A Stereospecific Route to Trisubstituted Olefins *via* β-Lactones [1]

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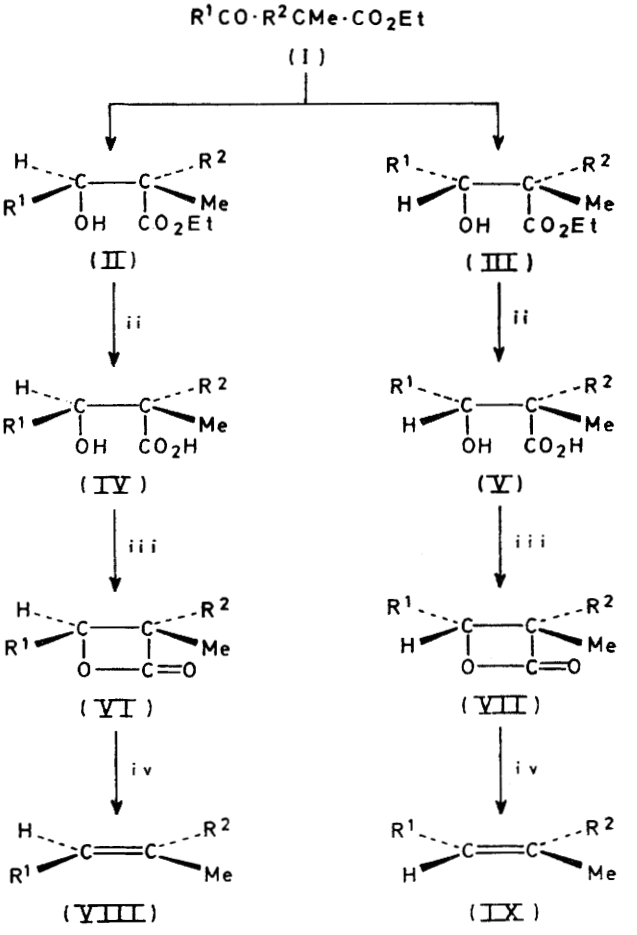
Diastereoisomeric αα-disubstituted β-hydroxy-acids have been converted into β-lactones, which on refluxing in collidine yielded *E*- or *Z*-olefins with high stereoselectivity. The mechanisms of these transformations are discussed.

As part of a study of the cyclisation of olefins to polycyclic systems,[2] new stereospecific methods for the synthesis of *Z*-trisubstituted olefins have been developed. The literature indicated that cycloreversion of β-lactones should provide olefins, but the stereospecificity was not defined.[3] However this reaction appeared attractive, as the required β-lactones could be prepared readily from the corresponding hydroxy-acids. In fact the β-lactones studied decomposed smoothly at moderate temperatures giving olefins with >95% stereospecificity.[1,4]

One of the olefins required for cyclisation studies was (*Z*)-12-benzyloxy-2,6-dimethyldodeca-1,5-dien-9-yne (VIIIb). It was envisaged that this could be obtained by thermolysis of the β-lactone (VIb), which in turn could be prepared by the sequence ethyl 6-methyl-3-oxohept-6-enoate [5] ⟶ ethyl 2-(6-benzyloxyhex-3-ynyl)-6-methyl-3-oxohept-6-enoate ⟶ (Ib) ⟶ (IIb) ⟶ (IVb) ⟶ (VIb) (Scheme 1). The feasibility of this sequence was tested with a model system. Thus ethyl 4-oxoheptanoate [6] was converted [7] *via* ethyl 2-butyl-3-oxoheptanoate into ethyl 2-butyl-2-methyl-3-oxoheptanoate (Ia) in 86% yield. Reduction of the oxo-ester (Ia) by borohydride afforded a mixture (52 : 48) of two diastereoisomeric alcohols, (IIa) and (IIIa), which were separated by preparative t.l.c.

