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STEREOCHEMICAL STUDIES OF TRICYCLO[6.2.1.0.^{1,6}]UNDECANES—I

THE STEREOCHEMISTRY OF INTERMEDIATES INVOLVED IN THE SYNTHESIS OF TRICYCLOVETIVANE SESQUITERPENES

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Abstract—The stereospecificity of addition to the double bond of 2-substituted bicyclo[6.2.1.0^{1,6}]undec - 5 - enes has been studied and shown to be influenced mainly by the bicycloheptyl moiety in the case of epoxidation and hydroboration. These reactions proceed to give predominantly products of *endo* attack on the double bond. However for osmylation the important effect is the stereochemistry of the C_2-substituent due to steric interactions involved in the cyclic osmate ester intermediate. This results in attack by OsO_4 on the double bond *trans* to the C_2-substituent.

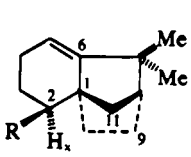
A key step in our synthesis of zizanoic acid (**8**) involved rearrangement of the monomesylate derived from the diol (**4** or **6**) produced by OsO_4 reaction with $\Delta^{5,6}$ - tricyclo-[6.2.1.0^{1,6}]undecene (**1**). Although the stereochemistry of the rearrangement product (**7**) could be assigned by direct comparison with authentic material obtained by degradation of methyl zizanoate (**9**), the stereochemistry of the diol (**4** or **6**) could only be tentatively assigned the β-diol structure (**6**) on the basis of preferential *exo*-attack on the bicyclo[2.2.1]heptyl system incorporated in **1**. A similar interpretation was made by Yoshikoshi[2]† and ourselves for the oxymylation product (**13**) derived from the epimeric ester (**10**), however in our hands this reaction was less stereospecific than for the β-COOMe epimer and led to a minor diol for which we ascribe the structure **15**. This stereochemical argument based on *exo*-attack, however, neglected the steric effect of the substituent at C_2. Comparison of the NMR spectra of the epimeric esters (**1** and **10**) indicated that the β-COOMe was axial (H, δ 2·69; AA' Xt, J = 4 Hz) and the α-COOMe equatorial (H, δ 2·50; AA'Xt, J = 12, 3 Hz). Conformational change to the half-boat form of **1** would place the C_2-β substituent in a pseudo-equatorial conformation but would at the same time, introduce eclipsing of the C_2-β substituent with the C_{11} methylene group. If the axial β-COOMe group in **1** hindered the approach of OsO_4 and, most importantly, the development of the cyclic osmate ester then the α-diol (**4**) would be expected. Rearrangement of the monomesylate (**5**) by a concerted process involving inversion of configuration at C_5 would lead to the 5β-H ketone (**7**) which was indeed the product having the important stereochemical features of the zizane or tricyclovetivane sesquiterpenes.

The earlier conclusion that rearrangement of **6** with inversion of configuration at C_5 would lead to **7** was in error. An analogy[3] for the rearrangement of **5** to **7** is to be found in the kinetically controlled conversion of **17** to **18**.

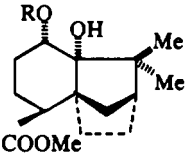
In order to settle the stereochemical problems outlined above it was decided to use X-ray methods to elucidate the structures of the diols formed by osmylation of the olefins **1** and **10**. Since this latter case was not stereospecific the major isomer was selected and converted into the monochloroacetate (**14**) in order to produce suitable crystals for X-ray analysis by direct methods. Crystallisation of the diol (**4**) afforded suitable crystals without the necessity of derivatisation. Full details of the analyses and molecular geometrics have been reported[4] elsewhere.

The X-ray data revealed that osmylation of **1** and **10** was directed by the stereochemistry of the COOMe group at C_2 i.e. *trans* to that substituent. From Dreiding models this can be rationalised by considering the steric interactions involved in the intermediate osmate esters in which the cyclohexane ring assumes a boat conformation in order to accommodate the *cis* fused 5-membered osmate ester. In the case of the β-COOMe substituent the cyclic osmate corresponding to the β-diol (**6**) would involve interactions between the OsO_4 moiety and the

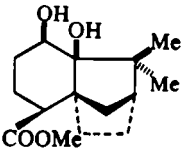
†We thank Professor Yoshikoshi for comparison of samples of the diol (**13**) and the keto ester (**16**) produced by rearrangement of the monomesylate. Production of the corresponding 5β-H epimer reported previously was probably derived from the minor diol (**15**).



1; R = COOMe
2; R = CH_2OH
3; R = Me



4; R = H
5; R = $MeSO_2$—



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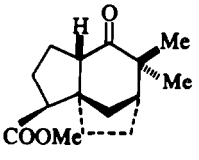

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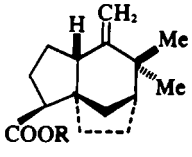
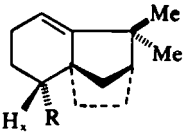
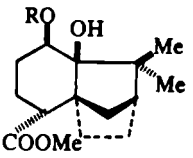


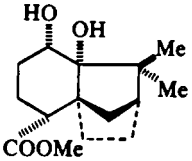
8; R = H
9; R = Me



10; R = COOMe
11; R = CH_2OH
12; R = Me



13; R = H
14; R = $ClCH_2CO$—



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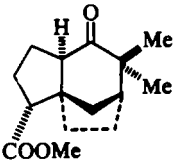

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β-COOMe group whereas these interactions are absent in the corresponding intermediate from which the α-diol (**4**) was derived. The same considerations applied to the intermediates produced by osmylation of **10** would favour the β-diol (**13**) found by X-ray analysis.

Osmylation of the olefin (**12**) gave similar results to that found in the case of the corresponding ester (**10**) in that two diols (**19** and **20**) were formed. It has been reported[5] that when OH and Me groups have a 1-3 diaxial relationship the Me is deshielded by 0·10–0·15 ppm. Thus the minor diol could be assigned the structure **20** in which the secondary C_2-Me and the tertiary OH are 1-3 diaxial and exhibits the expected 0·15 ppm deshielding of the secondary Me relative to the major diol (**19**). The change from COOMe to Me for the C_2 substituent in **10** and **11** does not affect the stereochemistry of osmylation.

In order to probe more deeply into the factors influencing the stereochemistry of addition reactions in the tricyclo[6.2.1.$0^{1,6}$]undec - 5 - ene system, it was decided to investigate reactions involving 3 or 4-membered intermediates i.e. expoxidation and hydroboration. Further, in order to ascertain whether the effect of the C_2 substituent was general or specific to the COOMe group a parallel series of reactions were carried out on the corresponding olefins (**3** and **12**) having a C_2-Me substituent. These were synthesised from the enone esters (**21** and **22**) by reduction (LAH/$AlCl_3$) to the alcohols (**2** and **11**) which were converted into the corresponding mesylates and further reduced (LAH).

Treatment of the β-Me olefin (**3**) with *m*-chloroperbenzoic acid in Et_2O afforded a single epoxide (**23/24**). Acid catalysed rearrangement (BF_3, Et_2O) produced a ketone (20%) and an alcohol (60%). The ketone (**25**) [νmax (CCl_4) 1712 cm^{-1}] was the product of kinetic control since it could be transformed into the C_6 epimer (**26**) [νmax (CCl_4) 1700 cm^{-1}] on acid treatment. Consideration of the CD spectra of the ketones (**25** and **26**) in the light of the octant rule[6] for cyclic ketones indicated the stereochemistry shown. Provided that the cyclohexanone moiety in **25** and **26** adopts a chair conformation we can consider the octant diagrams (**25** and **26**) for these respectively (Fig 1). The octant rule would predict that the ketone having the β-ring function (**25**) should exhibit a negative Cotton effect, whereas the ketone having the α-ring junction (**26**) would show a positive Cotton effect. Thus the epoxide produced from the β-Me olefin has the structure **24** resulting from epoxidation at the α-face trans to the β-Me substitute at C_2.

