Tetrahedron. 1967, Vol. 23, pp. 805 to 812. Pergamon Press Ltd. Printed in Northern Ireland

STUDIES ON BICYCLO[3.3.1]NONANES—II

TRANSANNULAR HYDRIDE SHIFTS IN BRIDGED BICYCLES

R. A. Appleton, J. R. Dixon, J. M. Evans and S. H. Graham
The Edward Davies Chemical Laboratory, Aberystwyth

(*Received* 13 *June* 1966)

Abstract—Formolysis of bicyclo[3,3,1]nonan-2β,3β-oxide and of 7β-methylbicyclo[3.3.1]nonan-2β,3β-oxide gives rise to products formed via transannular hydride shifts. No hydride shift has been observed in ionic reactions of [3.3.1]bicycles which carry oxygenated functions at C_9.

Carbonium ions derived from medium-sized rings are characterized by their tendency to undergo transference of hydride ion across the ring.[1] The bicyclo[3,3,1]nonane ring system has structural features in common with the unbridged medium-sized rings in as much as it is subject to serious steric strains. It has been shown[2-4] to exist as a double-chair conformation, and X-ray diffraction has shown the bond angles (except for C_1, C_5, and C_9) to be 114° (average value). This deformation of the rings allows the α-protons on C_3 and C_7 to move further apart and thus minimizes the trans-annular strain. These strains should largely be relieved in bicyclo[3,3,1]non-3-yl carbonium ions and it would be anticipated both that such ions should be formed with particular ease, and would give products formed via trans-annular hydride shifts, as in the case of analogous unbridged ions. Recently a preliminary account of hydride transfer in a bridged bicycle was published,[5] and similar hydride shifts have also recently been observed in the course of synthesizing certain alkaloids.[6,7] We now publish a full account of our investigations.

One of the typical experiments which demonstrated the occurrence of hydride shifts in monocyclic systems was the formation of non-vicinal diols, and of enols other than βγ-enols, in solvolytic opening of epoxide rings.[8] We therefore examined the effect of formic acid on bicyclo[3.3.1]nonan-2β,3β-oxide, (I), and on 7β-methylbicyclo[3.3.1]nonan-2β,3β-oxide, (II). From the latter was obtained a single product (GLC on tritolyl phosphate) the IR spectrum of which showed the absorptions of a trisubstituted ethylene (at 818 and 3004 cm^{-1}) and a formate ester (1182 cm^{-1}). The alcohol obtained on hydrolysis analysed for $C_{10}H_{16}O$, its PMR spectrum indicated the presence of allylic methyl (at τ8·33), axial secondary hydroxyl (at 6·20, too narrow to include any a,a coupling), and one olefinic proton. In addition, chromic acid oxidation of the alcohol gave a ketone, or mixture of ketones, the IR and UV spectra

---

[1] For review see J. Sicher, *Progress in Stereochemistry* (Edited by P.B.D. de la Mare and W. Klyne) Vol 3, pp 243–246. Butterworths, London.

[2] M. W. J. Pumphrey and M. J. T. Robinson, I.U.P.A.C. Congress, July, (1963).

[3] W. A. C. Brown, K. Eglinton, J. Martin, W. Parker and G. A. Sim, *Proc. Chem. Soc.* 57 (1964).

[4] W. A. C. Brown, J. Martin and G. A. Sim, *J. Chem. Soc.* 1844 (1965).

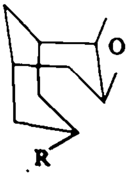
[5] R. A. Appleton and S. H. Graham, *Chem. Comm.* 297 (1965).

[6] H. Dugas, R. A. Ellison, Z. Valenta, K. Wiesner and C. M. Wong, *Tetrahedron Letters* 1279 (1965).

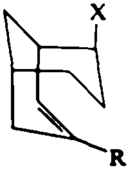
[7] W. A. Ayer and K. Piers, *Chem. Comm.* 541 (1965).

[8] A. C. Cope, S. W. Fenton and C. F. Spencer, *J. Amer. Chem. Soc.* 74, 5884 (1952).

