Tetrahedron. Vol. 27, pp. 2255 to 2269. Pergamon Press 1971. Printed in Great Britain

ENDO-TRICYCLO[3.2.1.$0^{2,4}$]OCT-6-ENE *EXO*-OXIDE

B. C. HENSHAW, D. W. ROME and B. L. JOHNSON
Department of Organic Chemistry, University of Western Australia,
Nedlands, Western Australia. 6009

(*Received in the UK 12 January* 1971; *Accepted for publication* 1 *March* 1971)

Abstract—Peracid oxidation of *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (X) yields epoxide XII. Lithium-ammonia reduction of XII gives rise to the known, unrearranged alcohol XIII whereas lithium aluminium hydride reduction of the epoxide XII forms the rearranged alcohols XIV and XV. Rearrangement also occurs when the epoxide XII is treated with hydrobromic acid to yield the bromohydrins XVI, XVII and XVIII. The mechanism of these acid catalysed rearrangements is discussed. Bromohydrin XVI was converted to the known alcohol XIV and also serves as a source of the previously unknown *exo*-tricyclo [3.2.1.$0^{2,4}$]oct-6-en-*anti*-8-ol (XIX). Debromination of bromohydrin XVII forms the methylnortricyclanol XV which was oxidised to the corresponding methylnortricyclanone XX. Reduction of ketone XX yields the diastereomeric methylnortricyclanol XXI stereospecifically. Oxidation of bromohydrin XVII gave the corresponding ketone XXII which on treatment with lithium aluminium hydride provided a mixture of XXIII and XXI. Treatment of bromohydrin XVII with alcoholic base yields the expected elimination and substitution products, XXIV and XXV respectively, and a small but significant amount of the methylnortricyclanone XX, the formation of which has been rationalized in terms of a 1,4-hydride-shift-substitution reaction. The same mechanism accounts for the formation of the diastereomeric alcohols XV and XXI when bromohydrin XVII was reacted with sodium hydride although competing reductive debromination also occurs. Bromohydrin XVIII was converted to the alcohols XXVIII and XXXVI as partial proof of structure.

ONE OF the most noteworthy features of the chemistry of the *exo*-oxides of norbornene,[1] norbornadiene[2] and benznorbornadiene[3] is the extent to which rearrangement accompanies cleavage of the epoxide ring. The recently reported deltacyclene oxide[4] behaves in a similar manner. For example, the predominant products formed by treatment of the *exo*-oxides of norbornene, benznorbornadiene and deltacyclene with HBr aq have rearranged structures.* The close similarity shown by these oxides in this reaction precludes any attempts to compare the oxides with regard to extent of and facility for rearrangement.

In contrast, the reduction of these oxides with LAH is a reaction which does allow for some differentiation in the propensities for rearrangement. It would appear that the proportion of rearranged products increases in the order: norbornadiene *exo*-oxide > benznorbornadiene *exo*-oxide > norbornene *exo*-oxide. Several groups of workers have reported[1b–1e] that LAH reduction of norbornene *exo*-oxide yields the unrearranged alcohol III exclusively. However, the proportion of rearranged alcohol II formed in this reduction does appear to depend on solvent and temperature since in one instance the reduction is reported[1f] to yield a mixture of rearranged alcohol II (8%) and unrearranged alcohol III (92%). Nevertheless the proportion of

* Under conditions (anhydrous HBr in ether) presumably less favourable for the formation of dissociated ions as distinct from ion-pair intermediates deltacyclene oxide yields, predominantly, unrearranged bromohydrins. See Ref. 4.

rearrangement is quite small. The *endo*-oxide of norbornene gives unrearranged alcohol only.[1f]

LAH reduction of the *exo*-oxide of benznorbornadiene IV[3a] yields mainly the rearranged alcohol, *anti*-7-benznorbornenol (V). However, the proportion of unrearranged alcohol formed in this reaction was not determined. It is worthy of note, that a Me derivative of the related 3,4-benzobicyclo[3.2.1]oct-6-ene oxide (mainly *exo*) under similar conditions forms a significant proportion (42%) of an alcohol, tentatively assigned the rearranged structure VI.[5]

Norbornadiene *exo*-oxide VII[2, 13] is unstable and undergoes very facile rearrangement to bicyclo[3.1.0]hex-2-ene-*endo*-6-carboxaldehyde (VIII).* LAH reduction of this oxide yields the corresponding rearranged alcohol IX. Rearranged products are formed exclusively with norbornadiene *exo*-oxide and furthermore, it would appear that the rearrangements are much more facile than with the oxides of benznorbornadiene and norbornene.

The formation of rearranged products in these reactions has been rationalized[1a, 1f, 3a] in terms of a mechanism involving acid (proton or aluminium) catalysed opening of the epoxide ring with intermediate formation of a carbonium ion. It seems plausible therefore that the increased reactivity of norbornadiene *exo*-oxide (and to a lesser extent benznorbornadiene *exo*-oxide) is due mainly to the presence of a favourably oriented double bond which may conceivably participate in the initial ionization step and would certainly stabilize the intermediate carbonium ion. Cyclopropane rings in related environments are known to behave like double bonds[6] and we thought it interesting to study the chemistry of the oxides of the known olefins, *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (X)[7] and *exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (XI).[8]

In conjunction with other studies we also required the previously unknown alcohol, *exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-en-*anti*-8-ol (XIX), and it was conceivable that this alcohol could be synthesised from the oxide of X. In the present paper we present the results of our study of the oxide of *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-ene (X)†. A preliminary account of the preparation and reactivity of the oxide of *exo*-tricyclo [3.2.1.$0^{2,4}$]oct-6-ene has been published recently.[10]

RESULTS AND DISCUSSION

Oxidation of the tricyclic olefin X[7] with monoperphthalic acid or more conveniently with commercial peracetic acid gave *exo*-3-oxa-*endo*-tetracyclo[3.3.1.$0^{2,4}$.$0^{6,8}$]nonane (XII) stereospecifically and in excellent yield. Analysis of the crude product on several VPC columns showed only one component. The NMR spectrum of XII displayed a two proton singlet at τ 7·12 which was assigned to the two equivalent oxirane protons at C-2 and C-4. The width at half-height of this singlet (2·5 Hz) suggested that the epoxide ring is in the *exo* configuration such that there is no appreciable coupling between the oxirane protons and the bridgehead protons at C-1 and C-5. A similar feature characterizes the NMR signal of oxirane protons in the *exo* oxide of norbornene (I).[11] The NMR signal due to H_{7s} occurs at τ 9·38 and

* An additional rearranged product is reported to be formed in this reaction. See Ref 2b.

† These results have been reported in preliminary form. See Ref 9.

approximates an octet. Simple first order analysis of this signal gives $J_{H_{7x}H_{7n}} = J_{H_{7x}}J_{H_8(H_6)} = 6{\cdot}5$ Hz and $J_{H_{7x}H_{9n}} = 2{\cdot}5$ Hz. The long range stereospecific coupling between H_{7x} and H_{9n} is reminiscent of the coupling observed[12] in olefin X between H_{3x} and H_{8n}. The observation of this coupling in epoxide XII provides some evidence for the configuration of the cyclopropane ring.

