Studies on Bicyclononanes. Part VII.[1] Reactions of (1-Bicyclo[3,3,1]-nonyl)methyl and Related Ions

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The solvolyses of esters of 1-hydroxymethylbicyclononane, 5-hydroxymethylmethylenecyclo-octane, and 1-methyl-5-hydroxymethylcyclo-octene are described, together with the deaminations of the corresponding amines. The occurrence of 1,3-hydride shifts is reported, and the implications of the results, as regards the π-route to bicyclic molecules, are discussed.

SOLVOLYTIC reactions of the tosylate (Ib) and the brosylate (Ic) were initially studied in the hope that they might serve as a synthetic route to the alcohol (V), an authentic sample of which was required for other work.[2] This hope was only partially realised.

The alcohol (Ia) and the amine (III) were prepared by the route shown. It was not possible to reduce the tosylhydrazone without at least partial reduction of the ester group.

The products from solvolyses of (Ib) and (Ic) are shown in Table 1. The esters which were formed were immediately hydrolysed to alcohols, and separated from the small quantities of olefin that accompanied them (these last were not investigated); the figures in Table 1 consequently refer to alcohols. The quantitative analyses were made by g.l.c.; identification of peaks was made both by comparison of g.l.c. retention times, and by the sequences of reactions which follow. The alcohol mixtures were oxidised, and separated into acidic, ketonic, and alcoholic fractions; the acidic fraction was

TABLE 1

Alcohols obtained in solvolyses of esters (Ib) and (Ic)

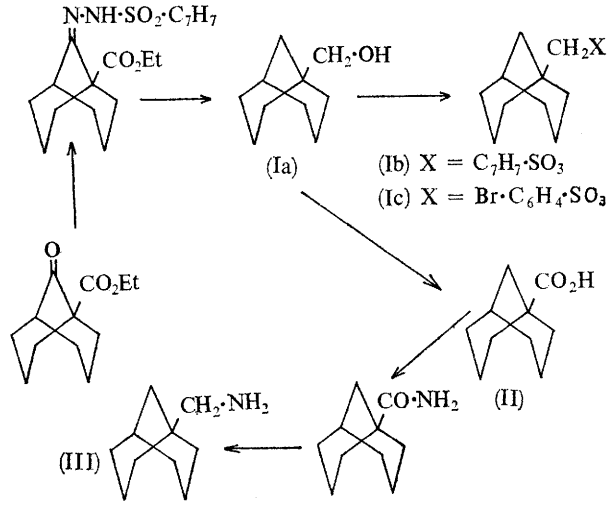
Substrate	Solvent	Time	% Product composition (I)	(IV)	(V)	(VI)	(VII)
(Ib)	Acetic acid	6 hr.	73	—	—	1	26
(Ib)	Acetic acid + 0·5% sodium acetate	72 hr.*	36	22	37	Trace	5
(Ib)	Formic acid	6 hr.†	64	7	—	1	28
(Ib)	Formic acid + 0·5% sodium formate	6 hr.	78	4	—	1	17
(Ib)	,, ,,	72 hr.	70	8	—	1	21
(Ib)	Trifluoroacetic acid	6 hr.	58	10	—	1	31
(Ic)	Acetic acid	6 hr.	65	4	—	—	31
(Ic)	Acetic acid + 0·5% sodium acetate	6 hr.	64	36	—	—	—
Deamination of amine (III)			35	30	32	3	

* No appreciable reaction after 6 hr. † No further reaction after 72 hr.

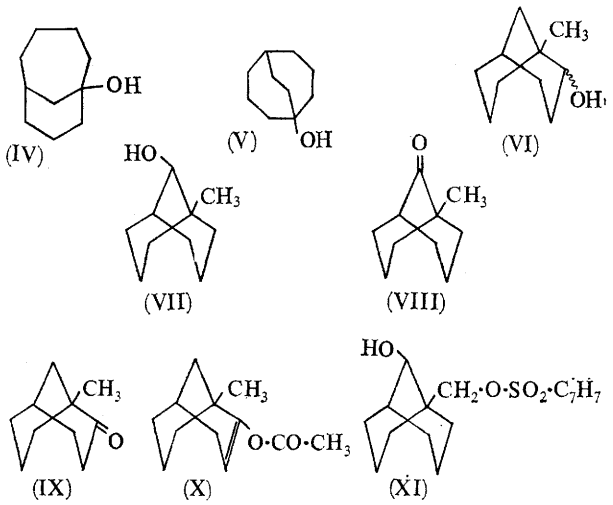
[1] Part VI, J. M. Davies and S. H. Graham, *J. Chem. Soc.* (*C*), 1968, 2040.