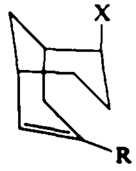
of which showed no olefinic-carbonyl conjugation. Assuming no skeletal rearrangement, a reasonable assumption in the light of the other experiments to be discussed, the formolysis product of II must be VI (X = O·CHO) or VII (X = O·CHO). No decision between these structures is possible and the material might well be a mixture of them, but it showed none of the normal signs of inhomogeneity, and we were able to resolve the analogous mixture III (X = OH) and IV (X = OH) on vapour phase chromatography.



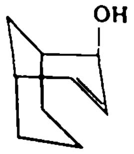
I, R = H
II, R = Me



III, R = H
VI, R = Me



IV, R = H
VII, R = Me



V

Formolysis of I gave a mixture of products which could be separated, after hydrolysis, into enol and diol fractions by steam distillation. The enol fraction comprised three substances in the ratios 46:46:8. Chromic acid oxidation of the mixture gave a ketone mixture which contained both conjugated and non-conjugated olefinic ketones. Oxidation with manganese dioxide gave a small amount of, mainly conjugated, ketone and a mixture of only two enols (TLC). Hydrogenation of the mixed enols gave only bicyclo[3.3.1]nonan-2β-ol, and oxidation (CrO_3) gave two olefinic ketones (TLC) which showed no olefinic-carbonyl conjugation (IR spectrum). These enols must therefore be III (X = OH) and IV (X = OH), the minor component being V.

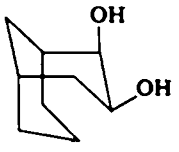
The diol fraction isolated after hydrolysis of the formolysis products of I consisted of two main components (TLC), a third was present in very small amount. Neither of the main components was the 2β,3β-diol VIII, a pure sample of which was prepared by osmic acid oxidation of bicyclonon-2-ene (it had the same R_F on TLC as the minor component of the diol fraction). Neither of the diols reacted with lead tetracetate, neither formed an isopropylidene ketal (differing from the 2β,3β-diol in both respects) but one was oxidized by periodate ion and, from the periodate consumed, it constituted 34% of the mixture (GLC analysis gave 40% of this component). This one is regarded as being the 2β,3α-diol IX, produced by normal *trans*-diaxial opening of the epoxide ring. After destruction of the vicinal diol with periodate the major component of the diol fraction was obtained in a state of purity. No evidence as to structure could be obtained from the PMR spectrum. An attempt was made at selective oxidation to a hydroxyketone since the C_7OH of a 2β,7β-diol (the product to be expected via a hydride shift) should be relatively resistant to oxidation because of its heavily sterically hindered α-proton. Model experiment on 2β- and 3β-hydroxybicyclononanes have shown that the former can be oxidized selectively in the presence of the latter.[9] In fact chromic acid oxidation of the diol led to the unsaturated ketone X. This could obviously be

---

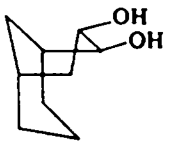
[9] C. Egan and S. H. Graham, to be published.

formed from a number of precursor diols, including XI (by a mechanism which would include a further hydride shift from C_3 to C_7) and its formation give no information as to the structure of the diol save to confirm that no skeletal rearrangement has taken place. While it is not possible to exclude absolutely the possibility of diequatorial opening of the epoxide ring, it seems to be unlikely in the present case. Equatorial opening of epoxide rings in sugars has been observed, but only as a very minor process competing with diaxial ring opening.[10] In the aluminohydride reduction of the trans-oxide of 4-t-butyl-1-methylcyclohexene 68% of (axial) secondary alcohol is produced as against 32% of (equatorial) tertiary alcohol, despite the known tendency of the reagent to attack secondary carbons.[11] The standard example of diequatorial ring opening is the conversion of 2β,3β-epoxylanost-8-en to 2α-bromolanost-8-en-3β-ol.[12] In this case, however, a ready explanation of the anomaly is found in the probable conformation of ring-A of the epoxylanostene as a half-boat. In the absence of any equivalent steric condition, it does not seem that serious amounts of products arising from a diequatorial opening of the epoxide ring are to be anticipated, and one of the two diols produced in the reaction must be non-vicinal. We are attempting to synthesise the diol XI to test the correctness of this conclusion, and are also investigating other ring opening reactions of I to determine if the Furst and Plattner rule applies rigidly to them.