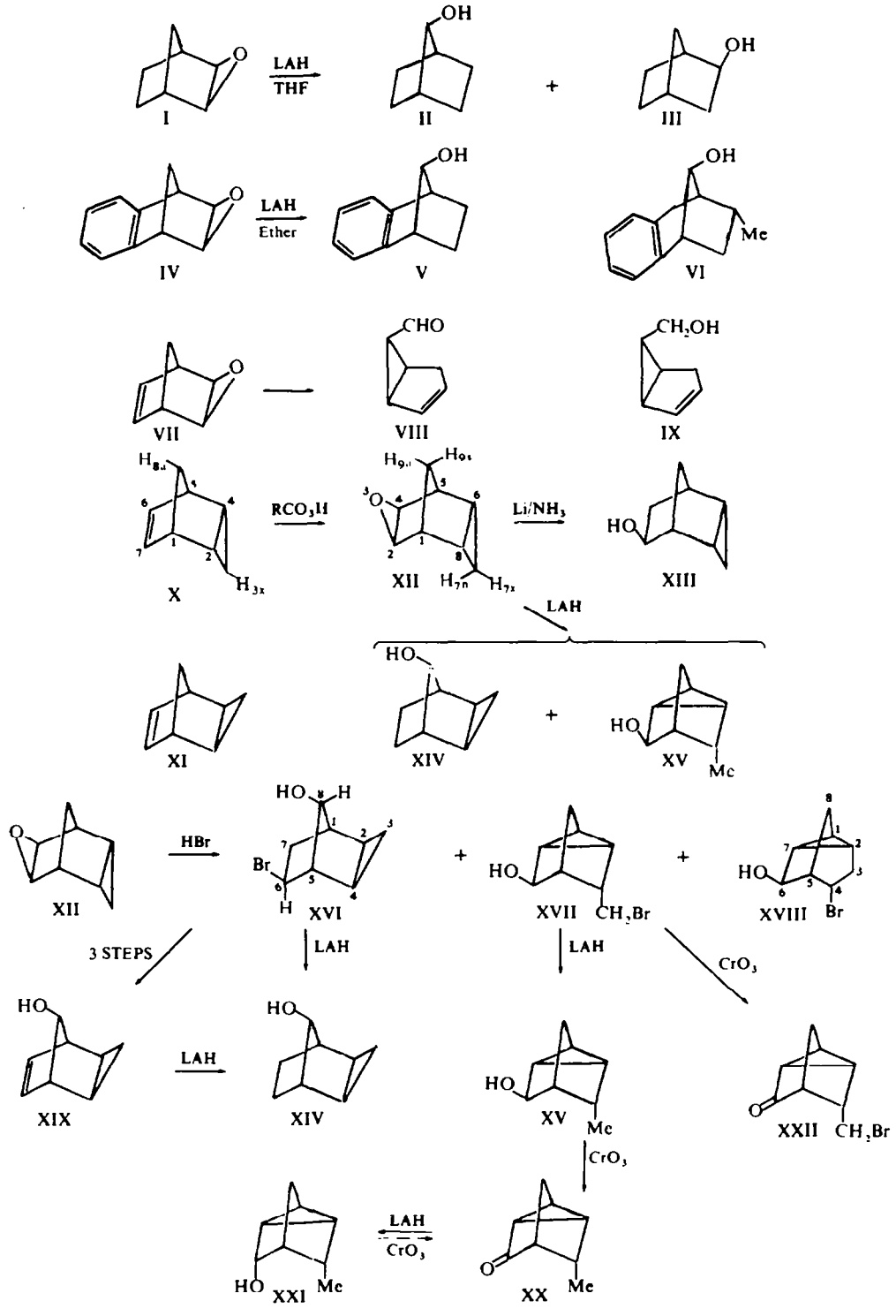
More definitive evidence for the proposed structure was obtained from chemical transformation. In seeking a reaction for this purpose it was noted that Li/EtNH_2 reduction of the *endo* oxide of norbornadiene is reported to proceed without rearrangement.[13] A reduction of this type therefore appeared to the most feasible for proof of the structure of epoxide XII. Accordingly the epoxide XII was reacted with Li/NH_3 and was converted cleanly to *endo*-tricyclo[3.2.1.$0^{2,4}$]octan-*exo*-6-ol (XIII). The product was identical to a sample of XIII prepared according to published procedure[6a] involving hydroboration of olefin X followed by oxidative work-up.

Reduction of epoxide XII with LAH/diglyme, following the recommended method of Yoon and Brown.[1c] yielded two alcohols. XIV (95%) and XV (5%), both of which have rearranged skeletons. By way of contrast, norbornene *exo*-oxide (I) under identical conditions gives exclusively the unrearranged alcohol III. Alcohol XIV was identified by comparison with an authentic sample prepared according to the literature.[14] Alcohol XV was identical with an authentic sample described further on.

Treatment of epoxide XII with HBr aq yielded a mixture of three bromohydrins, two of which were separated by chromatography on alumina and identified as *exo*-6-bromo-*exo*-tricyclo[3.2.1.$0^{2,4}$]octan-*anti*-8-ol (XVI) and *endo*-5-bromomethyltricyclo[2.2.1.$0^{2,6}$]heptan-*exo*-3-ol (XVII). The minor component XVIII could be obtained only as a mixture with XVII.

Reductive debromination of bromohydrin XVI with LAH in refluxing ether gave the known tricyclic alcohol XIV which was identified by comparison with an authentic sample.[14] This transformation defines the structures of XVI except for the configuration at C-6. The *exo* configuration for the 6-bromo substituent is preferred since the IR OH stretching frequency of XVI (3572 cm^{-1}) is some 64 cm^{-1} lower than that of alcohol XIV (3636 cm^{-1}), indicative of the presence of intramolecular hydrogen bonding. Further evidence for this configurational assignment was obtained from the NMR spectrum of the *p*-nitrobenzoate derived from XVI. The NMR signal due to the proton at C-6 appears as a triplet each line of which is further split by approximately 1 Hz into a doublet. As such, the pattern approximates the X part of an ABX pattern with $J_{obsd} = 5{\cdot}5$ Hz $= \frac{1}{2}(J_{H_6H_{7ex}} + J_{H_6H_{7en}})$ and $J_{H_6H_5} \approx 0$. The extra splitting (1 Hz) has been assigned to stereospecific coupling between the proton at C-6 and that at C-8, by analogy with the known coupling of this type in certain norbornane derivatives.[15] The significant feature of this pattern is the lack of coupling between the proton on C-6 and the vicinal bridgehead proton at C-5. This feature is characteristic of the *endo* proton at C-6 (and C-7) in tricyclo[3.2.1.$0^{2,4}$]octane derivatives.[6a]

Dehydrobromination of the tetrahydropyranyl ether of XVI and subsequent hydrolysis, following the well documented procedure[3a,16], provided the previously unknown *exo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-en-*anti*-8-ol (XIX). The IR OH stretching frequency of alcohol XIX occurred at 3567 cm^{-1} and indicated the presence of intramolecular hydrogen bonding and hence a *syn* relationship between the OH group and the double bond. Further evidence for this configurational assignment was obtained from the appearance of the vinyl signals in the NMR spectra of the alcohol


LAH
THF
I
II
III
LAH
Ether
IV
V
VI
VII
VIII
IX
RCO3H
Li/NH3
X
XII
XIII
LAH
XI
XIV
XV
HBr
XII
XVI
XVII
XVIII
3 STEPS
LAH
LAH
CrO3
XIX
XIV
XV
XXII
CrO3
LAH
CrO3
XXI
XX

