Studies on Terpenes. Part I. Rearrangement of 7-Oxatricyclo[4,3,0,$0^{3,9}$]-nonanes into 8-Substituted 1,3,3-Trimethylnorbornane Derivatives [1]

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9-Methyl-6-*p*-tolyl- (III; R = C_6H_4Me-*p*) and 6,9-dimethyl-7-oxatricyclo[4,3,0,$0^{3,9}$]nonane (III; R = Me) are readily rearranged into 8-substituted 1,3,3-trimethylnorbornan-2α-ols by treatment with boron trifluoride–ether. 9-Methyl-7-oxatricyclo[4,3,0,$0^{3,9}$]nonane (III; R = H) is rearranged (BF_3–OEt_2) to a mixture of *endo*-3α-acetoxymethyl-3-methylnorbornan-2α-yl acetate (VIII; R = Ac) and *exo*-7-acetoxymethyl-7-methylnorbornan-2β-yl acetate (IX; R = Ac).

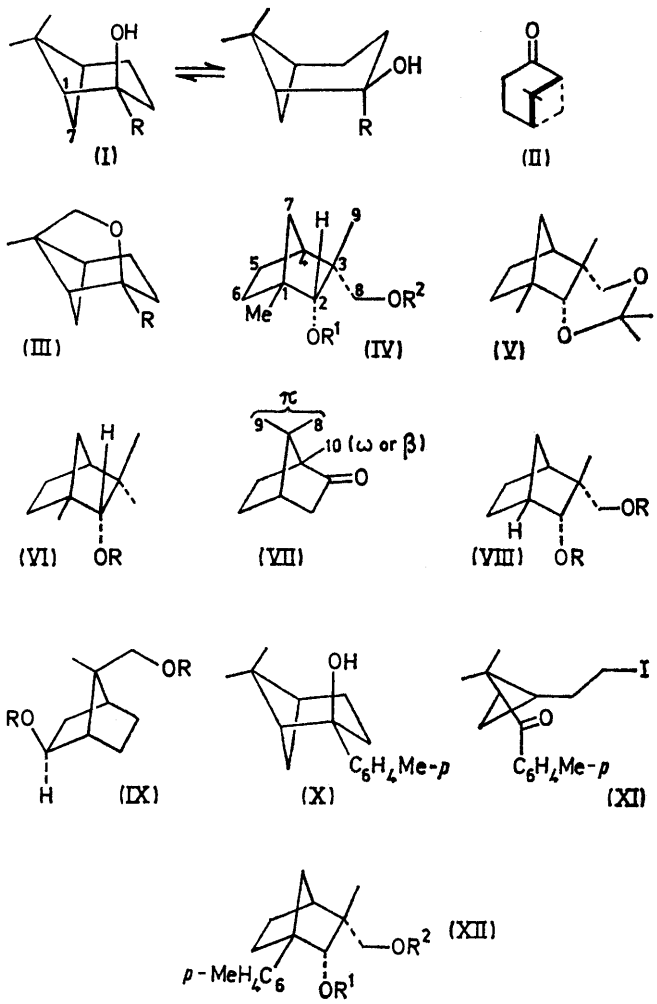
ESSENTIAL oil constituents based on the pinane skeleton represent an extensive series of compounds. The facility with which they are rearranged to other skeletal types has rendered them particularly useful as synthetic precursors. Unfortunately rearrangement of the pinane ring system often produces complex mixtures. Although interesting from a mechanistic stand-point and to the olfactory senses, the pinanes are not particularly attractive as starting materials for the synthesis of optically pure terpenes.

Consider the 6,6-dimethylnorpinan-2β-ols † (*trans*-nopinols) (I; R = H, alkyl, or aryl). These are readily available through nucleophilic addition to nopinone (II); the rearrangement of some of these nopinols has been studied and the results are given in the Table. The alcohol (I; R = H) benefits from anchimeric assistance in its solvolysis and a mixture of *endo*- and *exo*-secondary alcohols results.[2,3] Mere substitution of a methyl group for hydrogen at the position adjacent to the bridgehead, giving pinan-2β-ol (I; R = Me), produces a striking change in behaviour. Apart from ring-opened products, only *endo*-products are formed.[4,5] In the Table the last

† The αβ-notation has been used throughout; the isopropylidene bridge is considered to have the β-configuration.

[1] Preliminary communication, N. Bosworth and P. D. Magnus, *Chem. Comm.*, 1971, 618.
[2] E. C. Friedrich and S. Winstein, *J. Amer. Chem. Soc.*, 1964, **86**, 2721.
[3] P. von R. Schleyer, W. E. Watts, and C. Cupas, *J. Amer. Chem. Soc.*, 1964, **86**, 2722.
[4] W. D. Burrows and R. H. Eastman, *J. Amer. Chem. Soc.*, 1959, **81**, 245.
[5] N. A. Abraham and M. Vilkas, (*a*) *Bull. Soc. chim. France*, 1960, 1450; (*b*) *Ann. Chim.* (*France*), 1960, **5**, 961.

example, with the aryl compounds (I; R = [illegible]) is in effect a *cis*-elimination, but is more likely to occur *via* a benzylic carbonium ion in a non-concerted process.[6] The conformational flexibility of the alcohols (I; R = H and Me) might be implicated in the lack of clean *trans*-coplanar concerted migration of the 1,7-bond.



