The Structure of Laurenene, a New Diterpene from the Essential Oil of *Dacrydium cupressinum*. Part 1

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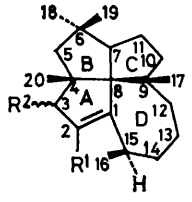
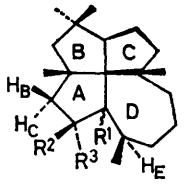
The chemistry of laurenene (1), an unusual new diterpene containing three five-membered rings, one seven-membered ring, one secondary and four tertiary methyl groups, isolated from the essential oil of *D. cupressinum*, is described

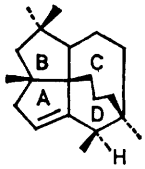
THE diterpene fraction of the volatile oil of *D. cupressinum* has been shown to contain rimuene,[1] phyllocladene, and isophyllocladene.[2] A new liquid diterpene hydrocarbon, for which the name laurenene is proposed, has now been isolated from this fraction and its structure (1) determined. Laurenene and rimuene have identical



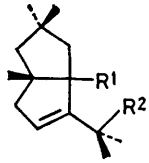
(1) R^1 = H, R^2 = H,H
(2) R^1 = H, R^2 = H,OH
(3) R^1 = Br R^2 = H,H
(4) R^1 = OAc, R^2 = H,H



	R^1	R^2	R^3
(5)	β-H	OH	H
(6)	β-H	—O—	
(7)	β-H	H	OH
(8)	—β-O—		H
(9)	α-H	—O—	
(10)	α-H	OH	H
(11)	α-H	H	OH
(12)	—β-O—		OAc
(13)	α-OAc	—O—	



(1a)



(1b)

R_F values on a 5% Apiezon L column (g.l.c.), but can be readily separated by preparative t.l.c. on silver nitrate-impregnated silica gel with hexane, or by column chromatography on silver nitrate-impregnated alumina with hexane, when the new diterpene moves almost with the solvent front. Laurenene constitutes *ca.* 12% of the total oil obtained by steam distillation of the leaves and terminal twigs.

On the basis of the experimental results described in this paper structure (1a) was earlier proposed[3] for laurenene. The degradative studies described had led to the conclusion that rings A—D met at C-8 and that there was a methyl group at the C—D ring junction. The size of rings C and D could not be deduced conclusively. While experimental studies designed to resolve these problems were in progress the diterpene was made the subject of an *X*-ray study and structure (1) established. The experimental work described in this paper relates largely to rings A and B and to the junctions of these rings with rings C and D, regions in which structures (1) and (1a) are identical.

Laurenene (1) analysed for $C_{20}H_{32}$. A positive tetranitromethane reaction showed the presence of unsaturation, which i.r. and n.m.r. spectra showed to be due to a trisubstituted double bond. Spin-decoupling experiments showed that the olefinic proton at C-2 was coupled with two allylic protons at C-3. The n.m.r. spectrum also showed four methyl singlets and a methyl doublet. The combination of five methyl groups and one double bond requires four rings and clearly pointed to an unusual structure.

Reactions of Ring A.—Laurenene (1) with diborane gave the alcohol (5) which on oxidation gave ketone (6). Lithium aluminium hydride (LAH) reduction of (6) gave alcohol (5) and as the major product, alcohol (7). The reconversion of (7) into diterpene (1) by dehydration with thionyl chloride precluded the possibility of skeletal rearrangements during the transformations (1)—(7).

The stereochemistry at C-1, -2, and -3 in compounds (5)—(7) can be deduced from their n.m.r. spectra. The n.m.r. spectrum of alcohol (7) showed a one-proton sextet ($H_A = R^2$), the multiplicity of which was shown, by a combination of europium-shift[4] and decoupling experiments, to arise from the coupling of H_A to three protons, H_B—$H_D = R^1$ (J_{AC} 2, J_{AB} 5, J_{AD} 5 Hz). Irradiation of H_A collapsed an eight-line pattern to a pair of doublets assigned to H_B and H_D. The H_B resonance showed characteristic geminal coupling (J_{BC} 14 Hz). Irradiation of H_B collapsed a broadened doublet attributable to H_C. That this latter pattern was a broadened doublet and not the expected four-line pattern can be explained in terms of paramagnetic broadening by the shift reagent. The fact that neither the H_B nor the H_C signals showed additional coupling is consistent with a fully substituted C-4. The pattern assigned to H_D, on irradiation of the H_A signal, collapsed to a doublet (J_{DE} 10 Hz) indicating coupling to one further proton (H_E). Irradiation of a one-proton multiplet caused collapse of the H_D quartet and also collapsed the doublet methyl signal. This multiplet was thus assigned to H_E. The absence of further coupling to H_D suggested that the additional adjacent carbon at C-8 was fully substituted.

Of the protons on carbons adjacent to that bearing the hydroxy-group. H_C was most affected by the shift reagent, and must thus lie on the same side of the molecule as the hydroxy-group, H_B and H_D, which were affected identically, bear the same relationship to the hydroxy-group. H_E was affected substantially more than the methyl group to which it was coupled, thus H_E lies relatively close to the hydroxy (*i.e.* α). Alcohol (5) is the C-2 epimer of alcohol (7). Formation of (5) from (1) indicates that the preferred mode of attack on hydrocarbon (1) is from the β-face. Likewise, reduction of ketone (6) occurs predominantly by β-face attack.

Laurenene (1) with *m*-chloroperbenzoic acid gave the epoxide (8). The epoxide was trisubstituted; the epoxidic proton showing coupling to one C-3 proton in the n.m.r. spectrum. The secondary methyl group now resonated at δ 0.74, because of shielding from the β-epoxide ring.[5]

The epoxide (8) rearranged with aqueous periodic acid, Jones reagent, or boron trifluoride–ether and gave the pentanone (9), $\nu_{max.}(CCl_4)$ 1 730 cm^{-1}.[6] The same ketone resulted from the reaction of compound (1) with performic acid. Ketones (6) and (9) are epimers; acidification of (6) giving (9). Deuteriation confirmed the presence of three allylic hydrogen atoms. The conversion of epoxide (8) to ketone (9) involves a 1,2 H shift and gives an α-H at C-1.

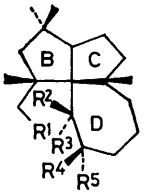
Lithium aluminium hydride reduction of ketone (9) gave two epimeric alcohols (10) and (11), isomeric at C-1 with alcohols (5) and (7). The major product (10) was the minor product when compound (9) was reduced with potassium in t-butyl alcohol. Models show a preference for α-face attack on ketone (9) consistent with the assignment of structure (10) to the major epimer from the lithium aluminium hydride reduction. Models also show that (11) would be the more stable alcohol. The regeneration of compound (1) in an attempt to convert alcohol (10) into a bromide with carbon tetrabromide–triphenylphosphine is consistent with a *trans*-configuration for 1-H and 2-OH.

Attempts to carry out addition reactions with the double bond in laurenene (1) gave unpredictable results. Compound (1) could not be hydrogenated at atmospheric pressure by any of the usual catalytic procedures, nor did it react with I_2–AgOAc. Prolonged reaction with OsO_4 gave 75% of unchanged (1) together with two allylic alcohols, assigned the epimeric structures (2) on the basis of their spectral characteristics. Reaction of compound (1) with bromine gave a monobromide (3), $C_{20}H_{31}Br$ (see following paper), and not the expected dibromide. The vinylic location of the bromine atom was confirmed by the i.r. absorption, $\nu_{max.}$ 1 628 cm^{-1}, and by conversion of (3) to a Grignard reagent [7] which regenerated laurenene (1) when treated with water. Compound (3) was also isolated in low yield from the reaction of laurenene (1) with aqueous *N*-bromosuccinimide. Ozonolysis of laurenene (1) produced a variety of products depending on the conditions used. At −70°, with hexane as solvent, ketone (9) and epoxide (8) were isolated. At the same temperature, using chloroform or dichloromethane as solvent, ketone (9) was the major product together with a small amount of a keto-acid (14).

The ketones (6) and (9) were the subjects of extensive investigation in attempts to find a method to open ring A in high yield.

Enol acetylation of ketones (6) and (9) led to the same enol acetate (4). Attempted epoxidation of (4) was slow and gave a mixture of products. The enol acetate epoxide (12) was produced in low yield by the treatment of compound (4) with ozone. Treatment of (12) with aqueous periodic acid gave the acetoxy-ketone (13); however, low yields in the production of (12) made this sequence unattractive.

Autoxidation of ketone (9) gave keto-acid (14) as major product, together with another keto-acid presumed to be the epimer (15). Methylation of the mixture gave the readily separable keto-esters (16) (major) and (17). I.r. solution studies on the three compounds (14), (16), and (17) showed carbonyl absorptions typical of a



	R^1	R^2	R^3	R^4	R^5
(14)	CO_2-H	—O—	CH_3	H	
(15)	CO_2-H	—O—	H	CH_3	
(16)	CO_2-Me	—O—	CH_3	H	
(17)	CO_2-Me	—O—	H	CH_3	
(18)	CH_2OH	—O—	H	CH_3	
(19)	Bz	Ph, OH	CH_3	H	
(20)	CH_2OH	OH	H	CH_3	H
(21)	CH_2OH	H	OH	CH_3	H

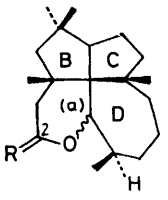
large ring ketone, $\nu_{max.}$ (CCl_4) 1 688, 1 687, and 1 689 cm^{-1}, respectively,[6] u.v. spectra showing the absence of any conjugation. The n.m.r. spectra of each of these compounds possessed four methyl singlets, a methyl doublet coupled to a one-proton apparent quartet, and an AB system. This latter is consistent with an allylic CH_2 grouping bonded to a tertiary centre. Autoxidation of (6) would be expected to rupture the C2-1–C-bond and give an oxo-function at C-1 and a carboxy-group at C-2. Since the oxo-functions produced are contained within a large ring, C-1 must lie at a ring junction between a five and a seven or larger membered ring. Although the keto-esters (16) and (17) are formulated as C-15 epimers, attempted basic epimerisation followed by methylation failed to demonstrate this, a new keto-ester, presumably the result of skeletal rearrangement, being formed. That keto-acid (14) was produced during ozonolysis of compound (1) and both keto-acids (14) and (15) were obtained from autoxidation suggests that (15) is the isomer differing

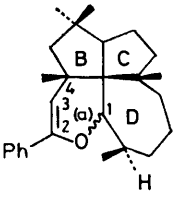
in stereochemistry at C-15 from compound (1). The keto-ester (17) did not react with sodium tris-(2-methoxyethoxy)aluminium hydride in an attempt to reduce the oxo-group selectively. Low temperature reaction with LAH gave the ketol (18) as did reaction in refluxing ether. Attempted autoxidation of (18) and allylic bromination of (17) were unsuccessful.

Since phenylmagnesium bromide reacted with keto-ester (16) to give keto-alcohol (19) this reaction could not be used as a first step in the Barbier–Wieland degradation of the methoxycarbonyl side chain of (16) by which it was hoped to gain access to ring B and investigate the stereochemistry at C-4.

Numerous methods of reduction of the 1-oxo-group in (16) were examined, most resulting in products of skeletal rearrangement. Reduction of (16) with LAH in ether, either at room temperature or under reflux, produced mixtures of two unstable hemiacetals (24) together with minor amounts of two diols (20) and (21). The higher R_F hemiacetal converted almost completely to the lower R_F isomer over 8 h at 0°. If left in contact with the reductant the higher R_F isomer predominated. These equilibrations suggest that the hemiacetals are isomeric at C-2, this being confirmed by oxidation with Jones reagent, both epimers giving the same lactone (23). The diol mixture was separated by multiple p.l.c. to give diols (20) and (21) in the ratio 2 : 1. The n.m.r. spectrum of (20) showed a one-proton singlet, δ 3.95, while that of (21) showed a one-proton doublet, δ 3.75 (J 8 Hz). By analogy with alcohol (7), (21) is the isomer with 1β-H. The diols (20) and (21) with Jones reagent gave lactones (22) and (23) respectively, together with in each case the keto-acid (14). Lactone (22) showed the 1-H resonance as a singlet, δ 4.35, while lactone (23) showed the signal as a doublet, δ 3.90 (J 9 Hz). By analogy with alcohol (7), lactone (23) can be ascribed the 1β-H stereochemistry. The lactone mixture could also be prepared in reduced yield by applying the same reduction–oxidation sequence to keto-acid (14).

Lactone (23) could not be opened by any of the conventional methods. Treatment with phenylmagnesium bromide produced the phenyl vinyl ether (25) rather

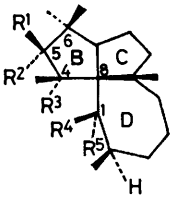




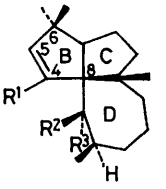
	R	(a)
(22)	—O—	β
(23)	—O—	α
(24)	H,OH	α

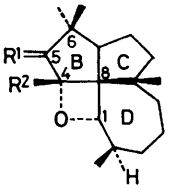
(25) (a) = α
(26) (a) = β

than the expected diol, presumably by dehydration of an intermediate hemiacetal. With phenyl-lithium the yield of phenyl vinyl ether was increased to over 90%. Lactone (22) under similar conditions gave the epimeric phenyl vinyl ether (26). The n.m.r. spectra of both compounds showed the C-3 olefinic proton signals as sharp singlets consistent with a fully substituted C-4.



	R^1	R^2	R^3	R^4	R^5
(27)	H	H	CHO	H	OBz
(28)	H	H	CO_2H	H	OBz
(29)	H	H	CHO	OBz	H
(30)	H	H	Ψ—CHOH	H	OH
(31)	H	H	Ψ—CHOH	H	OBz
(32)	H	H	CH_2OH	H	OBz
(33)	—O—		H	H	OH
(34)	—O—		H	—O—	
(35)	—O—		H	H	OAc
(36)	OH	H	H	H	OH
(37)	H	OH	H	H	OH
(38)	H	H	CH_2OH	H	OH
(39)	H	H	CH_2OH	OH	H
(40)	H	H	CH_2OTs	H	OBz
(41)	H	H	CH_2OAc	H	OH
(42)	H	H	CH_2OAc	—O—	





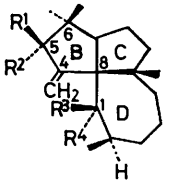
	R^1	R^2	R^3
(43)	CH_3	H	OBz
(44)	CH_3	OBz	H
(45)	CH_3	H	OH
(46)	CH_3	OH	H
(47)	CH_3	—O—	
(48)	CH_3	H	OAc

	R^1	R^2
(49)	H,H	CH_2OH
(50)	H,H	CH_2OAc
(51)	H,OH	CH_3
(52)	—O—	CH_3

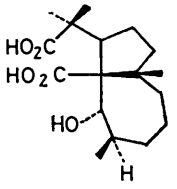
Cleavage of phenyl vinyl ether (25) with ruthenium tetraoxide or by ozonization gave a mixture containing aldehyde-benzoate (27) and acid benzoate (28). With performic acid compound (25) gave the aldehyde benzoate (27) in quantitative yield. The epimeric compound (29) could be produced in a similar fashion from compound (26).

Reaction of aldehyde-ester (27) with a Grignard reagent or an alkyl-lithium, followed by oxidation, was expected to give a diketone which might be selectively oxidised at C-3 under Baeyer–Villiger conditions. With phenyl-lithium or phenylmagnesium bromide, a mixture of diol (30) and alcohol-ester (31) was obtained. Lithium aluminium hydride reduced the mixture to diol (30).