The alcohol, which was the major rearrangement product of the epoxide (**24**) had spectral data suggestive of the alcohol (**27**) which was confirmed by controlled oxidative degradation to methyl ketopinate (**30**) via the ketone (**28**) which was converted into the furfurylidene derivative then ozonised to give an olefinic diacid resistant to O_3 even under moderately forcing conditions. The diester (**29**) was oxidised (K MnO_4/Na IO_4) to methyl ketopinate (**30**) which was identical with authentic material. This series of reactions is consistant with structure **27** in which the stereochemistry of the -OH substituent may be assigned from its derivation from the α-epoxide (**24**).

The production of **25** and **27** can be explained by

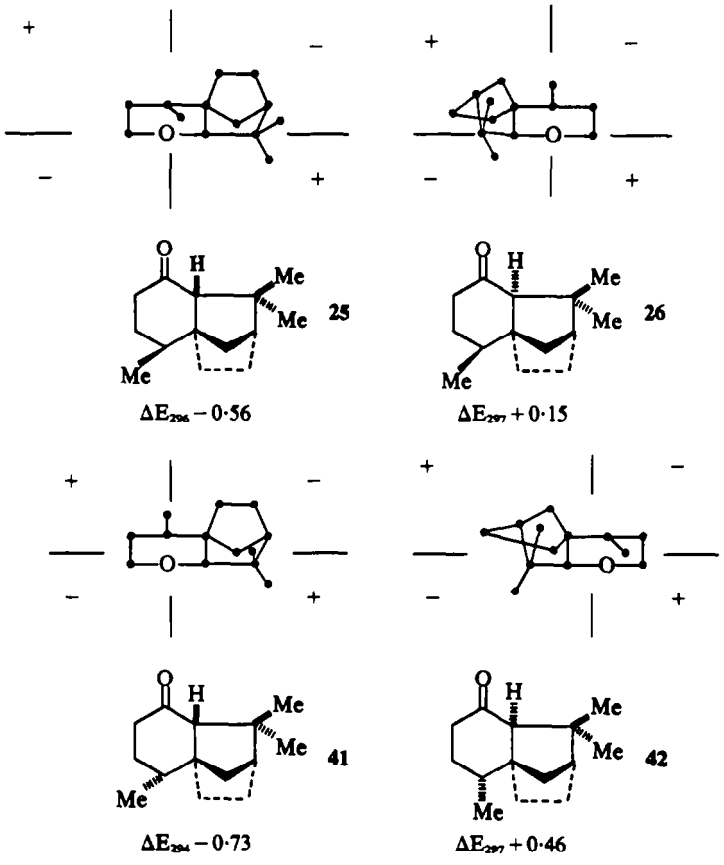


Fig 1

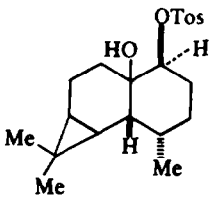
$BF_3 \cdot Et_2O$ fission of the oxirane ring in **24** to a carbonium ion which may subsequently be neutralised by a 1–2 hydride shift provided this is stereochemically favourable i.e. the C–H bond broken should be coplanar with the vacant p-orbital of the incipient carbonium ion (**38**).[7,8] Alternatively bond migration may occur followed by deprotonation to give the rearranged skeleton **27**. The *cis* relationship of the migrating alkyl substituent and the C–O bond cleaved in this rearrangement clearly indicates that this transformation is not concerted and involves an intermediate with high degree of carbonium ion character. This finding has important consequences in the reaction of isolongifolene epoxide which will be discussed in the following paper.

Examination of Dreiding models of an extreme form of such an intermediate (**38**) in which the epoxide has opened to the C_6 carbonium ion in the half-chair conformation shows that the C–H bond involved in formation of **25** does not have maximal overlap with the vacant p-orbital of the carbonium ion. Better overlap is observed between the carbonium ion and the 1–10 bond involved in the rearrangement to **27**.

Reduction (LAH) of the α-epoxide (**24**) afforded the tertiary alcohol (**32**) which was identical with the alcohol derived from epoxidation of **1** followed reduction (LAH), to **31a**, mesylation and further reduction (LAH). Thus epoxidation of the β-Me and β-COOMe C_2-substituted series have the same high stereospecificity as osmylation.

Hydroboration of the olefin (**3**) gave a secondary alcohol (**36**) which could be oxidised, under non-epimerising conditions, to the thermodynamically more stable ketone (**26**) identical to that produced by equilibration of the acid-catalysed rearrangement product of the α-epoxide (**24**). Again stereospecific α-attack of the C_2 β-substituted series was found to occur during hydroboration as in the case of osmylation and epoxidation.

Epoxidation of the C_2 α-Me olefin (**12**), in contrast to the β-series gave an inseparable mixture of epoxides (**39** and **40**) in which one predominated (80%). Acid-catalysed rearrangement of the epoxide mixture afforded the rearranged alcohol (**27**) together with a separable mixture of ketones **41** [νmax (CCl_4) 1712 cm^{-1}] and **42** [νmax (CCl_4) 1695 cm^{-1}]. The configuration of the OH group in **27** produced in this reaction showed that the α-epoxide (**40**) was the progenitor. For comparison the epimeric alcohol (**28**) was prepared by oxidation-reduction and was clearly distinguishable from **27**. The stereochemistry of the ketones (**41** and **42**) was assigned on the basis of the octant rule from consideration of the octant diagrams (Fig 1). Equilibration of these ketones led to a 1 : 1 mixture due to the gre-



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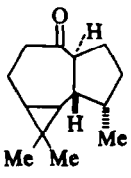

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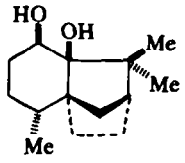

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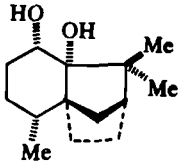

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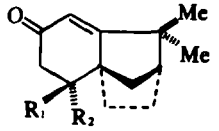
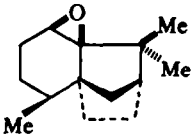


21; R_1 = COOMe R_2 = H
22; R_1 = H R_2 = COOMe



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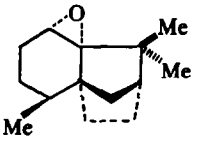

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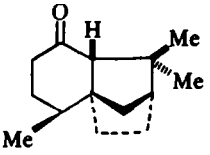

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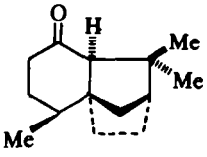

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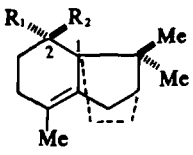
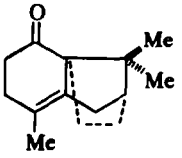


27; R_1 = OH R_2 = H
28; R_1 = H R_2 = OH



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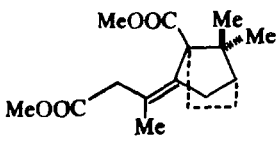
ater stability of the 5α-H ring junction in **42** being offset by forcing the C_2 α-Me into an axial conformation. Conformational change to the boat form to release the C_2 α-Me from the axial conformation would be destabilised by eclipsing of the C_7-Me substituent with the C_{10}-methylene group. In the case of the efficient transformation of **25** into **26** both factors favour **26** having an equatorial C_7-Me and the 5α-H ring junction. The isolation of the major acid-catalysed rearrangement products **27** and **41** (not equilibrated under the reaction conditions) would indicate that