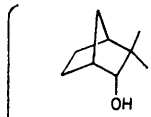
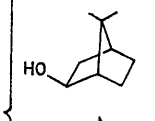
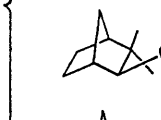
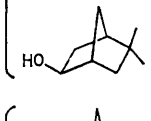
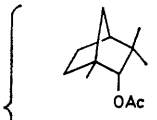
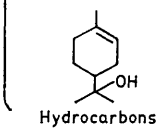
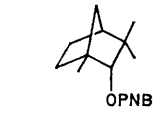
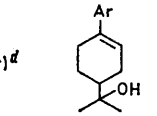
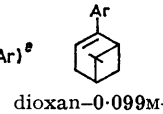
We felt that if the 2-hydroxy-group in the *trans*-nopinols could be confined to a strictly *trans*-coplanar relation to the 1,7-bond, a clean rearrangement to the fenchol (1,3,3-trimethylnorbornan-2-ol) series might result.

To create a conformationally defined system the 2-hydroxy-group is best incorporated into part of a ring structure. Formation of a carbon–oxygen bond to C-8 leads to the tricyclic 2,8-nopinyl ethers (III; R = H, alkyl, or aryl), having the desired conformational requirements.

6,9-Dimethyl-7-oxatricyclo[4,3,0,$0^{3,9}$]nonane [7,8] (III; R = Me) was prepared from (−)-pin-2(10)-ene *via* intramolecular (Br_2–HgO) oxidation of pinan-2β-ol (I; R = Me). Treatment of the ether (III; R = Me) in acetonitrile at 20° with acetyl toluene-*p*-sulphonate [9] did not give the 8-substituted pinane but the 8-substituted fenchol (IV; $R^1 = SO_2{\cdot}C_6H_1Me$-*p*, R^2 = Ac) (80%). Its structure was confirmed by n.m.r. spectroscopy.

Similarly, treatment of the pinanyl ether (III; R = Me) with acetic anhydride and boron trifluoride–ether [10] gave the diacetate (IV; $R^1 = R^2$ = Ac) (90%). The methylene AB system in the n.m.r. spectrum must

TABLE

Compound	Product(s)	Yield (%)
6,6-Dimethylnorpinan-2β-ol (I:R=H)[a]		59
		26
		4
		11
Pinan-2β-ol (I:R = Me)[b]		40–45
		5–10
	Hydrocarbons	40–50
Pinan-2β-yl *p*-nitrobenzoate[c]	 [f]	25–30
2-Aryl-6,6-dimethylpinan-2β-ol (I:R=Ar)[d]		61
2-Aryl-6,6-dimethylpinan-2β-ol (I:R=Ar)[e]		84

[a] Refs. 2 and 3; aqueous 70% dioxan–0·099M-$HClO_4$–75°. [b] Ref. 4; acetic anhydride. [c] Ref. 5. [d] Ref. 6; silica. [e] Ref. 6; Woelm I neutral alumina. [f] PNB = *p*-Nitrobenzoate.

[6] C. R. Hughes, D. F. MacSweeney, and R. Ramage, *Tetrahedron*, 1971, **27**, 2247.
[7] T. W. Gibson and W. F. Erman, *J. Amer. Chem. Soc.*, 1969, **91**, 4771.
[8] A. G. Hortmann and R. E. Youngstrom, *J. Org. Chem.* 1969, **34**, 3392.
[9] M. H. Karger and Y. Mazur, *J. Amer. Chem. Soc.*, 1968, **90**, 3878.
[10] (*a*) C. R. Narayanan and K. N. Iyer, *J. Org. Chem.*, 1965, **30**, 1734; (*b*) R. D. Youssefyeh and Y. Mazur, *Tetrahedron Letters*, 1962, 1287.

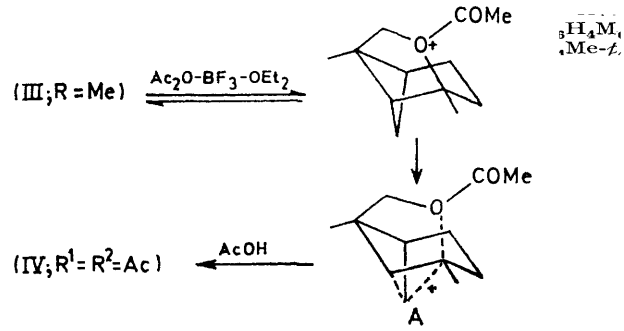
arise from a combination of intrinsic non-equivalence [11] due to the low symmetry (*cf.* $CH_AH_BU{\cdot}CXYZ$) [12] and unequal conformer population (UCP). It would appear likely that the former effect has precedence in this particular system. The long range 2—6β, 'W' coupling [12,13] (1·5 Hz) is in the expected range for a bicyclo-[2,2,1]heptane structure.

To establish the relative configuration of the two oxygen functions and the stereospecificity of the rearrangement, the following sequence of reactions was carried out. The diacetate (IV; $R^1 = R^2 = Ac$) was reduced with lithium aluminium hydride in ether to the diol (IV; $R^1 = R^2 = H$). The *cis*-disposition of the two hydroxy-groups was readily demonstrated by treatment of the diol (IV; $R^1 = R^2 = H$) with 2,2-dimethoxypropane–toluene-*p*-sulphonic acid to give the acetal (V). Reaction of the diol (IV; $R^1 = R^2 = H$) with toluene-*p*-sulphonyl chloride in pyridine [14] gave the tosylate (IV; $R^1 = H$, $R^2 = SO_2{\cdot}C_6H_4Me$-*p*). Acetylation of the tosylate (IV; $R^1 = H$, $R^2 = SO_2{\cdot}C_6H_4Me$-*p*) gave the acetate (IV; $R^1 = Ac$, $R^2 = SO_2{\cdot}C_6H_4Me$-*p*) as an unstable oil [*cf.* (IV; $R^1 = SO_2{\cdot}C_6H_4Me$-*p*, $R^2 =$ Ac)]. Its instability during chromatography on silica gel is readily explained by intramolecular displacement of the primary tosylate [15] by the 2-*endo*-acetate. Such a displacement is sterically impossible with the 2-tosylate (IV; $R^1 = SO_2{\cdot}C_6H_4Me$-*p*, $R^2 =$ Ac).