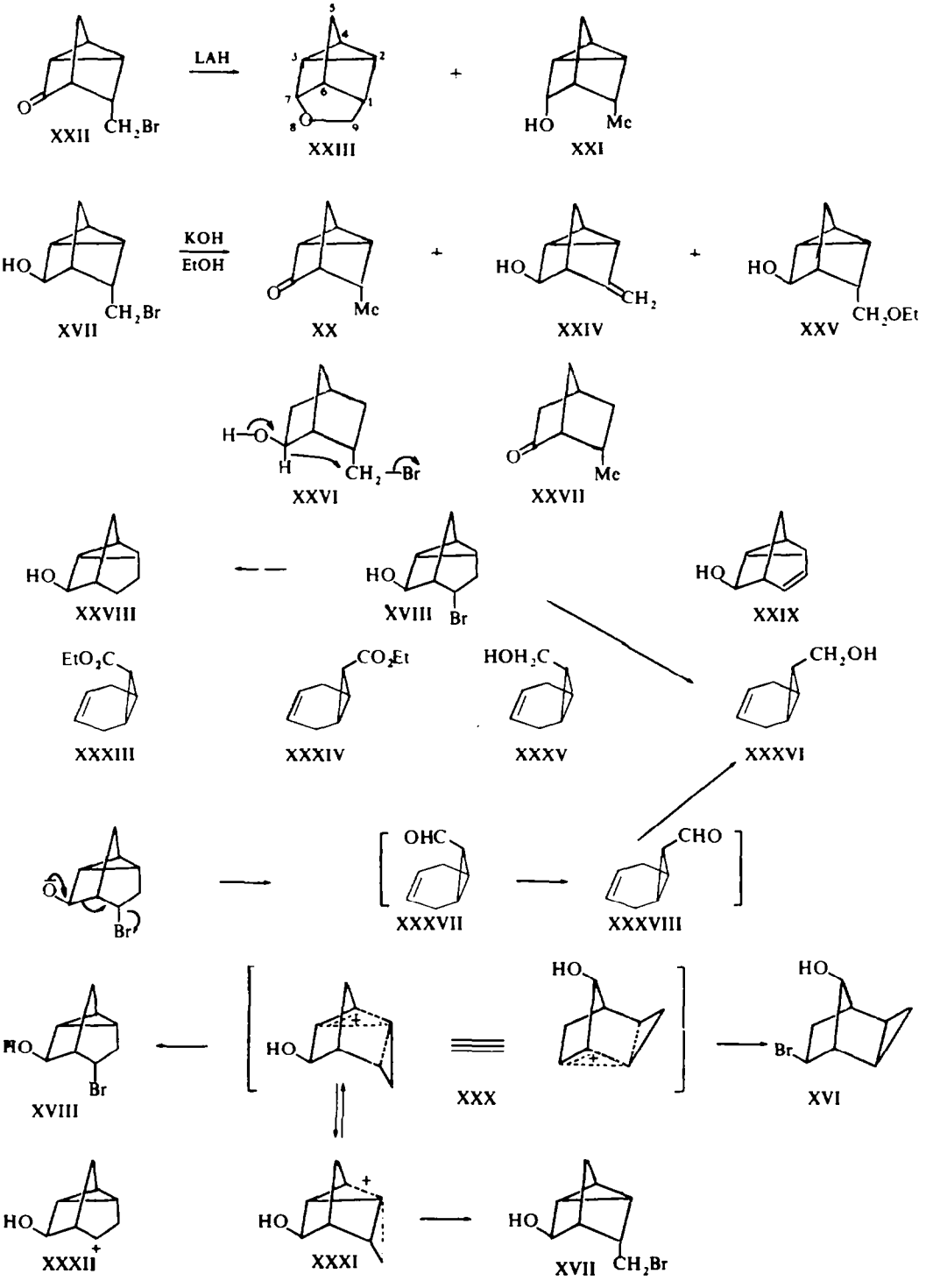

LAH
KOH
EtOH
XXII
XXIII
XXI
XVII
XX
XXIV
XXV
XXVI
XXVII
XXVIII
XVIII
XXIX
XXXIII
XXXIV
XXXV
XXXVI
XXXVII
XXXVIII
XVIII
XXX
XVI
XXXII
XXXI
XVII

TABLE 1. PRODUCT DISTRIBUTION FROM NaH/THF REDUCTION OF XVII AND XX

Reactant	Product Composition (%)		
	XX	XV	XXI
XVII	2	64	34
XX	2	23	75

XIX and of the derived tosylate. The appearance of both signals provided evidence for the presence of a long range stereospecific coupling between the vinyl protons and the *anti* proton at C-8[17]; the vinyl signal in the NMR spectrum of the parent alcohol was not clearly resolved and appeared as a broad multiplet whilst the corresponding signal in the NMR spectrum of the derived tosylate occurred as a well resolved doublet of triplets with the "triplet" separation equal to 2 Hz and the long range coupling equal to 1 Hz. However. conclusive evidence for this stereochemical relationship and for the overall structure was obtained by treatment of alcohol XIX with LAH in ether at room temperature. Under these conditions alcohol XIX was smoothly converted to the known alcohol XIV[14] which was shown to be identical to an authentic sample. Reduction of the double bond under these conditions is known to be characteristic of *syn*-norborn-2-en-7-ol derivatives[18] as well as *endo*-tricyclo[3.2.1.$0^{2,4}$]oct-6-en-*anti*-8-ol.[17]

The second bromohydrin resulting from HBr treatment was assigned structure XVII on the basis of physical data and chemical transformation. The IR spectrum of XVII displayed an OH stretching frequency at 3617 cm^{-1} and a medium intensity band at 3057 cm^{-1} which was assigned to the C-H stretching of the cyclopropane ring.[19] The NMR spectrum showed no absorption in the vinyl region; the signal at lowest field (τ 5·94) occurred as a poorly resolved triplet (one proton; J = 1 Hz)* and was assigned to the carbinol methine proton. A two proton doublet at τ 6·73 with J = 8 Hz was assigned to the protons of the bromomethyl substituent. Reductive debromination of bromohydrin XVII gave the corresponding methylnortricyclanol XV which displayed a characteristic Me doublet (J = 7 Hz) at τ 9·1 in the NMR spectrum. CrO_3 oxidation of XV yielded the corresponding methylnortricyclanone XX which readily formed a 2.4-dinitrophenylhydrazone and showed strong absorption in the IR spectrum at 1760 cm^{-1}. The frequency of this carbonyl absorption compares quite favourably with that reported (1753 cm^{-1}) for nortricyclanone.[21] LAH reduction of the methylnortricyclanone XX occurred stereospecifically and formed the diastereomeric methylnortricyclanol XXI. Oxidation of XXI regenerated the ketone XX.

The stereospecificity of this reduction does allow for some tentative conclusions with regard to the relative configurations of the carbinol carbon and Me substituted carbon in XV and XXI (and hence the stereochemistry of ketone XX and the parent bromohydrin XVII). One might expect that for a structure such as XX steric approach control of hydride reduction would favour the formation of one diastereomer (the *endo. endo* alcohol XXI) over the other (the *exo. endo* alcohol XV); whereas for the

* The NMR signals of the carbinol methine protons in nortricyclanol derivatives bear a close resemblance to this signal. See Ref. 20.

isomeric methylnortricyclanone in which the Me group was *syn* disposed to the methylene bridge the stereoselectivity of hydride reduction might be far less pronounced. However the result is indicative of structure rather than conclusive.

In an effort to resolve this question of stereochemistry. bromohydrin XVII was first oxidised to the corresponding ketone XXII which displayed characteristic IR absorption at 3067 cm^{-1} (cyclopropane C H stretch) and 1762 cm^{-1} (C=O stretch) and readily formed a 2.4-dinitrophenylhydrazone. Subsequent reduction of the bromomethylnortricyclanone XXII with LAH in ether at room temperature (conditions which are much milder than those used to convert XVII to XV) afforded a mixture of the tetracyclic ether XXIII (44%) and the *endo. endo*-methylnortricyclanol XXI (56%).

The identity of alcohol XXI was confirmed by oxidation to the ketone XX. The tetracyclic ether XXIII showed characteristic absorption in the IR spectrum at 3060 cm^{-1} (cyclopropane C H stretch). The NMR spectrum of XXIII displayed a broad triplet (J = 1·5 Hz) at τ 5·90 (one proton). ascribable to the proton on C-7. and a deceptively simple "doublet" at τ 6·31 (two protons) with a separation of 1·5 Hz which was assigned to the methylene protons at C-9. Formation of XXIII may be rationalized by assuming that the bromomethylnortricyclanone XXII is reduced stereospecifically (as is the case with the methylnortricyclanone XX) to give the alkoxide anion of the diastereomeric bromomethylnortricyclanol which undergoes facile intramolecular bromide ion displacement yielding the tetracyclic ether XXIII. We believe that the formation of XXIII under these conditions is firm evidence for the proposed stereochemistry of ketone XXII since if the ketone possessed the alternate stereochemistry with the bromomethyl substituent *anti* to the carbonyl group intramolecular ether formation would have been impossible. The *endo. endo* alcohol XXI appears to be formed by two pathways. Reductive ring opening of XXIII seems to be a minor pathway since separate treatment of XXIII under identical conditions gave a mixture of XXIII (95%) and XXI (5%). The major portion of XXI would appear to be derived via direct reductive debromination of ketone XXII to the methylnortricyclanone XX and subsequent known stereospecific reduction to yield the *endo. endo*-methylnortricyclanol XXI. The facility with which this reductive debromination occurs is worthy of note since it confirms the proposed stereochemistry of ketone XXII and hence the bromohydrin XVII. The conditions (refluxing LAH. ether for 108 hr) required for reductive debromination of bromohydrin XVII are more drastic than the conditions (LAH/ether at 15° for 30 min.) which lead to reductive debromination of the bromomethylnortricyclanone XXII. In the latter case it is plausible that the aluminium hydride complexes with the carbonyl oxygen leading to facile displacement of bromide ion by hydride at the favourably oriented bromomethyl carbon atom.

It was considered desirable at this stage to provide further evidence that the bromomethyl group in XVII was indeed attached to a tertiary carbon atom. Treatment of XVII with KOH/EtOH gave rise to mixture of three components. The two major components were assigned structures XXIV (38%) and XXV (56%) on the basis of the following data. The NMR spectrum of olefin XXIV showed two sharp singlets at τ 5·43 and 5·49 assigned to the two olefinic protons. a broad triplet (J = 2 Hz) assigned to the carbinol methine proton and a sharp singlet due to the OH proton. The IR spectrum of XXIV displayed characteristic absorption at 3616 (OH stretch).

3073 (olefinic and cyclopropyl C H stretch), 1673 (C=C stretch) and 860 cm^{-1} (=CH_2 deformation and nortricyclene skeleton[22]). The NMR spectrum of the ethyl ether XXV showed the characteristic ethoxy pattern comprised of a quartet (J = 7 Hz) at τ 6·61 and a triplet (J = 7 Hz) at τ 8·85 as well as a broad triplet (J = 2 Hz) at τ 6·01 assigned to the carbinol methine proton and a doublet (J = 7 Hz) at τ 6·72 due to the second group of methyleneoxy protons. The third component of the mixture proved to be the methylnortricyclanone XX (4%) identified by vpc peak enhancement and IR data from a collected sample.