Hydrolysis of the hydroxy esters (IIa) and (IIIa) with aqueous alcoholic sodium hydroxide gave the pure acids (IVa) and (Va), respectively, which reacted with methanesulphonyl chloride in pentane in the presence of anhydrous sodium carbonate giving the lactones (VIa) and (VIIa) in good yield. The lactones (VIa) and (VIIa) are formed stereospecifically and this conversion is assumed to take place with retention of configuration at the carbon atom carrying the hydroxy-group (*cf.* ref. 8). The mechanism (Scheme 2) involves initial



a; $R^1 = R^2 = [CH_2]_3Me$

b; $R^1 = CH_2·CH_2·CMe{:}CH_2$,

$R^2 = CH_2·CH_2·C{:}C·CH_2·CH_2·O·CH_2Ph$

SCHEME 1 Reagents: $NaBH_4$–MeOH; ii, aq. ethanolic NaOH, then H_3O^+; iii, $MeSO_2Cl$–$Me[CH_2]_3Me$–Na_2CO_3; iv, reflux in collidine

formation of the mixed anhydride (XI) followed by an internal nucleophilic displacement.

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[4] D. S. Noyce and E. H. Banitt, *J. Org. Chem.* 1966, **31**, 4043.

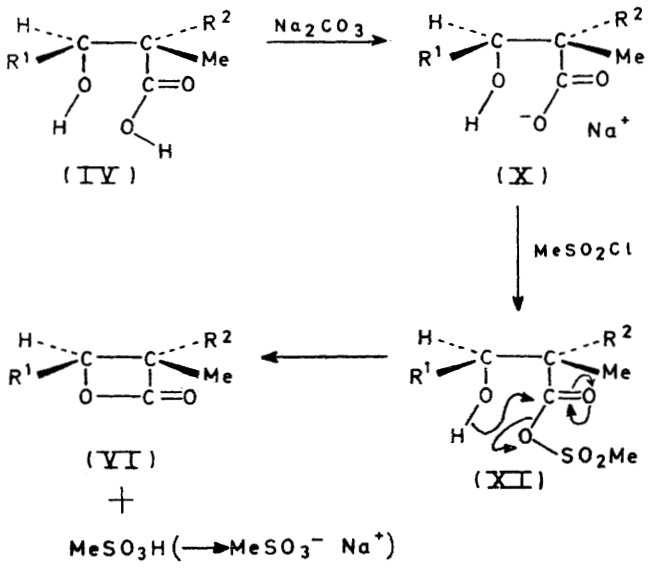
[5] M. S. Schechter, N. Green, and F. B. La Forge, *J. Amer. Chem. Soc.*, 1949, **71**, 3165.

[6] (*a*) G. W. Anderson, I. F. Halverstadt, W. H. Miller, and R. O. Roblin, *J. Amer. Chem. Soc.*, 1945, **67**, 2197; (*b*) D. S. Breslow, E. Baumgarten, and C. R. Hauser, *ibid.*, 1944, **66**, 1286.

[7] F. J. Marshall and W. N. Cannon, *J. Org. Chem.*, 1956, **21**, 245.

[8] (*a*) J. H. Brewster and C. H. Kucera, *J. Amer. Chem. Soc.*, 1955, **77**, 4564; (*b*) J. H. Brewster and C. J. Ciotti, *ibid.*, p. 6214; (*c*) W. Adam, J. Baeza, and J. C. Liu, *ibid.*, 1972, **94**, 2000.

