The Chemistry of Terpenes. Part VI.[1] Reactions involving the Isomeric Pinan-10-yl Carbonium Ions

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The relative yields of rearranged and unrearranged products obtained from the isomeric pinan-10-yl ions, produced during the deamination and deoxidation of the isomeric 10-aminopinanes and pinan-10-ols respectively, are compared with the yields of corresponding products resulting from methanolysis of the pinan-10-yl tosylates. The similarities and differences are rationalized in terms of the formation of ' free ' and solvated ions and of ion pairs.

' FREE ' carbonium ions, which are indiscriminate in their subsequent reactions, are produced during the deamination of aliphatic amines.[2] Similarly, ' free ' carbonium ions have been postulated as intermediates in the deamination of terpenoid amines,[2,3] and, although rearrangement of the terpenoid system may be concomitant with the loss of N_2 from the intermediate diazonium ions,[4] recent reports suggest that ion pairs control the formation of products.[5] There is no evidence, however, of concerted rearrangements or of the intervention of ion pairs during the deoxidation of alcohols with halogenoforms in a basic medium, which also proceeds *via* ' free ' carbonium ions.[2a] Conversely the products of the solvolysis of the corresponding tosylates generally result from unimolecular or bimolecular substitution or from elimination reactions where solvation plays an important part and all rearrangement products are generally formed *via* solvated non-classical carbonium ions. In order to compare the reactions of the ions formed under these three reaction conditions, we chose to study the pinan-10-yl system (I) and (II). ' Free ' or solvated primary carbonium ions produced from the pinan-10-yl compounds should be highly

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[1] Part V, R. A. Jones and T. C. Webb, *Tetrahedron*, 1972, **27**, 2877.

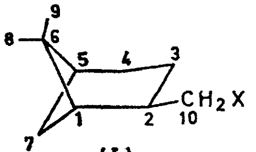
[2] ' Carbonium Ions,' eds. G. A. Olah and P. von R. Schleyer, Wiley-Interscience, New York, 1970, vol. II, (*a*) p. 573 *et seq.*; (*b*) p. 655 *et seq.*

[3] D. G. Cooper and R. A. Jones, *J. Chem. Soc.* (*C*), 1971, 3920.

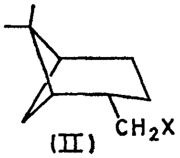
[4] W. Cocker, D. P. Hanna, and P. V. R. Shannon, *J. Chem. Soc.* (*C*), 1969, 1302.

[5] C. J. Collins, *Accounts Chem. Res.*, 1971, **4**, 315.

reactive and can either undergo a [1,2] hydride shift giving the pinan-2-yl ion or be stabilized through the formation of various non-classical ions.



(I)



(II)

a; X = NH_2
b; X = OH
c; X = $OSO_2C_6H_4CH_3$

During the course of our work Whittaker and his co-workers[6,7] reported their kinetic studies of the methanolysis of the pinan-10-yl tosylates. As our product analysis data for similar experiments (Table 1, cols. 4 and 10) differ little from those given by Whittaker, they will not be discussed in detail. The same group have also reported their investigations into the deamination of 2α*H*-10-aminopinane.[8,9,*]

TABLE 1

Products from the deamination and deoxidation of the isomeric 10-amino- and 10-hydroxy-pinanes and from the solvolysis of the corresponding tosylates