The formation of ketone XX under these conditions may be explained in terms of a mechanism recently proposed by Gwynn and Skillern.[23] These authors noted that basic treatment of *endo*-6-bromomethylnorbornan-*exo*-2-ol XXVI can give rise to ketone XXVII depending on the basic conditions. For example. NaH/THF reacts with XXVI to yield XXVII almost exclusively. This conversion was rationalized in terms of a novel intramolecular 1.4-hydride-shift-substitution reaction although the possibility of an intermolecular pathway was not discounted. It is entirely reasonable that the structurally related bromohydrin XVII could form ketone XX via the same pathway.

Accordingly. the bromohydrin XVII was treated with NaH/THF to give a mixture which contained ketone XX but in very low proportion (2%). The remaining products proved to be the diastereomeric *endo. endo* alcohol XXI (34%) and *exo. endo* alcohol XV (64%); (Table 1). It is known that enolizable ketones (such as XXVII) react with NaH to form the enolate anion rather than undergo hydride attack of the carbonyl carbon atom.[24] With nonenolizable ketones (such as XX) the latter process occurs. On the basis of these observations it would appear that bromohydrin XVII undergoes 1.4-hydride-shift-substitution to yield the methylnortricyclanone XX which. in contrast to ketone XXVII. suffers carbonyl reduction under these conditions giving a mixture of the diastereomeric alcohols XV and XXI. In support of this. ketone XX was found to give XV and XXI (and 2% reactant XX) under identical conditions. However. the proportions of XV (23%) and XXI (75%) were markedly different from the proportions resulting from identical treatment of bromohydrin XVII (Table 1). This difference in product distribution is not consistent with a single mechanistic pathway. involving 1.4-hydride-shift-substitution and subsequent carbonyl reduction. for reaction of bromohydrin XVII. We believe that XVII on treatment with NaH/THF. partitions between two competing reactions: one involving NaH debromination of XVII to give the *exo. endo* alcohol XV directly and the other involving 1.4-hydride-shift-substitution to give ketone XX which is reduced to alcohols XV and XXI. A comparison of the two product distributions suggests that these two pathways occur almost equally.

The third bromohydrin XVIII resulting from HBr treatment of epoxide XII could not be obtained homogeneous and consequently structural elucidation was performed on a sample which contained some of bromohydrin XVII (*ca* 5%). The NMR spectrum of XVIII showed a one proton singlet at τ 5·49 which was assigned to the carbinol methine proton on C-6. A one proton signal containing seven lines (doublet of doublets of doublets with J = 8. 5 and 3 Hz) occurred at τ 5·76 and was assigned to the proton on C-4. Characteristic IR absorption occurred at 3625 cm^{-1} (OH stretch) and 3045 cm^{-1} (cyclopropane C--H stretch). Reductive debromination of bromohydrin XVIII yielded the known tricyclic alcohol XXVIII[25] which was

identical to an authentic sample prepared from the corresponding tricyclic ketone* by reduction and subsequent equilibration of the epimeric alcohol.[25a]

Further evidence for structure XVIII. and in particular for the position of the bromo substituent, was sought by attempting to convert bromohydrin XVIII to the known unsaturated tricyclic alcohol XXIX[27] under dehydrobromination conditions. However, treatment of bromohydrin XVIII with KOH in EtOH afforded the bicyclic alcohol XXXVI. This alcohol was identical to the major component obtained from LAH reduction of a mixture of the known esters,[32] *exo*-7-carboethoxybicyclo-[4.1.0]hept-3-ene (XXXIV) (97%) and *endo*-7-carboethoxybicyclo[4.1.0]hept-3-ene (XXXIII) (3%). Although unexpected, the formation of alcohol XXXVI from bromohydrin XVIII under these conditions does provide some evidence for the position of the bromo substituent. If the bromo substituent is at C-4 in bromohydrin XVIII then one might expect this γ-bromoalcohol to undergo heterolytic cleavage under basic conditions to give initially the *endo* aldehyde XXXVII.[33] Subsequent epimerization of the *endo* aldehyde would yield the *exo* isomer XXXVIII which could well suffer hydride reduction under the above conditions[34] to afford the corresponding *exo* carbinol XXXVI.

Although these transformations define the parent skeleton and the configuration of C-6 of XVIII there still remains some ambiguity as to the configuration of C-4. The structural assignment shown in XVIII is preferred on the basis of mechanistic considerations.

Formation of rearranged products on treatment of epoxide XII with either HBr or LAH may be considered as a criterion for an ionic mechanism. Accordingly, acid catalysed cleavage of epoxide XII would lead directly to the intermediate tricyclooctyl cation which by analogy with extensive prior work[6, 28–30] is represented schematically as structure XXX and which is thought to be in equilibrium with cation XXXI. Subsequent nucleophilic capture of cation XXX by bromide ion results in stereospecific formation of bromohydrins XVI and XVIII. There appears to be very good evidence[29] that the *exo*-tricyclo[3.2.1.$0^{2,4}$]octyl product XVI is obtained solely from an intermediate such as XXX which ensures stereospecific nucleophilic capture. However, the results of Berson *et al.*[29] indicate that the tricyclo[3.2.1.$0^{2,7}$]octyl product XVIII may not be derived exclusively from the same ion but jointly from this ion and a tricyclo[3.2.1.$0^{2,7}$]oct-4-yl cation XXXII which is symmetrical with respect to nucleophilic attack. In this event, a bromohydrin diasteromeric with XVIII could well be formed and indeed the isolated tricyclo[3.2.1.$0^{2,7}$]octyl product may well have this alternate stereochemistry. We feel reasonably confident that only one such diasteromer is formed in the present instance but some caution should be exercised in this regard particularly in view of the experimental difficulties encountered in attenpting to recover this particular bromohydrin efficiently from the product mixture. We also feel that bromohydrin XVIII has the indicated stereochemistry since it might be expected that the present solvent system would not allow for significant leakage of cation XXX into the tricyclo[3.2.1.$0^{2,7}$]oct-4-yl cation XXXII. The absence of any hydride shifted tricyclo[3.2.1.$0^{2,7}$]oct-3-yl and the derived bicyclo-

* This ketone was originally prepared by LeBel ref 25. Subsequently, an alternate and more convenient method of preparation was reported almost simultaneously by three independent groups of workers ref 26.

[3.2.1]oct-2-en-7-yl products does add some support to this assumption. However, this question of the stereochemistry of XVIII must remain open at this stage.

The steps involving bromide ion capture of the intermediate cations are thought to be irreversible under the present conditions since in monitoring this reaction, and particularly the reaction of epoxide XII with $MgBr_2$ in ether, the product composition was observed to be independent of the extent of reaction.

A similar mechanism may account for the products formed from LAH reduction of epoxide XII. As might be expected the product distribution is quite different. The predominant formation of the *exo*-tricyclo[3.2.1.$0^{2,4}$]octyl derivative is indicative of major hydride capture of ion XXX from a hydrogen atom which is bonded to aluminium which in turn is bonded to the oxygen atom of XXX.

EXPERIMENTAL

All m.ps and b.ps were uncorrected. Microanalyses were performed at the Australian Microanalytical Service, Melbourne. NMR spectra refer to CCl_4 solns and were recorded using a Varian A-60 spectrometer. Chemical shifts were measured on the τ-scale relative to internal TMS. Multiplicities of signals are abbreviated as follows: s = singlet, d = doublet, tr = triplet etc. IR spectra refer to CCl_4 solns and were obtained with a Perkin–Elmer 337 spectrophotometer. Analytical vapour phase chromatography (VPC) was carried out using a Perkin–Elmer 880 gas chromatograph (F.I.D.) with the following columns:

1. 0·125 in O.D. × 10 ft Cu column of 5% TCEP on non acid washed Chromosorb W 80/100. 2. 0·125 in. O.D. × 10 ft Cu column of 5% Ucon 50 HB 2000 on non acid washed Chromosorb W 80/100. 3. 0·125 in. O.D. × 10 ft Cu column of 5% Hyprose SP-80 on non acid washed Chromosorb W 80/100. 4. 0·125 in. O.D. × 10 ft Cu column of 5% Carbowax 4000 on non acid washed Chromosorb W 80/100.

Percentage composition of mixtures were calculated from area percentages of each VPC trace without correction for molar response factors.