The β-lactones (VIa) and (VIIa) were stable in refluxing pyridine but underwent smooth cycloreversion in refluxing collidine to give the (*Z*)- (VIIIa) and (*E*)-(IXa) 5-methyldec-5-ene, respectively, in good yields. The *Z*-olefin (VIIIa) was a single stereoisomer (g.l.c., n.m.r.) and the *E*-olefin (IXa) was obtained >95%

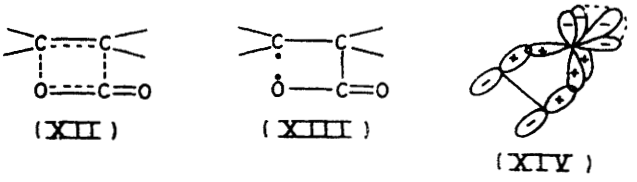


SCHEME 2

pure. Configurational assignments were based on the position of the =CMe n.m.r. signal, which appeared at τ 8.43 for the *Z*- and at τ 8.35 for the *E*-olefin.[9,10] Further support for the assignment of configurations was obtained from g.l.c. retention times[10] [(VIIIa) 4 min 54 s, (IXa) 4 min 15 s].

Ethyl 6-methyl-3-oxohept-6-enoate was prepared from 5-methylhex-5-en-2-one by reaction with diethyl carbonate in the presence of sodium hydride.[11] Alkylation of the oxo-ester with 6-benzyloxy-1-bromohex-3-yne in the presence of sodium ethoxide afforded ethyl 2-(6-benzyloxyhex-3-ynyl)-6-methyl-3-oxohept-6-enoate (52%), which reacted with methyl iodide in the presence of sodium hydride to give the dialkyl β-oxo-ester (Ib) in 67% yield. Reduction of the oxo-ester (Ib) with borohydride gave a mixture of diastereoisomeric alcohols, (IIb) and (IIIb), which were separated by t.l.c. These were converted into the β-lactones (VIb) and (VIIb), respectively, as described for the hydroxy-esters (IIa) and (IIIa). The lactone (VIIb) underwent smooth cycloreversion in refluxing collidine to give an olefin which was a single stereoisomer, assigned the structure (IXb). The lactone (VIb) under identical conditions gave a mixture containing at least 96% of the olefin (VIIIb). The olefin configurational assignments were again based on g.l.c. and n.m.r. evidence [(IXb) τ_{Me} 8.30, t_R 16 min 36 s; (VIIIb) τ_{Me} 8.39, t_R 17 min 54 s].

The thermal conversion of the β-lactones into olefins could be either a one-step reaction involving a cyclic transition state [*cf.* (XII)] or a two-step process involving a diradical intermediate [*cf.* (XIII)]. However the high degree of stereoselectivity observed supports the concerted mechanism, since a diradical of the type (XIII) would be expected to lose the stereochemical integrity rapidly.[12] A concerted thermal decarboxylation of the β-lactones would involve a four-membered cyclic transition state [*cf.* (XII)] and four electrons, and according to theories[13,14] of pericyclic reactions, such concerted processes have to be of the $[\sigma^2_s + \sigma^2_a]$ type. The transition state for this pathway would involve considerable twisting of the four-membered ring; therefore this pathway would be expected to be more energy-demanding than a stepwise reaction involving a 1,4-diradical [*cf.* (XIII)]. It has been found that the majority of cycloreversion reactions of cyclobutane derivatives[12] and the reverse reactions ([2 + 2] cycloaddition reactions of olefins[15]) take place by stepwise processes. However detailed studies on the cycloadditions of olefins to ketenes have shown that this reaction is a concerted process[16] and the preference for



a concerted pathway over the stepwise process in this case has been explained in terms of either a secondary orbital interaction[13] or an 'aromatic type transition state' involving six electrons.[14] For analogous reasons the cycloreversion reactions of β-lactones probably proceed by a concerted pathway rather than by a stepwise process. In the transition state (XIV) of this reaction the lactone ring is sufficiently twisted