2α*H*-Isomers						2β*H*-Isomers			
Deamination			Solvolysis in MeOH	Kovats' retention index [c]		Deamination			Solvolysis in MeOH
a	*b*	Deoxidation			Product	*a*	*b*	Deoxidation	
0·8	1·8	0·7	2·6	1028	Pin-2-ene	0·4	1·1	0·8	1·7
0·9	0·7	0·3	3·7	1062	α-Fenchene	0·9	0·9	0·3	0·0
2·2	2·7	0·6	2·7	1076	Camphene	2·1	1·3	0·8	2·3
6·0	6·8	0·6	21·5	1150	Pin-2(10)-ene	6·2	6·2	0·6	2·3
14·8	17·0	0·0	0·0	1169	(V)	19·1	15·2	0·0	0·0
4·7	6·1	0·5		1200	α-Terpinene	5·8	5·0	0·8	
3·0	1·3	0·5	6·6	1215	Limonene	3·0	2·9	0·8	2·9
1·3	1·8	0·9		1246	γ-Terpinene	1·3	1·3	0·5	
0·5	0·4	0·4	4·2	1286	Terpinolene	0·6	0·6	0·5	1·7
0·6	0·2	0·2		1331	*p*,α-Dimethylstyrene	0·4	0·1	0·0	
0·0	0·2	0·5	5·4 [d]	1435	*endo*-Fenchol	0·0	0·2	0·4	1·0 [d]
0·9	1·3	3·3	3·3 [d]	1544	Pinan-2β-ol	0·4	1·3	3·8	1·0 [d]
1·1	4·1	2·8		1592	4-Terpineol	0·9	3·0	4·1	
2·2 [e]	1·0	1·0	1·8 [d]	1629	Borneol	1·9 [e]	1·8	0·8	0·8 [d]
4·4 [e]	2·5	9·6	14·6 [d]	1661	α-Terpineol	3·7 [e]	2·4	25·9	7·8 [d]
6·7	3·1	27·5	14·5 [d]	1674	Pinan-2α-ol	5·1	1·5	9·5	5·0 [d]
8·0				1691	(IV; R = Ac)	8·3			
0·0	0·7	0·0		1702	An alcohol	0·0	4·9	16·3	
10·0				1708	(III; R = Ac)	10·5			
0·0	4·7	4·1		1715	An alcohol	0·0	4·9	4·3	
10·6				1723	An acetate	11·5			
12·0	13·8	2·7		1734	An alcohol	13·2	12·1	3·3	
0·0	4·6	3·6	10·6 [d]	1750	2α*H*-Pinan-10-ol	0·0	0·0	0·0	0·0
0·0	0·0	0·0	0·0	1761	2β*H*-Pinan-10-ol	0·0	3·0	0·0	67·1 [d]
0·0	1·5	0·0		1780	An alcohol	1·2	7·0	0·0	
0·9	18·4	23·1		1798	An alcohol	0·0	14·6	0·0	
8·4	5·3	17·1	8·5	Unidentified products [f]		3·5	8·7	26·5	6·4
(7)	(12)	(8)	(7)			(5)	(13)	(9)	(9)

[a] Deamination in glacial acetic acid. [b] Deamination in 5% sulphuric acid. [c] Measured at 120° on an LAC 2R-466 column. [d] Isolated as the methyl ether. [e] Combined yields of alcohol and acetate. [f] Number of unidentified products given in parentheses.

Deamination Studies.—With the exception of five new products, the number and identities of the deamination products obtained from the 10-aminopinanes in sulphuric acid (Table 1, cols. 2 and 8) were similar to those formed in the deamination of the isomeric 3-aminopinanes.[3] However, the relative yields of the non-rearranged alcohols resulting from direct substitution on the pinan-10-yl system were lower than those of the alcohols resulting from the corresponding substitution of the secondary pinan-3-yl ions confirming the lower susceptibility of the primary alkanediazonium group to react *via* an S_N1 mechanism. Comparison of the yields of the pinan-10-ols with those of the S_N2 methanolysis products of the corresponding tosylates also indicates that bimolecular substitution on the pinane-10-diazonium ions is of minor importance. Conversely, significant yields of pinan-2α- and -2β-ols illustrate the importance of a [1,2] hydride shift with the loss of nitrogen from the diazonium ions to give the tertiary pinan-2-yl ions.

N.m.r. measurements using a europium shift reagent showed that the preferred conformations of the pinan-10-yl compounds are similar to those of the 3-amino-[10] and 3-hydroxy-pinanes.[11,12] However, although the 2-CH_2X groups adopt a pseudo-equatorial position and the C-1—C-5 atoms are almost coplanar [(I) and (II)], there appears to be little difference in the migratory

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[*] The αβ notation has been used throughout; the isopropylidene bridge is considered to have the β-configuration. Wherever stereoisomers are possible only one structure has been given and can be considered to represent both isomers.

[6] J. R. Salmon and D. Whittaker, *Chem. Comm.*, 1967, 491.

[7] P. I. Meikle, J. R. Salmon, and D. Whittaker, *J.C.S. Perkin II*, 1972, 23.

[8] P. I. Meikle and D. Whittaker, *J.C.S. Chem. Comm.*, 1972, 789.

[9] P. I. Meikle and D. Whittaker, *J.C.S. Perkin II*, in the press.

