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endo-TRICYCLO[3.2.1.$O^{2,4}$]OCT-6-ENE OXIDE

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A study of the chemistry of the oxides of norbornene,[1] norbornadiene[2] and benzonorbornadiene[3] has revealed a propensity for these epoxides to undergo skeletal rearrangement. The synthesis and study of the oxide of endo-tricyclo[3.2.1.$O^{2,4}$]oct-6-ene I promised to be an interesting extension of this work.

Monoperphthalic acid oxidation of the tricyclic olefin I gave the epoxide 2 (mp 92-93°).[4] Assignment of the expected exo configuration to the oxirane ring was based in part on pmr evidence. The pmr signal ascribable to the oxirane protons at C-2 and C-4 appeared as a singlet ($W_{\frac{1}{2}h}$ = 2.5 Hz) with no detectable coupling to the bridgehead protons at C-1, C-5 - a characteristic feature of the pmr signal of the oxirane protons in the exo oxide of norbornene.[5] More definitive evidence, however, was obtained from Li/NH_3 reduction of 2 which proceeded cleanly and without rearrangement to yield the known endo,exo-tricyclo[3.2.1.$O^{2,4}$]octan-6-ol 3, identical with a sample of this alcohol prepared according to the published procedure.[6]

In contrast to this reduction, $LiAlH_4$/diglyme[1c] reduction of 2 gave rise to two main products 4 (95%) and 5 (5%) both of which had rearranged skeletons. Tricyclic alcohol 4 showed properties identical to those recorded in the literature.[7] Evidence supporting structure 5 for the minor component is presented further on.

Treatment of epoxide 2 with hydrobromic acid (or magnesium bromide-ether) gave three isomeric bromohydrins which have been assigned structures 6-OH, 7 and 8. Assignment of structure 8 to one of these bromohydrins is based on spectroscopic data and mechanistic considerations only and is therefore tentative. Bromohydrins 6-OH and 7, however, have been investigated more exhaustively.

Bromohydrin 6-OH was debrominated with $LiAlH_4$/ether to give the tricyclic alcohol 4,[7] a

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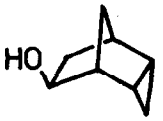

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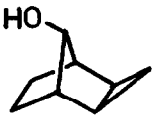

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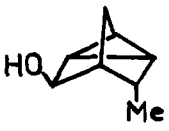

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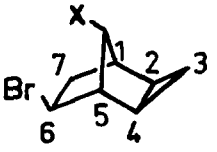

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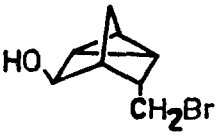

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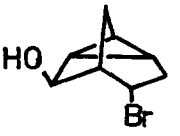

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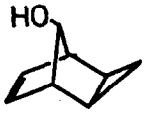

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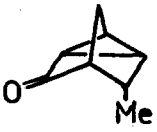

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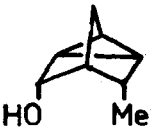

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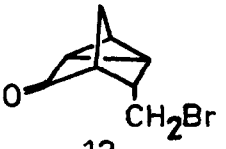

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transformation which defines the structure of 6-OH except for the configuration at C-6. The exo configuration of the bromo substituent is preferred because the observed infrared hydroxyl stretching frequency of 6-OH (ν_{OH} 3575 cm.$^{-1}$; cf for 4 ν_{OH} is 3636 cm.$^{-1}$) is consistent with the presence of intramolecular hydrogen bonding. Furthermore the pmr spectrum of the derived p-nitrobenzoate 6-OPNB shows the bromomethine signal as a triplet which approximates X part of an ABX pattern with J_{obsd} = 5.5 Hz = $\frac{1}{2}$ ($J_{H_6H_{7ex}} + J_{H_6H_{7en}}$) and $J_{H_6H_5} \simeq 0$.

Dehydrobromination of the derived tetrahydropyranyl ether 6-OTHP and subsequent hydrolysis, following the well documented procedure,[3,8] provided the previously unknown exo,anti-tricyclo [3.2.1.$O^{2,4}$]oct-6-en-8-ol 9. Alcohol 9 has the hydroxyl group syn disposed to the double bond and by analogy with the known behaviour of syn-7-norborneol[9] derivatives would be expected to undergo reduction of the double bond on reaction with $LiAlH_4$. This proved to be the case and 9 was smoothly converted to the known alcohol 4[7] with $LiAlH_4$/ether at room temperature.

Debromination of bromohydrin 7 (ν_{OH} 3615 cm.$^{-1}$) with refluxing $LiAlH_4$/ether (108 hrs) gave the methylnortricyclanol 5 (identical to the minor component obtained from $LiAlH_4$ reduction of 2). Oxidation[10] of 5 yielded the corresponding methylnortricyclanone 10 ($\nu_{C=O}$ 1760 cm.$^{-1}$; 2,4-DNP mp 192-194°) which on subsequent reduction formed the diastereomeric methylnortricyclanol 11 (mp 44-45°) stereospecifically. Oxidation[10] of 11 regenerated the ketone 10. These transformations, although entirely consistent with the proposed structure 7, still allow for some ambiguity with regard to the relative configuration of the hydroxyl and bromomethyl substituents. In an effort to resolve this ambiguity 7 was oxidised[10] to the bromomethylnortricyclanone 12 ($\nu_{C=O}$ 1762 cm.$^{-1}$; 2,4-DNP mp 213-214.5°C). Subsequent reduction ($LiAlH_4$/ether 20°, 30 min) gave the intramolecular ether 13 (44%) and the methylnortricyclanol 11 (56%). Formation of 13 may be rationalized by assuming that 12 is reduced stereospecifically to give the alkoxide anion of the diastereomiric bromomethylnortricyclanol which undergoes intramolecular bromide ion displacement yielding 13. Alcohol 11 appears to be formed by two pathways. Reductive ring opening of 13 seems to be a minor pathway since separate treatment of 13 under identical conditions gave a mixture of 13 (95%) and 11 (5%). The major portion of 11 would appear to be derived via direct debromination of 12 to give ketone 10 and subsequent stereospecific reduction of this ketone to yield 11.

The remarkable faculty for epoxide 2 to undergo rearrangement under protic and aprotic conditions parallels the behaviour of the oxides of other bicyclo[2.2.1]heptene derivatives.

Recent publications[6,11] concerned with the tricyclooctyl carbonium ion- intermediate are relevant to the mechanism of rearrangement of 2 and these will be discussed in a more detailed account of this work.

ACKNOWLEDGEMENT

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