Reduction of the tosylate (IV; $R^1 = H$, $R^2 = SO_2{\cdot}C_6H_4Me$-*p*) with lithium aluminium hydride gave 1,3,3-trimethylnorbornan-2α-ol (α-fenchol) (VI; R = H) as an impure oil. The τ value for 2-H (6·74) and J_{26} (1·3 Hz) are in agreement with the published data.[16] Further characterisation of the alcohol (VI; R = H) as its *p*-nitrobenzoate (VI; $R = CO{\cdot}C_6H_4NO_2$-*p*) confirmed the structure.

The remarkably high yield in the rearrangement of the ether (III; R = Me) to the diacetate (IV; $R^1 = R^2 =$ Ac) compared with the rearrangement of esters from pinan-2β-ol (I; R = Me) to α-fenchyl esters [4,5] suggests that the mechanism (Scheme 1) operates *via* A as an ion pair, and is completely concerted. Furthermore, the specific rotations of the fenchol (VI; R = H) and its *p*-nitrobenzoate (VI; $R = CO{\cdot}C_6H_4{\cdot}NO_2$-*p*) are the highest recorded in the literature.[5,17]

The 10ω- or 10β-, *cis*-8 π-, and *trans*-9 π-substituted bornan-2-one (camphor) derivatives (VII) have been described [18] but similar compounds in the fenchane series are virtually unknown. The only reported methyl substituted fenchane is Konovalov's 'hydroxyfenchane' [19] whose structure was established as 3,3-dimethylnorbornan-1-ylmethanol (10-hydroxyfenchane).[20,21]



SCHEME 1

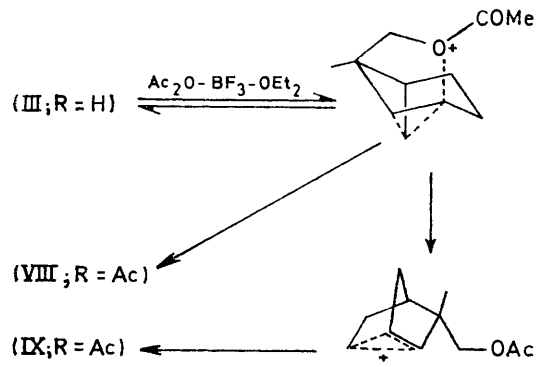
It would be expected from both Winstein's [2] and Schleyer's [3] study of α- and β-nopinol that the secondary ether (III; R = H) would benefit more from anchimeric assistance in its solvolysis than the tertiary ether (III; R = Me). As a consequence, products having the 7,7-dimethylnorbornan-2ξ-ol as well as the 3,3-dimethylnorbornan-2-ol structure may be formed.

9-Methyl-7-oxatricyclo[4,3,0,0 ^{3,9}]nonane [7] (III; R = H) [prepared from (−)-pin-2(10)ene *via* intramolecular oxidation with bromine–mercury(II) oxide of *cis*-nopinol [22]] was treated with acetic anhydride–boron trifluoride–ether at 0°. A rapid reaction took place [compared with the rearrangement of the pinyl ether (III; R = Me) to the acetate (IV; $R^1 = R^2 =$ Ac)] to give two compounds (VIII; R = Ac) and (IX; R = Ac) in the ratio 7 : 3 (calculated from n.m.r. data). This ratio is independent of the temperature at which the rearrangement is conducted (from −70 to 20°). The mixture of acetates (VIII; R = Ac) and (IX; R = Ac) could not be separated by the usual techniques (distillation, t.l.c., and g.l.c.). The n.m.r. spectrum indicated the skeletal types present in the mixture.

The mixture of the diacetates (VIII; R = Ac) and (IX; R = Ac) was reduced with lithium aluminium hydride to an inseparable mixture of diols (VIII; R = H) and (IX; R = H) which decomposed as silica, alumina, and g.l.c. Benzoylation of the diol mixture