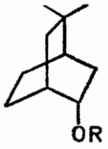
[10] Ee Chong-Sen and R. A. Jones, *Tetrahedron*, 1972, **28**, 2871.

[11] Ee Chong-Sen, Ph.D. Thesis, University of East Anglia, 1973.

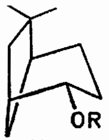
[12] D. V. Banthorpe and D. Whittaker, *Chem. Rev.*, 1966, **66**, 643, and references cited therein.

aptitude of the axial pinan-2α- and -2β-ols suggesting that the pinan-2-yl ion was not specifically solvated. Similarly, the formation of pin-2(10)-ene occurred with equal ease through the loss of a proton from 2α*H*- and 2β*H*-pinan-10-yl ions. As pin-2(10)-ene was not detected during the deamination of the 3-aminopinanes,[3] the alternative proton loss from the pinan-2-yl ion can be discounted and the shift of 2-H to C-10 is seen to be irreversible. This reaction should be compared with the solvolysis where base catalysed *E*2 elimination occurred with greater ease from the 2α*H*-isomer than from the 2β*H*-compound. This may be interpreted as being due to either a more favourable *syn*-elimination of toluene-*p*-sulphonic acid from the 2α*H*-isomer [13] or to the greater steric hindrance of the 2β*H*-isomer to the approach of the methoxide ion to the axial 2-H.[7]

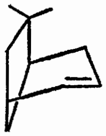
Although the pinan-2-yl ion, produced during the deamination of the 10-aminopinanes, underwent the normal rearrangements to the bornyl, fenchyl, and *p*-menthenyl systems, these compounds no longer constituted the major rearrangement products. Deaminations in sulphuric acid gave three new major products (>10%) with g.l.c. retention indices on an LAC 2R-466 column of 1169, 1734, and 1798. Mass spectral analysis showed the 1169 compound to be a hydrocarbon of molecular weight 136. The remaining compounds and three other new products with retention indices of 1702, 1715, and 1780 proved to be alcohols of molecular weight 154. The latter three alcohols were absent from the deaminations carried out in glacial acetic acid and were replaced by compounds with retention indices of 1691, 1708, and 1734. Of these, the first two proved to be identical both in their g.l.c. retention data and mass spectra with the acetates (III; R = Ac) and (IV; R = Ac) described by Whittaker.[8,9]



(III)

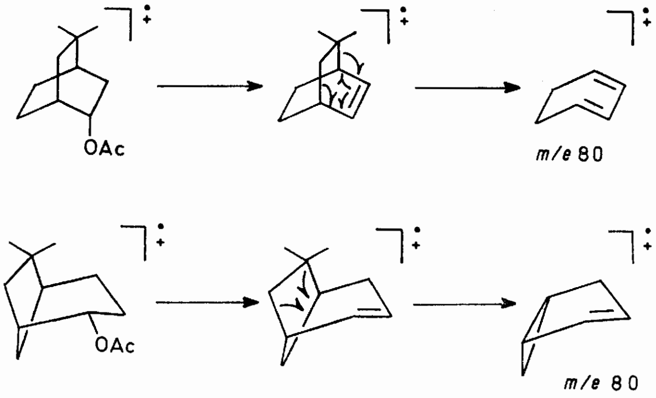


(IV)

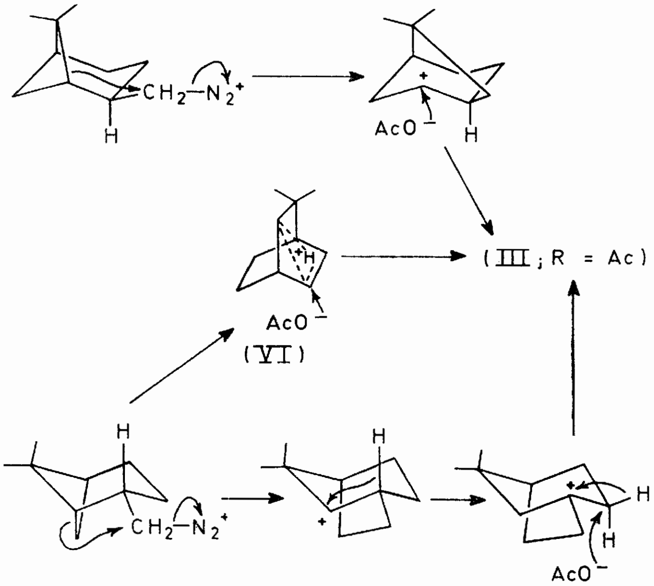


(V)