Jones oxidation of the diol gave a mixture of olefins (53) and (43) rather than the expected ketone. Scheme 1 gives a possible reaction pathway. Aldehyde-ester (27) could be reduced quantitatively with sodium borohydride to alcohol ester (32), which with acid-free lead



	R¹	R²	R³	R⁴
(53)	H	H	H	OBz
(54)	H	H	OBz	H
(55)	H	H	H	OH
(56)	H	H	OH	H
(57)	H	H	H	OAc
(58)	H	OH	—O—	
(59)	OH	H	—O—	
(60)	—O—		—O—	
(61)	OH	H	OH	H
(62)	H	H	—O—	



(63)

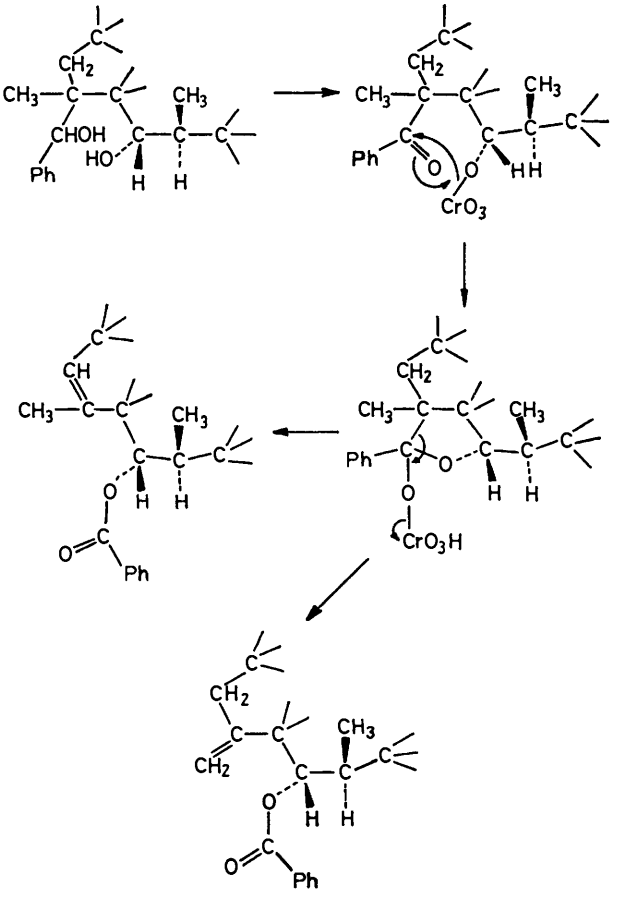
tetra-acetate gave a mixture of olefin-esters (53) and (43) in 50% yield, together with aldehyde-ester (27). Jones oxidation of aldehyde-ester (27) gave acid ester (28) in 50% yield; however, exclusion of oxygen raised the yield to 70%, the only side products, in this case, being the mixture of olefin-esters (53) and (43). Oxidative decarboxylation of acid-ester (28) gave the same mixture of olefin-esters. Because only partial separation of the mixture could be achieved by multiple p.l.c. it was debenzoylated with lithium aluminium hydride to the more easily separable mixture of olefin-alcohols (55) and (45). A similar series of reactions starting with aldehyde-ester (29) gave a mixture of olefin-esters (54) and (44), separated after lithium aluminium hydride debenzoylation as the olefin-alcohols (56) and (46).

That (45) and (46) were epimers was confirmed by oxidation to the same ketone (47). Treatment of exocyclic olefin (55) with toluene-*p*-sulphonic acid gave endocyclic olefin (45). That decarboxylation of (28) and its C-1 epimer gave only two isomeric olefins in each case is consistent with a fully substituted C-8 and with the bonding of C-4 to one methyl and one CH_2R grouping.

The n.m.r. spectrum of olefin alcohol (45) contained a one proton quartet, δ 5.185 (J 1 Hz) produced by the olefinic proton and a three proton doublet, δ 1.645 (J 1 Hz), produced by the C-4 methyl group. Irradiation of the C-4 methyl signal collapsed the C-5 olefinic proton resonance to a sharp singlet as required by a fully substituted C-6. Olefin-alcohol (46) showed similar features in the n.m.r. spectrum.

The n.m.r. spectrum of olefin-alcohol (55) contained two one-proton five-line patterns, δ 4.74 and 5.09, produced by the olefinic protons. Irradiation at δ 5.09 caused the multiplet at δ 4.74 to collapse to two broad lines while irradiation at δ 4.74 collapsed the δ 5.09 signal to a four line pattern. Both these irradiations produced changes in the proton envelope near δ 2.22. This is consistent with long-range coupling between the C-5 and -20 protons. In the n.m.r. spectrum of alcohol (56) the olefinic hydrogens produced a two proton multiplet.

Reactions of Ring B.—As a preliminary to the study of ring B, attempts were made to cleave the exocyclic double bond of olefin-alcohol (55). With *m*-chloroperbenzoic acid the alcohol (55) gave the oxetan (49) rather than an epoxide. The n.m.r. spectrum of the oxetan (49) revealed three methyl singlets, a methyl doublet, the typical 1β-H doublet, δ 4.07 (J 12 Hz), and an AB system attributable to the C-20 protons, δ 4.33 (H_A) and 3.63 (H_B) (J_{AB} 12 Hz). That the 20-hydroxy-function was primary was shown by acetylation with acetic anhydride



SCHEME 1

in pyridine, the n.m.r. spectrum of the resulting acetate (50) showing the C-20 proton signals further downfield, δ 4.39 (s). The expected epoxide could be an intermediate in the conversion of alcohol (55) into oxetan (49), acid-catalysed opening, with intramolecular nucleophilic substitution, giving the observed product.

Alcohol (55) with isopropenyl acetate–toluene-*p*-sulphonic acid gave an inseparable mixture of the *exo*-olefin-acetate (57) and the *endo*-olefin-acetate (48). The latter could be obtained in good yield from reaction of alcohol (45) with isopropenyl acetate–toluene-*p*-sulphonic acid. Oxidation of alcohol (55) gave ketone (62).

By analogy with the rearrangement of epoxide (8) to ketone (9), epoxide (64) was expected to give ketone (33). Epoxidation of alcohol (45) gave the epoxy-alcohol (64) together with alcohol-oxetan (51) which was also produced by the rearrangement of compound (64) on silica gel. Formation of the oxetan (51) must result from acid-catalysed epoxide opening with intramolecular nucleophilic attack on C-4 by the 1-hydroxy-group. Epoxide (64) with boron trifluoride–ether gave a mixture of oxetan (51) and an unstable aldehyde. Aldehyde formation from endocyclic epoxides has been reported and usually involves ring contraction.[8]

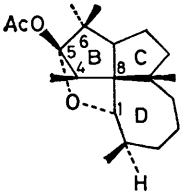
Oxidation of (51) gave the keto-oxetan (52), whose i.r. spectrum showed pentanone absorption at 1 737 cm^{-1}.[6] The two very low-field methyl resonances in the n.m.r. spectrum are attributed to methyl groups at C-4 and -6.

Alcohol (45) did not undergo hydroboration but with performic acid it gave the cyclopentanone, $\nu_{max.}$ (CCl_4) 1 724 cm^{-1}, (33), which on oxidation gave the diketone (34), $\nu_{max.}$ (CCl_4) 1 735 and 1 680 cm^{-1}.

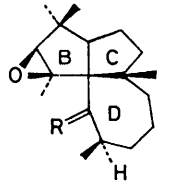
The absence of unexplained couplings in the C-5 proton signals in the n.m.r. spectra of derivatives of differing C-5 geometry [(45), (64), and (51)] is consistent with the fully substituted *gem*-dimethyl configuration at C-6.

Ozonolysis of compound (45) gave a minor product, olefin-ketone (47), and a major product, which contained a secondary hydroxy-group, a double bond, and a carbonyl group, and is assigned structure (58). Similar ozonolysis of (47) gave the epimeric alcohol (59). This implied that in the ozonolysis of alcohol (45), the double bond is attacked before the hydroxy-group is oxidised. The hydroxy-group must direct attack onto the double bond possibly by hydrogen bonding to the attacking ozone molecule in a similar fashion to the directing of peracid attack.[9] This would lead to an α-hydroxy-group at C-5. In ketone (47), in the absence of the directing influence of a 1-hydroxy, attack on the double bond occurs preferentially from the β-face. Oxidation of alcohols by ozone has been reported previously.[10] Formation of the allylic alcohol system can be envisaged as occurring by decomposition of the molozonide of the endocyclic double bond. That compounds (58) and (59) were epimers was shown by their oxidation to one compound (60). Ozonolysis of alcohol (46) gave the dihydroxy-olefin (61). Here the C-1 function is presumably inaccessible. Attack on the double bond should occur from the same side as in ketone (47). That substantial long-range coupling (>1 Hz) exists in the C-5 and -20 proton resonances of (58) and (61) but not in (59) (*J ca.* 0.5 Hz) appears contrary to the structures depicted. However, alcohols (55) and (56) and ketone (62) differ in the complexity of their C-20 proton signals, showing that the extent of long-range coupling between the C-20 and -5 protons is a function of the geometry of C-1. Comparison with derivatives discussed later supports the assignments given.

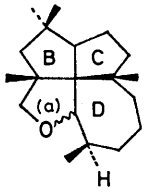
Epoxidation of acetate-olefin (48) gave epoxide acetate (65) which with 60% perchloric acid in tetrahydrofuran gave the keto-acetate (35). The n.m.r. spectrum of



(67)



(64) R = β-H, α-OH
(65) R = β-H, α-OAc
(66) R = O



(68) (a) = α
(69) (a) = β

(35) showed two methyl doublets, that at higher field (δ 0.91) being assigned to the 4-methyl on the basis of decoupling experiments. Decoupling studies on compound (33) located its 4-methyl resonance at δ 1.11. Conversion of a 1α-hydroxy-group to a 1α-acetate shields the 4-methyl strongly. Epoxidation of olefin (47) gave epoxy-ketone (66). Epoxides (65) and (66) are assumed to have the β-epoxide configuration in accord with the stereochemistry of the ozonolysis reactions.

Since attempted endocyclic double bond cleavage was unsuccessful, attempts were made to cleave the five-membered ring of ketol (33). *N*-Bromosuccinimide gave a high yield of keto-oxetan (52). Autoxidation of ketone (33) produced both acidic and neutral products. The neutral fraction was a complex mixture containing unchanged (33). The acid fraction was partially purified by p.l.c. to give a compound which appeared to be dicarboxylic acid (63).

With toluene-*p*-sulphonic acid–isopropenyl acetate (33) gave, as minor product, keto-acetate (35) and, as the major product, a hemiacetal acetate (67). The n.m.r. spectrum contained a one proton doublet, δ 3.79 (*J* 9 Hz), confirming the presence of a 1α-oxygenated function, and a quartet, δ 3.05 (*J* 6 Hz), which could be

shown to be coupled to the 4-methyl doublet, δ 1.08 (J 6 Hz), by decoupling experiments. That C-5 and -1 were oxygenated was confirmed when reduction of (67) with lithium aluminium hydride gave two epimeric alcohols, the major (37) and the minor (36). These same two diols were the sole reduction products of ketone-alcohol (33) and ketone-acetate (35), reduction of (33) yielding predominantly isomer (37) and reduction of (35) yielding almost exclusively isomer (36). These reductions also demonstrate that (33), (35), and (67) all have the same C-4 stereochemistry. Reduction of ketone-alcohol (33) required forcing conditions indicating severe steric hindrance of the oxo-group. This may be interpreted in terms of rapid alkoxy-hydride formation involving the 1-hydroxy, this group hindering attack on the 5-ketone from the α-face. Hence, attack would result from the β-face giving a predominance of alcohol (37). With ketone-acetate (35) attack on the 5-keto-group may occur before attack on the 1-acetate. Hence, an appreciable amount of α-face attack may occur. That the 5β-alcohol (36) is formed almost exclusively indicates substantial hindrance to β-face attack, consistent with a 4β-methyl. Steric hindrance to β-face attack is also consistent with the vigorous conditions required for reduction of (33). It has been [11] reported that an adjacent hydroxy-group has a stronger deshielding effect on a *trans*- than on a *cis*-methyl group and this is supported by data obtained by Nixon [12] on ring A substituted colensanes. The methyl proton resonances in the n.m.r. spectra of alcohols (36) and (37) support the assignments given (Table). Alcohols (36)

N.m.r. data for 5-hydroxy-derivatives

	4-Methyl doublet (δ)	Methyl singlets (δ)
(37)	1.10	0.85, 1.03, 1.05
(36)	1.04	0.98, 1.00, 1.09
(58)		0.54, 0.91, 1.06
(59)		0.66, 1.03, 1.04
(62)		0.73, 0.97, 0.97

and (37) each show one shielded methyl singlet as do the allylic alcohols (58) and (59). In both pairs of epimers, that assigned the 5α-hydroxy-stereochemistry has the highest-field methyl signal.

In the n.m.r. spectra of the *exo*-olefins (53), (55), (56), and (62) a shielded three-proton singlet appears. This signal must arise from a methyl group in close proximity to and lying within the shielding region of the double bond. It can be seen from a comparison of the *exo*-olefin-ketone (62) with the alcohols (58) and (59) (Table), that a 5β-hydroxy-group causes a further upfield shift in this methyl resonance of 0.07 p.p.m. while a 5α-hydroxy-group results in an upfield shift of 0.19 p.p.m. This is consistent with a methyl group bonded to C-6, having an α-orientation. Europium shift studies on the allylic alcohol (58) confirmed this assignment. Addition of shift reagent had the greatest effect on the C-5 proton signal, the highest-field methyl (that assigned to the 6α-position) being the signal next most affected. Hence, when complexed to the 5α-hydroxy group, the europium species lies closer to this methyl group than to either of the exocyclic double bond protons. An additional methyl signal, δ 1.06, was also affected substantially, moving as shift reagent was added at a similar rate to the least shifted olefinic proton resonance. This is undoubtedly due to the 6β-methyl group. Europium shift studies on the alcohol (59) support this assignment. Addition of europium shift reagent to the β-allylic alcohol (59) had the greatest effect on the 5α-proton with one of the methyl signals at lower field (either that at δ 1.03 or 1.04) being next most affected. The olefinic proton signals and the high-field, 6α-methyl singlet, δ 0.66, moved relatively little. This is consistent with bending the exocyclic double bond under the α-face of the molecule, the position expected for shielding of a 6α-methyl.[13]

On the basis of the chemistry of laurenene described so far the partial structure (1b) could be written.

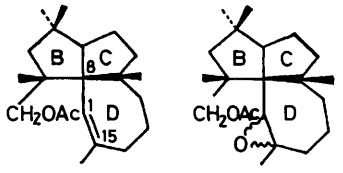
As removal of one functional group from aldehyde-ester (27) would facilitate study of the other, reduction of the aldehyde function was examined. Reduction of (27) with lithium aluminium hydride gave diol (38) as the only product. Care was necessary in work-up as heating in the presence of acid resulted in conversion to the ether (68). Compound (68) was also obtained from attempted tosylation of diol (38). Aldehyde-ester (29) gave ether (69) in a similar fashion, presumably *via* diol (39). Sodium borohydride reduction of (27) had given alcohol-ester (32), and this was converted to tosylate-ester (40). Reduction of (40) with lithium aluminium hydride gave ether (68) while sodium borohydride failed to react. Ether (68) was also isolated from attempts to replace the tosyl group with chlorine using pyridine hydrochloride.

Diol (38) was selectively acetylated with acid-free acetic anhydride in pyridine to give acetate-alcohol (41), which was rapidly converted to ether (68) on silica gel and could be oxidised with Jones reagent to acetate-ketone (42). Compound (42) proved resistant to Baeyer–Villiger oxidation and enol acetate formation.

Dehydration of acetate-alcohol (41) using mesyl chloride in pyridine gave acetate-olefin (70) in reasonable yield, the vinylic methyl, δ 1.75, signal in the n.m.r. spectrum being produced by the 15-methyl group. Epoxidation of (70) gave an isomeric mixture of epoxides (71) (7 : 2) which was partially separated by p.l.c. Formic acid in chloroform caused rearrangement of acetate-olefinic (70) into an isomeric primary acetate (72), which contained a trisubstituted double bond, four tertiary methyl groups, and a vinylic methyl. Epoxidation of (72) gave mainly one epoxide (73), the n.m.r. spectrum of which showed a sharp singlet for the methyl attached to the epoxide ring, δ 1.45, and a one-proton triplet for the epoxidic proton, δ 2.91 (J 3 Hz). These data are consistent with structure (73) but can be interpreted equally well on the basis of structure (1a) for laurenene.

Since the double bond in laurenene (1) has an allylic secondary methyl group, attempts were made to iso-

merise (1) to a tetrasubstituted olefin. Formic acid in benzene and *N*-lithioethylenediamine failed to produce any change. Formic acid in refluxing chloroform resulted in extensive rearrangement and gave an olefin (74) which retained the secondary methyl group and had two methyl groups attached to a tetrasubstituted double bond. Ozonolysis of this compound produced a dicarbonyl compound (75) containing two methyl ketone functions. This diketone was also prepared by osmylation of (74) and cleavage of the diol with lead tetra-acetate. Lithium aluminium hydride reduction of the diketone (75) gave three of the four possible diol isomers which were separated by multiple p.l.c. N.m.r. studies on the lowest R_F isomer showed one of the carbinol proton signals as a quartet which could be converted to a singlet by irradiation of a methyl doublet. This suggested that this CH_3CHOH grouping was connected to a quaternary carbon. The other carbinol proton resonated as a multiplet and was shown to be coupled to a methyl doublet and two other protons which produced simplified signals on irradiation of the carbinol multiplet. This showed the presence of a CH_3CHOH-CH_2 system bonded to a quaternary centre. The remaining two diols produced similar spectra. These data are in accord with structure (74) for the rearranged olefin. A plausible pathway for the formation of compound (74)



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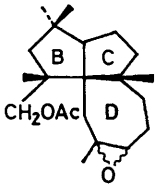
(71)



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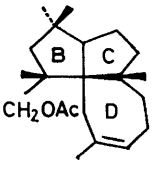

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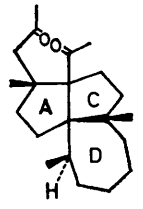
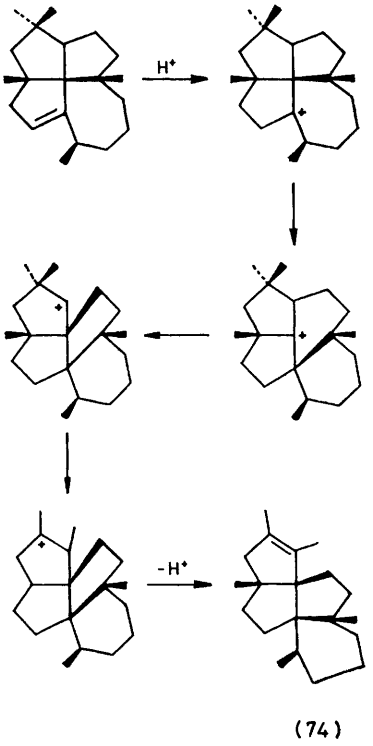


(75)

from laurenene (1) is outlined in Scheme 2. Generation of a secondary carbonium ion such as that at C-7, which the scheme required, has been noted previously.[14] The formation of structure (74) requires a 6,6-*gem*-dimethyl function and a proton at C-7.