[11] H. S. Gutowsky, *J. Chem. Phys.*, 1962, **37**, 2196.
[12] L. M. Jackman and S. Sternhell, 'Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon, pp. 372 and 334.
[13] M. J. Barfield, *J. Chem. Phys.*, 1964, **41**, 3825.
[14] A. J. Aasen and C. C. J. Culvenor, *J. Org. Chem.*, 1969, **34**, 4143.
[15] (*a*) Pl. A. Plattner and W. Long, *Helv. Chim. Acta*, 1944, **27**, 1872; (*b*) D. K. Fukushima, N. S. Leeds, H. L. Bradlow, T. H. Kritchevsky, M. B. Stokem, and T. F. Gallagher, *J. Biol. Chem.*, 1955, **212**, 449; (*c*) D. Taub, R. D. Hoffsommer, and N. L. Wendler, *J. Amer. Chem. Soc.*, 1959, **81**, 3291.
[16] (*a*) J. I. Mosher, *Mol. Phys.*, 1963, **6**, 93; (*b*) A. Coulombeau and A. Rassat, *Bull. Soc. chim. France*, 1965, 3338.
[17] 'Rodd's Chemistry of Carbon Compounds,' ed. S. Coffey, vol. II, 2nd edn., Part C, p. 240.
[18] J. L. Simonsen and L. N. Owen 'The Terpenes,' vol. II, 2nd edn., p. 386; ref. 17, p. 207; T. Hasselstrom, *J. Amer. Chem. Soc.*, 1931, **53**, 1097; E. J. Corey, M. Ohno, S. W. Chow, and R. A. Scherrer, *J. Amer. Chem. Soc.*, 1959, **81**, 6305; E. J. Corey, S. W. Chow, and R. A. Scherrer, *J. Amer. Chem. Soc.*, 1957, **79**, 5773; F. Dallacker, K. Ulrichs, and M. Lipp, *Annalen*, 1963, **667**, 50.
[19] S. S. Nametkin and V. A. Khokhrjakova, *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1611.
[20] G. Komppa and A. Klami, *Ber.*, 1935, **68***B*, 2001.
[21] T. Kuusinen, *Ann. Acad. Sci. Fennicae, Ser.* AII, 1956, **69**, 55 (*Chem. Abs.*, 1957, **51**, 4317).
[22] S. Winstein and N. J. Holness, *J. Amer. Chem. Soc.*, 1955, **77**, 3054.

(VIII; R = H) and (IX; R = H) gave two bis-benzoates (VIII; R = Bz) and (IX; R = Bz) that were separable (multiple elution t.l.c.). The n.m.r. spectra of the two benzoates do not supply sufficient information for unambiguous assignment of the orientation of the 2-proton in (IX; R = Bz). On mechanistic grounds (Scheme 2), however, it is reasonable that the 2-proton be assigned the *endo*-configuration.



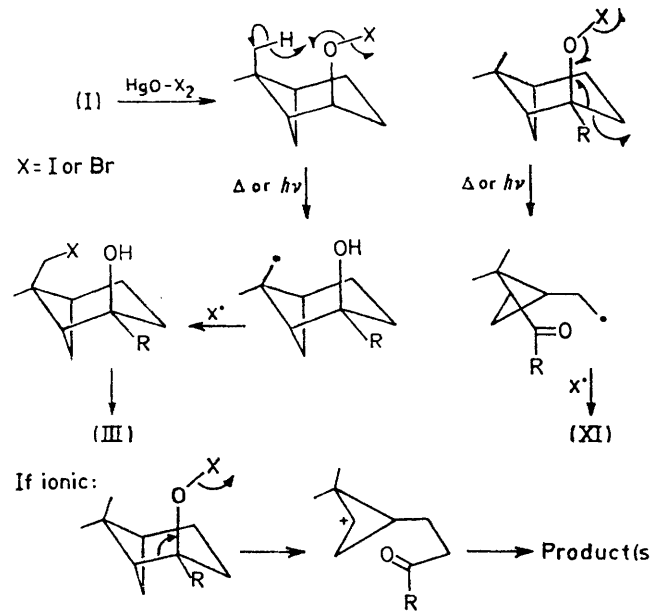
SCHEME 2

The (+)-ketone (II) was treated with *p*-tolylmagnesium bromide to give a single alcohol (X). The stereochemistry is assigned as *trans* on the basis of the usual Grignard additions to nopinone [7] and subsequent transformations. While the bromine–mercury(II) oxide [7,23] procedure for preparing the ethers (III) from *trans*-alcohol (I) was satisfactory for compounds (III; R = H or Me) (see Experimental section for modifications of Erman's [7] procedure), when applied to the *p*-tolyl compound (I; R = C_6H_4Me-*p*), a complex mixture of products were formed. With mercury(II) oxide–iodine–*hν* at −20° [24] the norpinanol (X) was cleanly transformed into two products; the required ether (III; R = C_6H_4Me-*p*) (80%) and the β-fragmentation product (XI) (20%). The structure of the crystalline ether (III; R = C_6H_4Me-*p*) followed from its n.m.r. spectrum. Similarly the n.m.r. and i.r. spectra of the cyclobutyl ketone (XI) are compatible with the assigned structure.

We found that intramolecular oxidations with both bromine– and iodine–mercury(II) oxide required continuous irradiation (tungsten 750 W lamp) during the whole reaction to achieve reasonable yields of the ethers. This is compatible with a radical process involving homolytic cleavage of hypohalite intermediates. Indeed the by-product (XI) from the iodine–mercury(II) oxidation is expected if radical intermediates are involved, whereas ionic intermediates would lead to rupture of the cyclobutane ring (see Scheme 3).

The ether (III; R = C_6H_4Me-*p*) was treated with acetic anhydride–boron trifluoride–ether at 0°. A single crystalline product (XII; R^1 = Ac, R^2 = H) was isolated in over 90% yield. If the reaction is conducted at 20°, the diacetate (XII; $R^1 = R^2$ = Ac) is the major product, accompanied by the mono-acetate (XII; R^1 = Ac, R^2 = H). For convenience, the rearrangement was carried out at 0° and worked-up with acetylation (pyridine–Ac_2O). Furthermore, to avoid a tedious separation of (III; R = C_6H_4Me-*p*) from the ketone (XI), the rearrangement of the mixture was carried out as before, but followed by acetylation (Ac_2O–pyridine). This expedient enabled the pure crystalline diacetate (XII; $R^1 = R^2$ = Ac) to be isolated in >90% yield; the by-product (XI) was removed during the aqueous work-up, presumably as the pyridinium iodide. The structure of the diacetate (XII; $R^1 = R^2$ = Ac) was readily deduced from the n.m.r. spectrum (see Experimental section). The absence of vinyl protons in the n.m.r. and styrene absorption in the u.v. spectrum eliminated 2-arylnorpinene- and 1-arylcyclohexene-like structures [6] (see Table).