[2] K. H. Baggaley, W. H. Evans, S. H. Graham, D. A. Jonas, and D. H. Jones, *Tetrahedron*, 1968, **24**, 3445.

composed solely of (II), confirming the presence of (I) in the original mixture. The alcohol fractions consisted



of the tertiary alcohol (IV) either alone or mixed with a second tertiary alcohol. Since (IV) was easily obtained pure its structure was assigned on the basis of its ^1H n.m.r. spectrum (no olefinic or methyl protons) and its non-identity with the known alcohol (V).[2] When a



second tertiary alcohol was present it had the same g.l.c. retention time as (V). The ketonic fraction gave a single peak on g.l.c., and this had the same retention time as the ketones (VIII) and (IX) [we were unable to resolve mixtures of these ketones on any stationary phase, nor could we resolve mixtures of (VI) and (VII), or of their acetate esters]. The ketonic fraction was therefore reacted with isopropenyl acetate to give a mixture of (VIII) and (X); this could be analysed quantitatively by g.l.c. [model experiments with a mixture of (VIII) and (IX) of known composition showed the method to be accurate] and separated on a preparative scale by chromatography on silica gel. In this way both (VI) and (VII) were positively identified in the alcohol mixtures. Owing to the small sample size available the secondary alcohols from the deamination of (III) were not analysed separately for (VI) and (VII).

Hartmann [3] found that, in reactions of the adamantylmethyl ion, substantial amounts of homoadamantyl product were formed only in buffered solution. Consequently it is not surprising that little tertiary alcohol was produced from (Ib) and (Ic) when re-protonation of products was possible (formic acid was obviously a sufficiently strong acid for this purpose). The bicyclo[3,3,1]nonane skeleton is not strain-free,[4] but it is apparently preferred to the skeletons of (IV) and (V). The production of secondary alcohol was not observed in the reactions of the adamantylmethyl ion; it is tempting to suggest that the formation of (VI) and (VII), which must involve a 1,3-hydride shift, is due to the increased energy, due to transannular strain, of the bicyclo[3,3,1]nonane system. In that case it might have been expected that migration from C-2 should have predominated over migration from C-9, because the former process better relieves the strain. (The introduction of a trigonal carbon at C-2 allows the *endo*-hydrogens on C-3 and C-7 to move somewhat apart, thereby diminishing transannular strain.[4]) The observed preference for migration from C-9 might arise in either of two ways, both related to the flattening of the bicyclononane skeleton about C-2, C-3, C-4, and C-6, C-7, C-8.[5] In the first place the geometry for hydride transfer from C-9 might be more favourable. Alternatively, the splaying outwards of the β-protons * on C-2, C-4, C-6, and C-8, which results from the flattening, leaves C-9 rather more open to solvent approach. If solvent attack is concerted with hydride shift, as it is known to be in other cases,[6] then both the preferential migration from C-9 and the enhanced tendency over the adamantyl compounds towards hydride shift might be explained. (In this connection it is relevant to note the relatively large O–O separation in bicyclo[3,3,1]nonane-2β,4β-diol.[1])

More puzzling is the absence of alcohol (V) from the products of solvolysis of (Ic) in buffered acetic acid, though it is formed from (Ib) and by deamination of (III). It would not be adequate to regard one of these solvolyses as being kinetically controlled (product distribution depending on energies of intermediate ions) and the other as thermodynamically controlled (product distribution depending on energies of esters) because while the absence of secondary esters from the products of brosylate solvolysis would establish that as the kinetically controlled process, the absence of (V) from

* The system of nomenclature in use is explained in Part IV of this series, C. S. Dean, J. R. Dixon, S. H. Graham, and D. O. Lewis, *J. Chem. Soc.* (*C*), 1968, 1491.

[3] M. Hartmann, *Z. Chem.*, 1964, 457.

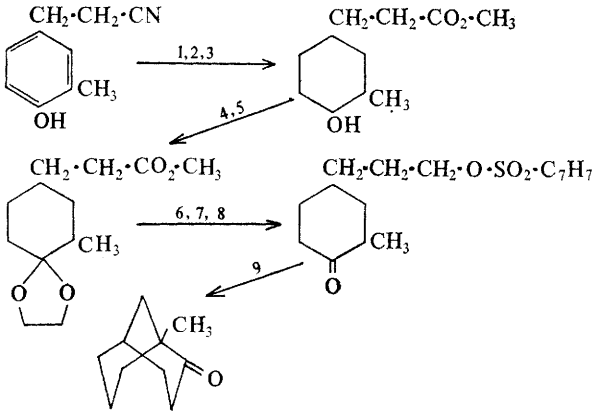
[4] R. A. Appleton, C. Egan, J. M. Evans, S. H. Graham, and J. R. Dixon, *J. Chem. Soc.* (*C*), 1968, 1110.

[5] W. A. C. Brown, J. Martin, and G. A. Sim, *J. Chem. Soc.*, 1965, 1844; M. Dobler and J. D. Dunitz, *Helv. Chim. Acta*, 1964, **47**, 695.

[6] A. C. Cope, M. M. Martin, and M. A. McKervey, *Quart. Rev.*, 1966, **20**, 119.

these products, and from the products in unbuffered media, would lead to the contrary conclusion. All three experiments must involve conditions of kinetic control, but it seems to be necessary to postulate the interposition of two sets of ionic intermediates. One set is generated from (Ib) and (III), and includes two pathways of comparable energy which lead to (IV) and (V); the other set, generated from (Ic) seem more akin to the final products in their energy relationships, in that the pathway leading to (IV) is now of lower energy than that leading to (V).