Preparative VPC was carried out using an Aerograph 700 Autoprep with following columns

5. 0·375 in. O.D. × 10 ft Al column of 15% Ucon 50 HB 2000 on non acid washed Chromosorb W 60/80. 6. 0·375 in. O.D. × 10 ft Al column of 10% Carbowax 20M on non acid washed Chromosorb W 60/80.

Epoxidation of endo-*tricyclo*[3.2.1.$0^{2,4}$]oct-6-ene (X). (a) *With monoperphthalic acid.* Olefin X[7] (8·1 g) was added to a soln of monoperphthalic acid (40 g) in dry ether (200 ml). The reaction mixture was allowed to stand for 3 days at 6° until a dense precipitate of phthalic acid had formed, and was then washed with satd Na_2CO_3 aq (8 × 100 ml), water (4 × 100 ml) and dried ($MgSO_4$). Evaporation of the ether under vacuum yielded *exo*-3-oxa-*endo*-tetracyclo[3.3.1.$0^{2,4}$.$0^{6,8}$]nonane (XII) as a white crystalline solid (7·5 g, 80%) m.p. 92–93°. The crude solid was greater than 99·5% one peak by VPC (col 1, 101°). An analytical sample, m.p. 92–93°, was obtained by vacuum sublimation of the crude solid. (Found: C, 78·55; H, 8·14; Calc for $C_8H_{10}O$: C, 78·65; H, 8·25%). NMR 7·12, s $W_{\frac{1}{2}h}$ = 2·5 Hz (2H); 7·53, br s $W_{\frac{1}{2}h}$ = 6·5 Hz (2H); 8·30, m (2H); 8·65, m (3H); 9·38, m (1H); IR 3070, 3030, 1046, 850 cm^{-1}. The purity of epoxide appears to be determined solely by the purity of the olefin used.

(b) *With peracetic acid.* Commercial peracetic acid (4·5 ml) was added dropwise to a stirred, cold (0°) mixture of the olefin X (2·0 g) in CH_2Cl_2 (25 ml) containing anhydrous NaOAc (0·2 g). The mixture was allowed to stand at room temp and after 30 min the temp had increased to 40°. The mixture was stirred at room temp for 11 hr and then poured into ether (200 ml). The ether soln was washed with satd aq Na_2CO_3 (4 × 75 ml), water (2 × 50 ml) and dried ($MgSO_4$). Evaporation of the ether gave the epoxide XII (2·1 g, 91%) which was identical (NMR and IR) to the epoxide described above.

Li, NH_3 *reduction of epoxide* XII. A soln of epoxide XII (600 mg) in ether (3 ml) was added dropwise to a mixture of Li shot (400 mg) and anhyd liquid NH_3 (70 ml) maintained at −33°. The mixture was stirred for 30 min and then EtOH added dropwise until the blue colour disappeared. The NH_3 was allowed to evaporate and the residue was diluted with H_2O (50 ml) and then extracted with ether (3 × 50 ml). The ethereal soln was washed with satd NH_4Cl aq (3 × 50 ml), H_2O (2 × 50 ml) and dried ($MgSO_4$). Evaporation of the ether gave an oil (480 mg, 80%) which showed one major component (98%) on VPC (col 2, 135°). The component was collected to give *endo*-tricyclo[3.2.1.$0^{2,4}$]octan-*exo*-6-ol (XIII) m.p. 74–77° (lit[6a] 75–79·5), identical NMR, IR and m.m.p.) to a sample prepared by the procedure of Wiberg and Wenzinger.[6a] NMR · 6·48, d of d, *J* = 2·5 and 6·0 Hz (1H) · 5·90, s, OH (1H); 7·5 to 8·1, br m (2H) 8·2, br

s $W_{\frac{1}{2}h}$ = 4 Hz (2H); 8·3 to 8·9 br m (4H); 8·9 to 9·5. br m (2H); IR: 3625. 3075. 3030. 3011. 1085. 1070. 1037. 1020 cm^{-1}.

LAH *reduction** *of epoxide* XII. Epoxide XII (440 mg) in dry diglyme (20 ml) was added to a suspension of LAH (100 mg) in dry diglyme (50 ml) and the mixture refluxed for 50 hr. Satd Na_2SO_4aq was added and the resultant mixture extracted with ether (3 × 200 ml). The ethereal soln was washed with H_2O (3 × 100 ml). dried ($MgSO_4$) and evaporated to give an oil (290 mg. 65%) which on analytical VPC (col 2. 135°) showed the presence of two components (5% and 95%). Separation of the two components was effected by preparative VPC (col 5. 160°). The minor component was shown to be identical (NMR and IR) to the methylnortricylanol XV which is characterized further on. The major component was shown to be *exo*-tricyclo[3.2.1.0^{2,4}]octan-*anti*-8-ol XIV m.p. 72–73° (lit[14] 75–76) by comparison of the IR and NMR spectra with those of an authentic sample of XIV prepared according to the published procedure[14].

Reaction of epoxide XII *with* HBraq. A soln of the epoxide XII (12·3 g) in petroleum ether (80 ml) at 10° was poured slowly into aq HBr soln (48%. 31 ml) with shaking and cooling. After 15 min the mixture was extracted with ether (3 × 150 ml) and the ether extract washed with sat Na_2CO_3aq (3 × 150 ml) and dried ($MgSO_4$). Evaporation of the ether yielded a brown oil (16·3 g) shown to be a mixture of three major components by analytical VPC (XVI 47%. XVII 42% and XVIII 11%; col 1. 105°). The components of the mixture appeared to be stable under these analytical VPC conditions but attempted separation of the components by preparative VPC at slightly higher temperatures and with thermal conductivity detection resulted in extensive decomposition.

The crude oil was chromatographed on neutral alumina (activity II; 70 g of alumina to 1 g of crude oil). In this manner homogeneous samples of XVI and XVII were obtained but in low yield due to incomplete separation. Elution with a mixture of 90% pet ether: 10% ether gave a solid (5·2 g) which showed only one peak on analytical VPC (col 1. 105°). Crystallization (twice) from pet ether yielded *exo*-6-bromo-*exo*-tricyclo[3.2.1.0^{2,4}]octan-*anti*-8-ol XVI as fine needles. m.p. 58·5–59·5°. (Found: C. 47·29; H. 5·66; Br 39·2; Calc for $C_8H_{11}BrO$; C. 47·32; H. 5·46; Br. 39·4%). NMR 5·92. br tr (1H); 6·13. br s $W_{\frac{1}{2}h}$ = 6 Hz (1H): 7·55. m (4H); 7·7 s. OH. (1H); 8·93. m (3H); 9·73. m (1H); IR 3550. 3056. 3005. 1053. 615. 585. The *p*-nitrobenzoate. prepared in the usual manner with *p*-nitrobenzoyl chloride and pyridine. was crystallized (three times) from pet ether and had m.p. 98–99°. (Found: C. 51·10; H. 4·15; N. 3·60; Br. 23·0; Calc for $C_{15}H_{14}O_4$ NBr: C. 51·15; H. 4·00; N. 3·89; Br. 22·7%).

Elution with a mixture of 80% pet ether: 20% ether yielded *endo*-5-bromomethyltricyclo[2.2.1.0^{2,6}] heptan-*exo*-3-ol (XVII) (1·6 g) as a colourless oil which displayed only one peak on analytical VPC (col 1. 105°). An analytical sample was prepared by microdistallation under vacuum. (Found: C. 47·35; H. 5·60; Br. 39·7; Calc for $C_8H_{11}BrO$: C. 47·32; H. 5·46; Br. 39·4%). NMR: 5·94. poorly resolved tr. J = 1 Hz (1H); 6·73. d J = 8 Hz (2H); 7·04. s. OH (1H); 7·77 to 8·26. m (3H); 8·50 to 8·86. m (4H); IR 3617. 3057. 1046. 624. 574 cm^{-1}.

Further elution with a mixture of 80% pet ether: 20% ether gave a low melting solid fraction (50 mg) which was enriched in the minor component (95%). An analytical sample was prepared by microdistillation under vacuum. (Found: C. 46·97; H. 5·42; Br. 39·7; Calc for $C_8H_{11}BrO$: C. 47·32; H. 5·46; Br. 39·4%): PMR: 5·49. s (1H); 5·76 d of d of d. J = 8. 5 and 3 Hz (1H); 6·58. s OH (1H); 7·3 to 8·0. br m (4H); 8·46. m (3H); 9·02. m (1H); IR: 3625. 3045. 1058 cm^{-1}.