This result is in agreement with the mechanism shown in Scheme 1; a clean *trans*-coplanar migration of the 1,7-bond with concerted C–O bond cleavage.



SCHEME 3

Rearrangement of the pinane ring system under carbonium ion conditions usually gives rise to many products.[25] The need to find defined conditions for selective rearrangement has been appreciated by us [1] and others.[6] It appears that when the oxonium–carbonium ion intermediate (Scheme 1) is stabilised (R = Me or Ar) high yields of 8-substituted fenchanes result. Whereas when R = H, the higher energy oxonium–carbonium ion is stabilised by anchimeric assistance, leading to the two observed products (VIII; R = Ac) and (IX; R = Ac).

[23] R. A. Sneen and N. P. Metheny, *J. Amer. Chem. Soc.*, 1964, **86**, 5503.
[24] M. Akhtar and D. H. R. Barton, *J. Amer. Chem. Soc.*, 1964, **86**, 1528.
[25] J. A. Berson, 'Molecular Rearrangements I,' ed. P. de Mayo, Interscience, New York, 1963, p. 111.

EXPERIMENTAL

M.p.s were determined on a Kofler hot-stage block and are uncorrected. I.r. spectra were measured for Nujol mulls and thin-films unless otherwise stated. N.m.r. spectra were recorded with a Varian A60 and HA 100 instruments for solutions in [^{2}H]chloroform with tetramethylsilane as internal standard.

All solvent were purified prior to use by standard techniques. Light petroleum refers to the fraction b.p. 40—60 °C.

Pinan-2β-ol [4] (I; R = Me).—This compound m.p. 57—59°, and $[\alpha]_D^{20}$ −4·4° (ether), was prepared by ozonolysis [26] of (−)-pin-2(10)-ene and treatment of the resulting (+)-6,6-dimethylnorpinan-2-one (II) with methylmagnesium bromide.

6,9-*Dimethyl-7-oxatricyclo*[4,3,0,0^{3,9}]*nonane* [7,8] (III; R = Me).—To a solution of pinan-2β-ol (I; R = Me) (52 g) in carbon tetrachloride (750 ml) containing yellow mercury(II) oxide (217 g) at 0° was added bromine (19 ml) during 1·5 h. The stirred mixture was protected from light. After 3 h at 0° the mixture was filtered and the filtrate was irradiated at 0° for 1·25 h with a tungsten lamp (500 W; 30 cm from the flask). Nitrogen was bubbled through the solution to remove hydrogen bromide. The solution was heated to reflux and after 1 h cooled and washed with aqueous sodium chloride solution. The solution was dried (Na_2SO_4) and evaporated to a straw-brown oil Distillation gave the pure ether (III; R = Me) (22 g), b.p. 60° at 9 mmHg.

1,3-*Dimethyl*-2α-p-*tolylsulphonyloxynorbornan*-3α-*ylmethyl Acetate* (IV; R^1 = SO_2·C_6H_4Me-*p*, R^2 = Ac). To a solution of the foregoing ether (III; R = Me) (1·0 g) in acetonitrile (10 ml) at −20° was added acetyl toluene-*p*-sulphonate (1·7 g) in acetonitrile (10 ml). After 14 h at room temperature (20°) the mixture was poured into water (50 ml) and extracted with light petroleum. The dried (Na_2SO_4) light petroleum layer on evaporation gave a yellow oil (2·0 g). The oil was dissolved in light petroleum containing 10% acetone and chromatographed on silica gel plates (60 × 20 cm). Elution with ether gave pure *acetate* (IV; R^1 = SO_2·C_6H_4Me-*p*, R^2 = Ac) (80%), m.p. 156—158° (from light petroleum), $\nu_{max.}$ 1725 and 1595 cm^{-1}, $[\alpha]_D^{25}$ +54·0° (*c* 1·9 in chloroform), τ * 8·95 (3H, s), 8·99 (3H, s), 7·95 (3H, s), 7·55 (3H, s), 6·13 (2H, ABq, *J* 10 Hz), 5·48br (1H, s), and 2·48 (4H, ABq, *J* 8 Hz) (Found: C, 62·0; H, 7·2. $C_{19}H_{26}O_5S$ requires C, 62·3; H, 7·2%).

2α-*Acetoxy*-1,3-*dimethylnorbornan*-3α-*ylmethyl Acetate* (IV; R^1 = R^2 = Ac).—The ether (III; R = Me) (5·0 g) in acetic anhydride (100 ml) at 0° was treated with boron trifluoride–ether (15 ml, 12% soln.). After 48 h at 0°, the mixture was poured into ice–water and extracted with ether (200 ml.). The extracts were washed with saturated aqueous sodium hydrogen carbonate solution and dried (Na_2SO_4). Evaporation left a dark red oil that slowly crystallised. Sublimation at 100° and 10^{-5} mmHg gave pure 2α-*acetoxy-acetate* (IV; R^1 = R^2 = Ac) (90%), m.p. 38—40°, $\nu_{max.}$ 2990, 1720, 1385, and 1280 cm^{-1}, $[\alpha]_D^{28·5}$ +36·0° (*c* 5·6 in chloroform), τ 8·92 (3H, s), 8·95 (3H, s), 7·96 (3H, s), 7·98 (3H, s), 6·4 (2H, ABq, *J* 6 Hz), and 5·45 (1H, d, *J* 1·5 Hz) (Found: C, 66·2; H, 8·7. $C_{14}H_{22}O_4$ requires C, 66·1; H, 8·7%).