[9] R. B. Bates and D. M. Gale, *J. Amer. Chem. Soc.*, 1960, **82**, 5749.
[10] A. van der Gen, K. Wiedhamp, J. J. Swoboda, H. C. Dunathan, and W. S. Johnson, *J. Amer. Chem. Soc.*, 1973, **95**, 2656.
[11] M. S. Schechter, N. Green, and F. B. La Forge, *J. Amer. Chem. Soc.*, 1949, **71**, 3165.
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[13] R. B. Woodward and R. Hoffmann, *Angew. Chem. Internat. Edn.*, 1969, **8**, 781.
[14] M. J. S. Dewar, *Angew. Chem. Internat. Edn.*, 1971, **10**, 761.
[15] (*a*) R. Gompper, *Angew, Chem. Internat. Edn.*, 1969, **8**, 312; (*b*) R. Huisgen, R. Grashey, and J. Sauer in 'The Chemistry of Alkenes,' ed. S. Patai, Interscience, New York, 1964, p. 741; (*c*) L. L. Muller and J. Hamer, '1,2-Cycloaddition Reactions,' Interscience, New York, 1967; (*d*) P. D. Bartlett, *Quart. Rev.*, 1970, **24**, 473; (*e*) P. D. Bartlett, *Science*, 1968, **159**, 833; (*f*) K. Kraft and G. Koltzenberg, *Tetrahedron Letters*, 1967, 4357, 4723.
[16] (*a*) R. Montague and L. Ghosez, *Angew. Chem. Internat. Edn.*, 1968, **1**, 221; (*b*) R. Huigen and P. Otto, *Tetrahedron Letters*, 1968, 4491; (*c*) R. Huisgen, K. A. Feiler, and P. Otto, *Chem. Ber.* 1969, **102**, 3405, 3444; (*d*) R. Huisgen, L. A. Feiler, and G. Binsch, *ibid.*, p. 3460; (*e*) R. Huisgen and L. A. Feiler, *ibid.*, pp. 3391, 3428; (*f*) R. Huisgen and P. Otto, *ibid.*, p. 3475.

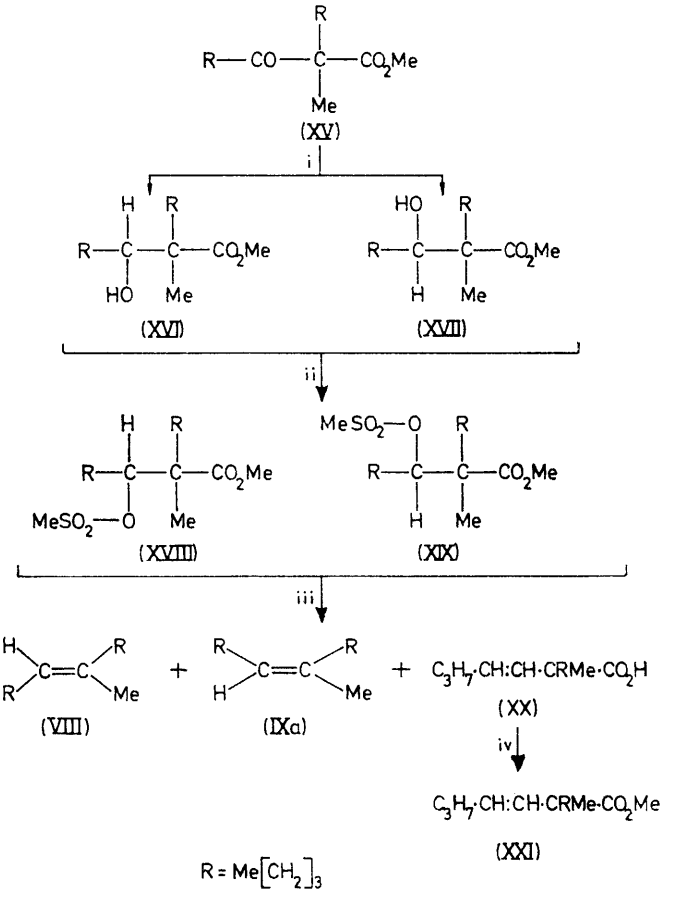
that the p orbitals of the incipient olefin overlap with the p orbitals of ring oxygen atom and the carbonyl carbon atom, which belong to different π-systems, and the second p orbital of the carbonyl oxygen atom couples the rest of the system together. Thus in the transition state there is a continuous cyclic overlap of atomic orbitals with no phase dislocation and involving six electrons, and therefore the transition state is stabilised.[14] Thus the cycloreversion involves a *cis*-elimination of carbon dioxide.

