl)ethanone prepared from an authentic sample (Found: C, 57.8; H, 5.9; N, 17.0. Calc. for $C_{16}H_{20}N_4O_4$: C, 57.8; H, 6.1; N, 16.9%).

Repetition of the nitrosation procedure on a 1 g scale of pure samples of (2) and (3) gave a near quantitative yield of (9) (95% by g.l.c.) from (2), whereas (9) was entirely absent in the nitrosation of (3), and (11) plus a minor

component [80 : 20 by g.l.c.; probably the *trans*-isomer of (11) from its retention time] were obtained.

N-*Nitroso*-5,7,7-*trimethyl*-6-*oxa*-3-*azabicyclo*[3.2.2]*nonane* (5).—To a solution of lithium aluminium hydride (10.0 g, 250 mmol) in anhydrous diethyl ether (200 ml), a solution of (1) (10.0 g, 55 mmol) in the same solvent (300 ml) was added dropwise with stirring. The mixture was heated under reflux for 48 h, and then cooled with ice and decomposed with water (10 ml), 4M-sodium hydroxide (10 ml), and water again (20 ml). The inorganic precipitate was washed thoroughly with ether and the combined ethereal solutions were treated with 1M-hydrochloric acid. The acid layer was cooled, made alkaline with 4M-sodium hydroxide, and extracted with ether. The combined extracts were dried (Na_2SO_4), filtered, and evaporated; the residue was distilled *in vacuo* to give a liquid (6.0 g), which showed two components (70 : 30) on g.l.c. The minor component was a mixture of (2) and (3).

Nitrosation of the reaction mixture (6 g) in 10% aqueous acetic acid (60 ml) was carried out in the usual manner with a solution of sodium nitrite (6 g, 87 mmol) in water (12 ml). A yellow liquid (6.40 g) was obtained, which exhibited three components on g.l.c. in the ratio 70 : 20 : 10. Chromatography on neutral alumina (grade I) gave, with pentane as eluant, the main compound (3.30 g, 30% overall) identified as the N-*nitroso-compound* (5), m.p. 95—96 °C (from light petroleum) (Found: C, 60.7; H, 9.3; N, 13.9. $C_{10}H_{18}N_2O_2$ requires C, 60.6; H, 9.2; N, 14.1%); $\lambda_{max.}$ 238 nm (ε 7 300); $\nu_{max.}(CCl_4)$ 1 450 cm^{-1}; δ(C_6H_6, 100 MHz) 1.17 (3 H, s, Me), 1.20 (6 H, s, 2Me), 2.76 (1 H, d, *J* 14.5 Hz, 2-NCH_{ax}), 3.62 (1 H, d, *J* 14 Hz, 4-NCH_{ax}), 4.36 (1 H, split d, *J* 14 and 1.6 Hz, 4-NCH_{eq}), 4.65 (1 H, split dd, *J* 15.5, 6, and 1.6 Hz, 2-NCH_{eq}); *m/e* 198, 168, 152, 139, 110, 55, 43 (base peak), 42, and 30.

Similar reduction of (1) with lithium aluminium hydride, but in di-isopropyl ether, afforded a mixture of (4) and (2) + (3) (7.3 g) in the ratio 75 : 25, respectively, from which (5) (4.60 g, 42% overall) was obtained as above.