2α-*Hydroxy*-1,3-*dimethylnorbornan*-3α-*ylmethanol* (IV; R^1 = R^2 = H).—To the crude diacetate (IV; R^1 = R^2 = Ac) (7·2 g) in ether (75 ml) was added lithium aluminium hydride (2·5 g) in ether (150 ml). After 1 h at room temperature the mixture was quenched with ethyl acetate and aqueous ammonium chloride solution. The ether layer was dried (Na_2SO_4) and evaporated to give the *diol* (IV; R^1 = R^2 = H) (3·3 g), m.p. 81° (from light petroleum–ether), $\nu_{max.}$ ($CHCl_3$) 3525, 3450, 1465, 1075, and 1030 cm^{-1}, $[\alpha]_D^{28·5}$ −21·2° (*c* 2·8 in chloroform), τ 8·9 (6H, s), 6·35 (2H, ABq, *J* 9 Hz), and 6·62 (1H, s) (Found: C, 70·7; H, 10·6. $C_{10}H_{18}O_2$ requires C, 70·5; H, 10·7%).

2α-*Hydroxy*-1,3-*dimethylnorbornan*-3α-*ylmethanol Isopropylidene Acetal* (V).—To the diol (IV; R^1 = R^2 = H) (100 mg) in 2,2-dimethoxypropane (5 ml) was added a crystal of toluene-*p*-sulphonic acid monohydrate. After 10 min, evaporation and sublimation of the mixture gave the *acetal* (V) (80%), m.p. 74—76°, $\nu_{max.}$ 2950, 1465, 1385, 1230, and 1090 cm^{-1}, τ 8·90 (3H, s), 8·86 (3H, s), 8·75 (3H, s), 8·71 (3H, s), 6·9 (1H, s), and 6·65 (2H, ABq, *J* 6 Hz). Mass spectrometry showed a molecular ion at *m/e* 210 corresponding to $C_{13}H_{22}O_2$.

2α-*Hydroxy*-1,3-*dimethylnorbornan*-3α-*ylmethyl Toluene*-p-*sulphonate* (IV; R^1 = H, R^2 = SO_2·C_6H_4Me-*p*).—The diol (IV; R^1 = R^2 = H) (1·1 g) in pyridine (20 ml) was treated with toluene-*p*-sulphonyl chloride (2·65 g) at 0°. After 24 h at 0° the mixture was poured into ice–water and extracted with ether. The extracts were washed with water, dried (Na_2SO_4), and evaporated. The residue was dissolved in light petroleum and treated with charcoal. The mixture was filtered and the filtrate was cooled to −70°. The *tosylate* (IV; R^1 = H, R^2 = SO_2·C_6H_4Me-*p*) (1·3 g) had m.p. 138—139° (from light petroleum), $[\alpha]_D^{28·5}$ +0·3° (*c* 0·66 in chloroform), $\nu_{max.}$ ($CHCl_3$) 3600, 1600, 1470, 1370, 1100, and 970 cm^{-1}, τ 8·98 (3H, s), 8·95 (3H, s), 7·55 (3H, s), 6·65br (1H, s), 6·01 (2H, s), 2·42 (4H, ABq, *J* 8 Hz), and 8·5 (1H, s, exchanged with D_2O) (Found: C, 63·0; H, 7·3. $C_{17}H_{24}O_4S$ requires C, 63·0; H, 7·4%).

1,3-*Dimethyl*-3α-p-*tolylsulphonylmethylnorbornan*-2α-*yl Acetate* (IV; R^1 = Ac, R^2 = SO_2·C_6H_4Me-*p*).—Vapour-phase dehydration of the 2α-hydroxy-tosylate (IV; R^1 = H, R^2 = SO_2·C_6H_4Me-*p*) (1465. mg) in pyridine (20 ml) was treated at 20° with acetyl chloride (0·2 ml). After 12 h the mixture was worked-up in the usual way to give an oil (80 mg) (purified by p.l.c.). The *acetate* (IV; R^1 = Ac, R^2 = SO_2·C_6H_4Me-*p*) has $[\alpha]_D^{24}$ +20·59 (*c* 0·53 in chloroform), $\nu_{max.}$ ($CHCl_3$) 1725 and 1602 cm^{-1}, τ 8·99 (3H, s), 8·94 (3H, s), 7·98 (3H, s), 7·55 (3H, s), 6·11 (2H, ABq, *J* 9 Hz), 5·43br (1H, s), and 2·43 (4H, ABq, *J* 8 Hz). Further purification lead to decomposition.