The presence of a proton at C-7 was clearly discernible from $Eu(dpm)_3$ shift studies on alcohols (7) and (45). In the case of alcohol (7), a one-proton triplet, δ 2.69 (*J* 8 Hz), which was affected almost as much by the addition of shift reagent as was the 15α-proton, was observed. The multiplicity is consistent with that required for a C-7 proton in (1) or (1a). To be affected so markedly,



(74)

SCHEME 2

this proton would be required to have the α-stereochemistry. A similar triplet, δ 2.42 (*J* 9 Hz), with similar behaviour was also observed in the case of olefin-alcohol (45). In the n.m.r. spectra of compounds where the 7α-proton would be expected to experience a deshielding interaction, an appropriate triplet [*e.g.* compounds (7), (32), (43), (45), and (64)] or double doublet [*e.g.* compound (52)] was observed.

Structure (1a) which was proposed on the basis of the experimental evidence described so far has the same stereochemistry at the ring junctions as structure (1) and the same stereochemistry for the allylic methyl group.

The discussion of the stereochemistry of derivatives of laurenene which follows was actually based on derivatives of the hypothetical structure (1a) but applies equally to derivatives of structure (1). Ketal-acetate (67) would be difficult to form if a 4α-methyl were present and impossible unless the 8(1) bond was α with respect to ring B. The large shielding of the 4-methyl signal shown on conversion of the 1α-alcohol (33) to the corresponding acetate (35) can be interpreted with the aid of models. When the acetate group is placed in the preferred conformation [15] with the carbonyl group eclipsing the C-1 proton the 4β-methyl group would lie almost directly above the carbon–oxygen double bond and hence would be shielded.[16] This additional evidence supports the 4β-methyl stereochemistry in the inter-related com-

pounds (33), (35)—(37), and (67). Oxetans (49)—(52) must have the 4α-oxygen stereochemistry, and further show that the 8(1) bond must be α with respect to ring B.

The stereochemistry at C-4 in (1) could also be deduced. Facile formation of the five-membered ring ethers (68) and (69), epimeric at C-1, involved C-1, C-3, C-4, and C-8 and requires a *cis*-fused C-4–C-8 ring junction. Hence, ethers (68) and (69) and, as a consequence, hydrocarbon (1) contain a 4β-methyl group. $Eu(dpm)_3$ shift studies on alcohol (7) supported this assignment. In this compound all tertiary methyl signals were affected less than the signals produced by the 1β- and 3β-protons. A 4α-methyl resonance would be affected more than either of these signals as it bears a 1,3-relationship to the 2α-hydroxy group.

In the experimental deduction of the laurenene structure a decision had to be made between (1a) and its enantiomer. Models of ketone (6) show that the structure based on (1a) would be expected to have a negative Cotton effect,[17] while the enantiomeric structure would display a positive Cotton effect. The o.r.d. and c.d. curves of ketone (6) show a negative Cotton effect which is consistent with structures (1) and (1a).

EXPERIMENTAL

Experimental procedures are as described in ref. 18. Solvents H, E, and B refer to hexane, sodium dried ether, and benzene, respectively.

Leaves and terminal twigs (1 100 kg) of *D. cupressinum* (Rimu, Red-pine) were collected by the State Forest Service at Hampden early in February 1968. The leaves were steam-distilled for 30 h and the distillate (1 208 ml) separated into four fractions by distillation under reduced pressure in a Claisen apparatus. The diterpene fraction (600 ml), b.p. 120—150° at 1—3 mmHg, was the subject of the present investigation.

Isolation of Hydrocarbons.—The diterpene fraction (74.5 g) was adsorbed on to alumina (1 500 g) from hexane. Hexane (1.0 l) eluted a hydrocarbon fraction (55 g, 74%) and ether (2.0 l) an oxygenated fraction (18 g, 23%).

Isolation of Laurenene (1).—The hydrocarbon mixture (10 g) was adsorbed from hexane onto silver nitrate impregnated alumina (550 g) and the column eluted with hexane until *laurenene* was removed (t.l.c.). The column was then stripped with ether and regenerated with hexane. This cycle was repeated with further batches (five) of the hydrocarbon mixture without obvious deactivation of the column. A total of 17.5 g (31%) of laurenene was recovered from the hydrocarbon fraction (55 g). Laurenene, a mobile colourless liquid, had b.p. 58° at 0.4 mmHg; $[\alpha]_D^{20}$ −7.1° (*c*, 0.78); $\nu_{max.}$ (film) 3 045 and 801 (CH=C) cm^{-1}; δ 0.93, 0.98, 1.05, 1.35 (3 H each, s, CH_3), 1.10 (3 H, d, *J* 7 Hz, CH_3CH), 5.39 (1 H, t, *J* 2 Hz, CH=C); δ(benzene) 0.98, 1.00, 1.07, 1.32 (3 H, each, s, CH_3), 1.09 (3 H, d, *J* 7 Hz, CH_3CH), 2.00 (2 H, m, CH_2C=C), 5.36 (1 H, t, *J* 2 Hz, CH=C); *m/e* 272 (M^+, 100%) and 257 (Found: C, 88.0; H, 11.9. $C_{20}H_{32}$ requires C, 88.2; H, 11.8%).

Hydroboration of Laurenene (1).—Laurenene (1) (1.070 g) and lithium aluminium hydride (960 mg) in dry ether (70 ml) was kept under dry nitrogen. A solution of boron trifluoride–ether (4.3 ml) in dry ether (80 ml) was added dropwise over 100 min at room temperature with stirring. After stirring for a further 150 min, saturated aqueous sodium sulphate (120 ml) was added. Work-up and evaporation of the solvent below 35° gave a moist oil which was dissolved in tetrahydrofuran (30 ml) and heated under reflux with 2M-sodium hydroxide (11 ml) and 30% hydrogen peroxide (11 ml) for 75 min. Work-up gave an oil (1.125 g) which was adsorbed from hexane on to alumina (40 g). Elution with hexane gave (1) (588 mg). Elution with ether gave *alcohol* (5) (476 mg), which after sublimation (67° at 0.02 mmHg) had m.p. 110—111°; $[\alpha]_D^{20}$ +14.2° (*c*, 0.74); $\nu_{max.}$ 3 045 (OH), 1 044, and 1 003 cm^{-1}; δ 1.02, 1.10, 1.13, 1.29 (3 H each, s, CH_3), 1.12 (3 H, d, *J* 7 Hz CH_3CH), and 4.18 (1 H, sextet, $W_{\frac{1}{2}}$ 25 Hz, CHOH), *m/e* 290 (M^+, 100%) and 275 (Found: C, 82.3; H, 11.8. $C_{20}H_{34}O$ requires C, 82.7; H, 11.8%).

Ketone (6).—Alcohol (5) (476 mg) in pure acetone (160 ml) was stirred at room temperate while Jones reagent (0.4 ml) was added slowly. After a further 2 min stirring, work-up gave an oil (501 mg). P.l.c. with E–H (1 : 4) gave *ketone* (6) (451 mg) which after distillation (67° at 0.02 mmHg) had $[\alpha]_D^{20}$ −2.4° (*c*, 0.78); $\nu_{max.}$ (film) 1 733 (C=O) and 1 420 cm^{-1}; $\nu_{max.}$ (CCl_4) 1 728 (C=O) cm^{-1}; δ 0.95, 0.99, 1.17, 1.37 (3 H each, s, CH_3) and 1.19 (3 H, d, *J* 6 Hz, CH_3CH); $\lambda_{max.}$ ($CHCl_3$) 290 nm (ε 34); *m/e* 288 (M^+, 100%) (Found: C, 83.5; H, 11.1. $C_{20}H_{32}O$ requires C, 83.3; H, 11.2%).

Lithium Aluminium Hydride Reduction of Ketone (6).—Ketone (6) (192 mg) in dry ether (40 ml) was heated under reflux with lithium aluminium hydride (200 mg) for 1 h. Work-up gave an oil (196 mg). P.l.c. with E–H (3 : 7) gave, at low R_F value, alcohol (5) (5 mg), and at higher R_F value, *alcohol* (7) (172 mg). The latter, after distillation (35° at 0.01 mmHg), had $[\alpha]_D^{20}$ −1.2° (*c*, 7.0); $\nu_{max.}$ (film) 3 624 and 3 483 (OH) and 1 038 cm^{-1}; $\nu_{max.}$ (0.1M in CCl_4) 3 627 (OH) cm^{-1}; δ 1.02, 1.04, 1.20, 1.24 (3 H each, s, CH_3), 1.10 (3 H, d, *J* 6 Hz, CH_3CH), 2.69 (1 H, t, *J* 8 Hz, $CHCH_2$), 4.31 (1 H, sextet, $W_{\frac{1}{2}}$ 12 Hz, CHOH) (Found: C, 82.4; H, 11.8. $C_{20}H_{34}O$ requires C, 82.7; H, 11.8%).

Dehydration of Alcohol (7).—Thionyl chloride (2 drops) was added to a solution of alcohol (7) (30 mg) in dry pyridine (1.5 ml). After 15 min at room temperature the reaction mixture was worked-up in the usual way. Chromatography on Spence H alumina with hexane gave laurenene (1) (25 mg).

Epoxide (8).—Laurenene (1) (178 mg) in chloroform (5 ml) was treated with *m*-chloroperbenzoic acid (133 mg) in chloroform (5 ml) at room temperature for 48 h. Work-up, including washing with 2M-sodium hydroxide, followed by p.l.c. with E–H (1 : 9) and immediate removal of the band of medium R_F value gave *epoxide* (8) (168 mg) which had, after sublimation (50° at 0.02 mmHg), m.p. 108—109°; $[\alpha]_D^{20}$ −12.8° (*c*, 1.26); $\nu_{max.}$ 3 020, 940, and 872 cm^{-1}; δ 0.96, 1.07, 1.19, 1.29 (3 H, each, s, CH_3), 0.745 (3 H, d, *J* 6 Hz, CH_3CH), 1.92 (1 H, d, *J* 15 Hz, CHCO), 2.00 (1 H, dd, *J* 2,15 Hz, CHCO), and 3.26 (1 H, d, *J* 2 Hz, CH of oxiran) (Found: C, 83.0; H, 11.3. $C_{20}H_{32}O$ requires C, 83.3; H, 11.2%).

Epoxide (8) gave ketone (9) in quantitative yield with each of Jones reagent, 30% hydrogen peroxide, zinc and acetic acid, periodic acid, and boron trifluoride–ether.

Ketone (9).—Laurenene (1) (1.129 g) in chloroform (10 ml) was treated with 85% *m*-chloroperbenzoic acid (1.055 g) in chloroform (40 ml) at room temperature. After 2 days boron trifluoride–ether (2 drops) was added. After a further 15 min work-up involving chloroform extraction and washing with 2M-sodium hydroxide, followed by p.l.c. with

E–H (3 : 17) gave, at medium R_F value, *ketone* (9) (1.111 g), which had, after sublimation (60° at 0.04 mmHg), m.p. 57.5—59°; $[\alpha]_D^{20}$ +8.7° (*c*, 0.90); $\nu_{max.}$ (film) 1 730 (C=O) and 1 405 cm^{-1}, $\nu_{max.}$ (CCl_4) 1 730 cm^{-1}; δ 0.98, 1.15, 1.16, 1.38 (3 H each, s, CH_3) and 1.25 (3 H, d, *J* 6 Hz, CH_3CH); $\lambda_{max.}$ ($CHCl_3$) 297 nm (ε 38); o.r.d. (*c*, 0.1, cyclohexane) $[\Phi]_{450}$ −126°, $[\Phi]_{328}$ −7 338°, $[\Phi]_{321}$ −5 124°, $[\Phi]_{318}$ −5 351°, $[\Phi]_{310}$ 0°, and $[\Phi]_{280}$ +10 121° (*a* −175); c.d. (*c* 0.1, cyclohexane) $[\Theta]_{337}$ 0, $[\Theta]_{321}$ −7 800 (shoulder), $[\Theta]_{310}$ −13 600, $[\Theta]_{305}$ −13 000, and $[\Theta]_{301}$ −13 700, $[\Theta]_{250}$ 0; *m/e* 288 (M^+, 100%) and 273. (Found: C, 83.5: H, 11.2. $C_{20}H_{32}O$ requires C, 83.3; H, 11.2%).

Epimerisation of Ketone (6).—(a) The ketone (21 mg) was adsorbed from hexane on to acidic alumina (2.5 g; grade 1). After 4 h elution with ether gave ketone (9) (18 mg).

(b) Ketone (6) (40 mg) was adsorbed from hexane on to alkaline alumina (6 g; grade 1). After 18 h elution with ether gave a complex mixture (35 mg) from which p.l.c. with E–H (1 : 4) separated ketone (9) (11 mg). Elution with ether–ethanol (1 : 1) after 7 h gave a similar complex mixture.

Deuteriation of Ketone (9).—Ketone (9) (12.5 mg) in deuterioethanol (1.5 ml) and deuterium oxide (0.2 ml) was treated with sodium (25 mg) and the mixture heated under reflux for 48 h. Work-up gave an oil (12.4 mg). Distillation (35° at 0.01 mmHg) gave the trideuterio-derivative, *m/e* 291 (M^+, 100%).

Lithium Aluminium Hydride Reduction of Ketone (9).—Ketone (9) (230 mg) in dry ether (40 ml) was heated under reflux with lithium aluminium hydride for 15 min. Work-up gave an oil (222 mg) which after p.l.c. with E–H (1 : 4) gave, at low R_F value, a mixture (8 mg) containing alcohol (11) (5 mg suggested by integral analysis of n.m.r. spectrum) and at medium R_F value, *alcohol* (10) (204 mg) which after distillation (50° at 0.02 mmHg) had $[\alpha]_D^{20}$ +93° (*c*, 2.57); $\nu_{max.}$ (film) 3 615 and 3 475 (OH) and 1 011 cm^{-1}; δ 1.06, 1.06, 1.26, 1.33 (3 H, each, s, CH_3), 1.10 (3 H, d, *J* 6 Hz CH_3CH), and 4.57 (1 H, $W_{\frac{1}{2}}$ 17 Hz, octet, CHOH) (Found: C, 82.8; H, 11.8. $C_{20}H_{34}O$ requires C, 82.7; H, 11.8%).

Potassium in t-Butyl Alcohol Reduction of Ketone (9).—Ketone (9) (106 mg) in t-butyl alcohol (30 ml) was treated with potassium (600 mg). When all the potassium had reacted, the mixture was stirred for 30 min. Dilution with water, acidification, and ether extraction gave an oil (106 mg) containing a number of products. Separation by p.l.c. with E–H (3 : 7) gave, in order of increasing R_F value, a keto-acid mixture (14) and (15) (24 mg), lactone (22) (7 mg), *alcohol* (11) (55 mg), and alcohol (10) (1 mg). Alcohol (11) after sublimation (45° at 0.01 mmHg) had m.p. 98—100°; $[\alpha]_D^{20}$ +83° (*c*, 1.38); $\nu_{max.}$ 3 620 and 3 340 (OH) and 1 019 cm^{-1}; δ 1.03, 1.08, 1.18, 1.24 (3 H, each, s, CH_3), 1.09 (3 H, d, *J* 8 Hz, CH_3CH), and 4.50 (1 H, sextet, $W_{\frac{1}{2}}$ 21 Hz, CHOH) (Found: C, 82.5; H, 11.6. $C_{20}H_{34}O$ requires C, 82.7; H, 11.8%).

Attempted Osmylation of Laurenene (1).—Laurenene (1) (511 mg) in dry pyridine (25 ml) and dioxan (18 ml) was treated with osmium tetraoxide (600 mg) at room temperature. Intermittent refluxing was continued for 18 days (total reflux time was 31 h), when the solvent was distilled off at atmospheric pressure to give a black solid. Tetrahydrofuran (125 ml) and lithium aluminium hydride (1 g) were added and the mixture refluxed for 5 h. Work-up gave an oil (507 mg) which was adsorbed from hexane on to alumina (15 g). Elution with hexane gave pure laurenene (1) (390 mg). Elution with ether gave a mixture (83 mg) containing two main components which were separated by p.l.c. with E–H (3 : 2) to give, in order of increasing R_F value, *product* 1 (2) (60 mg) and *product* 2 (2) (13 mg).