The *Z*-olefins (VIII) and the *E*-olefins (IX) were formed respectively from the slow- and the fast-moving hydroxy-esters (t.l.c.) by the sequence of reactions shown in Scheme 1. A concerted *cis*-elimination of carbon dioxide from the β-lactone, and formation of the β-lactone *via* a mixed anhydride as shown in Scheme 2, then implies the stereochemistries indicated in (II), (IV), and (VI), respectively, for the slow-moving β-hydroxy-esters and the β-hydroxy-acids and β-lactones derived from them. Similarly the fast-moving β-hydroxy-esters and the β-hydroxy-acids and β-lactones derived from them have the configurations shown in (III), (V), and (VII), respectively.

The decomposition of β-lactones to olefins appears to be a general method for the formation of *E*- and *Z*-trisubstituted olefins, and the overall yield from the β-hydroxy-ester is *ca.* 43%. Since our preliminary communication [1] other workers have also shown [8a] that the decarboxylation of β-lactones is stereospecific, and similar observations have also been made in the thermal decomposition of β-lactams to olefins.[17]

During the early part of our studies on stereospecific routes to trisubstituted olefins we investigated the decarboxylative elimination of β-mesyloxy-carboxylates. For this purpose the mixture of diastereoisomeric mesylates (XVIII) and (XIX) was prepared from methyl 2-butyl-2-methyl-3-oxoheptanoate (XV) by the sequence shown in Scheme 3. The mixture of mesylates when heated with lithium iodide in refluxing collidine gave (*E*)-5-methyldec-5-ene (IXa), (*Z*)-5-methyldec-5-ene (VIII), and 2-butyl-2-methylhept-3-enoic acid (XX), isolated as its methyl ester (XXI). The formation of the olefins (VIIIa) and (IXa) could be rationalised in terms of decarboxylative elimination of carbon dioxide and methanesulphonate from the carboxylate ions derived from the esters (XVIII) and (XIX) by reaction with lithium iodide.[18] The formation of the acid (XX) could be accounted for in terms of a β-elimination of methanesulphonic acid (induced by I^- – collidine), followed by demethylation with lithium iodide. As the major product from the above reaction is the acid (XX), this reaction was not studied further as a route to olefins.

Attempts were also made to change the ratio of the diastereoisomeric hydroxy-esters obtainable by reduction of the oxo-ester (XV) with borohydride. Thus the reduction of the sodium, potassium, or calcium salt of the oxo-acid obtained by hydrolysis of the ester (XV) was carried out with sodium or potassium borohydride in the presence of a variety of solvents and salts. In all cases except one the slow-moving diastereoisomer (t.l.c.)



SCHEME 3 Reagents: i, $NaBH_4$–MeOH; ii, $MeSO_2Cl$–C_5H_5N; iii, LiI–collidine (reflux), then H_3O^+; iv, CH_2N_2

was formed to the extent of *ca.* 70%. However when the reduction was carried out on the potassium salt of the oxo-acid with potassium borohydride in the presence of lithium chloride the major product was the fast-moving diastereoisomer (*ca.* 63%). Details of these experiments are available as Supplementary Publication No. SUP 21589 (3 pp.).*

EXPERIMENTAL

I.r. spectra were measured either for thin films (ν^a) with Perkin-Elmer Infracord model 137 or for 5% solutions in carbon tetrachloride (ν^b) with a Unicam SP 100 spectrophotometer. N.m.r. spectra were determined for solutions in carbon tetrachloride with a Varian A-60 spectrometer (tetramethylsilane as internal reference). G.l.c. analyses were conducted with an Aerograph Hy-Fi gas chromatograph equipped with flame ioniser detector and a disc chart

* For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin I*, 1975, Index issue.