Authentic samples of alcohol (VII) and ketone (VIII) were obtained by aluminohydride reduction of the diol monotosylate (XI),[2] and subsequent oxidation. The ketone (IX) was produced by the sequence of reactions shown.[7] In the final cyclisation only (IX) was formed, free from either epimer of the 3-methyl-2-one.[8] Reduction of the ketone gave the 2α-ol, and reaction of the tosylate of this with acetate ion gave the acetate of the 2β-ol. Both these alcohols had the same retention time as each other and as the 1-methyl-9-ol, and so also for their acetate and formate esters. Consequently it is not known which epimer was produced in the various solvolyses.



Reagents: 1, OH; 2, MeOH–H^+; 3, H_2/Rh; 4, CrO_3; 5, $(CH_2{\cdot}OH)_2$; 6, AlH_4^-; 7, H^+; 8, $C_7H_7SO_2Cl$; 9, BuO^-.

The solvolyses of the tosylate (XIIb) and brosylate (XIIc) were studied, since simple ionisation should give an ion isoelectronic with that derived from (Ib) and (Ic). However, the results (Table 2) showed that ionisation had been preceded by migration of the double bond into the ring. The esters did not react with a suspension of calcium carbonate in aqueous acetone;[9] reaction in buffered formic acid gave very little olefin and an ester mixture which was immediately hydrolysed: the resulting alcohol mixture showed three g.l.c. peaks. Oxidation gave (IX), free from other ketones, and a mixture of two tertiary alcohols. The ^{1}H n.m.r. spectrum of this mixture contained two singlet peaks. One at τ 9·1 could only arise from a methyl group and, as it integrated for one proton, it was assigned to the minor (30%) component of the mixture. The second singlet peak at τ 8·7 integrated for two protons and was therefore assigned to a methyl group (the chemical shift is correct for CH_3C–O) in the major (70%) component of the mixture. The mixture of tertiary alcohols obtained by deamination of (XV) (see below) was comprised of (V) (*ca.* 55%) and a second alcohol (*ca.* 45%) which corresponded in g.l.c. retention time to the tertiary alcohol produced in lesser amount from the solvolyses: the ^{1}H n.m.r. spectrum of that mixture included the peak at τ 9·1 (now integrating for 1·5 protons) but not that at 8·7, which confirms the correctness of the above assignments. In the case of both mixtures the absence of carbinol and of olefinic protons confirmed that they were composed solely of bicyclic tertiary alcohols. The two tertiary alcohols from the solvolyses were therefore assigned structures (XIV) and (XVII) respectively. An authentic sample of (XIV) was prepared from (XIII) and methyl magnesium iodide: it had the same g.l.c. retention time and the same infrared spectrum as the major component of the tertiary alcohol mixture. An attempt to synthesise an authentic sample of (XVII) was unsuccessful (see below). Since formation of esters of (VI) and (XIV) implied that rearrangement to esters of (XVIIIa) had preceded ionisation, a sample of this alcohol was synthesised by the route shown, which is shorter than the published procedure.[10] The result of solvolysing the tosylate (XVIIIb) (Table 2) confirmed that the esters (XIIb) and (XIIc) had rearranged before ionisation.

TABLE 2

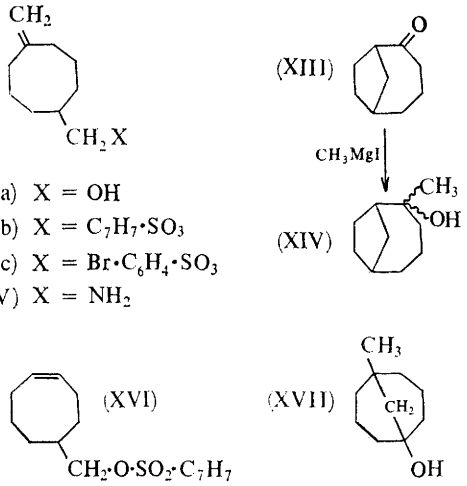
Solvolyses in formic acid containing 0·5% sodium formate, 48 hr. at room temp.

	Product distribution (after hydrolysis of esters)					
Substrate	(I)	(V)	(VI)	(XIIa)	(XIV)	(XVII)
(XIIb)	—	—	86	—	10	4
(XIIc)	—	—	85	—	11	4
(XVIIIb)	—	—	88	—	12	—
Deamination of (XV)	9	40	9	12	Trace	30

It has been demonstrated that formation of bicyclic products from (XVI) cannot involve a non-classical intermediate, *e.g.* (XIX).[11] These new results exclude bicyclic ions such as (XX), because the conversion of (XIIb) and (XIIc) into bicyclo[4,2,1]nonanes would go through a tertiary ion and be the favoured process. In actual fact, less [4,2,1]-product is formed from (XIIb) and (XIIc) than from (XVI),[12] and less olefin too. The only concept which is consistent with the results is that π-electron participation (formation of the 9,1-bond) is concerted with solvent attack. On this basis also the predominant formation of *endo*-alcohol from (XVI) is