Product 1 (2) had $\nu_{max.}$ 3 326br (OH), 3 045, 1 638, and 827 (CH=C) cm^{-1}; δ 0.98, 0.98, 1.06, 1.43 (3 H, each, s, CH_3), 1.12 (3 H, d, *J* 6 Hz, CH_3CH), 4.44 (1 H, s, CHOH), and 5.40 (1 H, s, CH=C) (Found: C, 83.6; H, 11.2. $C_{20}H_{32}O$ requires C, 83.3; H, 11.2%). Product 2 (2) had $\nu_{max.}$ 3 617 and 3 385br (OH), 3 045, and 1 634 (CH=C) cm^{-1}; δ 0.89, 1.00, 1.04, 1.32 (3 H each, s, CH_3), 1.11 (3 H, d, *J* 6 Hz, CH_3CH), 3.82 (1 H, d, *J* 3 Hz, CHOH), and 5.58 (1 H, d, *J* 3 Hz, CH=C) (Found: C, 83.7; H, 11.1. $C_{20}H_{32}O$ requires C, 83.3; H, 11.2%).

Attempted Allylic Oxidation of Laurenene (1).—Laurenene (1) (76 mg) in dioxan (9 ml) and water (1 ml) containing powdered calcium carbonate (56 mg) was stirred with recrystallised *N*-bromosuccinimide (115 mg) while being irradiated with visible light. The temperature of the solution was raised by the heat from the lamps. After 2 h, work-up gave a mixture (96 mg) of non-polar and polar material. P.l.c. with hexane gave, at high R_F value, *monobromide* (3) (22 mg), and p.l.c. rerun with E–H (1 : 9) gave, at low R_F value, an uncharacterised monobromide (29 mg). Monobromide (3) had $\nu_{max.}$ 1 629 (C=C), 1 255, and 1 125 cm^{-1}; δ 0.99, 1.02, 1.07, 1.34 (3 H each, s, CH_3) and 1.40 (3 H, d, *J* 7 Hz, CH_3CH) (Found: C, 68.4; H, 9.1; Br, 22.1. $C_{20}H_{31}Br$ requires C, 68.4; H, 8.9; Br, 22.7%). The uncharacterised monobromide had $\nu_{max.}$ 1 710 (C=O), 1 587 (C=C), and 1 002 cm^{-1}; δ 3.74 (1 H, s, CHBr); $\lambda_{max.}$ (cyclohexane) 210 (ε 3 800) and 252 nm (3 380) (Found: C, 66.4, 66.8; H, 8.4, 8.5; Br, 22.0. $C_{20}H_{29}BrO$ requires C, 65.8; H, 8.0; Br, 21.9%).

Ozonolysis of Laurenene (1).—(a) Laurenene (1) (1.384 g) in chloroform (200 ml) was treated with a stream of ozonised dry oxygen at −70° for 150 min, when a light blue colour had developed. Removal of the solvent *in vacuo* gave a crude oil (1.490 g). An identical oil was obtained in a repeat experiment when dichloromethane was used as solvent and when the blue solution was purged with nitrogen and hydrogenated with 10% palladium–charcoal at room temperature and atmospheric pressure. P.l.c. with E–H (1 : 4) gave ketone (9) (1.128 g) at high R_F value and keto-acid (14) (30 mg) at the base-line.

(b) Laurenene (1) (168 mg) in dry hexane (25 ml) was ozonised as in (a), and the blue solution purged with nitrogen. Treatment of the resulting solution by hydrogenation with 10% palladium–charcoal or by refluxing with ethanol and water gave identical mixtures. Work-up and separation by p.l.c. with E–H (1 : 9) gave, at medium R_F, ketone (9) (65 mg) and, at higher R_F, epoxide (8) (77 mg).

Enol Acetate (4).—(a) Ketone (6) (80 mg) was dissolved in acetic anhydride (15 ml) containing toluene-*p*-sulphonic acid (55 mg) and the solvent slowly distilled off through a packed column for 4.5 h by which time most of the solvent had been removed. Work-up included washing with saturated aqueous sodium hydrogencarbonate and gave an oil which after p.l.c. with E–H (1 : 19) gave, at medium R_F, *enol acetate* (4) (53 mg).

(b) Ketone (9) (216 mg) similarly gave enol acetate (4) (206 mg) which after distillation (50° at 0.1 mmHg) had $[\alpha]_D^{20}$ −11.2° (*c*, 0.76); $\nu_{max.}$ 1 758 (C=O), 1 678 (C=O), 1 212 (OAc), 1 168, and 1 008 cm^{-1}; δ 0.99, 1.06, 1.11, 1.33 (3 H, each, s, CH_3), 1.195 (3 H, d, *J* 7 Hz, CH_3CH), and

2.09 (3 H, s, OAc); $\lambda_{max.}$ ($CHCl_3$) 246 nm (ε 625) (Found: C, 80.3; H, 10.6. $C_{22}H_{34}O_2$ requires C, 80.0; H, 10.4%).

Ozonolysis of Enol Acetate (4).—Enol acetate (4) (53 mg) in chloroform (20 ml) was treated with a stream of ozonised dry oxygen at −70° for 75 min, then purged with nitrogen and heated under reflux with water (30 ml) for 4 h. Work-up gave an oil (59 mg) which after p.l.c. with E–H (3 : 17) gave, at medium R_F, *enol acetate epoxide* (12) (10 mg). Enol acetate epoxide (12) after sublimation (55° at 0.02 mmHg) had $\nu_{max.}$ 1 752 (C=O), 1 218 (OAc), 1 167, and 1 012 cm^{-1} (Found: C, 76.6; H, 10.1. $C_{22}H_{34}O_3$ requires C, 76.3; H, 9.9%).

Reaction of Periodic Acid with Enol Acetate Epoxide (12).—The epoxide (5 mg) in acetone (15 ml) was heated under reflux with 50% periodic acid dihydrate (0.025 ml) for 40 min. Work-up gave an oil (14 mg) which contained as the main product, *α-acetoxy-ketone* (13) which had $\nu_{max.}$ (film) 1 750 (C=O), 1 725 (C=O), 1 216 (OAc), and 1 030 cm^{-1}; δ 0.99, 1.03, 1.31, 1.58 (3 H each, s, CH_3), 1.21 (3 H, d, *J* 7 Hz, CH_3CH), and 2.09 (3 H, s, OAc) (Found: C, 76.3; H, 9.8. $C_{22}H_{34}O_3$ requires C, 76.3; H, 9.9%).

Autoxidation of Ketone (9).—Ketone (9) (271 mg) in t-butyl alcohol (20 ml) was added to a solution of potassium t-butoxide made by reacting potassium (1.83 g) with t-butyl alcohol (50 ml). The solution was stirred under oxygen at atmospheric pressure and room temperature for 5 h. Dilution with water and ether extraction gave a complex non-acidic fraction (45 mg) containing some unchanged starting material. Acidification and ether extraction of the aqueous layer gave a mixture of two keto-acids (279 mg) in the ratio 97 : 3. The major product, *keto-acid* (14), after recrystallisation from aqueous ethanol and sublimation (70° at 0.01 mmHg) had m.p. 129—132°; $\nu_{max.}$ 3 500—2 400 (OH of carboxylic acid), 1 694 (C=O), 1 676 (C=O), and 1 408 cm^{-1}, $\nu_{max.}$ (CCl_4) 1 688 cm^{-1}; δ 1.5, 1.15, 1.19, 1.45 (3 H each, s, CH_3), 1.03 (3 H, d, *J* 6 Hz, CH_3CH), 2.57 (1 H, d, *J* 14 Hz, $HCHCO_2H$), and 2.90 (1 H, d, *J* 14 Hz, $HCHCO_2H$); $\lambda_{max.}$ (EtOH) 220 (ε 312) and 281 nm (78) (Found: C, 75.3; H, 10.1. $C_{20}H_{32}O_3$ requires C, 75.0; H, 10.1%). The minor keto-acid (15) had $\nu_{max.}$ 1 706 (C=O) and 1 689 (C=O) cm^{-1}.

Autoxidation of large quantities of the ketone (1—10 g) was accomplished in 5 h by adding the ketone to a solution of potassium t-butoxide made by reacting potassium (7.8 g) with t-butyl alcohol (200 ml) and treating with oxygen as above.

Keto-esters (16) *and* (17).—The keto-acid mixture (1.3 g) obtained from autoxidation of ketone (9) was dissolved in ether (20 ml), treated with an excess of an ethereal solution of diazomethane, and kept overnight. Evaporation of the solvent under reduced pressure gave a mixture of keto-esters which was separated by multiple p.l.c. (3×) with E–B (1 : 99) to give *keto-ester* (16) (1.29 g) and *keto-ester* (17) (63 mg). Keto-ester (16) after distillation (50° at 0.02 mmHg) had $[\alpha]_D^{20}$ +58° (*c*, 0.64); $\nu_{max.}$ (film) 1 730 (C=O), 1 677 (C=O), 1 200 (ester), and 1 010 cm^{-1}, $\nu_{max.}$ (CCl_4) 1 687 cm^{-1}; δ 1.13, 1.15, 1.19, 1.39 (3 H each, s, CH_3), 1.02 (3 H, d, *J* 6.5 Hz, CH_3CH), 2.51 (1 H, d, *J* 14 Hz, $HCHCO_2R$), 2.92 (1 H, d, *J* 14 Hz, $HCHCO_2R$), 3.61 (3 H, s, CH_3OC=O), and 3.2 [apparent quartet, CH_3CH–C(O)C]; $\lambda_{max.}$ (EtOH) 212 (ε 131), 300 nm (30) (Found: C, 75.4; H, 10.4. $C_{21}H_{34}O_3$ requires C, 75.4; H, 10.3%). Keto-ester (17) after sublimation (90° at 0.1 mmHg) had $\nu_{max.}$ (film) 1 733 (C=O), 1 682 (C=O), 1 224 (ester), and 1 008 cm^{-1}; $\nu_{max.}$ (CCl_4) 1 689 cm^{-1}; δ 1.10, 1.27, 1.42, 1.49 (3 H each, s, CH_3), 1.07 (3 H, d, *J* 6 Hz, CH_3CH), 1.95 (1 H, d, *J* 13 Hz, $HCHCO_2R$), 2.61 (1 H, d, *J* 13 Hz, $HCHCO_2R$), 3.62 (3 H, s, CH_3OC=O), and 2.8 [apparent quartet, CH_3CH–C(O)C] (Found: C, 75.2; H, 10.2. $C_{21}H_{34}O_3$ requires C, 75.4; H, 10.3%).

Attempted Separation of Keto-ester Mixture on Alumina.—The crude keto-ester mixture (2.469 g) was adsorbed from hexane on to neutral alumina (300 g; grade 1). Elution with E–H (3 : 17) gave a mixture which indicated that rearrangement had occurred (t.l.c.). Elution with ether–ethanol (1 : 1) gave a complex mixture of neutral products (1.2 g) and elution with 2M aqueous potassium hydroxide gave a mixture of acidic products (1.1 g). Sequential reduction with lithium aluminium hydride in dry ether at room temperature and oxidation with Jones reagent in acetone at room temperature of both mixtures produced similar mixtures (t.l.c.) which were combined and separated into a neutral fraction (804 mg) and an acid fraction (1.4 g). Separation of the neutral fraction by p.l.c. with E–H (3 : 7) gave a mixture of lactones (22) and (23) (250 mg). Methylation of the acid fraction with diazomethane and separation by p.l.c. with E–H (1 : 4) gave, at lower R_F value, a new *keto-ester* (604 mg) and, at higher R_F, a mixture (200 mg) containing keto-ester (17) with a trace of keto-ester (16).

The new keto-ester after sublimation (80° at 0.01 mmHg) had $\nu_{max.}$ (film) 1 737 (C=O), 1 690 (C=O), 1 197 (ester), and 1 007 cm^{-1}; δ 1.03, 1.05, 1.10, 1.13 (3 H each, s, CH_3) 0.96 (3 H, d, *J* 8 Hz, CH_3CH), 2.42 (1 H, d, *J* 12 Hz, $HCHCO_2R$), 3.06 (1 H, d, *J* 12 Hz, $HCHCO_2R$), 3.61 (3 H, s, CH_3OC=O) (Found: C, 75.1; H, 10.3. $C_{21}H_{34}O_3$ requires C, 75.4; H, 10.3%).

Lithium Aluminium Hydride Reduction of Keto-ester (17).—A solution of keto-ester (17) (114 mg) in dry ether (10 ml) was stirred at room temperature with the hydride (10 mg) for 41 h. Work-up in the usual way followed by p.l.c. on silica gel with E–H (3 : 7) gave the *ketol* (18) (82 mg), m.p. 100—101° (sublimed sample); $\nu_{max.}$ 3 370 (OH) and 1 680 (C=O) cm^{-1}; δ 1.08, 1.23, 1.34, 1.45 (3 H each, s, CH_3), 1.09 (3 H, d, *J* 7 Hz, CH_3CH), and 3.64 (2 H, m, CH_2OH) (Found: C, 78.3; H, 11.4. $C_{20}H_{34}O_2$ requires C, 78.4; H, 11.2%).

Reaction of Phenylmagnesium Bromide with Keto-ester (16).—Keto-ester (16) (47 mg) in dry ether (10 ml) was heated under reflux with phenylmagnesium bromide prepared by reacting magnesium (150 mg) with dry bromobenzene (1.5 g) in dry ether (10 ml). After 2 h methanol was added and the mixture acidified and worked-up to give an oil (94 mg). P.l.c. with E–H (3 : 7) gave a keto-alcohol assigned structure (19) (19 mg) (high R_F) which had $\nu_{max.}$ 3 471sh (OH), 1 669 (C=O), 1 593, 775, 747, 700, and 693 (aromatic) cm^{-1}; δ 1.00, 1.00, 1.09, 1.23 (3 H each, s, CH_3), 1.035 (3 H, d, *J* 7 Hz, CH_3CH), 3.04 (2 H, s, CH_2CO-Ar), and 7.10—7.60 (10 H, m, Ar). A satisfactory analysis could not be obtained for this unstable compound.

Lithium Aluminium Hydride Reduction of Keto-ester (16).—Keto-ester (16) (197 mg) in dry ether (40 ml) was stirred with excess of lithium aluminium hydride at room temperature for 5 min. Work-up involved acidifying with 2M-HCl and evaporating the solvent at less than 35° and, gave an oil (190 mg). Multiple p.l.c. (3×) with E–H (1 : 4) gave, at medium R_F value, a hemiacetal (24) (70 mg) and, at slightly higher R_F value, the epimeric hemiacetal (24) (80 mg). Multiple p.l.c. (4×) of the remainder with E–H (1 : 1) gave, at lower R_F value, diol (20) (16 mg) and, at higher R_F value, diol (21) (9 mg). The unstable

hemiacetals (24) were kept overnight in hexane at 0° and equilibrated to a mixture containing almost completely [the lower R_F hemiacetal (24) which had $\nu_{max.}$ 3 603sh and 3 336 (OH), 1 142, 1 104, and 1 020 cm^{-1}; δ 1.11, 1.11, 1.17, 1.27 (3 H each, s, CH_3), 0.995 (3 H, d, J Hz, CH_3CH), 3.745 (1 H, d, J 9 Hz, $CHOR$), and 5.24 (1 H, t, J 7 Hz, $CHOH$). Diol (20) had $\nu_{max.}$ 3 560sh (OH), 3 320br (OH), and 1 021 cm^{-1}; δ 1.00, 1.09, 1.31, 1.31 (3 H, each, s, CH_3), 0.99 (3 H, d, J 7 Hz, CH_3CH), 3.58—3.79 (2 H, m, CH_2OH), 3.95 (1 H, s, $CHOH$). Diol (21) had $\nu_{max.}$ 3 440sh, 3 450sh, 3 356br and 3 230 (OH), and 1 020 cm^{-1}; δ 1.11, 1.11, 1.15, 1.33 (3 H each, s, CH_3), 3.70 (2 H, m, CH_2OH), and 3.75 (1 H, d, J 8 Hz, $CHOH$).

Reduction with lithium aluminium hydride in ether at either 0° or at reflux temperature gave a similar mixture to that obtained above. Satisfactory analyses could not be obtained but the structures were confirmed by subsequent reactions.

Lactone (23).—Oxidation of the mixture of hemiacetals (24) in acetone with Jones reagent at room temperature gave *lactone* (23) which after distillation (70° at 0.02 mmHg) had $\nu_{max.}$ 1 748 (C=O), 1 277 (ester), and 1 024 cm^{-1}; δ 1.09, 1.09, 1.20, 1.38 (3 H each, s, CH_3), 1.11 (3 H, d, J 6 Hz, CH_3CH), 2.20 (1 H, d, J 17 Hz, $HCHCO_2R$), 2.61 (1 H, d, J 17 Hz, $HCHCO_2R$), and 3.90 (1 H, d, J 9 Hz, $CHOC{=}O$) (Found: C, 78.7; H, 10.5. $C_{20}H_{32}O_2$ requires C, 78.9; H, 10.6%).