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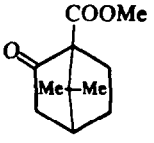

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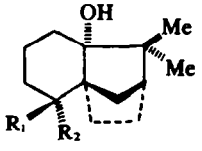
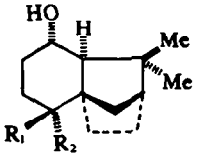
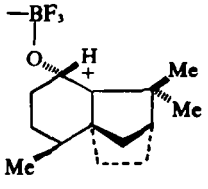


32; R_1 = Me R_2 = H
33; R_1 = CH_2OH R_2 = H
34; R_1 = H R_2 = Me
35; R_1 = H R_2 = CH_2OH



36: R_1 = Me R_2 = H
37: R_1 = H R_2 = Me



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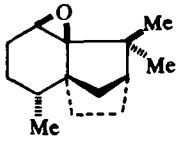

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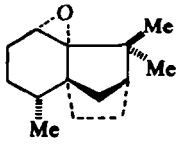

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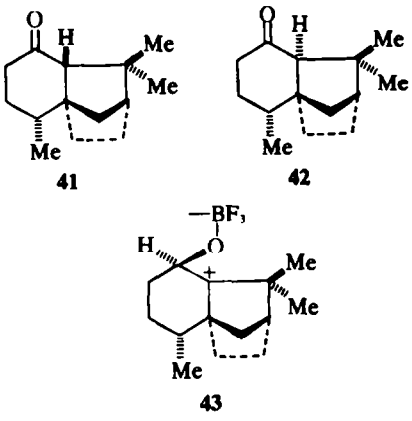

41 42 43

the α-epoxide (**40**) predominates in epoxidation of the $C_2\alpha$-Me olefin (**12**). Rearrangement of **40** to **27** and **41** can be explained exactly as in the case of the $C_2\beta$-Me epoxide (**24**). However, rearrangement of the minor epoxide (**39**) must only have produced the ketone (**42**) since none of the predicted rearrangement product could be identified in the products. Consideration of the Dreiding model of the carbonium ion intermediate (**43**) derived from **39** reveals that the C–H bond involved in production of the ketone (**42**) has good overlap with the developing carbonium ion centre. In this situation the 1–2 hydride shift is strongly preferred to the rearrangement process leading to **28**.

Reduction (LAH) of the epoxide (**40**) gave a tertiary alcohol (**34**) in which the C_2-Me and the OH group are 1–3 diaxial with the consequence that the secondary Me resonance was deshielded by 0·15 ppm relative to the epimer (**32**). Epoxidation of the C_2 α-COOMe (**10**) followed by reduction (LAH) to **35**, mesylation and further reduction (LAH) afforded the same tertiary alcohol (**34**). Thus peracid attacks **10** mainly from the α-face in contrast to the results discussed earlier for OsO_4 reaction which led predominantly to **13** resulting from *exo*-attack.

Hydroboration of the C_2 α-Me olefin (**12**) was found to be less stereospecific than the β series following the general pattern. The major product was oxidised (CrO_3/Et_2O) to give **42** [νmax (CCl_4) 1695 cm^{-1}] under conditions which did not equilibrate the product. From the configuration of the ring junction it could be discerned that B_2H_6 preferentially attacks the olefin from the α-face to give **37**.

The stereochemical results of osmylation, epoxidation and hydroboration of the $\Delta^{5,6}$ tricyclo[6.2.1.0^{1,6}]-undecenes (**1**, **3**, **10** and **12**) are shown in Fig 2. It can be seen that the steric effect of the C_2-β substituent supports the tendency for this ring system to react with B_2H_6 and peracid by *endo* attack whereas in the C_2-α series both effects are in opposition. In the case of osmylation the steric situation in the cyclic osmate ester must be considered and in the C_2-α series the interactions involved in this intermediate disfavour *endo* attack and lead to the *exo* product.

	Peracid/B_2H_6	OsO_4
β – C_2 substituent (1), (3)	endo (stereospecific)	endo
α – C_2 substituent (10), (12)	endo (major products)	exo

Fig 2

EXPERIMENTAL

All m.ps are uncorrected, UV spectra wrere measured in EtOH using a Unicam SP 800 spectrometer. IR spectra were determined in soln ($CHCl_3$ or CCl_4 as stated) using Unicam SP 200 or Perkin–Elmer 125 machines. NMR spectra were measured using Varian HA 100 spectrometer and TMS as internal standard. Mass spectra were obtained from A.E.I MS 12 And MS 902 instruments (the latter with on-line computer). Analytical GLC was carried out using a Perkin–Elmer F 11 chromatograph. Optical rotation measurements are for $CHCl_3$ solns using a Bendix–Ericsson ETL-NPL automatic polarimeter type 143A. CD measurements were carried out by Dr P. Scopes at Westfield College.

The silica for chromatography was Merck Kieselgel 70–325 mesh. Light petroleum refers to the fraction b.p. 40–60°.

2α - Carbomethoxy - 5β - chloroacetoxy - 6β - hydroxy - 7,7 - dimethyltricyclo[6.2.1.0^{1,6}]*undecane* (**14**). To a stirred soln containing **13** (104 mg, 0·39 mmole) and chloroacetyl chloride (55 mg, 0·49 mmole) in dry benzene (2 ml) was added dropwise a soln of pyridine (35 mg, 0·44 mmole) in dry benzene (1 ml). The mixture was stirred at room temp for 22 h, diluted with ether and washed with H_2O and brine. The ethereal soln was dried ($MgSO_4$) and the solvent removed *in vacuo* to give the crude product which was chromatographed over silica (10 g). Elution with 20% EtOAc in benzene afforded the pure **14** (123 mg, 91%) crystallised from hexane–MeOAc, m.p. 159–160°, νmax ($CHCl_3$) 3610, 1720 cm^{-1}, NMR ($CDCl_3$) δ 0·92 (3H,S), 1·04 (3H,S) 3·10 (H,m), 3·62 (3H,S), 4·00 (2H,S), 5·36 (H,m). (Found; C, 59·28 H, 7·53; Cl, 10·16. $C_{17}H_{25}O_5$ Cl requires: C, 59·21; H, 7·31; Cl, 10·29%).

2α - Carbomethoxy - 5α - 6 - oxo - 7,7 - dimethyltricyclo-[6.2.1.0^{1,6}]*undecane* (**16**). Dry Et_3N (4 ml) was added dropwise, with stirring, to an ice-cold soln containing recrystallised **15** m.p. 111–112° (184 mg, 0·69 mmole) and $MeSO_2$ Cl (63 mg, 0·55 mmole) in dry pyridine (8 ml). The deep red soln was stirred at room temp for 42 h and the solvent removed *in vacuo* at <35°. The residue was azeotroped 3X with benzene–heptane (1:1) followed by Et_2O/H_2O extraction. The aqueous layer was extracted with Et_2O and the combined Et_2O layer dried ($MgSO_4$) and concentrated *in vacuo*. Chromatography over silica (20 g) and elution with 20% EtOAc in benzene provided the pure mesylate (196 mg) which was dissolved in pyridine (9 ml) and Et_3N (4·5 ml) and refluxed 4 h. The solvent was removed *in vacuo* and partitioned Et_2O/H_2O. After the usual work up and chromatography over silica (12 g) the rearrangement product **16** (109 mg, 78%) was obtained on elution with 10% EtOAc in benzene followed by crystallisation from hexane, m.p. 94·5–95·5° $[\alpha]_D^{26}$ −78° (2·3% $CHCl_3$). This product was found to be identical with the sample of **16** provided by Prof. A. Yoshikoshi.