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[18] (*a*) F. Elsinger, J. Schreiber, and A. Eschenmoser, *Helv. Chim. Acta*, 1960, **43**, 113; (*b*) G. W. Krakover, J. W. Brown, and J. Fried, *J. Org. Chem.*, 1962, **27**, 4710.

integrator [7.5 ft × 0.125 in stainless steel column packed with 5% SE 30 (t_R[a]) or with 15% Carbowax on Chromosorb W (60—80 mesh) (t_R[b])]. T.l.c. was carried out with Merck silica gel G.

Ethyl 3-Oxoheptanoate.—(*a*) The reaction between n-butylmagnesium iodide and ethyl cyanoacetate gave ethyl 3-oxoheptanoate (18.5%), b.p. 42—45° at 0.15 mmHg (lit.,[6] 97—101° at 9 mmHg). n-Butylmagnesium bromide under the same conditions gave the oxo-ester in 9.5% yield.

(*b*) A mixture of magnesium (12.5 g), ethanol (12.5 ml), carbon tetrachloride (0.5 ml), and a part (15 ml) of a solution of diethyl malonate (70 g) in absolute ethanol (40 ml) was heated till a vigorous reaction set in. The rest of the malonate solution was then added to the refluxing solution, and the resulting mixture was refluxed for 2 h, cooled, treated with anhydrous ether (150 ml), and heated under reflux for a further 3½ h. A solution of n-valeryl chloride (59.8 g) in ether (50 ml) was then gradually added and the mixture was refluxed for 30 min, acidified with dilute sulphuric acid, and extracted twice with ether. The combined extracts were washed with water, dried ($MgSO_4$), and evaporated. Naphthalene-β-sulphonic acid monohydrate (10 g) was added to the residue (103 g), and the mixture was heated gradually to 200—210 °C in 30 min, then cooled. More naphthalene-β-sulphonic acid monohydrate (2 g) was then added and the mixture was again gradually heated to 200—210 °C (30 min). The product was cooled and dissolved in ether and the solution was washed successively with aqueous sodium hydrogen carbonate and water, dried ($MgSO_4$), and evaporated. Fractional distillation of the residue gave ethyl 3-oxoheptanoate (10 g, 12%), b.p. 69—73° at 3 mmHg.

Ethyl t-Butyl Butylmalonate.—This compound was prepared [6b] from diethyl butylmalonate; b.p. 95—96° at 1.3 mmHg (lit.,[6b] 126—128° at 15 mmHg).

Ethyl 2-Butyl-3-oxoheptanoate.—*Method* 1. Butyl bromide (7.19 g) was added in 30 min to a stirred, refluxing solution prepared by adding, under anhydrous conditions, ethyl 3-oxoheptanoate (8.19 g) to a solution of sodium (1.093 g) in absolute ethanol (24 ml), and the resulting mixture was stirred and refluxed for a further 17½ h. The alcohol was removed under reduced pressure and the residue (9.5 g) distilled through a 10 cm Vigreux column to give *ethyl 2-butyl-3-oxoheptanoate* (7.2 g, 65%), b.p. 83—84° at 0.1 mmHg, n_D^{27} 1.4328 (Found: C, 68.4; H, 10.6. $C_{13}H_{24}O_3$ requires C, 68.6; H, 10.8%); t_R[a] (145 °C) 6 min; $\nu_{max.}$[a] 1 745, 1 715, 1 180, 1 035, and 1 020 cm^{-1}.