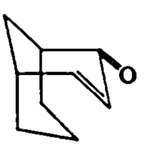
The percentages of enol (38), vicinal diol (24) and non-vicinal diol (36) formed are somewhat different from those (33·3, 13·3 and 53·3 respectively) reported by Cope for formolysis of *cis*-cyclooctene oxide.[13] In the cyclooctane series both 1,3 and 1,5-hydride shifts occur, the principal enol (3-cycloocten-1-ol) being formed almost exclusively via the latter, but non-vicinal diol being formed via both routes.[14] In the bicyclononane series only the equivalent of the 1,5-hydride shift is possible, and the production of rather more enol, and appreciably less non-vicinal diol is easily understood. The small amount of allylic alcohol (8% of the enol fraction, somewhat more than that found by Cope[13]) probably reflects the fact that the developing axial hydroxyl on C_2 will hinder solvent approach to C_4, leading to almost exclusive proton abstraction from C_6 and C_8. The vicinal diol formed in these reactions is regarded as resulting from concerted ring opening and solvation.[13] It might therefore have been expected that less vicinal diol would have been produced from I, as the second ring should hinder solvent approach to C_3: this does not seem to have been the case.



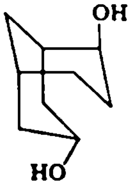
VIII



IX



X



XI

---

[10] F. H. Newth, *Quart. Rev.* **13**, 42 (1959).

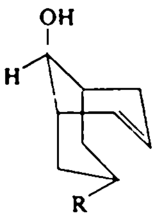
[11] N. A. Le Bel and G. G. Ecke, *J. Org. Chem.* **30**, 4316 (1965).

[12] D. H. R. Barton, D. A. Lewis and J. F. McGhie, *J. Chem. Soc.* 2907 (1957).

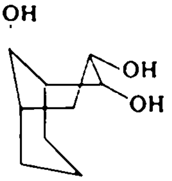
[13] A. C. Cope, J. M. Grisar and P. E. Peterson, *J. Amer. Chem. Soc.* **81**, 1640 (1959).

[14] A. C. Cope, G. A. Berchtold, P. E. Peterson and S. H. Sharman, *J. Amer. Chem. Soc.* **82**, 6366 (1960).

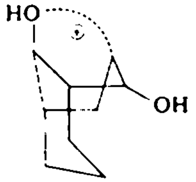
syn-Bicyclo[3.3.1]non-2-en-9-ol XII and its oxide have been prepared.[15] Action of formic acid on this oxide, followed by hydrolysis gave a single product analysing for $C_9H_{16}O_3$, which was not the 2β,3β,9-triol (prepared by osmic acid oxidation of XII). After preliminary mild oxidation with chromic acid, the product reacted with periodate, and the triol is therefore formulated as XIII. Its production at first suggested the interposition of an ion such as XIV. Such delocalisation has been observed in 4-methoxycyclohexyl carbonium ions.[16] The oxide of the epimeric alcohol XV (most conveniently prepared from a mixture of XII and XV) gave a single product, analysing as $C_9H_{14}O_2$. It took up one molecule of hydrogen to give the diol XVII (an authentic sample was prepared by LAH reduction of the oxide of XV), and on oxidation gave an unsaturated diketone with one conjugated carbonyl group. On oxidation with magnanese dioxide a monoketone with conjugated carbonyl group was isolated: the diol is therefore formulated as XVI. The formation of triol from one oxide and of endiol from the other may well be explained by the interposition of ion XIV in the first reaction. However, the failure to observe any transannular hydride shift in the second formolysis cannot be explained, unless the C_9 hydroxyl (axial with respect to the second ring) more effectively blocks approach of solvent to the axial protons on C_6 and C_8, than does the developing C_2 hydroxyl the approach of solvent to C_4. If this were so, then preferential loss of proton from C_4 could readily be understood.