2α - Hydroxymethyl - 7,7 - dimethyltricyclo[6.2.1.0^{1,6}] - *undec - 5 - ene* (**11**). A soln of LAH–$AlCl_3$ was prepared by careful addition of a soln of LAH (600 mg, 15·8 mmole) in anhyd Et_2O (30 ml) to a soln of $AlCl_3$ (6·2 g, 46·6 mmole) in Et_2O (30 ml). The enone **22** (1·68 g, 0·68 mmole) in Et_2O (20 ml) was added to this soln. The

mixture was stirred at reflux 1·5 h then cooled to room temp. Water was carefully added to decompose excess hydride followed by 2N H_2SO_4. The aqueous layer was extracted with Et_2O and the combined Et_2O soln washed with brine, $NaHCO_3$ aq, brine then dried ($MgSO_4$). Removal of the solvent afforded the crude alcohol which was chromatographed over silica (50 g). Elution with 30% Et_2O in light petroleum yielded **12** (0·91 g, 65%) as a viscous oil, b.p. 120°/0·5 mm; νmax ($CHCl_3$) 3600, 3450 cm^{-1}; NMR (CCl_4) δ 0·99 (3H,S), 1·03 (3H,S), 3·41 (H,q; J = 8, 10 Hz), 3·66 (H,q; J = 6, 10 Hz), 5·14 (H,t; J = 3 Hz). (Found C, 81·51, H, 11·03. $C_{14}H_{22}O$ requires: C, 81·50; H, 10·75%).

2β - *Hydroxymethyl* - 7,7 - *dimethyltricyclo*[6.2.1.0]^{1,6} - *undec* - 5 - *ene* (**2**). General directions as for **12**. The reagent was prepared by the addition of LAH (1·0 g, 26·3 mmole) in Et_2O (35 ml) to $AlCl_3$ (10·5 g, 79 mmole) in Et_2O (45 ml). The enone **21** (4·0 g, 16 mmole) was added in Et_2O (25 ml) and the mixture stirred under reflux for 1·5 h. Isolation as above afforded **2** which crystallised from hexane, m.p. 74–75°; νmax ($CHCl_3$) 3600, 3420 cm^{-1}; NMR (CCl_4) δ 0·98 (3H,S), 1·04 (3H,S), 3·37 (H,q; J = 8, 11 Hz), 3·55 (H,q; J = 6, 11 Hz), 5·13 (H,t, J = 4 Hz). (Found C, 81·62; H, 10·94. $C_{14}H_{22}O$ requires: 81·50; H 10·75%).

2α - *Methyl* - 7,7 - *dimethyltricyclo*[6.2.1.0^{1,6}] - *undec* - 5 - *ene* (**12**). To an ice-cold stirred soln of **11** (600 mg, 2·91 mmole) in CH_2Cl_2 (20 ml) containing Et_3N, (700 mg; 6·12 mmole) was added $MeSO_2Cl$ (700 mg, 6·12 mmole) in CH_2Cl_2 (3 ml). The mixture was stirred at 0° for 0·5 h then diluted with Et_2O and washed with H_2O, 1N HCl, $NaHCO_3$ aq and brine. After drying ($MgSO_4$) and removal of the solvent the crude mesylate (950 mg) was obtained as a colourless oil which was used directly for reduction, νmax ($CHCl_3$) 1180, 990, 970 cm^{-1}; NMR (CCl_4) δ 1·01 (3H,S), 1·04 (3H,S), 2·89 (3H,S), 4·03 (H,q; J = 8, 10 Hz), 4·23 (H,q; J = 6, 10 Hz), 5·20 (H,t; J = 3 Hz). Accurate mass *m/e* 284·1413 (30% M^+), $C_{15}H_{24}O_3S$ (+1 ppm); 188·1585 (18), $C_{14}H_{20}$ (+11); 173·1323 (31), $C_{13}H_{17}$ (−4); 145·1022 (100), $C_{11}H_{13}$ (+13).

The above mesylate (900 mg) in Et_2O (25 ml) was added to a stirred refluxing soln of LAH (1·0 g, 26 mmole) in Et_2O (30 ml). After 6 h reflux and 16 h at room temp the excess hydride was decomposed using sat. Rochelle salt soln. The ppt was removed by filtration through celite and the soln dried ($MgSO_4$). Removal of the solvent afforded **12** (1·7 g, 95%), b.p. 86°/12 mm; $[\alpha]_D^{27}$ +170° (1·2% $CHCl_3$); νmax ($CHCl_3$) 1678 cm^{-1} (weak); NMR (CCl_4) δ 0·96 (3H, d; J = 7 Hz), 1·01 (3H, S), 1·05 (3H,S) 5·15 (H,t; J = 3 Hz); GLC (15', 5% OV 17, 150°, 15 psi) Rt 22 min. (Found: C, 88·28; H, 11·48. $C_{14}H_{22}$ requires: C, 88·36; H, 11·64%).

2β - *Methyl* - 7,7 - *dimethyltricyclo*[6.2.1.0^{1,6}] - *undec* - 5 - *ene* (**3**). To an ice-cold stirred soln of **2** (1·0 g, 4·85 mmole) in CH_2Cl_2 (30 ml) containing Et_3N (3 ml) was added $MeSO_2Cl$ (1·1 g, 9·7 mmole) in CH_2Cl_2 (3 ml). The soln was stirred at 0° for 0·5 h. Work up as for **11** afforded the crude mesylate (1·52 g) which crystallised on standing, νmax ($CHCl_3$)1360, 970, 855 cm^{-1}; NMR (CCl_4) δ 0·99 (3H,S), 1·03 (3H,S), 2·86 (3H,S), 3·88 (H,q; J = 8, 10 Hz), 4·11 (H,q; J = 7, 10 Hz), 5·13 (H,t; J = 4 Hz). Accurate mass 284·1435 (4%, M^+), $C_{15}H_{24}O_3S$ (−4 ppm); 188·1554 (20), $C_{14}H_{20}$ (−6); 173·1331 (38), $C_{13}H_{17}(O)$; 145·1011 (100), $C_{11}H_{13}$(−4).

A soln of the crude mesylate (1·4 g) in Et_2O was added dropwise with stirring to a refluxing soln of LAH (1·2 g, 31·5 mmole) in Et_2O (40 ml). The mixture was refluxed for 5 h and worked up as previously described for **11** to give **3** (850 mg, 92%), b.p. 100°/0·1 mm; $[\alpha]_D^{23}$ +150° (1·25% $CHCl_3$); νmax ($CHCl_3$) 1680 cm^{-1} (weak); NMR (CCl_4) δ 0·86 (3H,d; J = 7 Hz), 0·96 (3H,S), 1·02 (3H,S), 5·12 (H,t, J = 4 Hz); GLC (15', 15% OV 17, 150°, 15 psi) Rt 22 min. (Found: C, 88·06; H, 11·45. $C_{14}H_{22}$ requires: C, 88·35; H, 11·65%).