5,7,7-*Trimethyl*-6-*oxa*-3-*azabicyclo*[3.2.2]*nonane* (4).—The *N*-nitrosoamine (5) (5.0 g, 25 mmol) was added slowly with ice-cooling to a solution of copper(I) chloride (10.0 g, 101 mmol) in concentrated hydrochloric acid (50 ml). After the evolution of nitrogen oxides was complete, the dark brown mixture was heated on a steam-bath for 15 min, cooled, and extracted with ether. The acid aqueous solution was made strongly alkaline with concentrated ammonia and extracted with ether. The combined extracts were dried (Na_2SO_4) and evaporated. Distillation *in vacuo* of the residue gave (4) as a liquid (3.50 g, 83%) which solidified on cooling, $[\alpha]_D^{22}$ +5.5° (*c* 4 in EtOH), b.p. 48—50 °C at 0.3 mmHg, $\nu_{max.}$(neat) 3 320 and 1 630 cm^{-1}; δ(CCl_4) 0.97 (3 H, s, Me), 1.24 (6 H, s, 2Me), 1.57 (1 H, s, NH; disappears with D_2O), 2.5—3.4 (5 H, m, 2-CH_2 + 4-CH_2 + 1-CH); *m/e* 169, 153, 137, 98, 82, 69, and 43 (base peak); its *hydrochloride* had m.p. 182—183 °C (from ethanol–ether) (Found: C, 58.2; H, 9.6; N, 7.0. $C_{10}H_{20}ClNO$ requires C, 58.4; H, 9.8; N, 6.8%).

5,7,7-*Trimethyl*-6-*oxa*-3-*azatricyclo*[3.2.2.0^{2,4}]*nonane* (6).—(i) *By reduction of* (1) *with lithium aluminium hydride in tetrahydrofuran.* This reduction was carried out in the same manner described for the preparation of (5), using anhydrous tetrahydrofuran instead of ether and distilling off the solvent before the treatment with 1M-hydrochloric acid. The residue was distilled *in vacuo* to give a liquid (6.5 g), b.p. 50—52 °C at 0.5 mmHg, which showed three components on g.l.c. (55 : 23 : 22). The last two peaks were attributed to (4) and (2) + (3), respectively, by their retention times.

(ii) *By reduction of* (1) *with sodium bis-(2-methoxyethoxy)-aluminium hydride in benzene* (*Red-al*®). To a 70% solution of sodium bis-(2-methoxyethoxy)aluminium hydride in benzene (Red-al®; 30 g, 148 mmol), a solution of (1) (10.0 g, 55 mmol) in anhydrous benzene (30 ml) was added dropwise with stirring. The solution was heated under reflux for 48 h, and then cooled and decomposed cautiously with 4M-sulphuric acid (30 ml). The acid layer was separated, made alkaline with 4M-sodium hydroxide, extracted with ether, and dried (Na_2SO_4). Evaporation left a residue which was distilled *in vacuo* to give a liquid (6 8 g), b.p. 55—60 °C at 0.6 mmHg. G.l.c. showed three peaks in the ratio 78 : 20 : 2, the last two being due to (4) and (2) + (3), respectively.

Separation of (6) from the other compounds was achieved by chromatography on neutral alumina (grade I) with pentane as eluant. The aziridine (6) was obtained as a white waxy product [3.0 g, 33% overall in the case of (i); 4.6 g, 50%, in the case of (ii)], $[\alpha]_D^{22}$ −8° (*c* in EtOH), m.p. 44—45 °C (from light petroleum) (Found: C, 71.5; H, 10.5; N, 8.1. $C_{10}H_{17}NO$ requires C, 71.8; H, 10.3; N, 8.4%); $\nu_{max.}$(neat) 3 275, 3 015, and 1 635 cm^{-1}; δ(CCl_4) 1.05 (3 H, s, Me), 1.10 (6 H, s, 2Me), 1.60 (1 H, m, NH; disappears with D_2O), and 2.08 and 2.31 (2 H, m, *J* 7 and 4.4 Hz, 2-CH + 4-CH); *m/e* 167, 149, 140, 109, 108, 81, 71, and 43 (base peak).

1,3,3-*Trimethyl*-2-*oxabicyclo*[2.2.2]*oct*-5-*ene* (7).—The aziridine (6) (3.34 g, 20 mmol) in 10% aqueous acetic acid (35 ml) was nitrosated with a solution of sodium nitrite (3.45 g, 50 mmol) in water (7 ml). A yellow liquid was obtained, which upon distillation *in vacuo* gave a g.l.c.-pure product (2.70 g, 89%), identified as (7) by its retention time, and i.r. and n.m.r. spectral data.[1]

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