The base peaks of the acetates were found at *m/e* 80 resulting from the loss of acetic acid and isobutene [14] (Scheme 1). The mass spectrum of the hydrocarbon also showed a base peak at *m/e* 80 and a detailed comparison of the fragmentation modes with those of the acetates indicated (V) to be the most probable structure. The formation of these compounds from the 2α*H*-10-aminopinane is readily explained by Whittaker's mechanism [8,9] through a [1,3] shift of C-6 (Scheme 2), but their formation from the 2β*H*-isomer is less obvious. However, it is reasonable to expect that a [1,3] shift involving C-7 of the 2β*H*-isomer should be as ready as that of C-6 of the 2α*H*-compound (Scheme 2). A subsequent [1,2] hydride shift to give a tertiary carbonium ion followed by acetate attack at C-3 with a simultaneous [1,2] hydride shift would give the bicyclo[2.2.2]octane. As an alternative pathway to the sequential [1,2] hydride shifts the ['6,2'] hydride shift [15] *via* the ion (VI) would also give (III; R = Ac). Ion pair stabilization of the intermediate ions allow for the conversion of the bicyclo[2.2.2]-system into the [3.2.1] compounds.[16] The importance of ion pairs in the stabilization of the intermediates of the [1,3] migrations is apparent from the decreased yields of these rearranged acetates as the glacial acetic acid is diluted with water (Table 2) and the complete absence of the corresponding alcohols (III and IV; R = H) from the deaminations conducted in aqueous sulphuric acid. However, the hydrocarbon (V) was produced in high yields both in glacial acetic acid and under dilute aqueous acidic conditions suggesting the preferential loss of a proton from the intermediate carbonium ion.



SCHEME 1



SCHEME 2

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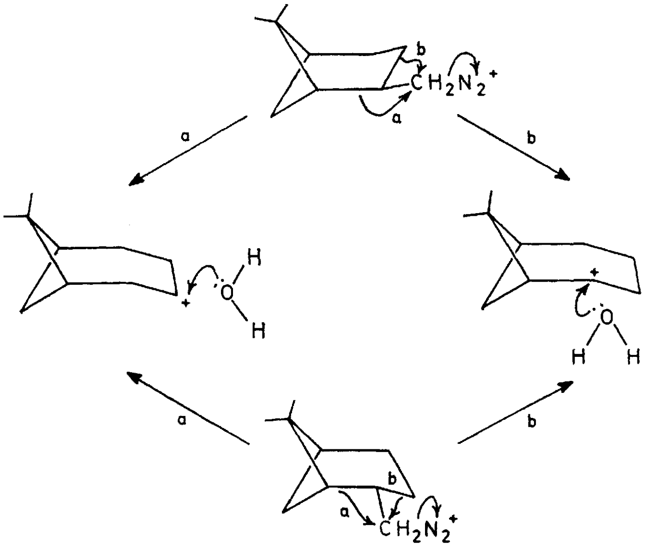
[13] P. S. Skell and W. L. Hall, *J. Amer. Chem. Soc.*, 1963, **85**, 2851.

[14] C. M. Cimarusti and J. Wolinsky, *J. Org. Chem.*, 1071, **36**, 1871.

[15] Ref. 2, p. 535 *et seq.* The [6,2] hydride shift should be described more accurately here as a [3,5] hydride shift.

[16] H. L. Goering and M. F. Sloan, *J. Amer. Chem. Soc.*, 1961, **83**, 1397.

None of the products were formed during the methanolysis of the tosylates.



SCHEME 3

The mass spectra of the remaining unidentified alcohols and the acetate with the retention index of 1723 were similar with base peaks at *m*/*e* 93, corresponding to the fragment ion $C_7H_9^+$ [$M - H_2O - H\cdot - (CH_3)_2C\cdot$]. Although the evidence is not unequivocal, by analogy with the fragmentation modes of pin-2-ene[17] it is possible that the unidentified products have the bicyclo[4.1.1]-octane structures referred to by Whittaker.[8,9] As comparable yields of the alcohols were obtained from both the 2α*H*- and the 2β*H*-10-aminopinanes it would appear that their formation was not a concerted reaction and that the intermediate ring-expanded ions (Scheme 3) were formed. However, deamination of the 2α*H*-isomer in aqueous acetic acid gave higher yields of the alcohols having retention indices of 1734 and 1798 and, although both isomers gave the ring-expanded acetate with a retention index of 1723, it was the 2β*H*-isomer which gave the higher yield indicating the intervention of ion pairs which sterically control the reaction course in acetic acid.