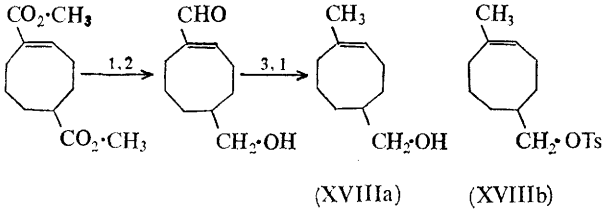
[7] E. N. Marvel, D. Sturmer, and C. Rowell, *Tetrahedron*, 1966, **22**, 861.
[8] C. Egan and S. H. Graham, to be published.
[9] T. L. Westman and R. D. Stevens, *Chem. Comm.*, 1965, 459.
[10] G. L. Buchanan, A. McKillop, and R. A. Raphael, *J. Chem. Soc.*, 1965, 833.
[11] H. Felkin, G. Le Ny, C. Lion, W. D. K. Macrosson, J. Martin, and W. Parker, *Tetrahedron Letters*, 1966, 157.
[12] K. H. Baggaley, J. R. Dixon, J. M. Evans, and S. H. Graham, *Tetrahedron*, 1967, **23**, 299.

more intelligible: it is in fact doubtful if reaction between (XX) and solvent could give so high a ratio of *endo* to *exo* product,[11] thermodynamic control of the



reaction would give about 30% of *exo*-ester,[12] and *endo*-approach of solvent would be at least partially inhibited by the C-8 methylene.

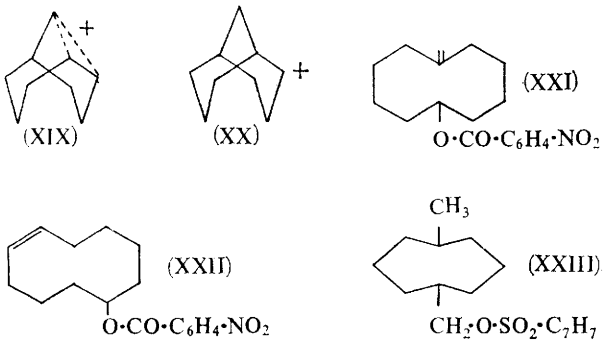
The products from deamination of (XV) were analysed as before. In this case these were two tertiary alcohols, one with the same g.l.c. retention time as (V): the second alcohol was assigned structure (XVII) for the



Reagents: 1, AlH_4^-; 2, MnO_2; 3, $C_7H_7·SO_2·N_2H_3$.

reasons discussed above. In this case it can be seen that double bond migration occurred to only a minor extent: 88% of the products were formed by π-electron participation, but for 30% this had been preceded by a 1,2-hydride shift. A comparable 1,2-hydride shift preceding the interaction of an endocyclic π-bond with an exocyclic positive charge has not been observed, and it therefore seems that interaction of an exocyclic π-bond with a positive centre is a less facile process interaction of an endocyclic one. This conclusion would be more certain if it was not based on a comparison between solvolytic reactions on the one hand, and a deamination on the other: it is worth noting however that the ester (XXI) is reported [9] to be stable under conditions which lead to solvolysis of (XXII). The formation of both (I) and (V) in the approximate ratio of 1 : 4 is not likely to reflect the relative stabilities of the two bicyclic ions and more probably indicates a duality of mechanism: formation of bicyclic tertiary ion and subsequent solvent capture competes with concerted π-electron participation and solvent attack. When contrasted with the exclusive formation of (V) by acid-catalysed hydration of 1,5-bismethylenecyclooctane [2] these results emphasise the highly concerted nature of that process.

The solvolysis of (XXIII) was studied in the hope that it might provide an authentic sample of (XVII).[13]



A complex mixture of esters was formed from which, by hydrolysis and oxidation, both alcohols and ketones could be isolated. The alcohol fraction included one component with the same g.l.c. retention time as that formed from (XV), and assigned structure (XVII). The ketone fraction included both cyclopentanones and cyclohexanones, and the ^1H n.m.r. spectrum showed an average of one methyl group per molecule. The esters of secondary alcohols must therefore have arisen by hydride shift after ring expansion (and have involved the isomerisation of a tertiary ester to a secondary one), and ring expansion must have led, at least in part, to a bicyclo[4,3,0]nonane.

EXPERIMENTAL

1-*Hydroxymethylbicyclo*[3,3,1]*nonane* (Ia).—1-Ethoxycarbonylbicyclo[3,3,1]nonan-9-one (25 g.) and toluene-*p*-sulphonylhydrazide (22·5 g.) in ethanol (200 ml.) were boiled for 1 hr., on cooling the *tosylhydrazone* crystallised as white cubes (38 g.), m.p. 148—150° (Found: C, 60·2; H, 6·8; N, 7·4. $C_{19}H_{26}N_2SO_4$ requires C, 60·3; H, 6·9; N. 7·4%). A solution of the tosylhydrazone (25 g.) in warm dioxan (500 ml.) was added to lithium aluminohydride (5 g.) in dioxan (500 ml.) at such a rate as to maintain reflux without external heating: the mixture was then boiled for 12 hr. and worked up normally to give after chromatography on alumina the *primary alcohol* (5·1 g.), b.p. 82°/0·5 mm., $\nu_{max.}$ (film) 3390br, no carbonyl absorption (Found: C, 77·4; H, 11·6. $C_{10}H_{18}O$ requires C, 77·9; H, 11·7%); *tosylate* (Ib), white cubes from ethanol, m.p. 75—76° (Found: C, 66·3; H, 7·7; S, 10·5. $C_{17}H_{24}SO_3$ requires C, 66·2; H, 7·8; S, 10·4%); *brosylate* (Ic), white needles from ethanol, m.p. 64° (not analysed).