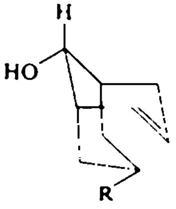
XII, R = H
XVIII, R = Me



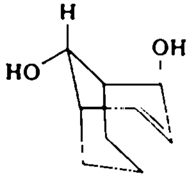
XIII



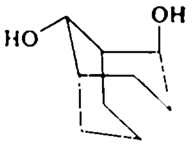
XIV



XV, R = H
XIX, R = Me



XVI



XVII

Although only such speculative explanations can be offered, it seems to be a general rule that transannular hydride shifts are not observable when C_9 is oxygenated. Both the *syn* (XVIII) and *anti*-epimers (XIX) of 7β-methylbicyclo[3.3.1]non-2-en-9-ol, and the related 9-ketone could be recovered unchanged, except for esterification of the

---

[15] J. R. Dixon, S. H. Graham and D. O. Lewis, to be published.

[16] D. S. Noyce and B. N. Bastian, *J. Amer. Chem. Soc.* **82**, 1246 (1960).

hydroxyl groups, after being refluxed with formic acid, and the composition of a mixture of XII (19%) and XV (81%) was unchanged by similar treatment. In the first three cases the starting materials (disubstituted ethylenes) could not have been of lower energy than the products (trisubstituted ethylenes). As for XII and XV, Le Bel and Spurlock[17] have shown that the syn epimer of the bicyclo[3.2.1]oct-2-en-8-ols (corresponding to XII) is in fact of higher energy than the *anti*. However we have equilibrated XII and XV and the equilibrium composition (55% XII and 45% XV) shows that, while ΔF(e → a) for cyclohexanol is only slightly greater than for 4-cyclohexenol, no hydride shift can have taken place during the attempted formic acid equilibration. The difference between the equilibria observed for bicyclooctenols and for bicyclononenols is a reminder that the steric interaction between a substituent on cyclohexane and a cis-vicinal methylene group is markedly dependent on the orientation of the latter. It is of interest to note that a transannular hydride shift has been observed in a hydroxy substituted bridged bicycle,[6] but the hydroxyl was attached to a bridgehead carbon. The apparent necessity of a C_9 methylene in order to realise a transannular hydride shift might tend to suggest that such shifts as are observed do in fact occur via the bridge, $C_7 \rightarrow C_9$, $C_9 \rightarrow C_3$. However, the hydride shift realised with II and the earlier reported isomerization of 7β-methylbicyclononene,[5] cannot be reconciled with this explanation: the configuration of the methyl group has been solidly established and precludes the possibility of a $C_7 \rightarrow C_9$ shift. Nor would $C_9 \rightarrow C_3$ shifts seem reasonable for the epoxides I and II, where again the oxide ring must necessarily be *cis* to the bridge: they could not occur in concert with opening of the oxide ring, as they do in monocyclic systems and almost certainly in bicyclic systems as well.

EXPERIMENTAL

7β-Methylbicyclo[3.3.1]*nonan-2β,3β-oxide* (II)

To a stirred ice-cold soln of 7β-methylbicyclo[3.3.1]non-2-ene[18] (4·0 g) in dry ether (20 ml) was added dropwise a soln of monoperhpthalic acid (7·1 g) in ether (40 ml) during 20 min, and the mixture kept at room temp for 4 days. After extraction with $NaHCO_3$aq (2 × 50 ml), water washing and drying ($MgSO_4$), solvent was removed and the residue distilled to give the *oxide* II (3·47 g, 78%), b.p. 82–82·5°,8 mm, n_D^{24} 1·4860. (Found: C, 79·30; H, 11·00. $C_{10}H_{16}O$ requires: C, 78·90; H, 10·60%.)