Oxidation of Diol (20).—Diol (20) (16 mg) in acetone (5 ml) was stirred with excess of Jones reagent at room temperature for 5 min. Work-up gave an oil (25 mg) from which multiple p.l.c. (4×) with E–H (3 : 7) gave, at low R_F value, keto-acid (14) (3 mg), and at medium R_F value, *lactone* (22) (10 mg) which after distillation (50° at 0.02 mmHg) had $\nu_{max.}$ (film) 1 736 (C=O), 1 260 (ester), and 1 006 cm^{-1}; δ 1.11, 1.11, 1.15, 1.38 (3 H each, s, CH_3), 1.08 (3 H, d, J 6 Hz, CH_3CH), 2.27 (1 H, d, J 18 Hz, $HCHCO_2R$), 2.82 (1 H, d, J 18 Hz, $HCHCO_2R$), and 4.35 ($CHOC{=}O$) (Found: C, 79.0; H, 10.7. $C_{20}H_{32}O_2$ requires C, 78.9; H, 10.6%).

Oxidation of Diol (21).—The diol (9 mg) in acetone (5 ml) was stirred with excess of Jones reagent at room temperature for 5 min. Work-up gave an oil (10 mg) from which multiple p.l.c. (4×) with E–H (3 : 7) gave, at low R_F value, keto-acid (14) (3 mg) and, at medium R_F value, lactone (23) (6 mg).

Preparation of Lactones (22) *and* (23).—(a) Keto-ester (16) (900 mg) in dry ether (70 ml) was stirred with lithium aluminium hydride at room temperature for 5 min. Work-up carried out at less than 35° gave an oil which was dissolved in pure acetone (100 ml) and stirred with Jones reagent (0.75 ml) at room temperature for 5 min. Dilution with water and extraction with ether gave an organic layer which was washed with 1M aqueous sodium hydroxide to extract acids. Further work-up as usual gave an acid fraction (28 mg) of keto-acid (14) and a neutral fraction (810 mg) from which p.l.c. with E–H (1 : 1) gave a mixture of lactones (22) and (23) (740 mg).

(b) Keto-acid (14) (84 mg) in dry ether (20 ml) was stirred with lithium aluminium hydride (50 mg) at room temperature for 5 min. Work-up carried out at <35° gave an oil which was dissolved in pure acetone (10 ml) and stirred with Jones reagent (0.1 ml) at room temperature for 5 min. Work-up gave an acid fraction (6 mg) of keto-acid (14) and a neutral fraction from which p.l.c. with E–H (1 : 1) gave a mixture of lactones (22) and (23) (55 mg).

(c) Lactones (22) and (23) could also be prepared by sequential reduction and oxidation of the mixture of keto-esters (16) and (17) as described above. The acid fraction contained the two keto-acids (14) and (15), and p.l.c. with E–H (1 : 1) of the neutral fraction gave a mixture of lactones (22) and (23) which were separated with difficulty by multiple p.l.c. (6×) with E–H (1 : 4).

Reaction of Phenylmagnesium Bromide with Lactone (23).—Lactone (23) (15 mg) in dry ether (10 ml) was heated under reflux with dry bromobenzene (0.6 g) and magnesium (60 mg) for 90 min. When cool, methanol was added to destroy excess of reagent and the mixture acidified with 2M-hydrochloric acid and worked-up to give an oil. P.l.c. with hexane solvent gave, at medium R_F value, *phenyl vinyl ether* (25) (11 mg) which after sublimation (90° at 0.02 mmHg) had m.p. 95.5—98°; $\nu_{max.}$ 1 667 (C=C), 1 598 and 1 574 (Ar), 814 (C=C), 763, and 688 (Ar) cm^{-1}; δ 1.01, 1.04, 1.24, 1.34 (3 H each, s, CH_3), 1.20 (3 H, d, J 7 Hz, CH_3CH), 3.395 (1 H, d, J 9 Hz, $CHOR$), 4.88 (1 H, s, CH=C), and 7.00—7.60 (5 H, m, phenyl) (Found: C, 85.7; H, 10.1. $C_{26}H_{36}O$ requires C, 85.7; H, 10.0%).

Reaction of Phenylmagnesium Bromide with Lactone (22).—The lactone (12 mg) was reacted with excess of phenylmagnesium bromide as for lactone (23). P.l.c. of the crude product with hexane gave *phenyl vinyl ether* (26) (6 mg) which after sublimation (90° at 0.02 mmHg) had m.p. 148—149°; $\nu_{max.}$ 1 643 (C=C), 762, 749, and 685 (Ar) cm^{-1}; δ 1.03, 1.11, 1.13, 1.42 (3 H each, s, CH_3), 1.13 (3 H, d, J 6 Hz, CH_3CH), 4.24 (1 H, s, CHOR), 5.20 (1 H, s, CH=C), and 7.00—7.60 (5 H, m, phenyl) (Found: C, 85.7; H, 10.0. $C_{26}H_{36}O$ requires C, 85.7; H, 10.0%).

Phenyl Vinyl Ethers (25) *and* (26).—The mixture of lactones (930 mg) from sequential reduction–oxidation of keto-ester (16) was dissolved in dry ether and stirred under nitrogen at 0°. Three equivalents of phenyl-lithium in ether were added quickly. After 1 min saturated aqueous ammonium chloride (20 ml) was added and the mixture worked-up to give an oil which was dissolved in ethanol (90 ml) and ether (40 ml). This solution was stirred with 2M-hydrochloric acid (40 ml) at room temperature. Work-up after 1 h gave an oil (1.48 g) which was adsorbed from hexane onto alumina (90 g). Elution with hexane gave an oil (1.14 g) and elution with ether gave an oil (195 mg). The ether fraction, after p.l.c., gave a mixture of lactones (22) and (23) containing mostly lactone (22). The hexane fraction, after p.l.c. with hexane, gave, at medium R_F, phenyl vinyl ether (25) (686 mg) and, at higher R_F, phenyl vinyl ether (26) (189 mg).

Cleavage of Phenyl Vinyl Ether (25).—(a) Vinyl ether (25) (40 mg) was dissolved in pure acetone (5.5 ml) containing water (0.3 ml) and stirred at room temperature with ruthenium dioxide (3 mg) and sodium periodate (150 mg) for 8 h. Sodium periodate (150 mg) was added and the mixture stirred for a further 28 h. Work-up gave an oil (58 mg) which after p.l.c. with E–H (1 : 4) gave, near the base-line, *acid-ester* (28) (14 mg) and, at medium R_F, aldehyde-ester (27) (19 mg). Acid-ester (28) had m.p. 165—180°; $\nu_{max.}$ 3 550—2 500 (OH of carboxylic acid), 1 724 (C=O), 1 690 (C=O), 1 598 and 1 581 (Ar), 1 310, 1 267 (ester), and 710 (Ar) cm^{-1}; δ (CCl_4), 1.15, 1.26, 1.50, 1.51 (3 H each, s, CH_3), 0.805 (3 H, d, J 7 Hz, CH_3CH), 5.575 (1 H, d, J 7 Hz, $CHOC{=}O$), and 7.16—7.93 (5 H, m, Ar) (Found: C, 75.4; H, 8.7. $C_{26}H_{36}O_4$ requires C, 75.7; H, 8.8%). Aldehyde-ester (27) had $\nu_{max.}$ (film) 2 723 (aldehyde), 1 710br (C=O), 1 599 and 1 580 (Ar), 1 310, 1 262 (ester), and 712 (Ar) cm^{-1}; δ(CCl_4) 1.20, 1.32, 1.34, 1.40 (3 H

each, s, CH_3), 0.835 (3 H, d, J 7 Hz, CH_3CH), 5.46 (1 H, d, J 8 Hz, $CHOC{=}O$), 7.34—7.99 (5 H, m, Ar), and 9.37 (1 H, s, $CH{=}O$). Aldehyde-ester (27) was unstable in air and could not be analysed satisfactorily but could be stored under vacuum.

(b) Vinyl ether (25) (2.03 g) in dry ether (45 ml) and 85% formic acid (28 ml) was heated to 35—40° and treated with 30% hydrogen peroxide (2.8 ml) with stirring under nitrogen at 35—40° for 1.2 h. Work-up included washing with saturated aqueous sodium hydrogencarbonate and gave an oil (2.2 g) containing only aldehyde-ester (27) (t.l.c.).

(c) Vinyl ether (25) (50 mg) in chloroform was treated with ozonised dry oxygen at −70° for 10 min by which time a blue colour had developed. The solvent was removed under reduced pressure at 25°, replaced by acetone (10 ml), and the mixture stirred with an excess of Jones reagent at room temperature for 1 h. Work-up gave an oil (57 mg) which after p.l.c. gave acid-ester (28) (14 mg) and aldehyde-ester (27) (13 mg).

(d) The vinyl ether (42 mg) was treated with ozone as in (c) and the solution after purging with nitrogen was stirred under hydrogen at room temperature with 10% palladium–charcoal. Work-up gave an oil (51 mg) containing aldehyde-ester (27) (16 mg).

Cleavage of Phenyl Vinyl Ether (26).—Vinyl ether (26) (25 mg) in ether (3 ml) and 85% formic acid (0.75 ml) was heated to 35—40° and treated with 30% hydrogen peroxide (0.08 ml) with stirring under nitrogen at 35—40° for 1.2 h. Work-up gave an oil (29 mg) from which p.l.c. with E–H (3 : 7) gave unstable crystalline aldehyde-ester (29) (22 mg) which was stored under vacuum. Aldehyde-ester (29) had $\nu_{max.}$ (film) 2 720 (aldehyde), 1 721br (C=O), 1 597 and 1 581 (Ar), 1 311, 1 260 (ester), and 711 (Ar) cm^{-1}; $\delta(CCl_4)$ 1.18, 1.24, 1.36, 1.49 (3 H each, s, CH_3), 1.08 (3 H, d, J 8 Hz, CH_3CH), 5.52 (1 H, s, CHOC=O), 7.20—8.00 (5 H, m, Ar), and 9.30 (1 H, s, CH=O).

Reaction of Phenyl-lithium with Aldehyde-ester (27).—Aldehyde-ester (27) (156 mg) in dry ether (14 ml) was stirred under nitrogen at room temperature with an excess of phenyl-lithium. Work-up after 20 min gave an oil (321 mg) which after p.l.c. with E–H (7 : 13) gave, at medium R_F, a main band (123 mg). Partial separation by multiple p.l.c. (4×) with E–H (1 : 9) gave, at lower R_F, *diol* (30) (46 mg) which after sublimation (85° at 0.01 mmHg) had m.p. 133—134.5°; $\nu_{max.}$ (film) 3 560br and 3 440br (OH), 1 596 (Ar), 754, and 704 (Ar) cm^{-1}; $\delta(CCl_4)$ 0.95, 0.99, 1.22, 1.42 (3 H each, s, CH_3), 1.005 (3 H, d, J 7 Hz, CH_3CH), 3.99 (1 H, d, J 8 Hz, $CHOH$), 5.34 (1 H, s, $ArCHOH$), and 7.18 (5 H, m, Ar) (Found: C, 81.0; H, 10.1. $C_{25}H_{38}O_2$ requires C, 81.0; H, 10.3%), and alcohol-ester (31) (59 mg) which had $\nu_{max.}$ (film) 3 498 (OH), 1 703 and 1 689 (C=O), 1 596 and 1 580 (Ar), 1 312, 1 274 (ester), and 712 and 703 (Ar) cm^{-1}, $\delta(CCl_4)$ 1.05, 1.27, 1.56, 1.74 (3 H each, s, CH_3), 0.89 (3 H, d, J 7 Hz, CH_3CH), 4.67 (1 H, s, $ArCHOH$), 5.885 (1 H, d, J 7 Hz, $CHOC{=}O$), and 6.80—7.90 (10 H, m, Ar). Reaction of aldehyde-ester (27) with phenylmagnesium bromide at room temperature for 1 h gave a similar mixture of products.

Reduction of Alcohol-ester (31).—The mixture of products from the reaction of phenylmagnesium bromide and aldehyde-ester (27) was heated under reflux in ether with excess of lithium aluminium hydride for 3 h. Work-up followed by p.l.c. gave diol (30).

Attempted Oxidation of Diol (30; R = Ph).—Crude diol (30) (60 mg) in pure acetone (10 ml) was stirred with Jones reagent at room temperature for 2 min. Work-up gave an oil (57 mg). P.l.c. with E–H (1 : 9) gave, at medium R_F value, a mixture of olefins (53) and (43) (24 mg).

Alcohol-ester (32).—Aldehyde-ester (27) (170 mg) in dioxan (22.5 ml) containing methanol (22.5 ml) and water (4.5 ml) was stirred with sodium borohydride (180 mg) at room temperature for 30 min. Work-up and p.l.c. with E–H (1 : 1) gave *alcohol-ester* (32) (151 mg) which had m.p. 124—128.5° (decomp.); $\nu_{max.}$ (film) 3 460br (OH), 1 706 (C=O), 1 598 and 1 581 (Ar), 1 312, 1 268 (ester), and 712 (Ar) cm^{-1}; $\delta(CCl_4)$ 1.17, 1.24, 1.31, 1.39 (3 H each, s, CH_3), 0.87 (3 H, d, J 7 Hz, CH_3CH), 2.375 (1 H, d, J 13 Hz, HCH), 2.71 (1 H, t, J 8 Hz, $CHCH_2$), 3.35 (2 H, s, CH_2OH), 5.30 (1 H, d, J 6 Hz, $CHOC{=}O$), and 7.33—8.10 (5 H, m, Ar) (Found: C, 77.8; H, 9.7. $C_{26}H_{38}O_3$ requires C, 78.4; H, 9.6%).

Reaction of Lead Tetra-acetate with Alcohol-ester (32).—The alcohol-ester (32) (180 mg) in dry benzene (5 ml) containing dry pyridine (0.3 ml) was stirred under dry nitrogen with acid-free lead tetra-acetate (232 mg) at room temperature for 30 min, then with heating under reflux for a further 4.5 h. Work-up gave an oil (169 mg) which was separated by multiple p.l.c. (2×) with E–H (3 : 17) to give, at low R_F, unchanged starting material (24 mg), at medium R_F, aldehyde-ester (27) (27 mg), at slightly higher R_F, an unidentified product (13 mg), and at highest R_F, the mixture of olefin-esters (53) and (43) (64 mg), $\nu_{max.}$ 1 710 (C=O), 1 698 and 1 581 (Ar), 1 311, 1 267 (ester), and 712 (Ar) cm^{-1}. The n.m.r. spectrum showed no acetate absorption.

Jones Oxidation of Aldehyde-ester (27).—The aldehyde (27) (2.2 g) in pure acetone (140 ml) was stirred with Jones reagent (10 ml) at room temperature under dry, oxygen-free nitrogen for 6 h. Additional Jones reagent (5 ml) was added and stirring was continued for a further 16 h. Jones reagent (5 ml) was again added, and stirring continued for a further 80 h, when the mixture was worked up to give an oil (2.351 g). Crystallisation from hexane gave acid-ester (28) (1.1 g) and p.l.c. of the residue with E–H (3 : 7) gave, at low R_F acid-ester (28) (0.5 g) and at high R_F, a mixture of olefin esters (53) and (43) (0.4 g).

Methyl Ester of (28).—Acid-ester (28) (25 mg) in ether (10 ml) was treated with excess of diazomethane in ether and kept at room temperature for 1.2 h. Evaporation of the solvent *in vacuo* and p.l.c. gave the methyl ester (16 mg) which after distillation (80° at 0.01 mmHg) had $\nu_{max.}$ (film) 1 742—1 712 (C=O), 1 600 and 1 583 (Ar), 1 310, 1 273—1 260 (ester), 770, and 707 (Ar) cm^{-1}; $\delta(CCl_4)$ 1.18, 1.29, 1.43, 1.51 (3 H each, s, CH_3), 0.825 (3 H, d, J 7 Hz, CH_3CH), 2.03 (3 H, s, OAc), 5.05 (1 H, d, J 7 Hz, $CHOC{=}O$), and 7.26—8.04 (5 H, m, Ar) (Found: C, 75.7; H, 9.0. $C_{27}H_{38}O_4$ requires C, 76.0; H, 9.0%).