Solvolyses of (Ib) *and* (Ic).—The ester (1 g.) was boiled with RCO_2H (50 ml.) with or without the addition of RCO_2Na for the time specified in Table 1, the mixture was poured into water (200 ml.), extracted with ether (4 × 50 ml.), and the extracts were washed, dried, and evaporated: the residual esters were analysed by g.l.c. (tricyanoethoxypropane at 100°), and peaks were identified by

[13] R. A. Flath, Thesis, University of California in Berkeley, cited by W. G. Dauben and C. D. Poulter, *J. Org. Chem.*, 1968, **33**, 1237.

comparison of retention times with those of authentic samples. The esters were reduced in the normal way with lithium aluminohydride (0·1 g.) and the resulting alcohols analysed by g.l.c. (butanediol succinate at 100°) after preliminary chromatography on alumina to remove olefins; these analyses agreed well with the ester analyses and the results are quoted in Table 1. The alcohols in ether were oxidised, at 35° for 4 hr., with sodium dichromate (1 g.) and 96% sulphuric acid (1 ml.) in water (50 ml.); the oxidation products were partitioned between ether and aqueous sodium hydrogen carbonate, acidification of the latter gave acid (II), m.p. 82—84° not depressed on admixture with an authentic sample [up to 0·3 g. of (II) could be recovered]. The neutral component in methylene chloride was chromatographed on alumina to give a ketone and alcohol fraction. In most runs this last was homogeneous (g.l.c.) and was sublimed to give *alcohol* (IV) as a white solid, m.p. 140°, $\nu_{max.}$ (film) 3390br and 1042 cm.$^{-1}$, ^{1}H n.m.r. absorption (in $CDCl_3$–D_2O) τ 8·3—8·7 (Found: C, 77·6; H, 11·5. $C_{10}H_{18}O$ requires: C, 77·9; H, 11·8%). In some runs the tertiary alcohol fraction contained two components with the g.l.c. retention times of (IV) and (V).[2] The ketonic fraction gave a single g.l.c. peak [with retention time of (VIII) and (IX)]: the ketonic fraction (*ca.* 0·02 g.), isopropenyl acetate (0·07 g.) and a crystal of toluene-*p*-sulphonic acid were boiled for 2 hr., the cooled mixture was diluted with water and extracted into ether, washed, and dried. Analysis of the mixture by g.l.c. (butanediol succinate at 100°) gave two peaks with the g.l.c. retention times of (VIII) and (X). Repetition of the process on a larger sample of ketone fraction 0·4 g.) [from reaction of (Ib) with HCO_2H for 72 hr.] gave a mixture of (VIII) and (X) (0·42 g.) which was eluted by petroleum from an alumina column to give (VIII) (0·4 g.), identical infrared spectrum and g.l.c. retention times with those of an authentic sample, semicarbazone, m.p. and mixed m.p. 222°, and also (X) (0·02 g.), identical infrared spectrum and g.l.c. retention time with an authentic sample. This enol acetate was hydrolysed (with 2N-sodium hydroxide) and converted into the semicarbazone of (IX), m.p. and mixed m.p. 202°.

1-*Carboxybicyclo*[3,3,1]*nonane* (II).—Sodium dichromate (1 g.) and 99% sulphuric acid (1 ml.) in water (50 ml.) were added dropwise to the alcohol (Ia) (1 g.) in ether (50 ml.) and the mixture was boiled for 4 hr. Normal work-up gave the *acid* (II) (0·9 g.), white needles from petroleum, m.p. 82—84° (Found: C, 71·5; H, 9·8. $C_{10}H_{16}O_2$ requires C, 71·4; H, 9·6%).

1-*Aminomethylbicyclo*[3,3,1]*nonane* (III).—The acid (II) (1·2 g.) was heated to 40—60° for 3 hr. with thionyl chloride (1·4 g.), the excess of thionyl chloride was removed *in vacuo*, and 0·88 ammonia (3 ml.) was added to the residue: the usual separations gave the crude amide (0·7 g.) which was used without further purification. The amide (0·7 g.) in dry ether was reduced with lithium aluminohydride (0·18 g.) for 4 hr. at reflux temperature: the mixture was worked up using 3N-sodium hydroxide to dissolve alumina, the basic fraction of the products extracted into 2N-hydrochloric acid and isolated normally to give the colourless oily amine (0·55 g.), $\nu_{max.}$ (film) 3380br and 1600 cm.$^{-1}$. The amine (0·5 g.) without further purification was dissolved in acetic acid–sodium acetate buffer (25 ml.) at pH 4·5, and sodium nitrite (0·23 g.) was added in portions at 0°, nd the whole then kept at room temperature for 4 days. The products were then extracted into ether, washed, and dried: removal of solvent left an oil (0·2 g.) which contained 5% of hydrocarbon. The oil was analysed by g.l.c. (butanediol succinate at 100°).