Formolysis of 7β-methylbicyclo[3.3.1]*nonan-2β,3β-oxide* (II)

A soln of II (1·0 g) in 98% formic acid (5 ml) was kept at room temp for 2 weeks, then poured into water (30 ml), neutralized with solid Na_2CO_3, and ether extracted (4 × 15 ml). Removal of solvent after drying ($MgSO_4$) left a liquid (0·92 g), b.p. 107–108°/8 mm, n_D^{24} 1·4979. This was homogeneous [GLC on tritolyl phosphate (TTP) at 118°] and had absorptions at 818, 1182 and 3004 cm^{-1}. It was immediately hydrolysed by refluxing a sample (0·42 g) with 4N NaOH (20 ml) and MeOH (2 ml) for 3 hr. Ether extraction of the cooled mixture gave the *alcohol* III or IV (0·35 g), b.p. 113–115°/8 mm, m.p. 44–46°. (Found: C, 78·4; H, 10·5 $C_{10}H_{16}O$ requires: C, 78·9; H, 10·6%.) The PMR spectrum showed a 3-proton singlet at τ 8·33, a single-proton multiplet at τ 6·20 (W_H, 6 c/s), and a single-proton multiplet at τ 4·55.

Oxidation of alcohol III or IV. The alcohol (0·32 g) in ether (10 ml) and sodium dichromate (0·85 g) and conc H_2SO_4, (0·8 ml) in water (4·5 ml) were stirred at room temp for 4 hr. The ether layer was separated, the aqueous phase extracted (3 × 10 ml), the combined extracts washed (water, $NaHCO_3$aq) and dried ($MgSO_4$). Evaporation of solvent left a colourless liquid (0·19 g, 60%), b.p. 106°/9 mm, IR absorption at 1710 cm^{-1}; UV λ max 301 mμ, ϵ max 148 (0·0044 molar in hexane).

---

[17] N. A. Le Bel and L. A. Spurlock, *Tetrahedron* **20**, 215 (1964).

[18] R. A. Appleton and S. H. Graham, to be published.

Formolysis of syn-*9-hydroxybicyclo*[3.3.1]*nonan-2β*: *3β-oxide*

The oxide (1·5 g) and 85% formic acid (50 ml) were refluxed for 30 min, cooled poured into water and extracted with chf. After washing the extracts (water, $NaHCO_3$aq), the chf was evaporated and crude formate ester boiled with KOH (6·5 g) in EtOH (40 ml) for 8 hr. Evaporation of the bulk of the EtOH, dilution with water and ether extraction gave, after evaporation of solvent, *bicyclo*[3.3.1]*nonan-2β,3α-9-triol.* purified by sublimation at 80°/15 mm, m.p. 197°. (Found: C, 62·48; H, 9·70. $C_9H_{16}O_3$ requires: C, 62·76; H, 9·43%.)

Bicyclo[3.3.1]*nonan-2β,3β,9-triol.* The alcohol XII (0·5 g) was added to osmic acid (1 g) in ether (10 ml) and pyridine (1 ml): after 24 hr the crystalline complex was filtered off, and stirred with 5% NaOHaq (80 ml), mannitol (10 g) and chf (20 ml) for 6 hr. The chf soln was washed (HCl, water) and dried ($MgSO_4$) and evaporated to give the *triol* (0.22 g, 32%), m.p. 195°, depressed on admixture with the triol from the formolysis. (Found: C, 63·01; H, 9·55. $C_9H_{16}O_3$ requires: C, 62·76; H, 9·43%.)

Oxidation of triol from formolysis. The triol (0·5 g) in ether (15 ml) was strired with sodium dichromate (0·9 g), conc H_2SO_4 (1·0 ml), and water (10 ml) at room temp for 8 hr. The ether phase was washed (water) dried ($MgSO_4$) and evaporated. The crude oxidation product (0·22 g) was allowed to stand at room temp with 0·11N potassium periodate soln (100 ml) and 2N H_2SO_4 (10 ml). Excess of KI was added, titration with standard thiosulphate showed 95 ml 0·11N KIO_4 had been consumed (81% of theory).

Formolysis of bicyclo[3.3.1]*nonan-2β-3β-oxide* (I)

A soln of the oxide[19] (3 g) in 90% formic acid (90 ml) was stirred at room temp for 2 days (at reflux temp decomposition occurred). Solvent was evaporated at room temp and the residue boiled with 30% NaOHaq (40 ml) under reflux for 2 hr: steam distillation of the mixture gave a fraction (a) (0·94 g), and extraction of the cooled alkaline liquor with chf (2 × 100 ml) gave, after the usual washing and drying a second fraction (b) (1·55 g).