Reduction of the 2α-*Hydroxy-tosylate* (IV; R^1 = H, R^2 = SO_2·C_6H_4Me-*p*) *to* 1,3,3-*Trimethylnorbornan*-2α-*ol* (VI; R = H).—The 2α-Hydroxy-tosylate (IV; R^1 = H, R^2 = SO_2·C_6H_4Me-*p*) (200 mg) in ether (10 ml) was treated with lithium aluminium hydride (120 mg). The mixture was heated at reflux for 0·5 h then worked-up in the usual way. The alcohol (VI; R = H) (65 mg) was isolated as an impure oil, $\nu_{max.}$ (CCl_4) 3650 and 1220 cm^{-1}, $[\alpha]_D^{24}$ +14·5° (*c* 0·32 in methanol), τ 9·13 (3H, s), 9·04 (3H, s), 8·98 (3H, s), and 6·74 (1H, d, *J* 1·3 Hz).

The *p*-nitrobenzoate (VI; R = CO·C_6H_4·NO_2-*p*) was prepared in the usual way, (m.p. 107° (lit.,[5,27] 108—109°), $[\alpha]_D^{24}$ +17·9° (*c* 0·66 in CS_2), and was identical with an authentic sample prepared by the method of Abraham and Vilkas.[5]

* The methylene signals occurred at τ 7·9—9·0 and only diagnostic signals are mentioned (similarly for all subsequent n.m.r. data).

[26] J. Meinwald and P. G. Gassman, *J. Amer. Chem. Soc.*, 1960, **82**, 5445.

[27] J. Kenyon and H. E. M. Priston, *J. Chem. Soc.*, 1925, 1472.

9-*Methyl*-7-*oxatricyclo*[4,3,0,$0^{3,9}$]*nonane* [7] (III; R = H).—Pinan-2α-ol [22] (10 g) in pentane (250 ml; purified by stirring with conc. H_2SO_4 then 0·3N-$KMnO_4$ in 3N-H_2SO_4, followed by distillation from CaO) containing yellow mercury(II) oxide (22·0 g; previously dried at 100°) was treated with a solution of bromine (14·5 g) in pentane (50 ml), added dropwise over a period of 2 h. During the addition, the flask containing the pinanol was irradiated (tungsten lamp, 500 W) whilst the bromine–pentane solution was protected from light. During the addition and for 1 h afterwards the pentane mixture was kept at reflux under nitrogen. The mercury(II) oxide was filtered off, and the filtrate was washed with aqueous sodium hydrogen carbonate, dried (Na_2SO_4), and evaporated. The resulting oil was passed through a column of neutral alumina (50 g) eluting with pentane. Evaporation gave an oil (70%). N.m.r. showed that the ether (III; R = H) was sufficiently pure for the next stage.

Rearrangement of 9-*Methyl*-7-*oxatricyclo*[4,3,0,$0^{3,9}$]*nonane* (III; R = H).—The ether (III; R = H) (1·0 g) in acetic anhydride (20 ml) at 0° was treated with boron trifluoride–ether (6 ml). After 1 h at 0° the mixture was poured onto ice–water and extracted with ether. The extracts were washed with aqueous sodium hydrogen carbonate and water, and dried (K_2CO_3). Evaporation gave an oil (1·5 g), distillation of which at 88° and 0·2 mmHg did not separate the two components. Neither could the mixture be separated by t.l.c. or g.l.c. $\nu_{max.}$ (CCl_4) 1730 and 1250 cm^{-1}, τ 8·90 (3H, s), 7·9 (6H, s), 6·2 (2H, ABq, *J* 9 Hz), and 5·5 (1H, m) assignable to endo-3α-*acetoxymethyl*-3-*methylnorbornan*-2α-*yl acetate* (VIII; R = Ac), and τ 8·95 (3H, s), 8·04 (6H, s), 5·86 (2H, s), and 5·0 (1H, m), assignable to exo-7-*acetoxymethyl*-7-*methylnorbornan*-2β-*yl acetate* (IX; R = Ac) (Found: C, 64·9; H, 8·1. $C_{13}H_{20}O_4$ requires C, 65·0; H, 8·4%). Mass spectrometry of the two-component mixture gave a single molecular ion at *m/e* 220 corresponding to $C_{13}H_{20}O_4$.

endo-3α-*Benzoyloxymethyl*-3-*methylnorbornan*-2α-*yl Benzoate* (VIII; R = Bz) *and* exo-7-*Benzoyloxymethyl*-7-*methylnorbornan*-2β-*yl Benzoate* (IX; R = Bz).—The mixture of diacetates (VIII; R = Ac) and (IX; R = Ac) (613 mg) in ether (20 ml) was treated with lithium aluminium hydride (500 mg). The mixture was heated at reflux for 5 h and worked-up in the usual way to give the diols (VIII; R = H) and (IX; R = H), $\nu_{max.}$ 3600 and 3400 cm^{-1}. All attempts to separate these by p.l.c., g.l.c., and selective formation of isopropylidene acetal, borate esters, carbonate, oxalate, *p*-nitrobenzoates, and cholesteryl carbonate failed. Benzoylation (benzoyl chloride–pyridine) gave a mixture of the two benzoates (VIII; R = Bz) and (IX; R = Bz), which were separated by multiple elution p.l.c. The *benzoate* (VIII; R = Bz) had m.p. 98—100° (from light petroleum), $\nu_{max.}$ (CCl_4) 1720 cm^{-1}, τ 8·8 (3H, s), 5·85 (2H, ABq, *J* 9 Hz), 5·1 (1H, m), and 1·8—2·7 (10H, m) (Found: C, 75·8; H, 6·7. $C_{21}H_{24}O_4$ requires C, 75·8; H, 6·6%), the *benzoate* (IX; R = Bz) had m.p. 98—100° (from light petroleum), $\nu_{max.}$ (CCl_4) 1720 cm^{-1}, τ 8·8 (3H, s), 5·8 (2H, s), 5·1 (1H, m), and 1·8—2·7 (10H, m) (Found: C, 75·6; H, 6·6. $C_{21}H_{24}O_4$ requires C, 75·8; H, 6·6%).