1-*Methylbicyclo*[3,3,1]*nonan*-9-*one* (VIII).—The monotosylate (XI)[2] (3 g.) in ether (50 ml.) was added to lithium aluminohydride (0·75 g.) in ether (50 ml.) at such a rate as to maintain reflux, and the mixture was then stirred and boiled for 3 hr. Normal work-up then gave the *alcohol* (VII) (1·1 g.) as a waxy solid, m.p. 39°, $\nu_{max.}$ (CCl_4 solution) 3623 and 1062 cm.$^{-1}$, ^{1}H n.m.r. absorptions at τ 6·70 (1H, d) and 9·18 (3H, s) (Found: C, 77·3; H, 11·7. $C_{10}H_{18}O$ requires C, 77·9; H, 11·7%). Oxidation of the alcohol (1 g.) in ether with sodium dichromate (0·66 g.) and 96% sulphuric acid (1 ml.) in water (50 ml.) gave the *ketone* (VIII) (0·85 g.), b.p. 74°/0·8 mm., $\nu_{max.}$ (film) 1700 cm.$^{-1}$ (Found: C, 78·9; H, 10·6. $C_{10}H_{16}O$ requires C, 78·9; H, 10·6%); *semicarbazone*, m.p. 222° (Found: C, 63·1; H, 9·2. $C_{11}H_{19}N_3O$ requires C, 63·1; H, 9·2%).

β-(4-*Hydroxy*-3-*methylphenyl*)*propionitrile*.— Aluminium chloride (84 g.) was added in portions to *o*-cresol (136·5 g.) and acrylonitrile (80 g.) at 15—20° while hydrogen chloride was bubbled through the mixture: while passage of gas was maintained the temperature was allowed to rise to 80° during 3 hr. and kept there for 30 min. Normal work-up gave the *nitrile* (124·7 g.), b.p. 160—165°/1 mm., m.p. 60° not raised by recrystallisation (Found: C, 74·3; H, 6·8; N, 8·2. $C_{10}H_{11}NO$ requires C, 74·5; H, 6·9; N, 8·7%).

Methyl β-(3-*Methyl*-4-*hydroxyphenyl*)*propionate*.—The nitrile (100 g.) was boiled with 2N-sodium hydroxide (250 ml.) for 4 days (when evolution of ammonia ceased); the solution, was cooled, acidified, and the precipitated β-(3-*methyl*-4-*hydroxyphenyl*)*propionic acid* recrystallised from benzene (charcoal) to give colourless needles, m.p. 58° (Found: C, 63·5; H, 6·9. $C_{10}H_{12}O_3,\frac{1}{2}H_2O$ requires C, 63·5; H, 6·9%). The acid (80 g.) was boiled for 8 hr. with methanol (200 ml.), dichloroethane (400 ml.), and 96% sulphuric acid (4 ml.), then worked up normally to give the *ester* (58 g.), b.p. 150—152°/1·2 mm., m.p. 33° (Found: C, 67·9; H, 7·3. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·3%).

2-*Methyl*-4-(ω-*hydroxypropyl*)*cyclohexanone*.—The phenolic ester (20 g.) in methanol (250 ml.) was hydrogenated over 5% rhodium–charcoal (2 g.) at 60—80 lb. in.$^{-2}$ and 20° to give *methyl* β-(4-*hydroxy*-3-*methylcyclohexyl*)*propionate* (19·5 g.), b.p. 114—116°/0·6 mm., n^{20} 1·4708 (Found: C, 66·3; H, 9·9. $C_{11}H_{20}O_3$ requires C, 66·0; H, 10·1%). To this ester (22·5 g.) in acetone (300 ml.) at 0° was added chromium trioxide (14 g.) in 30% (w/w) sulphuric acid (60 ml.); the mixture was then stirred at room temperature for 24 hr. The usual work-up gave methyl β-(3-methyl-4-oxocyclohexyl)propionate (16·3 g.), b.p. 118°/0·1 mm., n^{22} 1·4583, $\nu_{max.}$ 1733 and 1703 cm.$^{-1}$. The keto-ester (17·5 g.) was treated with ethylene glycol (6 g.) and toluene-*p*-sulphonic acid (0·5 g.) in benzene (100 ml.) in the usual way to yield the ketal (20·5 g.), $\nu_{max.}$ 1733, 1172, and 1098 cm.$^{-1}$ (not analysed). This was reduced with lithium aluminohydride (1·7 g.) in the usual way and the ethereal solution subsequently stirred with 2N-sulphuric acid, then worked-up to give the *keto-alcohol* (11·9 g.), b.p. 92°/0·1 mm., n^{20} 1·4772, $\nu_{max.}$ (film) 3450br and 1709 cm.$^{-1}$ (Found: C, 70·8; H, 10·5. $C_{10}H_{18}O_2$ requires C, 70·6; H, 10·6%).