Examination of fraction (a). The IR spectrum showed absorptions at 3623 cm^{-1} (OH) and 3029 cm^{-1} (disubstituted ethylene). Hydrogenation of a portion (0·5 g) in EtOH soln over Pt gave bicyclononan-2β-ol, m.p. 169° undepressed on admixture with an authentic sample[19]. Fraction (a) (0·1 g) in ether (25 ml) was stirred with 5% chromic acid (10 ml) for 4 hr. After the usual work-up the oily mixture of ketones showed IR absorptions at 1712 and 1678 cm^{-1}. Fraction (a) (0·8 g) in chf (100 ml) was stirred with active MnO_2 (10 g)[20,21] for 12 hr at room temp. After filtration and evaporation of solvent the mixture constisted of two alcohols (each 45·5%) and a ketone (9%). (GLC on tritolyl phosphate at 120°). The components were separated by chromatography of a petrol soln on alumina to give ketone (0·07 g) and *alcohols* (0·7 g). (Found: C, 78·03; H, 10·17. $C_9H_{14}O$ requires: C, 78·25; H, 10·14%.) The alcohol fraction comprised two components (TLC on alumina, ether as developer) Oxidation of a portion with chromic acid as above gave a mixture of ketones which showed IR absorption only at 1712 cm^{-1} in the carbonyl region.

Examination of fraction (b). This showed IR absorptions at 3590 and 3401 cm^{-1} but no absorptions characteristic of olefins: it showed two spots on TLC (alumina, developed with MeOH), and three components (2, 58 and 40%) on GLC (fluorosilicone at 160°). Fraction (b) (1 g), was stirred in solution in 0·1N potassium periodate soln (1000 ml) and 2N H_2SO_4 (100 ml) for 24 hr. Back titration of a 25 ml aliquot showed 633 ml of periodate had been consumed corresponding to 34·7% of vicinal diol in the mixture (GLC on fluorosilicone at 160° showed 42% α-diol). The mixture was concentrated *in vacuo* to about 200 ml, saturated with common salt and extracted with chf (3 × 100 ml). Evaporation of solvent after washing and drying left pure *diol* (0·53 g), m.p. 204°. (Found: C, 68·97; H, 10·34. $C_9H_{16}O_2$ requires: C, 69·20; H, 10·32%.) Only the faster moving component of the original mixture was present (TLC on alumina).

Attemped reaction of fraction (b) *with acetone.* The diol mixture (50 mg) was stirred with AnalaR acetone (20 ml) (dried over K_2CO_3) and anhyd $CuSO_4$ (0·5 g) for 48 hr at room temp, then excess of solvent was evaporated from the filtered mixture. Both main components of the original mixture were present unchanged but a small spot on a TLC plate (alumina, developed with ether) corresponded

---

[19] K. Baggaley, J. R. Dixon, J. M. Evans and S. H. Graham, in the press.

[20] R. J. Gritter and T. J. Wallace, *J. Org. Chem.* **24**, 1051 (1959).

[21] F. Sondheimer, C. Amendolla and G. Rosenkranz, *J. Amer. Chem. Soc.* **75**, 5932 (1953).

to the isopropylidene derivative of the 2β,3β-diol, and this was also detected on GLC (5% butanediol succinate at 85°). The diol mixture (0·2 g) was refluxed with acetone (30 ml), petrol (30 ml) and toluenesulphonic acid (0·1 g) for 48 hr,[22] both major components of the mixture remained unchanged under these conditions and also when the petrol was replaced by chf (30 ml).[23]