TABLE 2

Products from the deamination of 2α*H*- and 2β*H*-10-aminopinane in acetic acid–water (w/w%)

2α*H*-Isomer							Kovats retention index	Product	2β*H*-Isomer						
100%	83%	76%	67%	50%	33%	17%			100%	83%	76%	67%	50%	33%	17%
0·8	0·6	0·6	1·0	1·2	1·5	2·3	1029	Pin-2-ene	0·6	0·4	0·6	0·6	1·0	1·5	2·5
0·9	0·7	0·7	0·9	0·7	1·1	1·3	1062	α-Fenchene	0·9	0·7	0·9	0·8	0·9	1·1	1·7
2·2	2·2	1·8	2·3	1·9	2·5	2·8	1075	Camphene	2·1	1·3	1·6	1·6	2·3	3·1	4·4
6·0	6·0	6·1	6·0	5·9	6·3	7·8	1151	Pin-2(10)ene	6·2	4·0	3·9	3·9	3·7	5·0	6·6
14·8	16·4	16·6	17·3	15·7	16·1	15·1	1169	(V)	19·1	12·6	14·0	13·8	12·9	14·3	12·7
4·7	4·8	4·8	5·7	4·7	5·0	5·0	1200	α-Terpinene	5·8	6·3	6·3	6·1	6·2	6·3	7·3
3·0	2·6	2·7	3·0	2·5	2·6	2·7	1215	Limonene	3·0	3·5	3·3	2·7	3·4	3·8	5·7
1·3	1·2	1·4	1·4	1·4	1·5	1·6	1246	γ-Terpinene	1·3	1·4	1·4	1·5	1·4	1·7	1·9
0·5	0·3	0·4	0·5	0·5	0·6	0·7	1286	Terpinolene	0·6	1·2	1·5	1·9	2·1	2·0	2·3
0·6	0·2	0·3	0·5	0·5	0·4	0·4	1331	*p*,α-Dimethylstyrene	0·4	0·7	0·5	0·5	0·5	0·4	0·5
0·0	0·0	0·0	1·9	2·8	0·0	0·0	1430	*endo*-Fenchol	0·0	0·0	0·0	0·0	0·0	0·0	0·0
0·9	1·5	2·0	1·1	1·8	1·6	2·0	1544	Pinan-2β-ol	0·4	2·2	1·9	1·9	2·4	2·5	3·0
1·3	1·0	1·1	0·9	1·1	1·0	1·2	1558	Bornyl acetate	0·3	2·4	1·9	2·0	2·3	2·3	2·2
1·1	2·5	3·1	2·6	3·9	4·2	4·3	1592	4-Terpineol	0·9	2·4	2·5	2·5	2·0	2·7	3·2
0·9	0·7	0·8	0·8	0·9	0·9	1·0	1629	Borneol	1·6	2·4	2·3	2·3	2·3	2·1	1·9
4·4	2·9	2·8	2·5	2·4	2·2	2·0	1661	α-Terpineol	0·0	1·6	1·7	1·4	1·4	1·5	1·6
6·7	6·0	6·1	6·3	5·3	4·7	3·2	1674	Pinan-2α-ol	5·1	9·0	9·1	9·0	7·6	6·2	3·7
8·0	5·9	5·5	4·8	3·5	2·8	2·1	1691	(IV; R = Ac)	8·3	5·0	4·6	4·3	3·3	2·5	1·3
10·0	9·3	5·3	4·7	3·9	2·7	0·0	1708	(III; R = Ac)	10·5	5·4	5·1	4·6	4·1	3·0	2·3
10·6	6·4	6·0	4·6	4·6	4·1	5·8	1723	An acetate	11·5	12·8	11·8	10·8	9·8	8·7	7·9
12·0	15·7	16·3	18·0	16·8	18·2	17·1	1734	An alcohol	13·2	8·2	8·7	9·4	10·0	10·6	9·9
0·0	3·1	4·2	3·2	6·7	5·5	6·7	1750	2α*H*-Pinan-10-ol	0·0	0·0	0·0	0·0	0·0	0·0	0·0
0·0	0·0	0·0	0·0	0·0	0·0	0·0	1761	2β*H*-Pinan-10-ol	0·0	1·4	1·6	2·0	2·3	2·9	2·6
0·0	0·0	0·0	0·0	0·0	0·0	0·0	1780	An alcohol	1·2	2·8	3·3	4·1	4·8	6·0	7·7
0·9	4·4	5·1	6·8	8·5	9·6	10·7	1798	An alcohol	0·0	2·3	3·0	3·8	4·5	4·8	5·4