Reaction of epoxide XII *with* $MgBr_2$ *in ether*. The procedure is similar to that used by Crandall[16a] with norbornene oxide. Bromine (244 mg. 2 mmol) was added to a stirred mixture of Mg turnings (56 mg. 2·3 mmol) in anhyd ether (50 ml) at 0°. When the exothermic reaction had subsided the mixture was brought to room temp and then stirred for a further 3 hr. At this stage the mixture consisted of two phases a colourless upper phase and a slightly turbid lower phase. A soln of epoxide XII (170 mg. 1·4 mmol) in ether (20 ml) was added and the mixture stirred for 3 hrs at 15°. Cold 10% NH_4Claq (40 ml) was added and the ether layer was separated and washed with 5% $NaHCO_3$aq (2 × 20 ml). water (3 × 20 ml) and then dried ($MgSO_4$). Evaporation of the ether yield a pale yellow oil (280 mg) which on VPC analysis showed four peaks corresponding to epoxide XII (10%) and bromohydrins XVI (33%). XVII (48%) and XVIII (9%). The epoxide XII was identified by peak enhancement and the bromohydrins were identified from IR spectra of samples separated by chromatography on alumina (see separation above).

Debromination of exo-6-*bromo*-exo-*tricyclo*[3.2.1.0^{2,4}]*octan*-anti-8-*ol* (XVI). A mixture of bromohydrin XVI (78 mg). LAH (50 mg) and dry ether (50 ml) was refluxed for 43 hr. The reaction was monitored by VPC. Sat Na_2SO_4aq (25 ml) was added carefully and the ether layer separated and washed with water

* This reduction was carried out according to the procedure recommended in Ref 1*c*.

(2 × 10 ml) and dried $MgSO_4$). Evaporation of the ether yielded a solid (27 mg. 59%) which was sublimed (once) under vacuum to give *exo*-tricyclo[3.2.1.$0^{2,4}$]octan-*anti*-8-ol (XIV) m.p. 72·5–73·5° (lit[14] 75–76°). A mixed m.p. with an authentic sample of XIV. prepared according to the published procedure[14], was undepressed. The IR spectrum was identical to that of the authentic sample.

Preparation of exo-*tricyclo*[3.2.1.$0^{2,4}$]*oct-6-en*-anti-8-*ol* (XIX). One drop of 32% HClaq was added to a cold. stirred soln of bromohydrin XVI (2·14 g) in dihydropyran (2·54 g). The soln was allowed to come to room temp and then stirred for a further 16 hr. The mixture was diluted with ether (500 ml) and the ethereal soln was washed with sat $NaHCO_3$aq (3 × 100 ml). water (2 × 100 ml) and dried ($MgSO_4$). Evaporation of the solvent yielded the crude tetrahydropyranyl ether as an oil (3·27 g) which was purified by distillation (120–140° bath temp. 0·1 mm).

The tetrahydropyranyl ether (3·0 g) was dissolved in 4M KOMe–MeOH (25 ml) and the soln heated to 110° (oil bath temp) for 16 hr. The reaction mixture was poured into water (200 ml) and the product extracted into ether (4 × 100 ml). The ethereal soln was washed with water (4 × 100 ml). dried ($MgSO_4$) and evaporated to yield an oil (2·0 g). The crude product was dissolved in MeOH (20 ml) and the soln diluted with a soln of HCl in MeOH (25 ml; prepared from MeOH. 200 ml. and 32% HClaq. 16 ml). The mixture was refluxed for 1 hr. then neutralized with solid Na_2CO_3 and diluted with H_2O (500 ml). The aq mixture was extracted with ether (3 × 250 ml) and the ethereal soln was washed with water (4 × 200 ml). dried ($MgSO_4$) and evaporated to yield an oil (1·5 g). A preliminary purification of the crude oil was effected by chromatography on activity II neutral alumina. Most of the impurities were removed by eluting the column with pentane. Subsequent elution with ether gave the crude alcohol (0·80 g) which was purified by preparative VPC (col 5. 160°). Alcohol XIX was obtained as a colourless liquid (Found: C. 78·78; H. 8·34; Calc for $C_8H_{10}O$: C. 78·65; H. 8·25%). NMR: 3·68. unresolved m (2H); 6·38 unresolved m (1H); 7·33. s $W_{\frac{1}{2}h}$ = 5 Hz (2H); 7·80. s. OH (1H); 8·07. m (1H); 8·96. m (3H); IR: 3567. 3115. 3074. 3060. 3022. 1100. 1040. 695. 64 cm^{-1}.

The *p*-toluenesulphonate was prepared in the usual manner with TsCl in pyridine and was crystallized from pentane. m.p. 81·5–82° (Found: C. 65·29; H. 5·90; S. 11·53; Calc for $C_{15}H_{16}O_3S$: C. 65·22; H. 5·80; S. 11·59%).

LAH *reduction of* exo-*tricyclo*[3.2.1.$0^{2,4}$]*oct-6-en*-anti-8-*ol* (XIX). A soln of XIX (75 mg) in ether (15 ml) was added dropwise to a stirred suspension of LAH (30 mg) in ether (20 ml). The mixture was stirred for a further 3 hr at room temp. Sat Na_2SO_4aq (10 ml) was added and the mixture extracted with ether (2 × 50 ml). The ethereal soln was washed with water (2 × 50 ml). dried ($MgSO_4$) and evaporated to give an oil (72 mg; 96%) which was shown to consist of two components (XIX 10% XIV 90%) by VPC (col 2. 130°). The mixture was separated by preparative VPC (col 5. 160°). As collected the product had m.p. 74–75° (lit[14] 75–76) and was shown to be identical (IR. VPC retention time and m.m.p.) to an authentic sample of *exo*-tricyclo[3.2.1.$0^{2,4}$]octan-*anti*-8-ol (XIV) prepared according to the method of Pincock and Wells.[14]

Debromination of endo-5-*bromomethyltricyclo*[2.2.1.$0^{2,6}$]*heptan*-exo-3-*ol* (XVII). A mixture of bromohydrin XVII (2 g). LAH (0·5 g) and dry ether (200 ml) was refluxed for 108 hr. The reaction was monitored by VPC. Isolation as above gave *endo*-5-methyltricyclo[2.2.1.$0^{2,6}$]heptan-*exo*-3-ol (XV) (1·08 g. 88%) as a colourless liquid which was shown to be greater than 98% one peak by analytical VPC (col 2. 120°). An analytical sample was prepared by microdistillation under vacuum. (Found: C. 77·20; H. 9·89; Calc for $C_8H_{12}O$: C. 77·40; H. 9·73%). NMR: 5·95. br s $W_{\frac{1}{2}h}$ = 5 Hz (1H); 6·23. s. OH (1H): 8·0 to 9·3. br m (10H); IR: 3615. 3050. 1050 cm^{-1}.

Oxidation of endo-5-*methyltricyclo*[2.2.1.$0^{2,6}$]heptan-*exo*-3-*ol* (XV). The procedure used was similar to that described by Meinwald *et al*[31] for the oxidation of nortricyclanol. Under these conditions the methylnortricylanol XV (1·05 g) gave *endo*-5-methyltricyclo[2.2.1.$0^{2,6}$]heptan-3-one (XX) (0·76 g. 72%) as a colourless liquid which was shown to be greater than 99% one peak by VPC (col 2. 120°); IR: 3061. 3012. 1760 cm^{-1}. Satisfactory elemental analyses could not be obtained presumably because the ketone is hygroscopic. This behaviour is reminiscent of that of nortricyclanone.[21]

The 2,4-dinitrophenylhydrazone was prepared according to standard procedure and was crystallized (three times) from MeOH to give orange needles m.p. 192–194°. (Found: C. 55·53; H. 4·68; N. 18·89; Calc for $C_{14}H_{14}O_4N_4$: C. 55·62; H. 4·67; N. 18·54%).

Reduction of endo-5-*methyltricyclo*[2.2.1.$0^{2,6}$]*heptan*-3-*one* (XX) *with LAH*. Ketone XX (150 mg) in dry ether (10 ml) was added dropwise to LAH (100 mg) in ether (10 ml) and the mixture stirred for ½ hr at 15°. The reaction mixture was decomposed with satd Na_2SO_4aq (15 ml) and the ether layer was separated and washed with water (3 × 10 ml) and dried ($MgSO_4$). Evaporation of the ether gave a solid (120 mg. 83%) which was greater than 98% one peak on VPC (col 3. 120°). The solid was sublimed (once. 40°. 0·1 mm) to

give XXI. m.p. 44–45° (Found: C. 77·23; H. 9·83; Calc for $C_8H_{12}O$: C. 77·40; H. 9·73%). NMR: 6·15. d J = 1·5 Hz (1H); 6·49. s. OH (1H); 8·1 to 8·5. m (2H); 8·7 to 9·1. m (8H); IR: 3630. 3062. 1075 cm^{-1}.