Bicyclo[3.3.1]*nonan-2β,3β-diol*

Bicyclonon-2-ene (0·24 g) in dry ether (5 ml) was added to osmic acid (0·5 g) in dry ether (10 ml) and pyridine (1 ml). Separation of pale brown complex commenced immediately; after 36 hr it was filtered off and stirred with mannitol (5 g), 5% NaOHaq (40 ml) and chf (20 ml) for 7 hr. The chf layer was separated, the aqueous phase extracted with chf, and the extracts washed with 2N HCl containing NaCl (100 ml). Evaporation of solvent gave the diol (0·28 g, 91%), crystals from petrol b.p. 120° m.p. 139°. (Found: C, 69·17; H, 10·26. $C_9H_{16}O_2$ requires: C, 69·20; H, 10·32%.) TLC (on alumina, developed with MeOH) showed it to differ from both major components of fraction (b)

Mixture of epimeric bicyclo[3.3.1]*non-2-en-9-ols*

Reduction of bicyclo[3,3,1]non-2-en-9-one[24] (8 g) with LAH in the usual way yielded a mixture of two alcohols; IR absorptions at 3623, 3584, 3472 cm^{-1}. Hydrogenation of a portion of the mixture (in soln in AcOH over Pt) gave bicyclo[3.3.1]nonan-9-ol, m.p. 207° (lit[24] 207°). VPC (tritolyl phosphate at 120°) gave the composition as 19% of *syn*-epimer,[14] and 81% *anti*.

Attempted equilibration of epimeric alcohols with formic acid

The mixture of alcohols (0·8 g) in 90% formic acid (35 ml) was heated gently for 0·5 hr, during which time the solution darkened somewhat. The cooled soln was concentrated *in vacuo* and the residue refluxed with 40% NaOHaq (30 ml) for 2 hr. Steam distillation, ether extraction and the usual washing and drying gave a solid (0·63 g) which had the same composition as the original mixture (GLC on tritolyl phosphate at 120°)

Equilibration of epimeric alcohols[25]

Isopropanol was refluxed over and distilled from CaO, acetone was refluxed over and distilled from $CaSO_4$. Equilibrations were carried out starting from both *syn* and *anti* alcohols. The alcohol (0·5 g), redistilled aluminium isopropoxide (0·5 g), acetone (0·6 ml) in isopropanol (13 ml) were refluxed for 72 hr. After cooling reaction mixtures were poured into water (80 ml) and 10N HCl (5 ml), and extracted with ether (50 ml). The ether extracts were washed (water, $NaHCO_3$aq) and dried ($MgSO_4$). The crude solutions were analysed (GLC on tritolyl phosphate at 120°) Starting from *syn*-alcohol the product composition was 57% *syn* and 43% *anti*; starting from *anti*-alcohol the percentages were 53 and 47% respectively.

Anti-9-*Hydroxybicyclo*[3.3.1]*nonan-2β,3β-oxide*

A mixture of the epimeric bicyclo[3.3.1]non-2-en-9-ols (7·7 g) in chf (25 ml) was added dropwise with stirring to an ice cooled soln of perbenzoic acid (8·55 g) in chf (185 ml), and the soln kept in the refrigerator for 2 days. Extraction with $NaHCO_3$aq water washing, drying ($MgSO_4$), and removal of solvent left a semisolid mixture, which gave two spots on TLC. Recrystallization from petrol gave the *oxide* of the *anti* alcohol (3·5 g), white fluffy crystals, m.p. 233°, IR absorptions at 3623 and 3497 cm^{-1}. (Found: C, 65·95; H, 8·93. $C_9H_{14}O_2$ requires: C, 70·13; H, 9·09%.)

anti-*bicyclo*[3.3.1]*nonan-2β,9-diol*

A suspension of LAH (0·1 g) in dry THF (20 ml) was stirred and refluxed for 15 min; after cooling, the above oxiran (0·5 g) in dry THF (30 ml) was added dropwise, with stirring over 15 min. The mixture was refluxed for 4 hr, cooled, cautiously treated with water, and filtered from inorganic solids. Evaporation of the filtrate gave the *diol* (0·51 g, 88·8%), purified by recrystallization from 120° petroleum, m.p. 244°. (Found: C, 69·9; H, 10·10. $C_9H_{16}O_2$ requires: C, 69·20; H, 10·32%.)

[22] M. S. Newman and M. Renoll, *J. Amer. Chem. Soc.* **47**, 1621 (1945).