Deoxidation Studies.—Compared with the deamination reactions, deoxidation of the pinan-10-ols gave fewer products and, although it has frequently been postulated that deamination and deoxidation reactions both proceed *via* ' free ' or ' hot ' carbonium ions,[2] it is equally apparent that in the deamination reactions the formation of ion pairs is a controlling factor in the rearrangement reactions. This is particularly obvious with the pinan-10-yl system, where there is no evidence in the deoxidation reactions of the [1,3] rearrangements to the bicyclo[2.2.2]- and -[3.2.1]-octanes, which occurred to the extent of *ca.* 35% in the deamination reactions.

Owing to its high encounter rate with hydroxide ions, the carbonium ion formed under the basic deoxidation reactions has a limited life-time compared with that formed under the acidic deamination conditions.[18] Thus, whilst the yields of alcohols were considerably higher for the deoxidation reactions, the yields of the olefins were lower than those produced in the deamination reactions. The major reaction pathways followed in the deoxidation of the pinan-10-ols involved a [1,2] hydride

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[17] H. C. Hill, R. I. Reed, and M. J. Robert-Lopes, *J. Chem. Soc.* (*C*), 1968, 93; R. I. Reed in ' Mass Spectrometry of Organic Ions,' ed. F. W. McLafferty, Academic Press, New York, 1963.

[18] *Cf.* P. S. Skell and R. J. Maxwell, *J. Amer. Chem. Soc.*, 1962, **84**, 3963.

shift followed by simple Wagner–Meerwein [1,2] migrations. However, the most remarkable feature of the rearrangement reactions was the preferential formation (27·5%) of pinan-2α-ol from 2α*H*-pinan-10-ol and the correspondingly high yield (25·9%) of α-terpineol from the 2β*H*-isomer. These observations are difficult to rationalize unless one assumes that, subsequent to the shift of 2-H to give the pinan-2-yl ion, capture of the hydroxide ion is so rapid that the tertiary ions essentially retain the conformation of their pinan-10-yl ion precursor. Attack on the less hindered α-side of the tertiary ion produced through the rearrangement of 2α*H*-pinan-10-ol would give pinan-2α-ol, whereas in the corresponding reaction on the tertiary ion obtained from 2β*H*-pinan-10-ol, both the α- and β-sides of the ion would be sterically hindered for nucleophilic attack by the hydroxide ion. Attack at C-6 with simultaneous cleavage of the C-6–C-1 bond to give α-terpineol would, however, be favoured.

EXPERIMENTAL

Spectroscopic analyses of the reaction products were performed as described previously.[3] G.l.c. analysis were carried out at 120° on a 4 m × 0·125 in column of LAC 2R-466 on Chromosorb W (15% w/w) in a Perkin-Elmer F11 chromatograph, with a flame ionization detector and nitrogen as the carrier gas (10 lb in^{-2}). Chromatographic peak areas were measured with an accuracy of better than ±3% with an Allbrit planimeter.

10-*Amino*-2α*H*-*pinane* (Ia).—Hydroboration of pin-2(10)-ene at room temperature and subsequent reaction with amino-oxysulphonic acid gave 10-amino-2α*H*-pinane (49%), b.p. 84—86° at 10 mmHg (lit.,[19] b.p. 60—61° at 2 mmHg). Treatment of an ethereal solution of the amine with dry hydrogen chloride gave the *hydrochloride*, m.p. 270° (Found: C, 63·8; H, 10·8; N, 7·2. $C_{10}H_{20}ClN$ requires C, 63·5; H, 10·6; N, 7·2%).