Oxidative Decarboxylation of Acid-ester (28).—Acid (28) (1.6 g) in dry benzene (40 ml) containing dry pyridine (2.4 ml) was stirred under dry, oxygen-free nitrogen with acetic acid-free lead tetra-acetate (1.76 g) at room temperature for 1 h and then with heating under reflux for 40 min. When cool, ethylene glycol (0.5 ml) was added, and the mixture worked up. Washing with 2M-hydrochloric acid removed any lead salt and gave an oil (1.4 g). P.l.c. with E–H (1 : 19) gave a mixture of olefin-esters (1.3 g). Partial separation of this mixture by multiple p.l.c. (4×) with E–H (1 : 4) gave, at medium R_F, olefin-ester (53) and, at slightly higher R_F, olefin-ester (43). Olefin-ester (53) had $\nu_{max.}$ (film) 3 069 ($CH_2{=}C$), 1 707 (C=O), 1 643 (C=C), 1 599 and 1 580 (Ar), 1 311, 1 269 (ester), 889, 880 (C=C), and

706 (Ar) cm^{-1}; δ(CCl_4) 0.98, 1.00, 1.07 (3 H each, s, CH_3), 0.845 (3 H, d, *J* 7 Hz, CH_3CH), 4.72br (1 H, HC*H*=C), 4.77br (1 H, HC*H*=C), 5.46 (1 H, d, *J* 8 Hz, CHOC=O), and 7.26—7.97 (5 H, m, Ar). Olefin-ester (43) had $\nu_{max.}$ (film) 3 063 (C=C), 1 705 (C=O), 1 642 (C=C), 1 599 and 1 580 (Ar), 1 311, 1 270 (ester), 858, 842 (C=C), and 710 (Ar) cm^{-1}; δ(CCl_4) 0.94, 0.94, 1.04 (3 H each, s, CH_3), 0.865 (3 H, d, *J* 7 Hz, CH_3CH), 1.595 (3 H, d, *J* 1 Hz, CH_3C=C), 2.60 (1 H, t, *J* 9 Hz, $CHCH_2$), 4.85br (1 H, CH=C), 5.33 (1 H, d, *J* 8 Hz, CHOC=O), and 7.22—8.00 (5 H, m, Ar). A mixture of (53) and (43) (1.6 g) in dry ether (100 ml) was heated under reflux with excess of lithium aluminium hydride for 5 h. Work-up and multiple p.l.c. (2×) with E–H (1 : 19) gave, at medium R_F, *olefin-alcohol* (45) (760 mg) and, at higher R_F, *olefin-alcohol* (55) (240 mg). Olefin-alcohol (45) after distillation (35° at 0.01 mmHg) had $\nu_{max.}$ (film) 3 551sh (OH), 861, and 848 (C=C) cm^{-1}; δ 0.94, 1.00, 1.08 (3 H each, s, CH_3), 1.00 (3 H, d, *J* 7 Hz, CH_3CH), 1.64 (3 H, d, *J* 1 Hz, CH_3C=C), 2.42 (1 H, t, *J* 9 Hz, $CHCH_2$), 3.455 (1 H, d, *J* 9 Hz, CHOH), 5.18 (1 H, q, *J* 1 Hz, C*H*=CCH_3) (Found: C, 82.7; H, 11.6. $C_{18}H_{30}O$ requires C, 82.4; H, 11.5%) Olefin-alcohol (55) after distillation (35° at 0.01 mmHg) had $\nu_{max.}$ (film) 3 567sh (OH), 3 064 and 1 634 (C=C), and 887 (C=CH_2) cm^{-1}; δ 0.89, 1.03, 1.03 (3 H each, s, CH_3), 0.995 (3 H, d, *J* 7 Hz, CH_3CH), 3.665 (1 H, d, *J* 7 Hz, CHOH), 4.74 (1 H, m, *W* 6 Hz, HC*H*=C), and 5.09 (1 H, m, *W* 4 Hz, HC*H*=C) (Found: C, 82.7; H, 11.5. $C_{18}H_{30}O$ requires C, 82.4; H, 11.5%).

Similar Jones oxidation of aldehyde-ester (29) followed by oxidative decarboxylation gave a mixture of olefin-esters (54) and (44). The intermediate acid-ester was not isolated.

Reduction of Olefin-esters (54) *and* (44).—Reduction as described above of a mixture of (54) and (44) (160 mg) gave olefin-alcohols (56) and (46). Multiple p.l.c. (2×) with E–H (1 : 19) gave, at lower R_F, *olefin-alcohol* (46) (90 mg) and, at higher R_F value, olefin-alcohol (56) (20 mg; estimated from mixtures). Olefin-alcohol (56) after distillation (55° at 0.01 mmHg) had $\nu_{max.}$ (film) 3 626 and 3 492 (OH), 882, 856, and 839 (C=C) cm^{-1}; δ 0.95, 1.00, 1.03 (3 H each, s, CH_3), 0.965 (3 H, d, *J* 7 Hz, CH_3CH), 1.915 (3 H, d, *J* 1 Hz, CH_3C=C), 3.595 (1 H, d, *J* 3 Hz, CHOH), and 5.095 (1 H, d, *J* 1 Hz, C*H*=CCH_3) (Found: C, 82.2; H, 11.5. $C_{18}H_{30}O$ requires C, 82.4; H, 11.5%). Olefin-alcohol (56) had $\nu_{max.}$ (film) 3 520br (OH), 3 077 and 1 635 (C=C), and 897 (C=CH_2) cm^{-1}; δ 0.82, 0.96, 0.98 (3 H each, s, CH_3), 0.94 (3 H, d, *J* 7 Hz, CH_3CH), 3.45 (1 H, s, CHOH), 5.03 (2 H, m, $W_{\frac{1}{2}}$ 9 Hz, CH_2=C). The alcohol could not be obtained completely free from the olefin-alcohol (46) (Found: C, 82.5; H, 11.7. $C_{18}H_{30}O$ requires C, 82.4; H, 11.5%).

Olefin-ketone (47).—(a) Olefin-alcohol (45) (34 mg) in pure acetone was stirred with an excess of Jones reagent at room temperature for 5 min. Work-up and p.l.c. with E–H (1 : 9) gave olefin-ketone (47) (30 mg) which after distillation (50° at 0.01 mmHg) had $\nu_{max.}$ (film) 1 692 (C=O) and 855 (C=C) cm^{-1}; δ 0.85, 0.97, 1.07 (3 H each, s, CH_3), 1.035 (3 H, d, *J* 7 Hz, CH_3 CH), 1.795 (3 H, d, *J* 1 Hz, CH_3 C=C), and 5.115 (1 H, q, *J* 1 Hz, C*H*=C–CH_3) (Found: C, 82.8; H, 11.2. $C_{18}H_{28}O$ requires C, 83.0; H, 10.8%).

(b) Olefin-alcohol (46) was oxidised as in (a) and gave olefin-ketone (47).

Isomerisation of Olefin-alcohol (55).—A solution of olefin alcohol (55) (100 mg) and toluene-*p*-sulphonic acid (100 mg) in chloroform (3 ml) was kept at room temperature for 50 h. Work-up in the usual way followed by p.l.c. on silica gel with E–H (1 : 19) gave olefin-alcohol (45) (75 mg).

Oxetan (49).—Olefin-alcohol (55) (50 mg) in chloroform (5 ml) was treated with 85% *m*-chloroperbenzoic acid (52 mg) and kept at room temperature for 12 h. Work-up and p.l.c. with E–H (1 : 1) gave *oxetan* (49) (40 mg) which after sublimation (65° at 0.01 mmHg) had m.p. 80—83°; $\nu_{max.}$ (film) 3 430br (OH), 1 012, 985, and 845 cm^{-1}; δ 1.02, 1.15, 1.37 (3 H each, s, CH_3), 0.905 (3 H, d, *J* 7 Hz, CH_3CH), 3.63 (1 H, *J* 12 Hz, HCHOH), 4.33 (1 H, d, *J* 12 Hz, HC*H*-OH), and 4.07 (1 H, d, *J* 12 Hz, CHOR) (Found: C, 77.8; H, 10.8. $C_{18}H_{30}O_2$ requires C, 77.6; H, 10.7%).

Acetylation of Oxetan (49).—Oxetan (49) (28 mg) in dry pyridine (5 ml) was treated with acetic anhydride (2 ml) and kept at room temperature for 3 days. Work-up and p.l.c. with E–H (1 : 1) gave *acetate-oxetan* (50) which after distillation (65° at 0.01 mmHg) had $\nu_{max.}$ (film) 1 742 (C=O), 1 236 (OAc), 1 019, 970, and 847 cm^{-1}; δ 1.03, 1.12, 1.38 (3 H, each, s, CH_3), 0.915 (3 H, d, *J* 7 Hz, CH_3CH), 2.06 (3 H, s, OAc), 4.33 (1 H, d, *J* 12 Hz, CHOR), and 4.39 (2 H, s, CH_2OAc) (Found: C, 75.0; H, 10.1. $C_{20}H_{32}O_3$ requires C, 75.0; H, 10.1%).

Olefin-ketone (62).—Olefin-alcohol (55) (32 mg) in pure acetone (5 ml) was stirred with excess of Jones reagent (0.5 ml) at room temperature for 5 min. Work-up and p.l.c. with E–H (1 : 19) gave *olefin-ketone* (62) (27 mg) which after distillation (50° at 0.01 mmHg) had $\nu_{max.}$ (film) 3 088 (C=C), 1 700 (C=O), 1 648 (C=C), 886, and 880 (C=CH_2) cm^{-1}; δ 0.73, 0.97, 0.97 (3 H each, s, CH_3) 1.035 (3 H, d, *J* 7 Hz, CH_3CH), 3.14 (1 H, m, $W_{\frac{1}{2}}$ 22 Hz), 4.90 (1 H, m, HC*H* = C), and 5.30 (1 H, m, HC*H* = C) (Found: C 83.2; H, 10.9. $C_{18}H_{28}O$ requires C, 83.0; H, 10.8%).

Acetylation of Olefin-alcohol (45).—A solution of olefin alcohol (45) (90 mg) and toluene-*p*-sulphonic acid in isopropenyl acetate (3 ml) was kept at room temperature for 66 h. Work-up in the usual way, followed by p.l.c. on silica gel with E–H (1 : 24) gave *olefin acetate* (48) (75 mg) (distilled at 89° and 0.02 mmHg); $\nu_{max.}$ 1 730, 1 240 (acetate), and 1 640 (C=C) cm^{-1}; δ 0.88, 0.95, 1.10 (3 H each, s, CH_3), 0.82 (3 H, d, *J* 6.5 Hz, CH_3CH), 1.56 (3 H, d, *J* 1 Hz, CH_3C=CH), 1.94 (3 H, s, $OCOCH_3$), 4.92 (1 H, s, C*H*=C), and 5.01 (1 H, d, *J* 8.5 Hz, *H*COAc) (Found: C, 78.7; H, 10.7. $C_{20}H_{32}O_2$ requires C, 78.9; H, 10.6%).

Attempted Acetylation of Olefin-alcohol (55).—(a) A solution of olefin alcohol (55) (107 mg) in dry pyridine (0.5 ml) and acetic anhydride (0.5 ml) was kept at room temperature for 48 h. Work-up in the usual way gave unchanged starting material (100 mg).

(b) A solution of olefin alcohol (55) (99 mg) and toluene-*p*-sulphonic acid (10 mg) in isopropenyl acetate (3 ml) was kept at room temperature for 41 h. Work-up in the usual manner gave an inseparable mixture of olefin acetates (57) and (48) (Found: C, 78.6; H, 10.7. $C_{20}H_{32}O_2$ requires C, 78.9; H, 10.6%).

Epoxidation of Olefin-alcohol (45).—Olefin alcohol (45) (43 mg) in chloroform (3 ml) was treated with *m*-chloroperbenzoic acid (35 mg) at room temperature for 24 h. Work-up gave an oil (49 mg), and p.l.c. with E–H (1 : 9) gave, in order of increasing R_F, *alcohol-oxetan* (51) (9 mg) and epoxide-alcohol (64) (23 mg). Since (64) rearranged to (51) on silica gel, the bands were removed directly on developing. Alcohol-oxetan (51) after sublimation (65° at 0.01 mmHg) had $\nu_{max.}$ 3 318 (OH), 1 067, and 1 010 cm^{-1}; δ 1.08, 1.14, 1.22 (3 H each, s, CH_3), 0.895 (3 H, d, *J* Hz, CH_3CH), 1.51 (3 H, s, CH_3CO), 3.39 (1 H, s, CHOH), and

4.36 (1 H, d, J 12 Hz, C*H*OR) (Found: C, 77.8; H, 10.8. $C_{18}H_{30}O_2$ requires C, 77.7; H, 10.9%). Epoxide-alcohol (64) had $\nu_{max.}$ (film) 3 450 (OH), 1 383, 1 125, 843, and 736 cm^{-1}; δ 1.10, 1.10, 1.11 (3 H each, s, CH_3), 0.995 (3 H, d, J 7 Hz, CH_3CH), 1.53 (3 H, s, CH_3CO), 2.56 (1 H, t, J 8 Hz, C*H*CH_2), 2.99 (1 H, s, CH of oxiran), and 3.775 (1 H, d, J 9 Hz, C*H*OH).

Rearrangement of Epoxide-alcohol (64).—The epoxide-alcohol (64) (23 mg) in dry ether (10 ml) was treated with boron trifluoride–ether (1 drop) and kept at room temperature for 25 min. Work-up gave an oil (23 mg) containing alcohol-oxetan (51) and an aldehyde, estimated in the ratio 1 : 1 by integral analysis of the n.m.r. spectrum. The aldehyde was unstable in air and was not isolated. The crude oil had $\nu_{max.}$ (film) 3 430 (OH), 2 695 (CHO), 1 725 (C=O), and 1 010 cm^{-1}; δ 3.39 (s, C*H*OH), 4.37 (d, J 12 Hz, C*H*OR), and 9.58 (s, CH=O).

Ketone-oxetan (52).—Alcohol-oxetan (51) (11 mg) in pure acetone (5 ml) was stirred with excess of Jones reagent at room temperature for 15 min. Work-up and p.l.c. with E–H (1 : 3) gave *ketone-oxetan* (52) (8 mg) which after distillation (70° at 0.01 mmHg) had $\nu_{max.}$ 1 737 (C=O), 1 007, 981, and 823 cm^{-1}; δ 1.05, 1.13, 1.47, 1.50 (3 H each, s, CH_3), 0.90 (3 H, d, J 6 Hz, CH_3CH), 2.785 (1 H, dd, J 7, 10 Hz, C*H*CH_2), and 4.58 (1 H, d, J 11 Hz, C*H*OR) (Found: C, 78.0; H, 10.4. $C_{18}H_{28}O_2$ requires C, 78.2; H, 10.2%).

Reaction of Performic Acid with Olefin-alcohol (45).—The olefin-alcohol (45) (115 mg) in ether (8 ml) and 85% formic acid (8 ml) was heated to 35° and treated with 30% hydrogen peroxide (0.8 ml). The mixture was stirred at 35—40° for 1 h, and then worked-up to give an oil (131 mg). P.l.c. with E–H (1 : 1) gave, at low R_F, alcohol-oxetan (51) (6 mg) and, at medium R_F, *ketone-alcohol* (33) (118 mg) which after sublimation (75° at 0.02 mmHg) had m.p. 143—145°; $\nu_{max.}$ 3 450 (OH), 1 725 (C=O), and 982 cm^{-1}; $\nu_{max.}$ (0.1M in CCl_4) 1 736 (C=O) cm^{-1}; δ 0.97, 1.09, 1.13 (3 H each, s, CH_3), 0.95 (3 H, d, J 6 Hz, CH_3CH), 1.11 (3 H, d, J 7 Hz, CH_3CH), 2.43 (1 H, m, C*H*CH_3), and 3.56 (1 H, d, J 9 Hz, C*H*OH) (Found: C, 78.0; H, 10.9. $C_{18}H_{30}O_2$ requires C, 77.6; H, 10.9%). When the reaction temperature was increased to 40—45°, the ratio of (51) : (33) was changed to 1 : 6.

Diketone (34).—Ketone-alcohol (33) (76 mg) in pure acetone (10 ml) was stirred with excess of Jones reagent at room temperature for 10 min. Work-up and p.l.c. with E–H (3 : 7) gave *diketone* (34) (64 mg) which after sublimation (60° at 0.01 mmHg) had m.p. 104—107°; $\nu_{max.}$ 1 735 (C=O), 1 680 (C=O), and 1 015 cm^{-1}; δ 0.97, 1.02, 1.18 (3 H, each, s, CH_3), 1.02 (3 H, d, J 6 Hz, CH_3CH), and 1.215 (3 H, d, J 7 Hz, CH_3CH) (Found: C, 78.3; H, 10.3. $C_{18}H_{28}O_2$ requires C, 78.2; H, 10.2%).

Ozonolysis of Olefin-alcohol (45).—The olefin-alcohol (45) (95 mg) in chloroform (30 ml) was treated with ozonised dry oxygen at −70° for 1 h, then kept at −70° for 1.8 h. Removal of the solvent at room temperature gave a mixture (103 mg). P.l.c. with E–H (1 : 9) gave, at medium R_F value, olefin-ketone (47) (12 mg), and p.l.c. of the remainder with E–H (1 : 1) gave, at low R_F, the *olefin-ketol* (58) (51 mg) which after sublimation (65° at 0.01 mmHg) had $\nu_{max.}$ (film) 3 440br (OH), 3 094 (C=C), 1 691 (C=O), 1 650 (C=C), 892 (C=CH_2), and 841 cm^{-1}; δ 0.54, 0.91, 1.06 (3 H each, s, CH_3), 1.025 (3 H, d, J 7 Hz, CH_3CH), 3.16 (1·H, m, $W_{\frac{1}{2}}$ 20 Hz), 4.06 (1 H, t, J 2 Hz, C*H*OH), 5.17 (1 H, d, J 2 Hz, HC*H*=C), and 5.52 (1 H, d, J 2 Hz, HC*H*=C) (Found: C, 78.3; H, 10.4. $C_{18}H_{28}O_2$ requires C, 78.2; H, 10.2%).