Oxidation of alcohol XXI (30 mg) according to the method of Meinwald *et al*[31] gave the corresponding ketone (25 mg. 83%) which was greater than 98% one peak on VPC and displayed and IR spectrum identical to that of XX.

Oxidation of endo-5-*bromomethyltricyclo*[2.2.1.0^{2,6}]*heptan*-exo-3-*ol* (XVII). The procedure used was similar to that described by Meinwald *et al*[31] for the oxidation of nortricyclanol. Bromohydrin XVII (1·5 g) gave the corresponding ketone XXII (1·2 g. 83%) as a colourless liquid which was shown to be greater than 98% one peak by VPC (col 1. 120°). An analytical sample was prepared by microdistillation under vacuum. (Found: C. 48·07; H. 4·62; Br. 39·5; Calc for C_8H_9OBr: C. 47·79; H. 4·51; Br. 39·7%); NMR: 6·68. m (2H); 7·3 to 8·3. br m (5H); 8·4 to 8·8. m (2H); IR: 3067. 3012. 1762. 633. 612 cm^{-1}.

The 2,4-dinitrophenylhydrazone. prepared in the usual manner. was crystallized (three times) from MeOH to give orange flakes m.p. 213–214·5° (Found: C. 43·90; H. 3·45; Br. 20·8; N. 14·85; Calc for $C_{14}H_{13}O_4BrN_4$: C. 44·11; H. 3·44; Br. 21·0; N. 14·70%).

Treatment of endo-5-*bromomethyltricyclo*[2.2.1.0^{2,6}]*heptan*-3-*one* (XXII) *with LAH*. Ketone XXII (1 g) in dry ether (20 ml) was added dropwise to a suspension of LAH (250 mg) in ether (20 ml) and the mixture stirred for ½ hour at 15°. The reaction mixture was decomposed with satd Na_2SO_4 aq (30 ml) and the ether layer was separated and washed with water (3 × 15 ml) and dried ($MgSO_4$). Evaporation of the ether gave a colourless oil (610 mg) which was shown by VPC (col 2. 120°) to consist of two components (XXIII 44%. XXI 56%). The mixture was separated by preparative VPC (col 5. 140°).

8-Oxatetracyclo[4.3.0.0^{2,4}0^{3,7}]nonane (XXIII) was collected as a colourless oil which was purified by microdistillation under vacuum (Found: C. 78·65; H. 8·58; Calc for $C_8H_{10}O$: C. 78·65; H. 8·25%); NMR: 5·90. br tr J = 1·5 Hz (1H) 6·31. d "J" = 1·5 Hz (2H); 7·70 br s (1H); 8·11. br s (1H); 8·34. br s (2H); 8·84. br s (3H); IR: 3060. 1043. 1023. 923 cm^{-1}.

endo-5-Methyltricyclo[2.2.1.0^{2,6}]heptan-*endo*-3-ol (XXI) was collected as a solid which after sublimation (once. 40°. 0·1 mm) had m.p. 44–45° and was identical (IR. PMR. R_f) to a sample of this alcohol described previously.

Under identical conditions of reduction (LAH in ether for ½ hr at 15°) the tetracyclic ether XXIII gave a mixture of reactant (95%) and alcohol XXI (5%) both of which were identified by VPC peak enhancement only.

Reaction of endo-5-*bromomethyltricyclo*[2.2.1.0^{2,6}]*heptan*-exo-3-*ol* XVII *with KOH–EtOH*. Bromohydrin XVII (430 mg) was refluxed in 5% KOH in EtOH (30 ml) for 24 hr. The reaction was monitored by analytical VPC. The brown soln was diluted with water (150 ml) and then extracted with ether (3 × 50 ml). The ethereal soln was washed with sat NH_4Cl aq (2 × 25 ml). H_2O (2 × 25 ml) and dried ($MgSO_4$). Evaporation of the ether yielded a red oil (230 mg) which was shown by VPC (col 2. 120°) to consist of three components. (XX 4%. XXIV 38%. XXV 58%). The components were separated by preparative VPC (col 5. 140°).

Ketone XX was collected as a liquid. identified by comparison of the IR spectrum with that of XX described previously. Olefin XXIV was collected as a liquid and an analytical sample prepared by microdistillation under vacuum (Found: C. 78·98; H. 8·23; Calc for $C_8H_{10}O$: C. 78·65; H. 8·25%); NMR: 5·43 and 5·49. s (2H); 6·22 tr J = 2 Hz (1H); 6·47. s. OH (1H); 7·97. m (1H); 8·1 to 8·8 br m (5H); IR: 3616. 3073. 1673. 860 cm^{-1}. Hydroxyether XXV was collected as a liquid. An analytical sample was prepared by microdistillation under vacuum (Found: C. 71·34; H. 9·54; Calc for $C_{10}H_{16}O_2$: C. 71·39; H. 9·59%); NMR: 6·01. tr J = 2 Hz (1H); 6·61. q J = 7 Hz and 6·72. d J = 7 Hz (4H); 7·00. s. OH (1H); 7·9 to 8·3. m (3H); 8·5 to 9·0 m with a superimposed tr at 8·85. J = 7 Hz (7H); IR: 3624. 3072. 1097. 1066. 841 cm^{-1}.

Reaction of endo-5-*bromomethyltricyclo*[2.2.1.0^{2,6}]*heptan*-exo-3-*ol* (XVII) *with NaH in THF*. Bromohydrin XVII (1·1 g) was refluxed in THF (40 ml) with NaH (350 mg) for 50 hr. The reaction was monitored by VPC. The brown reaction mixture was diluted carefully with water (200 ml) and the aq mixture extracted with ether (4 × 100 ml). The ethereal soln was washed with H_2O (4 × 50 ml) and dried ($MgSO_4$). Evaporation of the ether gave a yellow liquid which was shown by VPC (col 2 and col 3. both 120°) to consist of three major components: XX 2%. XXI 34%. XV 64%. The ketone XX was identified by VPC peak enhancement only. Alcohols XV and XXI were identified by peak enhancement and by comparison of the IR spectra of collected samples with those of samples of the alcohols described previously.

Reaction of endo-3-*methyltricyclo*[2.2.1.0^{2,6}]*heptan*-3-*one* XX *with NaH in THF*. The conditions used were identical to those described above. The ketone XX yielded a mixture of three components: XX (2%). XV (23%). XXI (75%). Each component was identified by VPC peak enhancement only.

Debromination of bromohydrin XVIII. A soln of XVIII (3·0 g, contaminated with minor proportions of XVI and XVII) in ether (5 ml) was added dropwise to a mixture of Li shot (0·5 g) and anhyd NH_3 (70 ml) maintained at −33°. The mixture was stirred for 45 min and then EtOH was added dropwise until the blue colour disappeared. The NH_3 was allowed to evaporate and the residue was diluted with H_2O (50 ml) and then extracted with ether (3 × 100 ml). The ethereal soln was washed with H_2O (3 × 50 ml) and dried ($MgSO_4$). Evaporation of the ether gave an oil (1·4 g, 76%) which was separated into three components by preparative VPC (col 6, 140°). Two of these components (arising from the contaminating bromohydrins XVI and XVII) were shown to be identical (IR, PMR and R_t) to alcohols XIV and XV. The third component was shown to be identical (NMR, IR, R_t and m.m.p.) to *endo*-tricyclo[3.2.1.$0^{2,7}$]octan-6-ol (XXVIII) prepared according to the published procedure.[25,26]

exo- *and* endo-7-*Hydroxymethylbicyclo*[4.1.0]*hept*-3-*ene* (XXXVI and XXXV). Addition of ethyl diazoacetate to cyclohexa-1,4-diene according to the published procedure[32] gave a mixture of *endo*-7-carboethoxybicyclo[4.1.0]hept-3-ene XXXIII (2%), *exo*-7-carboethoxybicyclo[4.1.0]hept-3-ene XXXIV (59%), diethyl fumarate (23%) and diethyl maleate (16%). The composition of the product was determined by NMR spectroscopy and VPC.

A soln of this mixture (8·2 g) in anhyd ether (50 ml) was added dropwise to a stirred suspension of LAH (5·7 g) in ether (150 ml) at 0°. Addition was complete in 30 min and stirring was continued for another 1·5 hr at room temp. Work-up in the usual manner gave a liquid (3·3 g) which on vpc analysis (col 14, 145°) showed three componenents: Component 1 (2%), Component 2 (88%) and Component 3 (10%) in order of increasing R_t. The NMR spectrum of the mixture indicated that none of these components corresponded to products arising from LAH reduction of fumaric and maleic esters and presumably the latter were extracted into the aqueous phase during work-up. The components of the mixture were separated by preparative VPC (col 6, 160°).