1-*Methylbicyclo*[3,3,1]*nonan*-2-*one* (IX).—The keto-alcohol (2 g.) was converted into its tosylate (3·4 g.) in the usual way: the colourless gum, $\nu_{max.}$ (film) 1192 and 1182 cm.$^{-1}$ and no OH absorptions, was used without further purification. The tosylate (3·4 g.) in tetrahydrofuran (50

ml.) was added in a nitrogen atmosphere to potassium t-butoxide (1·9 g.) in tetrahydrofuran (250 ml.), and the mixture was then stirred at 50—55° for 24 hr. Work-up gave the *bicyclic ketone* (IX) (1 g.), b.p. 54°/0·4 mm., $\nu_{max.}$ (film) 1706 cm.$^{-1}$ (Found: C, 79·2; H, 11·6. $C_{10}H_{16}O$ requires C, 78·9; H, 11·6%); *semicarbazone*, m.p. 202° (Found: C, 63·4; H, 9·2; N, 19·9. $C_{11}H_{19}N_3O$ requires C, 63·2; H, 9·2; N, 20·1%). A mixture of ketone (VIII) (22%) and ketone (IX) (78%) was analysed using isopropenyl acetate as for the ketones obtained from (Ib) etc.: the two g.l.c. peaks had relative areas 11 : 39.

1-*Methylbicyclo*[3,3,1]*nonan*-2α-*ol* (VI).—Reduction of (IX) (0·75 g.) in the normal way with lithium aluminohydride (0·06 g.) gave the *alcohol* which was purified by sublimation *in vacuo*, m.p. 40°, $\nu_{max.}$ (CCl_4 solution) 3390br, 1381, and 1055 cm.$^{-1}$, ^{1}H n.m.r. absorptions at τ 6·70 (1H, m) and 9·13 (3H, s) (Found: C, 77·5; H, 11·8. $C_{10}H_{18}O$ requires C, 77·9; H, 11·8%). Reaction with toluene-*p*-sulphonyl chloride in the usual way gave the tosylate ester which partially solidified, $\nu_{max.}$ (film) 1375, 1190, and 1183 cm.$^{-1}$. A solution of the tosylate (0·7 g.) and tetraethylammonium acetate (7 g.) in dry acetone (30 ml.) was kept at room temperature for 14 days: chromatography of the solute on alumina gave unreacted tosylate (0·5 g.) and 1-methyl-2β-acetoxybicyclo[3,3,1]nonane (0·05 g.), $\nu_{max.}$ (film) 1724 and 1375 cm.$^{-1}$. This had the same g.l.c. retention time as the acetate of the 1-methyl-2α-ol. Reduction of this acetate with lithium aluminium hydride gave a sample of 2β-ol which had the same g.l.c. retention time as the 1-methyl-2α-ol.

Solvolysis of Esters (XIIb) *and* (XIIc).—The alcohol (XIIa) [12] was converted into ester (XIIb), an oil, $\nu_{max.}$ (film), 3076, 1639, 1190, 1176, and 885 cm.$^{-1}$ (not analysed), and ester (XIIc), an oil, $\nu_{max.}$ 3076, 1639, 1190, 1183, and 885 cm.$^{-1}$ (not analysed). The esters (1 g.) and sodium formate (0·25 g.) in formic acid (50 ml.) were stirred at room temperature for 48 hr., poured into water, and extracted into petroleum. The mixed products in ether were reduced with lithium aluminohydride and chromatographed on alumina, eluting first with petroleum then with benzene, to give alcohols (0·4 g.) and hydrocarbons (0·05 g.): the alcohol fraction gave three g.l.c. peaks (butanediol succinate at 100°) with the retention times of (VI), (XIV), and (XVII). The alcohol mixture was oxidised as described above to give ketone (0·3 g.) and alcohols (0·04 g.): the former had the same infrared spectrum (and g.l.c. retention time) as (IX) and gave the semicarbazone, m.p. and mixed m.p. 202°. The major (70%) and minor (30%) components of the alcohol fraction had the same g.l.c. retention times as (XIV) and (XVII) respectively; the ^{1}H n.m.r. spectrum included absorptions at τ 8·70 (~2H, s) and 9·10 (~1H, s). Two distillations gave a sample containing 90% of the major component and the infrared spectrum could not then be distinguished from that of an authentic sample of (XIV).

Deamination of Amine (XV).—Sodium nitrite (1·5 g.) was added in portions to a solution of (XV) [2] (3 g.) in aqueous acetic acid–sodium acetate, pH 4·5 (150 ml.), at 0°, and the solution was kept at room temperature for 4 days: then the products were extracted, washed, and dried. Chromatography of the products on alumina gave hydrocarbons (0·3 g.) and alcohols (1·9 g.): the hydrocarbons gave three g.l.c. peaks, 10%, 54%, and 36% (on tricyanoethoxypropane at 25°); they were not further investigated. The alcohol fraction gave five g.l.c. peaks (butanediol succinate at 100°) with the retention times of (I), (V), (VI), (XIIa), and (XVII). The alcohol mixture was oxidised in the same way as before, the acidic products, $\nu_{max.}$ 2976, 1639, and 890 cm.$^{-1}$, were removed and the neutral fraction (1·9 g.) now gave three g.l.c. peaks corresponding to (V), (IX), and (XVII); chromatography on alumina gave the ketonic fraction (0·12 g.), semicarbazone m.p. and mixed m.p. 202°, and an alcohol fraction (1·3 g.) which solidified after distillation and the ^{1}H n.m.r. spectrum of which showed an absorption at τ 9·11 (~1·5H, s).