Ozonolysis of Olefin-ketone (47).—A stream of dry ozonised oxygen was passed through a solution of the olefin-ketone (47) (118 mg) in chloroform (30 ml) at −70° for 1 h then the solvent removed at room temperature. P.l.c. on silica gel with E–H (2 : 3) gave *olefin-ketol* (59) (77 mg), m.p. 132—134° (sublimed sample); $\nu_{max.}$ 3 505 (OH), 3 075, 1 645, 915 (C=CH_2), and 1 685 (C=O) cm^{-1}; δ 0.66, 1.03, 1.04 (3 H, each, s, CH_3), 1.01 (3 H, d, J 6.5 Hz, CH_3–CH), 3.87br (1 H, *H*C–OH), 5.16br (1 H, HC*H*=C), 5.66br (1 H, HC*H*=C) (Found: C, 78.5; H, 10.2. $C_{18}H_{28}O_2$ requires C, 78.2; H, 10.2%).

Oxidation of Olefin-ketol (58).—Chromium trioxide (67 mg) was added to a stirred solution of dry pyridine (110 mg) in dry dichloromethane (2 ml) at room temperature. After stirring for 45 min a solution of the olefin-ketol (58) (31 mg) in dry dichloromethane (3 ml) was added and stirring continued for a further 25 min. Excess of reagent was destroyed by the addition of methanol (1 ml), hexane (50 ml) was added, and the mixture filtered. The filtrate was washed with water, dried over magnesium sulphate, and evaporated. P.l.c. on silica gel with E–H (1 : 1) gave *olefin-diketone* (60) (20 mg), m.p. 77—80° (distilled sample); $\nu_{max.}$ 3 090, 1 625 (C=CH_2, conjugated), 1 720 (conjugated ketone), and 1 695 (C=O) cm^{-1}; δ 0.78, 0.78, 1.09 (3 H each, s, CH_3), 1.06 (3 H, d, J 6.5 Hz, CH_3CH), 5.45 (1 H, d, J 0.7 Hz, HC*H*=C), and 6.44 (1 H, d, J 0.7 Hz, HC*H*=C); $\lambda_{max.}$ 230 nm (ε 8 800) (Found: C, 78.9; H, 9.8. $C_{18}H_{26}O_2$ requires C, 78.8; H, 9.6%).

Oxidation of Olefin-ketol (59).—Chromium trioxide (22 mg) was added to a stirred solution of dry pyridine (37 mg) in dichloromethane (1 ml) at room temperature. After stirring for 45 min, a solution of the olefin-ketol (59) (9 mg) in dry dichloromethane (1.5 ml) was added and stirring continued for a further 25 min. Work-up as for oxidation of olefin-ketol (58) followed by p.l.c. on silica gel with E–H (1 : 1) gave olefin diketone (60) (6 mg).

Ozonolysis of Olefin-alcohol (46).—A stream of dry ozonised oxygen was passed through a solution of the olefin-alcohol (46) (157 mg) in chloroform (30 ml) at −70° for 1 h. The resulting solution was kept at −70° for 1 h then the solvent removed at room temperature. P.l.c. on silica gel with E–H (2 : 3) gave *olefin-diol* (61) (32 mg) in addition to complex aldehyde mixtures. Olefin diol (61) had $\nu_{max.}$ 3 430 (OH), 3 080, 1 640, and 900 (C=CH_2) cm^{-1}; δ 0.76, 0.99, 1.05 (3 H each, s, CH_3), 1.02 (3 H, d, J 6.5 Hz, CH_3-CH), 3.10br (1 H, C*H*–OH), 3.97 (1 H, t, J 2 Hz, C*H*OH), 5.12 (1 H, d, J 2 Hz, HC*H*=C), and 5.31 (1 H, d, J 2 Hz, HC*H*=C) (Found: C, 77.7; H, 10.7. $C_{18}H_{30}O_2$ requires C, 77.7; H, 10.9%).

Epoxidation of Olefin-acetate (48).—A solution of the olefin-acetate (48) (32 mg) in dichloromethane (5 ml) was treated with *m*-chloroperbenzoic acid (32 mg) at room temperature for 48 h. Work-up in the usual way, followed by p.l.c. on silica gel with E–H (1 : 9) gave *epoxy-acetate* (65) (29 mg) (distilled at 100° and 0.02 mmHg); $\nu_{max.}$ 1 730 (acetate) cm^{-1}; δ 1.02, 1.18, 1.23, 1.19 (3 H each, s, CH_3), 0.82 (3 H, d, J 6 Hz, CH_3CH), 2.03 (3 H, s, OCOCH_3), 2.66 (1 H, s, O·C·C*H*), and 5.06 (1 H, d, J 7 Hz, C*H*OAc). (Found: C, 75.2; H, 9.9. $C_{20}H_{32}O_3$ requires C, 75.0; H, 10.1%).

Attempted Opening of Epoxy-acetate (65).—A solution of epoxy-acetate (65) (96 mg) in tetrahydrofuran (14 ml) was treated with 60% perchloric acid (7 ml) at room temperature for 20 min. Work-up in the usual way followed by

p.l.c. on silica gel with E–H (2 : 3) gave *keto-acetate* (35) (82 mg) (distilled at 100° and 0.012 mmHg); $\nu_{max.}$ 1 742 (C=O), 1 730 (C=O), 1 225 (OAc), 1 011, and 951 cm^{-1}; δ 1.01, 1.11, 1.19 (3 H, each, s, CH_3), 0.80 (3 H, d, *J* 7 Hz, CH_3CH), 0.91 (3 H, d, *J* 7 Hz, CH_3CH), 1.85 (3 H, s, $OCOCH_3$), 2.48 (1 H, m, $CHCH_3$), and 4.89 (1 H, d, *J* 8 Hz, CHOAc) (Found: C, 75.4; H, 10.4. $C_{20}H_{32}O_3$ requires C, 75.0; H, 10.1%).

Epoxide-ketone (66).—Olefin-ketone (47) (20 mg) in chloroform (10 ml) was treated with *m*-chloroperbenzoic acid (25 mg) and kept at room temperature for 12 h. Work-up and p.l.c. with E–H (1 : 19) gave *epoxide-ketone* (66) (15 mg) which after sublimation (55° at 0.01 mmHg) had m.p. 107—115°; $\nu_{max.}$ 1 688 (C=O), 1 129, and 748 cm^{-1}; δ 0.82, 1.03, 1.25 (3 H each, s, CH_3), 1.035 (3 H, d, *J* 7 Hz, CH_3CH), 1.67 (3 H, s, CH_3CO), and 2.84 (1 H, s, CH of oxiran) (Found: C, 78.0; H, 10.2. $C_{18}H_{28}O_2$ requires C, 78.2; H, 10.2%).

N-*Bromosuccinimide on Ketol* (33).—A solution of the ketol (33) (150 mg) in carbon tetrachloride (15 ml) was refluxed with *N*-bromosuccinimide (143 mg) for 35 min. The reaction mixture was cooled in ice and the succinimide removed by filtration. Evaporation and p.l.c. on silica gel with E–H (1 : 1) gave keto-oxetan (52) (32 mg) and, at lower R_F, unchanged ketol (33) (51 mg).

Autoxidation of Ketol (33).—A solution of the ketol (33) (140 mg) and potassium t-butoxide (1.5 g) in t-butyl alcohol (37 ml) was stirred under oxygen for 24 h at 30°. The mixture was acidified with 2M-sulphuric acid and extracted with ether (3×). The combined ether extracts were washed with water, then extracted with sodium hydrogencarbonate solution (3×). Drying the ether portion (Na_2SO_4) and evaporation gave a complex neutral fraction (69 mg) which was not investigated further. The combined hydrogencarbonate extracts were acidified with 2M-sulphuric acid and extracted with ether (3×). The combined ether extracts were washed with water, dried (Na_2SO_4), and evaporated to give an acid fraction (72 mg). P.l.c. on silica gel with ethyl formate–toluene–formic acid (4 : 5 : 1) gave a compound, possibly the *hydroxydicarboxylic acid* (63) (45 mg) (distilled at 150° 0.01 mmHg); $\nu_{max.}$ 2 700—3 400 (OH) and 1 700 (C=O) cm^{-1} (Found: C, 65.9; H, 8.6. $C_{17}H_{28}O_5$ requires C, 65.4; H, 9.0%).

Attempted Enol Acetylation of Ketone-alcohol (33).—The ketone-alcohol (33) (125 mg) in isopropenyl acetate (20 ml) containing toluene-*p*-sulphonic acid monohydrate (30 mg) was heated at 40° for 16 h. Work-up and p.l.c. with E–H (3 : 7) gave, in order of increasing R_F value, starting material (16 mg), keto-acetate (35) (22 mg), and *hemiacetal acetate* (67) (73 mg). Hemiacetal acetate (67) after sublimation (64° at 0.01 mmHg) had $\nu_{max.}$ 1 750 (C=O), 1 247 and 1 240 (OAc), 1 121, 1 094, and 947 cm^{-1}; δ 0.93, 1.08, 1.14 (3 H each, s, CH_3), 1.08 (3 H, d, *J* 6 Hz, CH_3CH), 1.11 (3 H, d, *J* 6 Hz, CH_3CH), 2.06 (3 H, s, OAc), 3.05 (1 H, q, *J* 6 Hz, $CHCH_3$), and 3.795 (1 H, d, *J* 9 Hz, CHOR) (Found: C, 75.2; H, 10.2. $C_{20}H_{32}O_3$ requires C, 75.0; H, 10.1%). When the reaction was carried out under reflux for 4 h with a slow distillation of the solvent, complete reaction to a similar mixture of (35) and (67) resulted.

Reduction of Hemiacetal Acetate (67).—The hemiacetal acetate (67) (15 mg) in dry ether (10 ml) was treated with excess of lithium aluminium hydride and kept at room temperature for 59 h. Work-up and p.l.c. with E–H (1 : 1) gave diol (37) (6 mg) and diol (36) (3 mg).

Reduction of Ketone-alcohol (33).—The ketone-alcohol (33) (21 mg) in dry ether (9 ml) was heated under reflux with excess of lithium aluminium hydride for 1 h. Work-up and p.l.c. with E–H (1 : 1) gave, in order of increasing R_F value, *diol* (36) (3 mg) and *diol* (37) (12 mg). Diol (36) after sublimation (75° at 0.02 mmHg) had m.p. 178—180°; $\nu_{max.}$ 3 180br (OH) and 1 016 cm^{-1}; δ 0.98, 1.00, 1.09 (3 H each, s, CH_3), 0.995 (3 H, d, *J* 7 Hz, CH_3CH), 1.045 (3 H, d, *J* 7 Hz, CH_3CH), 3.435 (1 H, d, *J* 7 Hz, CHOH), and 3.555 (1 H, d, *J* 9 Hz, CHOH) (Found: C, 76.7; H, 11.4. $C_{18}H_{32}O_2$ requires C, 77.1; H, 11.5%). Diol (37) after sublimation (85° at 0.02 mmHg) had m.p. 65—67.5°; $\nu_{max.}$ (crystals) 3 430 (OH), 1 418, 1 356, 1 337, 1 050, and 982 cm^{-1}; δ 0.85, 1.03, 1.05 (3 H each, s, CH_3), 0.935 (3 H, d, *J* 7 Hz, CH_3CH), 1.10 (3 H, d, *J* 6 Hz, CH_3CH), 3.645 (1 H, d, *J* 7 Hz, CHOH), 3.97 (1 H, d, *J* 10 Hz, CH–OH) (Found: C, 77.3; H, 11.5. $C_{18}H_{32}O_2$ requires C, 77.1; H, 11.5%).

Reduction of Keto-acetate (35).—The keto-acetate (35) (20 mg) in dry ether (10 ml) was treated with excess of lithium aluminium hydride and kept at room temperature for 30 min. Work-up gave a product (17 mg) consisting mainly of diol (36) with a trace of diol (37) (t.l.c.).

Diol (38).—Aldehyde ester (27) (90 mg) in dry ether was stirred with excess of lithium aluminium hydride at room temperature for 15 min. Work-up included washing with 2M-hydrochloric acid and evaporation of solvents under reduced pressure at less than 45° and gave an oil (81 mg) Purification by p.l.c. gave *diol* (38) (58 mg) which after sublimation (80° at 0.03 mmHg) had m.p. 97—100°; $\nu_{max.}$ (film) 3 320br (OH), 1 056, and 1 022 cm^{-1}; δ 1.14, 1.14, 1.14, 1.35 (3 H each, s, CH_3), 1.005 (3 H, d, *J* 7 Hz, CH_3CH), 3.48 (1 H, d, *J* 11 Hz, HCHOH), 4.05 (1 H, d, *J* 11 Hz, HCHOH), 3.745 (1 H, d, *J* 7 Hz, CH–OH) (Found: C, 77.7; H, 11.7. $C_{19}H_{34}O_2$ requires C, 77.5; H, 11.6%). When the product was subjected to strong heat during work-up, the main product isolated was ether (68).

Ether (68).—Diol (38) (15 mg) in dry pyridine (1 ml) was stirred with recrystallised toluene-*p*-sulphonyl chloride (11 mg) at 0° for 1 h. Little reaction had occurred and the mixture was kept at room temperature for 25 h. Work-up and p.l.c. with E–H (1 : 49) gave *ether* (68) (9 mg) which after distillation (51° at 0.04 mmHg) had $\nu_{max.}$ (film) 1 079 and 1 064 cm^{-1}; δ 0.99, 1.15, 1.18, 1.19 (3 H each, s, CH_3), 1.04 (3 H, d, *J* 6 Hz, CH_3CH), 3.23 (1 H, d, *J* 9 Hz, HCHOR), 3.61 (1 H, d, *J* 9 Hz, HCHOR), and 3.45 (1 H, d, *J* 9 Hz, CHOR) (Found: C, 82.5; H, 11.8. $C_{19}H_{32}O$ requires C, 82.5; H, 11.7%).

Ether (69).—Aldehyde-ester (29) (17 mg) in dry ether (5 ml) was stirred with excess of lithium aluminium hydride at room temperature for 10 min. Work-up gave an oil (18 mg) which had $\nu_{max.}$ (film) 3 250 (OH) cm^{-1}. This oil was dissolved in dry pyridine (1 ml) and treated with recrystallised toluene-*p*-sulphonyl chloride at room temperature. Work-up after 74 h and p.l.c. with E–H (3 : 47) gave *ether* (69) (8 mg) which after distillation (50° at 0.02 mmHg) had $\nu_{max.}$ (film) 1 048 and 944 cm^{-1}; δ 1.10, 1.12, 1.18, 1.31 (3 H each, s, CH_3), 1.065 (3 H, d, *J* 7 Hz, CH_3CH), 3.49 (1 H, d, *J* 9 Hz, HCHOR), 3.73 (1 H, d, *J* 9 Hz, HCHOR), and 4.22 (1 H, s, CHOR). (Found: C, 82.3; H, 11.6. $C_{19}H_{32}O$ requires C, 82.5; H, 11.7%).

Tosylate-ester (40).—Alcohol-ester (32) (125 mg) in dry pyridine was treated with recrystallised toluene-*p*-sulphonyl chloride (120 mg) at room temperature for 26 h. Work-up included washing with 2M-hydrochloric acid and removal of solvents under reduced pressure at less than 35° and gave the crystalline *tosylate-ester* (40) which had

$\nu_{max.}$ (film) 1 705 (C=O), 1 597 and 1 581 (Ar), 1 357 (SO_2–O), 1 260 (ester), 1 188, and 1 174 (SO_2–O) cm^{-1}; δ(CCl_4) 1.19, 1.19, 1.29, 1.42 (3 H each, s, CH_3), 0.785 (3 H, d, *J* 7 Hz, CH_3CH), 2.36 (3 H, s, CH_3Ar), 3.71 (1 H, d, *J* 10 Hz, HC*H*OTs), 3.89 (1 H, d, *J* 10 Hz, HC*H*OTs), 5.15 (1 H, d, *J* 5 Hz, CHOC=O), and 7.01—7.96 (9 H, m, Ar). The tosylate decomposed during sublimation (90° at 0.01 mmHg).

Reduction of Tosylate-ester (40).—The tosylate-ester (40) (170 mg) in dry ether (20 ml) was treated with excess of lithium aluminium hydride at room temperature for 30 min. Work-up and p.l.c. gave ether (68) (62 mg).

Attempted Replacement of Tosylate by Chlorine.—Tosylate ester (40) (69 mg) in dry pyridine containing absolute ethanol (0.3 ml) was treated with pyridine hydrochloride (65 mg) at room temperature for 17 h. As no reaction occurred, the mixture was heated to 70—80° for 3 days. Work-up and p.l.c. gave ether (68) (21 mg).