2α - *Methyl* - 5α - *hydroxy* - 6αH - 7,7 - *dimethyltricyclo*-[6.2.1.0^{1,6}] - *undecane* (**37**). A soln of $BF_3{\cdot}Et_2O$ (0·45 ml, 4·1 mmole) in anhyd THF (4 ml) was added during 1 h to a stirred soln of **12** (100 mg, 0·53 mmole) and $NaBH_4$ (100 mg, 2·6 mmole) in anhyd THF (3 ml) under N_2. After 2 h, excess hydride was decomposed with H_2O. 3N NaOH (0·8 ml) was added followed by 30% H_2O_2 (0·8 ml, 8 mmole) and the mixture was saturated with NaCl and extracted with Et_2O. The Et_2O was washed with brine and dried ($MgSO_4$). Removal of the solvent followed by chromatography of the residue over silica (5 g). Elution with 20% Et_2O in light petroleum gave a mixture of alcohols. The major epimer (**37**) m.p. 105·5–106·5° was obtained by recrystallisation from hexane, $[\alpha]_D^{21}$ +12·7° (1·27% $CHCl_3$); νmax ($CHCl_3$) 3610, 3480 cm^{-1}; NMR (CCl_4) δ 0·95 (3H, d; J = 6 Hz), 1·04 (3H,S), 1·11 (3H,S) 3·42 (H,m) 0·92 (H,S exchanges with D_2O); GLC (10', 10% carbowax, 190° 20 psi) Rt 15·75 (major) 13·75 (minor) min. (Found: C, 80·42; H, 11·58. $C_{14}H_{24}O$ requires: C, 80·71; H, 11·61%).

2β - *Methyl* - 5α - *hydroxy* - 6αH - 7,7 - *dimethyltricyclo*-[6.2.1.0^{1,6}] - *undecane* (**36**). A soln of 1 MB_2H_6 in THF (10 ml, 10 mmole) was added to a soln of **3** (1·08 g, 5·7 mmole) in anhyd THF (10 ml) and the reactants stirred at room temp for 18 h. Excess hydride was cautiously decomposed with H_2O and 3N NaOH (10 ml) added followed by 30% H_2O_2 (5 ml, 50 mmole). After work up as for **37** the crude product was chromatographed over silica (40 g). Elution with 20% Et_2O in pentane afforded **36** (1·05; 90%) crystallised from pentane, m.p. 81–82° $[\alpha]_D^{22}$ +78° (1·04%, $CHCl_3$); νmax (CCl_4) 3580, 3470 cm^{-1}; NMR (CCl_4) δ 0·80 (3H,d; J = 7 Hz); 1·00 (3H,S); 1·03 (3H,S) 3·30 (H,m); GLC (9', 7% carbowax 150°, 20 psi) Rt 18·5 min. (Found: C, 80·83; H, 11·55. $C_{14}H_{24}O$ requires: C, 80·71; H, 11·61%).

2α - *Methyl* - 5 - *oxo* - 6αH - 7,7 - *dimethyltricyclo*[6.2.1.0^{1,6}]-*undecane* (**42**). 1 M aqueous chromic acid (0·15 ml, 50% excess) was added to a soln of **37** (30 mg, 0·144 mmole) in Et_2O (1 ml). The mixture was stirred at room temp, diluted with Et_2O and washed with $NaHCO_3$ and brine then dried ($MgSO_4$). Removal of the solvent followed by silica chromatography (eluate 20% Et_2O in pentane) gave **42**. b.p. 120°/0·1 mm; m.p. 30° $[\alpha]_D^{26}$ +143° (0·93% $CHCl_3$); νmax (CCl_4) 1695 cm^{-1}; NMR (CCl_4) δ 0·93 (3H,S), 0·98 (3H,d; J = 7 Hz), 1·15 (3H,S) 2·16 (2H, m); GLC (20', 20% DEGS +2% bentonite 200° 30 psi) Rt 17·5 min; CD (0·113% MeOH) ΔE_{333} 0, ΔE_{297} +0·46, ΔE_{242} +0·65 (Found: C, 81·79; H, 10·90. $C_{14}H_{22}O$ requires: C, 81·50; H, 10·75%).

2β - *Methyl* - 5 - *oxo* - 6αH - 7,7 - *dimethyltricyclo*[6.2.1.0^{1,6}]-*undecane* (**26**). To a soln of **36** (943 mg, 4·54 mmole) in ether (12 ml) was added 1 M aqueous chromic acid (3·34 Ml, 10% excess). The heterogeneous mixture was gently stirred at room temp for 2·25 h then diluted with H_2O. The ether layer was washed with $NaHCO_3$ aq, brine and dried ($MgSO_4$). Removal of the solvent and silica chromatography (eluate 10% Et_2O in pentane) afforded **26**, b.p. 124°/0·15 mm; m.p. 30° $[\alpha]_D^{26}$ +142° (1·01% $CHCl_3$); νmax (CCl_4) 1700 cm^{-1}; NMR (CCl_4) δ 0·96 (3H,S), 0·98 (3H,d, J = 6 Hz), 1·17 (3H,S); CD (0·114% MeOH) ΔE_{333} −0·03, ΔE_{303} +0·16, ΔE_{297} +0·15, ΔE_{240} 0, ΔE_{211} +0·55 (Found: C, 81·74; H, 10·76. $C_{14}H_{22}$ requires: C, 81·50; H, 10·75%).

2α - *Methyl* - 5,6α/β *epoxy* - 7,7 - *dimethyltricyclo*[6.2.1.0^{1,6}]-*undecane* (**39**) *and* (**40**). A soln of **12** (250 mg, 1·32 mmole) in Et_2O (8 ml) was cooled to 0° and a soln of *m*-chloroperbenzoic acid (295 mg, 1·72 mmole) in Et_2O (8 ml) added. After 15 h at room temp in the absence of light the excess peracid was decomposed by 10% $NaHSO_3$ aq. The Et_2O layer was washed with $NaHCO_3$ aq, brine, and dried ($MgSO_4$). Removal of the solvent gave the crude epoxide mixture (**39** and **40**) as a colourless oil, νmax (CCl_4) 925, 945, 970 cm^{-1}; NMR (CCl_4) δ 0·75 (3H,S) 3·10 (H, broad s); minor isomer ( H) 2·08 (H,m). Ratio of epoxides from NMR 4:1; Mass Spec *m/e* 206 (M^-).

2β - *Methyl* - 5,6α - *epoxy* - 7,7 - *dimethyltricyclo* - [6.2.1.0^{1,6}] - *undecane* (**24**). In the way described for epoxidation of **12**, **24** was prepared from **3** (250 mg, 1·32 mmole) in Et_2O (5 ml) and *m*-chloroperbenzoic acid (290 mg, 1·69 mmole) in Et_2O (5 ml) as a colourless oil (277 mg), b.p. 95°, 0·4 mm; $[\alpha]_D^{23}$ +11° (0·64%, $CHCl_3$); νmax (CCl_4) 1000, 965, 930 cm^{-1}; NMR (CCl_4) δ 0·79 (3H,

d J = 7 Hz), 0·72 (3H,S), 0·86 (3H,S) 2·95 (H,d J = 5 Hz). Mass spec. *m/—e* 206·1667 (85%, M^+), $C_{14}H_{22}O$ (−2 ppm); 191·1443 (63) $C_{13}H_{19}O$ (4); 162·1122 (100), $C_{11}H_{13}O$ (−1). (Found; C, 81·58 H, 10·89. $C_{14}H_{22}O$ requires: C, 81·50; H, 10·75%).