7,7-*Dimethyl*-2-p-*tolylnorpinan*-2β-*ol* (X).—7,7-Dimethylnorpinan-2-one (II) (5·2 g) was added to a solution of *p*-tolylmagnesium bromide [prepared from *p*-bromotoluene (6·44 g) and magnesium (0·95 g) in ether (50 ml)]. The mixture was heated at reflux for 3·5 h and worked-up by adding a saturated aqueous solution of ammonium chloride. The ether layer was dried (Na_2SO_4) and evaporation gave the alcohol (X) (60%), m.p. 97—99° (from light petroleum–ethyl acetate), $\nu_{max.}$ ($CHCl_3$) 3650 and 3550 cm^{-1}, $[\alpha]_D^{26}$ −4·5° (*c* 0·07 in chloroform), τ 8·75 (3H, s), 8·70 (3H, s), 8·20 (1H, s exchanged by D_2O), 7·7 (3H, s), and 2·75 (4H, ABq, *J* 8 Hz) (Found: C, 83·6; H, 9·5. $C_{16}H_{22}O$ requires C, 83·4; H, 9·6%).

9-*Methyl*-6-p-*tolyl*-7-*oxatricyclo*[4,3,0,$0^{3,9}$]*nonane* (III; R = C_6H_4Me-*p*).—The norpinanol (X) (12 g) in carbon tetrachloride (200 ml) was treated at −20° with mercury(II) oxide (24 g). To this stirred mixture was added a solution of iodine (13·25 g) in carbon tetrachloride (50 ml), protected from light. The iodine solution was added during 1 h, whilst the mixture was being irradiated (tungsten lamp, 500 W). After a further 2 h at −20° the mixture was filtered. The solution was washed with aqueous sodium chloride solution, dried (Na_2SO_4), and the carbon tetrachloride layer was evaporated. Chromatography over alumina (G3) (light petroleum) gave the *ether* (III; R = C_6H_4Me-*p*) (80%), m.p. 84° (from light petroleum), $\nu_{max.}$ ($CHCl_3$) 1030 and 985 cm^{-1}, $[\alpha]_D^{29}$ +11·6° (*c* 0·6 in chloroform), τ 8·65 (3H, s), 7·6 (3H, s), 6·2 (2H, ABq, *J* 9 Hz), and 2·8 (4H, ABq, *J* 6 Hz) (Found: C, 83·9; H, 8·7. $C_{16}H_{20}O$ requires C, 84·2; H, 8·8%).

Further elution of the column with light petroleum–benzene (10 : 1) gave 3-(2-*iodoethyl*)-2,2-*dimethylcyclobutyl* p-*tolyl ketone* (XI) (20%), m.p. 78° (from light petroleum), $\nu_{max.}$ ($CHCl_3$) 1660 and 1610 cm^{-1}, $[\alpha]_D^{26}$ +41·2° (*c* 0·1 in chloroform), τ 9·3 (3H, s), 8·7 (3H, s), 7·6 (3H, s), 6·85 (2H, t, *J* 7 Hz), 6·3 (1H, t, *J* 7 Hz), 2·7 (2H, d, *J* 9 Hz), and 2·15 (2H, d, *J* 9 Hz) (Found: C, 54·1; H, 6·0. $C_{16}H_{21}IO$ requires C, 53·9; H, 5·9%).

3α-*Hydroxymethyl*-3-*methyl*-1-p-*tolylnorbornan*-2α-*yl Acetate* (XII; R^1 = Ac; R^2 = H).—The ether (III; R = C_6H_4Me-*p*) (271 mg) in acetic anhydride (1 ml) and ether (2 ml) was treated with boron trifluoride–ether (0·5 ml) at 0°. After 1 h work-up in the usual way gave the *hydroxyacetate* (XII; R^1 = Ac, R^2 = H) (314 mg), m.p. 108—109° (from light petroleum–ethyl acetate), $\nu_{max.}$ ($CHCl_3$) 3550 and 1720 cm^{-1}, $[\alpha]_D^{24}$ +46·8° (*c* 0·2 in chloroform), τ 8·75 (3H, s), 8·0 (3H, s), 7·7 (3H, s), 6·4 (2H, ABq, *J* 10 Hz), 5·25 (1H, s), and 2·85 (4H, s) (Found: 74·8; H, 8·2. $C_{18}H_{24}O_3$ requires C, 75·0; H, 8·4%).

Conducting the above experiment at −20° followed by acetylation (Ac_2O–pyridine) gave 3α-*acetoxymethyl*-3-*methyl*-1-p-*tolylnorbornan*-2α-*yl acetate* (XII; R^1 = R^2 = Ac) (95%), m.p. 110—112° (from light petroleum–ethyl acetate), $\nu_{max.}$ 1720 cm^{-1}, $[\alpha]_D^{26}$ +50·2° (*c* 0·4 in chloroform), τ 8·8 (3H, s), 8·04 (3H, s), 8·00 (3H, s), 7·6 (3H, s), 6·04 (2H, ABq, *J* 8 Hz), 5·28br (1H, s), and 2·98 (4H, s) (Found: C, 72·7; H, 7·8. $C_{20}H_{26}O_4$ requires C, 72·7; H, 7·9%).

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