Acetate-alcohol (41).—Diol (38) (347 mg) in dry pyridine (2 ml) was treated with a 1M solution of acid-free acetic anhydride in pyridine (2 ml) and kept for 25 h at room temperature. Work-up included washing with 2M-hydrochloric acid then with saturated aqueous sodium hydrogencarbonate and removal of solvents under reduced pressure at $<35°$ and gave the crude crystalline acetate-alcohol (41) (354 mg) which had $\nu_{max.}$ 3 465 (OH), 1 731br and 1 706 (C=O), 1 265 (OAc), and 1 023 cm^{-1}; δ 1.12, 1.12, 1.19, 1.39 (3 H each, s, CH_3), 0.985 (3 H, d, *J* 7 Hz, CH_3CH), 2.03 (3 H, s, OAc), 3.63 (1 H, d, *J* 8 Hz, C*H*OH), 4.23 (1 H, d, *J* 10 Hz, HC*H*OAc), and 4.63 (1 H, d, *J* 10 Hz, HC*H*OAc). Acetate-alcohol (41) rapidly rearranged on p.l.c. to ether (68) and no attempt was made to purify this product.

Acetate-ketone (42).—Crude acetate-alcohol (41) (43 mg) in pure acetone was stirred at room temperature with Jones reagent (0.02 ml) for 2 min, then Jones reagent (0.02 ml) was added, and stirring continued for a further 3 min. Work-up and p.l.c. with E–H (3 : 7) gave *acetate-ketone* (42) (33 mg) which after distillation (50° at 0.02 mmHg) had $\nu_{max.}$ (film) 1 728 (C=O), 1 676 (C=O), 1 230br (OAc), and 1 030 cm^{-1}; δ 1.08, 1.11, 1.20, 1.37 (3 H each, s, CH_3), 1.03 (3 H, d, *J* 6 Hz, CH_3CH), 2.02 (3 H, s, OAc), 3.87 (1 H, d, *J* 11 Hz, HC*H*OAc), and 4.19 (1 H, d, *J* 11 Hz, HC*H*OAc) (Found: C, 75.6; H, 10.4. $C_{21}H_{34}O_3$ requires C, 75.4; H, 10.3%).

Acetate-olefin (70).—Crude acetate-alcohol (41) (354 mg) in dry pyridine (20 ml) containing mesyl chloride (6 ml) was kept at room temperature with exclusion of moisture for 12 h, and then for a further 47 h at 35°. Work-up included washing with 2M-hydrochloric acid then with saturated aqueous sodium hydrogencarbonate and gave an oil (337 mg). P.l.c. with E–H (1 : 9) gave, at medium R_F, *acetate-olefin* (70) (158 mg), and, at higher R_F, ether (68) (20 mg). Acetate-olefin (70) after distillation (80° at 0.02 mmHg) had $\nu_{max.}$ (film) 1 739 (C=O), 1 233 (OAc), and 870 (CH=C) cm^{-1}; δ 1.09, 1.12, 1.27, 1.32 (3 H each, s, CH_3), 1.75br (3 H, s, CH_3C=CH), 2.02 (3 H, s, OAc), 4.05 (2 H, s, CH_2OAc), and 5.32br (1 H, s, CH=C) (Found: C, 79.3; H, 10.9. $C_{21}H_{34}O_2$ requires C, 79.2; H, 10.8%).

Epoxidation of Acetate-olefin (70).—Olefin (70) (62 mg) in chloroform (5 ml) was treated with *m*-chloroperbenzoic acid (50 mg) and the mixture kept at room temperature for 10 h. Work-up gave an oil (69 mg) containing the isomeric acetate epoxides (71). Partial separation was achieved by p.l.c. with E–H (3 : 7) which gave, at lower R_F, acetate-epoxide (71)—1 (36 mg) and, at higher R_F, acetate-epoxide (71)—2 (11 mg). Acetate-epoxide (71)—1 had $\nu_{max.}$ 1 738 (C=O), 1 241 (OAc), 1 026, and 900 cm^{-1}; δ 1.11, 1.15, 1.19, 1.33, 1.36 (3 H each, s, CH_3), 2.03 (3 H, s, OAc), 3.13 (1 H, s, CH of oxiran), 4.26 (1 H, d, *J* 11 Hz, HC*H*OAc), and 4.42 (1 H, d, *J* 11 Hz, HC*H*OAc). Acetate-epoxide (71)—2 had $\nu_{max.}$ (film) 1 743 (C=O), 1 233 (OAc), and 1 028 cm^{-1}; δ 1.12, 1.17, 1.19, 1.32, 1.32 (3 H each, s, CH_3), 2.06 (3 H, s, OAc), 2.84 (1 H, s, CH of oxiran), 4.08 (1 H, d, *J* 11 Hz, HC*H*OAc), and 4.23 (1 H, d, *J* 11 Hz, HC*H*OAc).

Rearrangement of Acetate-olefin (70).—The acetate-olefin (70) (14 mg) in a solution of chloroform (2 ml) and 98—100% formic acid (2 ml) was heated under reflux for 30 h. Work-up and p.l.c. with E–H (1 : 3) gave the rearranged *olefin* (72) (8 mg) which after distillation (80° at 0.01 mmHg) had $\nu_{max.}$ (film) 1 743 (C=O), 1 239 (OAc), and 838 (CH=C) cm^{-1}; δ 0.96, 1.10, 1.13, 1.31 (3 H each, s, CH_3), 1.71 br (3 H, s, CH_3C=CH), 2.02 (3 H, s, OAc), 4.08 (2 H, s, CH_2-OAc), and 5.37 (1 H, s, $W_{\frac{1}{2}}$ 11 Hz, C*H*=C) (Found: C, 79.4; H, 10.9. $C_{21}H_{34}O_2$ requires C, 79.2; H, 10.8%).

Epoxidation of Acetate-olefin (72).—Olefin (72) (30 mg) in chloroform (5 ml) was treated with *m*-chloroperbenzoic acid (40 mg) and kept at room temperature for 4 h. Work-up and p.l.c. with E–H (2 : 3) gave the *epoxide* (73) which after distillation (80° at 0.01 mmHg) had $\nu_{max.}$ (film) 1 740 (C=O), 1 237 (OAc), 1 026, and 748 cm^{-1}; δ 1.07, 1.12, 1.16, 1.32 (3 H each, s, CH_3), 1.45 (3 H, s, CH_3CO), 2.03 (3 H, s, OAc), 2.91 (1 H, t, *J* 3 Hz, CH of oxiran), 3.97 (1 H, d, *J* 11 Hz, HC*H*OAc), and 4.15 (1 H, d, *J* 11 Hz, HC*H*OAc) (Found: C, 75.1; H, 10.2. $C_{21}H_{34}O_3$ requires C, 75.4; H, 10.3%).

Rearrangement of Laurenene (1).—Laurenene (1) (110 mg) in chloroform (3 ml) containing 98—100% formic acid (3 ml) did not react at room temperature during 26 h. After heating under reflux for 15 h, the pink solution was worked up, including washing with saturated aqueous sodium hydrogencarbonate to give an oil (120 mg). P.l.c. on silver nitrate impregnated silica gel with hexane gave, at high R_F, *olefin* (74) (80 mg) which after distillation (50° at 0.01 mmHg) had $\nu_{max.}$ (film) 1 313, 1 150, and 975 cm^{-1}; δ 0.92, 0.99 (3 H each, s, CH_3), 0.72 (3 H, d, *J* 6 Hz, CH_3CH), and 1.53sbr and 1.58br (3 H each, s, CH_3–C=C) (Found: C, 88.2; H, 12.0. $C_{20}H_{32}$ requires C, 88.2; H, 11.8%).

Ozonolysis of Olefin (74).—Olefin (74) (60 mg) in ethyl acetate (20 ml) was treated with a stream of ozonised dry oxygen at $-70°$ for 15 min and the blue solution purged with nitrogen. The solution was then shaken with 10% palladium–charcoal under hydrogen at atmospheric pressure and room temperature for 100 min. Work-up gave an oil which after p.l.c. with E–H (1 : 3) gave, at medium R_F value, *diketone* (75) (26 mg) which after distillation (65° at 0.02 mmHg) had $\nu_{max.}$ (film) 1 713 (C=O), 1 672 (C=O), 1 428, 1 400, and 1 193 cm^{-1}; δ 1.05, 1.13 (3 H each, s, CH_3) 0.995 (3 H, d, *J* 7 Hz, CH_3CH), 1.98, and 2.32 (3 H each, s, CH_3C=O); $\lambda_{max.}$ (EtOH) 223 (ε 350), 225 (350), 251 (140), 276 (130), and 283 nm (130) (Found: C, 79.1; H, 10.7. $C_{20}H_{32}O_2$ requires C, 78.9; H, 10.6%).

Osmylation of Olefin (74).—Olefin (74) (97 mg) in dry dioxan (6 ml) and dry pyridine (7.5 ml) was stirred with osmium tetraoxide (100 mg) at room temperature. After 11 days water (10 ml) and sodium metabisulphite (3 g) were added and the mixture stirred at room temperature for 17 h. Work-up gave a solid (120 mg). P.l.c. (×2) with E–H (1 : 1) gave, at medium R_F a *diol* (56 mg) which after sublimation (85° at 0.01 mmHg) had $\nu_{max.}$ 3 446, 3 330 (OH), 1 181, 1 113, and 912 cm^{-1}; δ 1.04, 1.20 (3 H each,

s, CH_3), 1.015 (3 H, d, J 7 Hz, CH_3CH), 1.32, and 1.35 (3 H each, s, CH_3CO) (Found: C, 78.5; H, 11.3. $C_{20}H_{34}O_2$ requires C, 78.4; H, 11.2%). The diol (27 mg) in dry benzene (5 ml) was stirred under nitrogen at room temperature with lead tetra-acetate (99 mg; acetic acid-free) for 20 min, then ethylene glycol (9 drops) added. Work-up included washing with 2M-hydrochloric acid and gave pure diketone (75) (27 mg).

Epoxidation of Olefin (74).—The olefin (56 mg) in chloroform (5 ml) was treated with *m*-chloroperbenzoic acid (53 mg) at room temperature for 20 h. Work-up involved chloroform extraction and washing with 2M-sodium hydroxide and gave an oil (57 mg). P.l.c. with E–H (1 : 4) gave, at low R_F, a *hydroxy-epoxide* (11 mg) and, at high R_F, an *epoxide* (40 mg). The hydroxy-epoxide after sublimation (70° at 0.02 mmHg) had $\nu_{max.}$ 3 520sh (OH), 1 183, 1 176, 1 138, and 949 cm^{-1}; δ 1.02, 1.18 (3 H each, s, CH_3), 0.83 (3 H, d, J 6 Hz, CH_3CH), 1.25 (3 H, s, CH_3CO), 3.06 (1 H, d, J 4 Hz, $HCH{\cdot}C{\cdot}O$), 3.36 (1 H, d, J 4 Hz, $HCH{\cdot}C{\cdot}O$) (Found: C, 78.7; H, 10.7. $C_{20}H_{32}O_2$ requires C, 78.9; H, 10.6%). The epoxide after sublimation (40° at 0.01 mmHg) had $\nu_{max.}$ 842 cm^{-1}; δ 0.98, 1.01 (3 H, s, CH_3), 0.74 (3 H, d, J 7 Hz, CH_3CH), 1.29, 1.36 (3 H each, s, CH_3CO), 1.68 (2 H, s, CH_2CO) (Found: C, 83.1; H, 11.3. $C_{20}H_{32}O$ requires C, 83.3; H, 11.2%).

Reduction of Diketone (75).—Diketone (75) (50 mg) in dry ether was stirred at room temperature with excess of lithium aluminium hydride for 1.5 h. Work-up gave an oil (45 mg) which after multiple p.l.c. (4×) with E–H (3 : 2) gave, in order of increasing R_F value, *diol*-1 (15 mg), *diol*-2 (12 mg), and *diol*-3 (14 mg). Diol-1 after distillation (95° at 0.01 mmHg) had $\nu_{max.}$ 3 320br (OH) and 1 110br cm^{-1}; δ 1.07, 1.25 (3 H each, s, CH_3), 1.015 (3 H, d, J 7 Hz, CH_3CH), 1.22 (3 H, d, J 6 Hz, CH_3CHO), 1.34 (3 H, d, J 6 Hz, CH_3CHO), 1.825 (1 H, 'd, J 3 Hz', CH–C–O), 1.945 (1 H, 'd, J 7 Hz', $CHCO$), 4.05 (1 H, m, $W_{\frac{1}{2}}$ 15 Hz, $CHOH$), and 4.44 (1 H, q, J 7 Hz, CH–OH) (Found: C, 78.0; H, 11.7. $C_{20}H_{36}O_2$ requires C, 77.9; H, 11.8%). Diol-2 after sublimation (95° at 0.01 mmHg) had $\nu_{max.}$ 3 410 (OH), 1 118, 1 070, and 1 019 cm^{-1}; δ 1.00, 1.12 (3 H each, s, CH_3), 0.965 (3 H, d, J 7 Hz, CH_3CH), 1.205 (3 H, d, J 7 Hz, CH_3CHO), 1.25 (3 H, d, J 6 Hz, CH_3CHO), 3.95 (1 H, m, $W_{\frac{1}{2}}$ 17 Hz, $CHOH$), and 4.19 (1 H, q, J 6 Hz, $CHOH$) (Found: C, 78.0; H, 11.8. $C_{20}H_{36}O_2$ requires C, 77.9; H, 11.8%). Diol-3 after sublimation (95° at 0.01 mmHg) had $\nu_{max.}$ 3 425 (OH), 3 320 (OH), 1 099, and 1 012 cm^{-1}; δ 1.07, 1.13 (3 H each, s, CH_3), 1.055 (3 H, d, J 7 Hz, CH_3CH), 1.23 (3 H, d, J 6 Hz, CH_3CHO), 1.31 (3 H, d, J 6 Hz, CH_3CHO), 3.99 (1 H, m, $W_{\frac{1}{2}}$ 16 Hz, $CHOH$), and 4.43 (1 H, q, J 6 Hz, $CHOH$) (Found: C, 78.3; H, 11.5. $C_{20}H_{36}O_2$ requires C, 77.9; H, 11.8%).

[8/1018 *Received*, 1st *June*, 1978]

REFERENCES

[1] F. H. McDowell and H. J. Findlay, *J. Soc. Chem. Ind.*, 1925, **44**, 42T.
[2] L. H. Briggs and M. D. Sutherland, *J. Org. Chem.*, 1948, **13**, 1.
[3] D. R. Lauren, Ph.D. Thesis, University of Otago, 1971.
[4] (*a*) C. C. Hinckley, *J. Amer. Chem. Soc.*, 1969, **91**, 5160; (*b*) J. K. M. Sanders and D. H. Williams, *Chem. Comm.*, 1970, 422; (*c*) P. V. Demarco, T. K. Elgay, R. B. Lewis, and E. Wenkert, *J. Amer. Chem. Soc.*, 1970, **92**, 5734, 5737; (*d*) D. G. Buckley, G. H. Green, E. Ritchie, and W. C. Taylor, *Chem. and Ind.*, 1971, 298.
[5] M. Kitadani, H. Uda, and Y. Yoshikoshi, *Tetrahedron Letters*, 1966, 4843.
[6] P. S. Kalsi, *Perfumery and Essential Oil Record*, 1968, 786.
[7] R. D. Riecke and S. E. Bates, *J. Amer. Chem. Soc.*, 1974, **96**, 1775.
[8] (*a*) J. M. Coxon, M. P. Hartshorn, and D. N. Kirk, *Tetrahedron*, 1969, **25**, 2603; (*b*) R. C. Cambie and R. A. Francich, *Austral. J. Chem.*, 1970, **23**, 93.
[9] P. Chamberlain, M. L. Roberts, and G. H. Whitham, *J. Chem. Soc.* (*B*), 1970, 1374.
[10] W. L. Waters, A. J. Rollin, C. M. Bardwell, J. A. Schneider, and T. W. Aanerud, *J. Org. Chem.*, 1976, **41**, 889.
[11] A. C. Gripper Gray and H. Hart, *J. Amer. Chem. Soc.*, 1968, **90**, 2569.
[12] L. N. Nixon, Ph.D. Thesis, University of Otago, 1970.
[13] L. M. Jackman and S. Sternhell, 'Applications of Nuclear Magnetic Resonance in Organic Chemistry,' International Series of Monographs in Organic Chemistry, Pergamon Press, Oxford, 1969, vol. 5, p. 83.
[14] (*a*) E. J. Corey and S. Nazoe, *J. Amer. Chem. Soc.*, 1965, **87**, 5733; (*b*) O. E. Edwards and B. S. Mootoo, *Canad. J. Chem.*, 1969, **47**, 1189.
[15] C. R. Narayanan, M. R. Sarma, T. K. K. Srinivasan, and M. S. Wadia, *Canad. J. Chem.*, 1969, **47**, 1601.
[16] Ref. 13, p. 88.
[17] C. Djerassi, 'Optical Rotatory Dispersion,' McGraw–Hill, New York, 1960.
[18] R. E. Corbett and R. A. J. Smith, *J. Chem. Soc.* (*C*), 1969, **44**.