Rearrangement of epoxide (**24**); *2β - Methyl - 5 - oxo - 6β - 7,7 - dimethyltricyclo*[6.2.1.0^{1,6}] *- undecane* (**25**) *and 2α - hydroxy - 5 - methyl - 11,11 - dimethyltricyclo*[6.2.1.0^{1,6}] *- undec - 5 - ene* (**27**). $BF_3{\cdot}Et_2O$ (0·2 ml, 1·6 mmole) was added to a soln of **24** (215 mg, 1·04 mmole) in anhyd Et_2O (4 ml). The reactants were mixed and allowed to stand at room temp for 23 h and the soln was then diluted with Et_2O, washed with $NaHCO_3$ aq, brine and dried ($MgSO_4$). The solvent was removed and the crude product chromatographed over silica (10 g). Elution with 10% Et_2O in pentane gave **25** (42 mg, 19%), b.p. 70°/0·1 mm; m.p. 26–31°; $[\alpha]_D^{24}$ −9·3° (0·75% $CHCl_3$); νmax 1712 cm^{-1}; NMR (CCl_4) δ 0·98 (3H,S), 1·16 (3H,d J = 7 Hz), 1·20 (3H,S); CD (0·038% MeOH) ΔE_{330} 0, ΔE_{296} −0·56, ΔE_{254} 0. (Found: C, 81·79; H, 10·65. $C_{14}H_{22}O$ requires: C, 81·50, H, 10·75%). Elution with 20% Et_2O in pentane gave **27** (130 mg, 6%), m.p. 76–77 (hexane); $[\alpha]_D^{23}$ −157° (1·96% $CHCl_3$); νmax (CCl_4) 3480, 3600 cm^{-1} 0·77 (3H,S), 1·05 (3H,S) 1·49 (3H,S), 1·20 (H,S—exchanges with D_2O), 3·60 (H,q; J = 4 11 Hz); GLC 10′, 10% carbowax, 150°, 30 psi Rt 26 min; Mass spec. *m/e* 206·1660 (29% M^+), $C_{14}H_{22}O$ (−5 ppm); 188·1560 (23), $C_{14}H_{20}$ (−2); 145·1024 (100), $C_{11}H_{13}$(5). (Found: C, 81·56; H, 10·74. $C_{14}H_{22}O$ requires: C, 81·50; H, 10·75%).

Equilibration of ketone (**25**) *to 6α-isomer* (**26**). The ketone **25** (10 mg) νmax 1712 cm^{-1} was dissolved in CCl_4 (1 ml) and 70% $HClO_4$ aq (2 drops) added. After 2 h stirring at room temp the soln was diluted with pentane and washed with $NaHCO_3$ aq, brine and dried ($MgSO_4$). Removal of the solvent gave a colourless oil (8 mg) which was identical by IR to **26**, νmax (CCl_4) 1700 cm^{-1}; GLC 10′ 10% carbowax, 180° 25 psi Rt 12 min (26, 86%), 10·75 min (25, 14%).

2 - Oxo - 5 - methyl - 11,11 - dimethyltricyclo[6.2.1.0^{1,6}]*undec - ene* (**29**). 1 M Chromic acid (0·95 ml, 0·95 mmole) was added to a soln of **27** (236 mg, 1·14 mmole) in Et_2O (6 ml). After 2·25 h stirring the mixture was diluted with Et_2O and washed with H_2O, $NaHCO_3$ aq, brine and dried ($MgSO_4$). The solvent was removed and chromatography over silica (20 g) (eluate 10% Et_2O in light petroleum) afforded **29** (230 mg, 98%) as a colourless oil, b.p. 60°/0·01 mm; $[\alpha]_D^{24}$ +72° (0·89% $CHCl_3$); νmax ($CHCl_3$) 1690 cm^{-1}; NMR (CCl_4) δ 0·86 (3H,S), 1·12 (3H,S), 1·63 (3H,S), Mass spec. *m/e* 204·1515 (88%, M^+), $C_{14}H_{20}O$ (0 ppm); 189·1275 (12), $C_{13}H_{17}O$ (−2); 161·0962 (72) $C_{11}H_{13}O$ (−3); 125·0956 (100), $C_8H_{13}O$ (−8). GLC 10′, 10% carbowax 180°, 20 psi, Rt 12 min. (Found: C, 82·39; H, 9·93 $C_{14}H_{20}O$ requires: C, 82·30; 9·87%).

Methyl ketopinate (**31**). Furfuraldehyde (94 mg, 0·98 mmole) in MeOH was added to a soln of **29** (100 mg, 0·49 mmole) in MeOH (10 ml). 40% KOH aq (0·5 ml) was then added and the mixture allowed to stand in the dark for 20 h under N_2. Brine was added and the mixture was extracted with Et_2O which was washed with brine then dried ($MgSO_4$). Removal of the solvent and crystallisation of the residue from hexane–ether gave the pure furfurylidene ketone (96 mg, 70%) as pale yellow rods, m.p. 166–166·5°; $[\alpha]_D^{24}$ −34° (0·77%, $CHCl_3$); νmax ($CHCl_3$) 1670 cm^{-1}; λmax (EtOH) 327 nm (18·050), NMR (CCl_4) δ 0·84 (3H,S), 1·25 (3H,S), 1·71 (3H,S), 3·36 (2H, broad m), 6·45 (H,m), 6·57 (H,m), 7·25 (H,m), 7·52 (H,m); Mass spec. *m/e* 282·1628 (71%, M^+), $C_{19}H_{22}O_2$ (3 ppm); 267·1270 (92), $C_{18}H_{19}O_2$ (−6); 239·1068 (100), $C_{16}H_{15}O_2$ (−2). (Found: C, 80·60; H, 8·10. $C_{19}H_{22}O_2$ requires: C, 80·81; H, 7·85%).

The furfurylidene ketone (60 mg, 0·213 mmole) in CH_2Cl_2 (20 ml) was cooled to −70° and ozonised until blue. Excess O_3 was evaporated under N_2 and the soln warmed to room temp then reduced in volume to *ca* 10 ml. 50% HIO_4 aq (0·3 ml), HOAc (10 ml) and water (3 ml) were added and the resulting homogeneous soln stirred at room temp for 20 h. Brine was added and Et_2O extract washed with $NaHCO_3$ aq. The alkaline layer was acidified and extracted with Et_2O. Removal of the Et_2O gave crude acidic material which was converted into the methyl esters (58 mg) by CH_2N_2/Et_2O. Chromatography over silica (3 g) and elution with 20% Et_2O in pentane gave **30** (40 mg), NMR (CCl_4) δ 1·03 (3H,S), 1·29 (3H,S), 1·60 (3H,S) 2·60 (2H,S allylic), 3·61 (3H,S), 3·63 (3H,S).

The diester **30** (40 mg) in t-BuOH (10 ml) was treated with a soln of $NaIO_4$ (0·17 g), K_2CO_3 (0·04 g) and $KMnO_4$ (0·04 g) in H_2O (10 ml). The mixture was warmed at 60° for 3 h followed by removal of t-BuOH *in vacuo* and acidification with 6N HCl. Na_2SO_4 was added and the resulting clear soln extracted with Et_2O. The Et_2O was washed with $NaHCO_3$, brine and dried ($MgSO_4$). Removal of the solvent and preparative TLC allowed the isolation of pure methyl ketopinate (5·2 mg) which was identical to authentic material by comparison of TLC, NMR, IR, Mass spec and GLC TLC (pentane–ether 7:3) R_f 0·34; νmax ($CHCl_3$) 1748 cm^{-1}; 1723 cm^{-1}; NMR (CCl_4), δ 1·06 (3H,S), 1·15 (3H,S), 3·69 (3H,S) GLC 10′, 10% carbowax 200°, 20 psi Rt 9·25 min, mass spec *m/e* 196 (M^+), 168, 165.