Component 1 formed a liquid the NMR spectrum of which showed no absorption in the vinyl region. This component was not investigated further. Component 2 was distilled under vac to give *exo*-7-*hydroxymethylbicyclo*[4.1.0]*hept*-3-*ene* (XXXVI) as a clear liquid. (Found: C, 76·97; H, 9·84; Calc for $C_8H_{12}O$: C, 77·37; H, 9·73%) NMR: τ 4·75, br s (1·98, vinyl); 6·08, s (1·03, hydroxyl); 6·58, d, J = 6·5 Hz (2·03, carbinol methylene); 7·68, br s (3·92, allylic); 8·8 to 9·2, m (3·04, cyclopropane): IR: 3617, 3026, 3005, 1010, 655 cm^{-1}. Component 3 was collected as a solid which after vac sublimation (80°, 4 mm) gave *endo*-7-*hydroxymethylbicyclo*[4.1.0]*hept*-3-*ene* (XXXV) as white crystals, m.p. 66–67°. (Found: C, 77·67; H, 10·01; Calc for $C_8H_{12}O$: C, 77·37; H, 9·73%). PMR: τ 4·45, br s (1·99, vinyl); 6·51, m (2·03, carbinol methylene); 7·79, br s (3·98, allylic); 8·04, s (1·15, hydroxyl); 8·94, m (2·84, cyclopropane); IR: 3638, 3018, 1024 and 668 cm^{-1}.

Treatment of bromohydrin (XVIII) *with KOH/EtOH*. A mixture of bromohydrins (XVII) and (XVIII) (5 g, containing 30% (XVIII) in 5% KOH/EtOH (200 ml) was refluxed for 30 hr. The mixture was cooled, poured into water (600 ml) and the product extracted with ether (4 × 120 ml). The ethereal soln was washed with water (2 × 200 ml), dried and evaporated to leave a brown oil (3·0 g) which on analytical VPC (col 2, 135°) showed five components: Component 1 (3%), Component 2 (4%), Component 3 (31%), Component 4 (17%) and Component 5 (45%). The crude oil was separated into its components by preparative VPC (col 6, 165°).

Components 1, 3 and 5 were shown to be identical (IR, NMR) to ketone (XX) and alcohols (XXIV) and (XXV) respectively by comparison with samples of these compounds arising from identical base treatment of pure bromohydrin (XVII). NMR spectroscopy indicated that Component 2 was an unsaturated aldehyde but this component was collected in such poor yield that further investigation was precluded. Component 4 was identified as *exo*-7-hydroxymethylbicyclo[4.1.0]hept-3-ene (XXXVI) by comparison of its IR and NMR spectra with those of a sample of this alcohol described above.

Acknowledgement This work was supported by a grant from the Australian Research Grants Committee. We wish to express our gratitude for the award of Commonwealth Scholarships to B.C.H. and D.W.R.

REFERENCES

[1] [a] J. K. Crandall, *J. Org. Chem.* **29**, 2830 (1964)
[b] S. B. Soloway and S. J. Cristol, *Ibid.* **25**, 327 (1960)
[c] N. M. Yoon and H. C. Brown, *J. Am. Chem. Soc.* **90**, 2927 (1968)
[d] H. M. Walborsky and D. F. Loncrini, *Ibid.* **76**, 5396 (1954)
[e] K. Watanabe, C. N. Pillai and H. Pines, *Ibid.* **84**, 3934 (1962)

[1] H. Kwart and T. Takeshita. *J. Org. Chem.* **28**. 670 (1963)
[2] [a] J. Meinwald. S. S. Labana. L. L. Labana and G. H. Wahl. *Tetrahedron Letters* 1789 (1965)
[b] J. E. Franz. M. Dietrich and A. Henshall. *Chem. and Ind.* 1177 (1966)
[3] [a] P. D. Bartlett and W. P. Giddings. *J. Am. Chem. Soc.* **82**. 1240 (1960)
[b] G. A. Wiley. 137th Meeting. A.C.S. Cleveland. Ohio. April. 1960. Abstracts p. 280 (1960)
[4] R. M. Coates and J. L. Kirkpatrick. *J. Am. Chem. Soc.* **90**. 4162 (1968)
[5] K. Kitahonoki. Y. Takano. A. Matsuura and K. Kotera. *Tetrahedron* **25**. 335 (1969)
[6] [a] K. B. Wiberg and G. R. Wenzinger. *J. Org. Chem.* **30**. 2278 (1965)
[b] A. K. Coulter and R. C. Musso. *Ibid.* **30**. 2462 (1965)
[7] [a] K. B. Wiberg and W. Bartley. *J. Am. Chem. Soc.* **82**. 6375 (1960)
[b] G. L. Closs and K. D. Krantz. *J. Org. Chem.* **31**. 638 (1966)
[8] H. E. Simmons. E. P. Blanchard and R. D. Smith. *J. Am. Chem. Soc.* **86**. 1347 (1964)
[9] [a] B. C. Henshaw. D. W. Rome and B. L. Johnson. *Tetrahedron Letters* 6049 (1968)
[b] D. W. Rome and B. L. Johnson. *Ibid.* 6053 (1968)
[10] G. D. Sargent. M. J. Harrison and G. Khoury. *J. Am. Chem. Soc.* **91**. 4937 (1969)
[11] K. Tori. K. Kitahonoki. Y. Takano. H. Tanida and T. Tsuji. *Tetrahedron Letters* 559 (1964)
[12] K. Tori and M. Ohtsuru. *Chem. Comm.* 886 (1966)
[13] J. T. Lumb and G. H. Whitham. *J. Chem. Soc.* 1189 (1964)
[14] [a] R. E. Pincock and J. I. Wells. *J. Org. Chem.* **29**. 965 (1964)
[b] J. Haywood-Farmer. R. E. Pincock and J. I. Wells. *Tetrahedron* **22**. 2007 (1966)
[15] R. V. Meon and H. S. Makowski. *Anal. Chem.* **39**. 1860 (1967)
[16] S. Winstein and E. T. Stafford. *J. Am. Chem. Soc.* **79**. 505 (1957)
[17] S. C. Clarke. K. J. Frayne and B. L. Johnson. *Tetrahedron* **25**. 1265 (1969)
[18] B. Franzus and E. I. Snyder. *J. Am. Chem. Soc.* **87**. 3423 (1965)
[19] U. R. Nayak and S. Dev. *Tetrahedron* **24**. 4099 (1968)
[20] R. S. Neale and E. B. Whipple. *J. Am. Chem. Soc.* **86**. 3130 (1964)
[21] J. P. Schaefer. *Ibid.* **82**. 4091 (1960)
[22] J. Passivirta. *Suomen Kemi* **31B**. 115 (1958)
[23] D. E. Gwynn and L. Skillern. *Chem. Comm.* 490 (1968)
[24] F. W. Swamer and C. R. Hauser. *J. Am. Chem. Soc.* **68**. 2647 (1946)
[25] [a] N. A. LeBel and J. E. Huber. *Ibid.* **85**. 3193 (1963)
[b] N. A. LeBel. J. E. Huber and L. H. Zalkow. *Ibid.* **84**. 2226 (1962)
[26] [a] W. von E. Doering. E. T. Fossel and R. L. Kaye. *Tetrahedron* **21**. 25 (1965)
[b] H. O. House. S. G. Boots and V. K. Jones. *J. Org. Chem.* **30**. 2519 (1965)
[c] V. Ioan. M. Poporici. E. Mosanu. M. Elican and C. D. Nenitzescu. *Rev. Roumaine Chim.* **10** (2). 185 (1965)
[27] S. Winstein. *Quart. Rev.* **23**. 141 (1969)
[28] R. R. Sauers. J. A. Beisler and H. Feilich. *J. Org. Chem.* **32**. 569 (1967)
[29] J. A. Berson. R. G. Bergman. G. M. Clarke and D. Wege. *J. Am. Chem. Soc.* **90**. 3236. 3238. 3240 (1968)
[30] G. N. Fickes. *J. Org. Chem.* **34**. 1513 (1969)
[31] J. Meinwald. J. Crandall and W. E. Hymans. *Org. Syn.* **45**. 77 (1965)
[32] H. Musso and U. Biethan. *Ber. Dtsch. Chem. Ges.* **97**. 2282 (1964)
[33] C. A. Grob and P. W. Schiess. *Angew. Chem. internat. Edit.* **6**. 1 (1967)
[34] F. P. van der Maeden. H. Steinberg and Th. J. de Boer. *Tetrahedron Letters* 4521 (1967)