2-*Methylbicyclo*[4,2,1]*nonan*-2-*ol* (XIV).—Bicyclo[4,2,1]-nonan-2-one [12] (0·5 g.) was added to the Grignard reagent from methyl iodide (1 g.), and the mixture was boiled for 3 hr., then worked up using saturated aqueous ammonium chloride. This gave the *alcohol* (XIV) (4·9 g.), b.p. 80°/1·5 mm., $\nu_{max.}$ (film) 3390br and 1117 cm.$^{-1}$ (Found: C, 77·8; H, 11·6. $C_{10}H_{18}O$ requires C, 77·9; H, 11·8%).

Solvolysis of Ester (XXIII).—1-Methyl-5-hydroxymethylbicyclo[3,3,0]octane [14] was converted into an oily tosylate, $\nu_{max.}$ 1190 and 1183 cm.$^{-1}$, in the usual way. This ester (0·5 g.) was boiled for 6 hr. with acetic acid (50 ml.) [the addition of sodium acetate (0·25 g.) did not affect the results]. The products were worked up and oxidised as before to give 1-methyl-5-carboxybicyclo[3,3,0]octane [14] m.p. and mixed m.p. 184°; an alcohol fraction with two components, one of which had the same g.l.c. retention time as (XIV); a ketonic fraction with four components (g.l.c. on butanediol succinate at 100°), $\nu_{max.}$ (CCl_4 solution) 1742 and 1709 cm.$^{-1}$, ^{1}H n.m.r. absorption at τ 8·8 (complex, 3H).

1,5-*Bismethoxycarbonylcyclo-octene*.— 1-Ethoxycarbonylbicyclo[3,3,1]non-3-en-9-one (60 g.) was boiled with a solution of sodium (3·5 g.) in methanol (600 ml.) for 15 hr., the solution was acidified with acetic acid, concentrated *in vacuo* to 200 ml., and worked up normally to give a mobile liquid (49 g.). This was boiled for 2 hr. with Girard P reagent (35 g.) and acetic acid (3 ml.) in ethanol (400 ml.), then worked up normally to give the pure diester (42·2 g.), b.p. 112—116°, $\nu_{max.}$ (film), 1739, 1715, 1639, and 763 cm.$^{-1}$. From the aqueous solution of the Girard complexes some starting material was recovered.

1-*Formyl*-5-*hydroxymethylcyclo-octene*.—The diester (42 g.) was reduced in the usual way with lithium aluminohydride (15 g.) to give 1,5-*bishydroxymethylcyclo-octene* (26·1 g.) as a viscous liquid, b.p. 142—146°/0·2 mm., $\nu_{max.}$ ($CHCl_3$ solution) 3620 cm.$^{-1}$ (Found: C, 70·9; H, 10·7. $C_{10}H_{18}O_2$ requires C, 70·6; H, 10·7%). The diol (5 g.) in AnalaR chloroform (200 ml.) was stirred with active manganese dioxide [15] for 7 days at room temperature: the *hydroxyaldehyde* (4 g.) was isolated as a viscous liquid, b.p. 130°/0·2 mm., $\nu_{max.}$ (film) 3390br, 2732, 1684, and 1650 cm.$^{-1}$ (Found: C, 71·6; H, 10·4. $C_{10}H_{16}O_2$ requires C, 71·4; H, 10·5%).

1-*Methyl*-5-*hydroxymethylcyclo-octene* (XVIIIa).—The hydroxy-aldehyde (4 g.) and toluene-*p*-sulphonylhydrazide (4·2 g.) in ethanol were boiled for 4 hr. Removal of the solvent left the tosylhydrazone as a viscous yellow oil, $\nu_{max.}$ (film) 1175, 1170, and 820 cm.$^{-1}$, no carbonyl absorptions. This oil was used without further purification. The tosylhydrazone (2 g.) in methanol (50 ml.) was treated with sodium borohydride (2·5 g.) in portions and the solution then boiled for 12 hr., and worked up to give the alcohol (XVIIIa) (0·7 g.), b.p. 95°/8 mm., n^{20} 1·4941 (lit.,[10]

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n_D^{18} 1·4938), $\nu_{max.}$ (film) 3400br and 830 cm.$^{-1}$ (Found: C, 77·8; H, 11·5. Calc. for $C_{10}H_{18}O$: C, 77·8; H, 11·7%). The viscous tosylate (XVIIIb), $\nu_{max.}$ (film) 1192, 1178, and 820 cm.$^{-1}$, was solvolysed without further purification as described for the solvolysis of (XIIb), and the products were analysed similarly.

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