[23] L. Hartman, *Chem. & Ind.* **711** (1960).

[24] S. Foote and R. B. Woodward, *Tetrahedron* **20**, 687 (1964).

[25] E. L. Eliel and R. S. Ro, *J. Amer. Chem. Soc.* **79**, 5992 (1957).

Solvolysis of 2β,3β-oxide of XV

The oxide (2 g) in 90% formic acid (90 ml) was kept at room temp for 2 days with occasional stirring. The greater part of the solvent was removed by evaporation *in vacuo*, and the residue refluxed with 30% NaOH (100 ml) for 3 hr; the cooled alkaline soln was saturated with salt, extracted with chf (3 × 20 ml). Evaporation of solvent, after washing and drying gave a *diol* (1·65 g), white plates from 120° petroleum, m.p. 204°, which gave only one spot on TLC (alumina, developed with MeOH). IR absorptions at 3623, 3367 and 3030 cm^{-1}. (Found: C, 69·88, H, 9·17. $C_9H_{14}O_2$ requires: C, 70·09; H, 9·15%.) Hydrogenation of a sample in acetic acid over Pt (correct absorption for one double bond) gave the saturated diol, m.p. 244° undepressed on admixture with a sample prepared as described above.

Oxidation of solvolysis product

(a) *With chromic acid.* To the unsaturated diol (0·12 g) in ether (65 ml) was added 6% chromic acid soln (5 ml) dropwise with stirring: after stirring at room temp for 4 hr the usual work-up gave oily material which showed IR absorptions at 3030, 1709, and 1666 cm^{-1}.

(b) *With manganese dioxide.* The unsaturated diol (0·1 g) in chf (30 ml) was stirred with activated MnO_2[20,21] (3 g) for 12 hr at room temp. Solvent was evaporated from the filtered soln to leave a semi-solid ketone, which showed IR absorption at 1664 cm^{-1}.

Reaction of syn-*7β-methylbicyclo*[3.3.1]*non*-2-en-9-*ol with formic acid*

The alcohol[18] (1·0 g) was boiled under reflux with 98% formic acid (5 ml) for 1 hr, water added to the cooled soln and the mixture ether extracted. Evaporation of ether after washing and drying ($MgSO_4$) left an oily *formate ester* (0·91 g), b.p. 62°/0·25 mm, homogeneous on gas chromatography (TTP at 105°). (Found: C, 73·4; H, 9·3. $C_{11}H_{16}O_2$ requires: C, 73·3; H, 8·9%.) IR absorptions at 1176, 1718, and 3025 cm^{-1}. The ester was hydrolysed by refluxing with 6N NaOH for 5 hr (some white solid collected in the condenser), then the mixture was extracted with ether and the extracts washed and dried ($MgSO_4$). Evaporation of solvent left a white solid (0·3 g), m.p. 93–93·5° undepressed on admixture with the original alcohol and showing the same IR absorptions as that alcohol.

Reaction of anti-*7β-methylbicyclo*[3.3.1]*non-2-en-9-ol with formic acid*

The alcohol[18] (0·9 g) was boiled under reflux with 98% formic acid (5 ml) and worked up as above to give a formate ester (0·82 g), b.p. 101°/8 mm, homogeneous on gas chromatography (TTP at 105°) showing IR absorptions at 1176, 1724 and 3025 cm^{-1}. This was not analysed but was immediately hydrolysed as above to yield the original alcohol (0·53 g), m.p. 97–99° undepressed on admixture with starting material.

Reaction of 7β-methylbicyclo[3.3.1]*non-2-en-9-one with formic acid*

The ketone[18] (1·0 g) was refluxed with 98% formic acid (5 ml) for 5 hr and worked up as before to give the original ketone (0·92 g), identified by its IR spectrum (16 peaks in the region 5–15 μ).

Acknowledgements—The authors wish to thank Dr. D. A. Wilson, Univeristy College of South Wales and Monmouthshire for running P.M.R. spectra and for much helpful discussion, and to thank the Science Research Council for maintenance grants (to R.A.A., J.R.D. and J.M.E.). Analyses are by Drs. Weiler and Strauss, Oxford.