Reduction of 2 - oxo - 5 - methyl - 11,11 - dimethyltricyclo-[6.2.1.0^{1,6}] *- undec - 5 - ene* (**29**). A mixture (35 mg) containing 37% **27** and 63% **29** was reduced by $NaBH_4$ (150 mg, 4 mmole) in MeOH at room temp for 1 h then heated under reflux for 1 h. The soln was cooled, diluted with brine and extracted with Et_2O which was dried ($MgSO_4$). Removal of the solvent gave a mixture of **27** (56%) and **28** (44%); νmax ($CHCl_3$) 3480, 3620 cm^{-1}; GLC 10′, 10% carbowax, 150°, 30 psi, Rt (27), 27·5 min; (28) 21 min; NMR (CCl_4) δ 0·97 (3H,S), 1·03 (3H,S), 1·56 (3H,S) in addition to Me signals of **27**.

Rearrangement of epoxide mixture **39/40**; *2α - methyl - 5 - oxo - 6α/β - 7,7 - dimethyltricyclo*[6.2.1.0^{1,6}]*undecane* **41/42** *and 2α - hydroxy - 5 - methyl - 11,11 - dimethyltricyclo*[6.2.1.0]*undec - 5 - ene* (**27**). $BF_3{\cdot}Et_2O$ (0·1 ml, 0·8 mmole) was added to the total mixture **39/40** (300 mg, 1·46 mmole) in dry Et_2O. After 19 h at room temp the soln was diluted with Et_2O, washed $NaHCO_3$, brine and dried ($MgSO_4$). Removal of the solvent gave a crude product which was chromatographed over silica (15 g). Elution with 10% Et_2O in pentane afforded **41** and **42** (95 mg, 35% based on olefin). The major epimer **41** was obtained from early chromatographic fractions as an oil, b.p. 120°/0·1 mm; $[\alpha]_D^{26}$ − 16° (0·84%, $CHCl_3$); νmax (CCl_4) 1712 cm^{-1} NMR (CCl_4) δ 1·00 (3H,S), 1·22 (3H,S), 0·99 (3H,d, J = 7 Hz); Mass spec *m/e* 206·1669 (74%, M^+), $C_{14}H_{22}O$ (−1 ppm); 191·1437 (37), $C_{13}H_{19}O$ (0); 177·1287 (100), $C_{12}H_{17}O$ (4), CD (0·098% MeOH) ΔE_{330} 0, ΔE_{294} −0·73, ΔE_{233} 0. (Found: C, 81·43 H, 10·55 $C_{14}H_{22}O$ requires: C, 81·50; H, 10·75%).

The minor ketone was shown to be **42** by IR NMR, and GLC comparison.

Further elution with 20% Et_2O in pentane gave rearranged **27** (68 mg, 35% based on olefin) identical to that obtained *via* rearrangement of **24**.

The epimer **28** was not detected by GLC analysis of the crude product of rearrangement of the mixture **39** and **40**.

Equilibration of ketones **41** *and* **42**. A mixture (10 mg) of the ketones **41** and **42** in ratio 2:1 dissolved in CCl_4 (1 ml) containing 2 drops 70% $HClO_4$ aq. After 2 h the soln was diluted with pentane and washed with $NaHCO_3$ aq, brine and dried ($MgSO_4$). Removal of the solvent gave a mixture (9 mg) of **41** and **42** in the ratio 1:1 by GLC analysis. A similar epimerisation of **41** and **42** in ratio 2:3 gave the same 1:1 equilibrium ratio of **41** and **42**.

2α - Methyl - 5β,6β - dihydroxy - 7,7 - dimethyltricyclo-[6.2.1.0^{1,6}]*undecane* (**19**). OsO_4 (300 mg, 1·18 mmole) was added to **12** (200 mg, 1·05 mmole) in dry Et_2O (10 ml). Pyridine (0·5 ml) was then added and the mixture was stirred with a soln of sodium metabisulphite (750 mg) in H_2O (6 ml)/pyridine (4·5 ml) for 2·5 h. The solvent was then removed *in vacuo* and the residue extracted with Et_2O, washed with H_2O and dried ($MgSO_4$). Removal of the solvent followed by chromatography over silica (15 g) gave a mix-

ture of diols, **19** was obtained by recrystallisation from hexane, m.p. 122–123°; νmax ($CHCl_3$) 3570 cm^{-1}; NMR (CCl_4) δ 0·85 (3H,d J = 7 Hz), 1·01 (3H,S), 1·10 (3H,S), 4·10 (H,m); mass spec *m/e* 224·1767 (7%, M^+), $C_{14}H_{24}O_2$ (−4 ppm); 206·1667 (100), $C_{14}H_{22}O$ (−2). (Found: C, 75·26; H, 10·74 $C_{14}H_{24}O_2$ requires: 74·95; H, 10·78%). The minor diol **20** was obtained from an early fraction from the chromatography; NMR (CCl_4) δ 0·91 (3H,S), 1·01 (3H,d J = 7 Hz), 1·14 (3H,S), 3·80 (H,m).

2α - Methyl - 6α - hydroxy - 7,7 - dimethyltricyclo-[6.2.1.0^{1,6}]undecane (**34**)

(a) *From olefin* **12**. The mixture of **39**/**40** (300 mg, 1·46 mmole) in anhyd Et_2O (8 ml) was added to a soln of LAH (400 mg, 10·5 mmole) in anhyd Et_2O (15 ml). The mixture was stirred under reflux for 2·5 h then cooled to room temp. Excess hydride was carefully decomposed by sat Rochelle salt and the inorganic ppt was removed by filtration through celite. The Et_2O soln was dried ($MgSO_4$) and the solvent removed followed by chromatography over silica (12 g). Elution with 10% Et_2O in pentane gave **34** together with 20% of the 6β epimer by GLC analysis. recrystallisation from pentane afforded the pure 6α alcohol **34**, m.p. 79–80° $[\alpha]_D^{23}$ −13·4 (1·76%, $CHCl_3$), νmax ($CHCl_3$) 3650 cm^{-1}; NMR (CCl_4) δ 0·87 (3H,S), 0·91 (3H,S), 1·02 (3H,d J = 7), mass spec *m/e* 208·1823 (27%, M^+) $C_{14}H_{22}O$ (−2 ppm); 193·1596 (21), $C_{13}H_{21}O$ (2); 190·1724 (13), $C_{14}H_{22}$ (1); 165·1269 (60), $C_{11}H_{17}O$ (−6); 147·1167 (60), $C_{11}H_{15}$ (−5); 125·0961 (100), $C_8H_{13}O$ (−4); GLC 9′, 7% carbowax, 150°, 20 psi, Rt 9 min (6βOH) 9·75 min (6αOH). (at higher temp small amounts of dehydration products detected) (Found: C, 80·61; H, 11·48. $C_{14}H_{22}O$ requires: C, 80·71; H, 11·61%).

(b) *From the olefinic ester* **10** *via diol* **35**. *m*-Chloroperbenzoic acid (153 mg, 0·89 mmole) in Et_2O was added to an ice-cold soln of **10** (160 mg, 0·68 mmole) in Et_2O. After 24 h at room temp in the dark the reaction was worked up as for above epoxidation. A mixture of epoxides (170 mg) was obtained; NMR (CCl_4) major isomer δ 0·84 (3H,S), 1·00 (3H,S) 3·16 (H,m ), 3·60 (3H,S); minor isomer δ 0·91 (3H,S), 0·98 (3H,S), 3·05 (H,m ), 3·60 (3H,S); ν_{max}(CCl_4) 1735 cm^{-1}; mass spec *m/e* 250 (M^+).