10-*Amino*-2β*H*-*pinane* (IIa). Boron trifluoride–ether complex (11 ml) was added dropwise to a stirred mixture of pin-2(10)-ene (20 g) and sodium borohydride (2·5 g) in bis-(2-methoxyethyl) ether (75 ml) under nitrogen and the stirring was continued at room temperature for 30 min. The 2α*H*-pinan-10-ylborane was heated at 130° for 3 h and the solution then cooled to 0°. A suspension of amino-oxysulphonic acid (20 g) in bis-(2-methoxyethyl) ether (75 ml) was added and stirring was continued at *ca.* 20° for 1 h and then at 100° for a further 1 h. The cooled solution was acidified with hydrochloric acid, extracted with ether (4 × 100 ml) to remove non-basic components, and then made alkaline. Steam distillation gave the crude amine as an oil. The distillate was extracted with ether (3 × 10 ml) and the combined extracts were dried ($MgSO_4$) and saturated with dry hydrogen chloride to give the *hydrochloride*, m.p. 235° (decomp.) (Found: C, 63·8; H, 10·4; N, 7·4%). Treatment of the hydrochloride with base gave the *amine* (10·2 g, 45%), b.p. 87—89° at 10 mmHg.

2αH-*Pinan*-10-*yl Tosylate* (Ic).—Reaction of 2α*H*-pinan-10-ol (Ib) with toluene-*p*-sulphonyl chloride in pyridine at room temperature for 48 h gave the tosylate (49%), m.p. 76—77° (lit.,[7] 75·5—76°).

2β*H*-*Pinan*-10-*yl Tosylate* (IIc).—Using a similar procedure to that described for the 2α*H*-isomer, 2β*H*-pinan-10-ol (IIb) gave 2β*H*-pinan-10-yl tosylate (56%), m.p. 45—47° (lit.,[7] 50—50·5°)(Found: C, 66·2; H, 7·8; S, 10·3. Calc. for $C_{17}H_{24}O_3S$: C, 66·2; H, 7·8; S, 10·4%).

Samples of pinan-2α- and -2β-ols were prepared by standard methods and were converted into their methyl ethers by reaction of the potassium alcoholates with methyl iodide. The methyl ethers of the isomeric pinan-10-ols and α-terpineol were prepared by analogous procedures whilst the methyl ethers of borneol and *endo*-fenchol were prepared by the boron trifluoride catalysed reaction with diazomethane. Samples of the acetates were obtained by the acid catalysed esterification of the alcohols with isopropenyl acetate.

Authentic samples of the other products were obtained from commercial sources.

Deamination Conditions.—(a) *In acetic acid*. Recrystallized sodium nitrite (0·22 g) was added in portions over a period of 15 min to a well stirred solution of the amine (0·5 g) in the appropriate concentration of glacial acetic acid in water (total volume 3 ml) at 0°. Stirring was continued at room temperature for 3 h and the mixture was then extracted with ether (4 × 5 ml). The extracts were washed with a saturated solution of sodium hydrogen carbonate (5 ml) and then with water (5 ml), dried (Na_2SO_4), and concentrated to 2 ml under reduced pressure. The residual solution was analysed by g.l.c.

(b) *In sulphuric acid*. Aqueous sodium nitrite (15%; 10 ml) was added rapidly with stirring to the amine (0·5 g) in sulphuric acid (1·0 g) and water (10 ml) at 0°. Stirring was continued at room temperature for 3 h and the mixture was then worked-up as described above.

Deoxidation Reactions.—The alcohol (0·5 g) and potassium hydroxide (5·0 g) in water (2 ml) were heated at 100° for 1 h. Bromoform (3·0 g) was added and the mixture heated under reflux for a further 3 h. The cooled mixture was diluted with water (10 ml) and extracted with ether (5 × 20 ml). The extracts were washed with water until the washings were no longer basic, dried ($MgSO_4$), and concentrated to 2 ml under reduced pressure. The residual solution was analysed by g.l.c.

Methanolysis Reactions.—The tosylate (1·0 g) and sodium methoxide (0·2 g) in methanol (100 ml) were stirred at 85° under nitrogen for 7 days. The reaction mixture was diluted with water (100 ml) and extracted with ether (4 × 50 ml). The extracts were washed with water (2 × 50 ml), dried ($MgSO_4$), and concentrated to 2 ml under reduced pressure. The residual solution was analysed by g.l.c.

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