The epoxide mixture (160 mg, 0·64 mmole) in Et_2O (5 ml) was added to a soln of LAH (160 mg, 4·2 mmole) in anhyd Et_2O and the mixture stirred under reflux for 3·5 h and worked up as described for **34**. The crude product contained 26% of the minor isomer by GLC. Chromatography over silica (8 g) and elution with 30% Et_2O in pentane gave **35** plus the 6β epimer. Recrystallisation from pentane–Et_2O of fractions rich in the major diol (**35**) provided pure material, m.p. 158–158·5°; $[\alpha]_D^{24}$ −12·6° (0·52% $CHCl_3$); νmax 3620 (weak) 3400 cm^{-1}; NMR (CCl_4) δ 0·95 (3H,S), 0·98 (3H,S), 3·03 (2H,S exch. D_2O), 3·76 (2H,m); mass spec *m/e* 224·1771 (12% M^+), $C_{14}H_{24}O_2$ (−2 ppm); 206·1663 (20), $C_{14}H_{22}O$ (−4); 193·1594 (34), $C_{13}H_{21}O$ (1); 69·0712 (100), C_5H_9 (11); GLC 10′, 10% carbowax, 220°, 40 psi Rt 18 min (minor), 20 min (major). (Found: C, 74·66; H, 10·70. $C_{14}H_{24}O_2$ requires: C, 74·95; H, 10·78%).

To the homogeneous diol **35** (60 mg, 0·27 mmole) in CH_2Cl_2 (4 ml)/Et_3N (0·4 ml) was added CH_3SO_2Cl (100 mg, 0·88 mmole)) in CH_2Cl_2 at 0° with stirring. After 1 h the soln was diluted with Et_2O and washed with 0·5 NHCl, $NaHCO_3$ aq, brine then dried ($MgSO_4$). Removal of the solvent gave an oil (95 mg) νmax ($CHCl_3$) 3580, 1360, 1185, 990, 960 cm^{-1}; NMR (CCl_4), δ 0·89 (3H,S), 0·94 (3H,S), 2·85 (3H,S), 4·47 (H,t: J = 10 Hz), 4·14 (H,q; J = 4, 10 Hz).

The crude mesylate (70 mg, 0·23 mmole) in Et_2O (5 ml) was added to a stirred refluxing soln of LAH (100 mg, 2·63 mmole) in anhyd Et_2O (10 ml). After 5 h reflux and 10 h at room temp the reaction was worked up as in method (a) for (**34**) to give a tert alcohol (42 mg, 90%) identical with **34** produced from **12** by IR, NMR, MS, and GLC.

2β - Methyl - 6α - hydroxy - 7,7 - dimethyltricyclo - [6.2.1.0^{1,6}]undecane (**32**)

(a) *From olefin* (**3**). Following the procedure described for the α-Me series (**34**), epoxide **24** (270 mg, 1·31 mmole) in anhyd Et_2O (8 ml) was added to LAH (200 mg, 5·27 mmole) in anhyd Et_2O (10 ml). After 2·25 h reflux, the reaction was worked up as for **34** to give an oil which was chromatographed on silica (20 g) to yield starting epoxide (80 mg, 30%), eluted with 5% Et_2O in pentane followed by the tert alcohol **32** (124 mg, 46%) eluted with 10% Et_2O in pentane. Recrystallisation from pentane at low temp gave **32**, m.p. 48·5–49·5°; $[\alpha]_D^{22}$ 46·7° (1·91% $CHCl_3$); νmax 3620, 3480 cm^{-1}; NMR (CCl_4) δ 0·91 (6H,S), 0·87 (3H,d J = 6 Hz); mass spec 208·1824 (23%, M^+), $C_{14}H_{22}O$ (−2 ppm); 193·1597 (15), $C_{13}H_{21}O$ (2); 190·1718 (11), $C_{14}H_{22}$ (−2); 125·0963 (100), $C_8H_{13}O$ (−3); GLC 10′ 10% carbowax, 180°, 20 psi Rt 15·5 min. (Found: C, 80·78; H, 11·61 $C_{14}H_{24}O$ requires: C, 80·71; H, 11·61%).

(b) *From the olefinic ester* **1** *via diol* **33**. *m*-Chloroperbenzoic acid (310 mg, 1·8 mmole) in Et_2O (6 ml) was added to **1** (320 mg, 1·37 mmole) in Et_2O (6 ml) at 0°. After 16 h at room temp the reaction was worked up as for **35** to give the epoxy ester (325 mg); νmax (CCl_4) 1735 cm^{-1}; NMR (CCl_4) δ 0·75 (3H,S, 0·94 (3H,S), 3·07 (H,d; J = 5 Hz); 3·59 (3H,S); mass spec *m/e* 250·1558 (65% M^+), $C_{15}H_{22}O_3$ (−4 ppm); 235·1332 (46), $C_{14}H_{19}O_3$ (−5); 232·1468 (55), $C_{15}H_{20}O_2$ (2); 221·1182 (95), $C_{13}H_{17}O_3$ (2); 91·0549 (100), C_7H_7 (1).

The crude epoxy ester (275 mg, 1·1 mmole) in anhyd Et_2O (10 ml) was added to a soln of LAH (300 mg, 7·9 mmole) in anhyd Et_2O (5 ml). After 2 h reflux the reaction was worked up as for **35** and the crude product chromatographed over silica (10 g). Elution with 50% EtOAc in benzene afforded the pure **33** (129 mg, 53%), m.p. 142–143° (Et_2O); $[\alpha]_D^{24}$ +51° (0·65% $CHCl_3$); νmax ($CHCl_3$) 3620, 3480 cm^{-1}; NMR ($CDCl_3$) δ 0·95 (6H,S) 1·30 (3H, S exch. D_2O), 3·40 (H,q; J = 8, 11 Hz), 3·84 (H,q J = 4, 11 Hz); mass spec *m/e* 224·1780 (13%), $C_{14}H_{24}O_2$ (2 ppm); 206·1675 (25), $C_{14}H_{22}O$ (2); 141·0906 (100), $C_8H_{13}O_2$ (−7). (Found: C, 74·84; H, 10·73. $C_{14}H_{24}O_2$ requires: C, 74·95; H, 10·78%).

A soln of CH_3SO_2Cl (77 mg, 0·67 mmole) in CH_2Cl_2 (1 ml) was added to **33** (75 mg, 0·336 mmole) in CH_2Cl_2 (4 ml) as 0–5°. After 30 min the product was isolated as in the case of **35**, as an oil (95 mg, 94%); νmax ($CHCl_3$) 3600 (weak), 1360, 960, 980 cm^{-1}; NMR (CCl_4) δ 0·93 (6H,S), 2·87 (3H,s), 3·95 (H,q; J = 2, 10 Hz), 4·28 (H,q, J = 4, 10 Hz).

The crude mesylate (70 mg, 0·232 mmole) in anhyd Et_2O (5 ml) was added to a stirred refluxing soln of LAH (120 mg, 3·16 mmole) in anhyd Et_2O (10 ml). The mixture was stirred under reflux for 5 h and worked up as for the preparation of **34** by method (b) to give a crude product which was chromatographed over silica (5 g). Elution with 10% Et_2O in pentane gave **32** (28 mg, 58%) identical with material prepared from **3**.

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