Method 2. Ether-washed sodium hydride (1.089 g) and a solution of ethyl t-butyl butylmalonate (7.33 g) in benzene (150 ml) were refluxed first at 55 °C for *ca.* 100 min, and then at 80 °C for 90 min, treated with a solution of valeryl chloride (3.654 g) in benzene (60 ml), refluxed for 30 min, and set aside at room temperature overnight. The mixture was stirred at room temperature for 1 h with anhydrous toluene-*p*-sulphonic acid (2.40 g), filtered, and evaporated. A solution of the residue (9.5 g) in benzene (60 ml) was freed from water (Dean–Stark apparatus), treated with anhydrous toluene-*p*-sulphonic acid (0.5 g) and refluxed for 1 h. The solution was then washed with aqueous sodium hydrogen carbonate, dried ($MgSO_4$), and evaporated. Fractional distillation (10 cm Vigreux column) of the residue (6.7 g) gave ethyl 2-butyl-3-oxoheptanoate (2.15 g, 31%).

Ethyl 2-Butyl-2-methyl-3-oxoheptanoate (I).—Ethyl 2-butyl-3-oxoheptanoate (7.9 g) was added in 10 min to a stirred suspension of ether-washed sodium hydride (0.85 g) in a solution (50% v/v; 70 ml) of dry dimethylformamide in benzene maintained at 5—10 °C (ice–water bath). The resulting mixture was stirred for 20 min, treated with methyl iodide (5.77 g) in 5 min, stirred for 30 min at 5—10 °C and then for 90 min at 40—50 °C (external), and set aside overnight at room temperature. As the mixture was still faintly alkaline, methyl iodide (1.0 g) was added and the resulting mixture was stirred at 40—50 °C for 2 h, cooled, diluted with water, and extracted twice with benzene. The combined extracts were washed successively with sodium thiosulphate solution and water, dried ($MgSO_4$), and evaporated. The residue (8.7 g) was distilled under reduced pressure through a Vigreux column (10 cm) to give *ethyl 2-butyl-2-methyl-3-oxoheptanoate* (7.33 g, 86%), b.p. 82—83° at 0.1 mmHg, n_D^{25} 1.4350 (Found: C, 69.0; H, 10.9. $C_{14}H_{26}O_3$ requires C, 69.4; H, 10.8%), $\nu_{max.}$[a] 1 745, 1 725, and 1 615 cm^{-1}; τ 5.83 (2 H, q, *J* 7.5 Hz, O·C*H*$_2$Me), 7.65 (2 H, t, *J* 7 Hz, CH$_2$·CO), 8.13—9.32 (16 H, m, C$_4$*H*$_9$·C and C$_3$*H*$_7$·CH$_2$·CO), 8.75 (3 H, t, *J* 7.5 Hz, O·CH$_2$·C*H*$_3$), and 8.76 (3 H, s, CMe).

Ethyl 2-Butyl-3-hydroxy-2-methylheptanoates (IIa) *and* (IIIa).—A solution of ethyl 2-butyl-2-methyl-3-oxoheptanoate (Ia) (2.24 g) in methanol (75 ml) was stirred for 6 h with sodium borohydride (0.57 g), concentrated, diluted with water, acidified, and extracted twice with ether. The combined extracts were dried ($MgSO_4$) and evaporated and the residue (2.18 g) was shown by g.l.c. [15% Carbowax (neutral)] to be a mixture (52 : 48) of two diastereoisomers in which the compound with lower retention time predominates. Preparative t.l.c. [silica gel; benzene–ethyl acetate (90 : 10)] gave (i) the slow-moving *diastereoisomer* (IIa), which was further purified by distillation (bath temp. 110 °C; 0.05 mmHg); n_D^{25} 1.4427; R_F 0.31 (Found: C, 68.9; H, 11.6. $C_{14}H_{28}O_3$ requires C, 68.8; H, 11.55%); t_R[b] 9 min 30 s; $\nu_{max.}$[b] 3 515, 1 730, and 1 045 cm^{-1}; τ 5.87 (2 H, q, *J* 7 Hz, O·C*H*$_2$Me), 6.27—6.72br (1 H, C*H*·OH), 7.65br (1 H, s, OH), 8.25—9.30 (18 H, m, 2 × C$_4$H$_9$), 8.74 (3 H, t, *J* 7 Hz, O·CH$_2$*Me*), and 8.95 (3 H, s, CMe); and (ii) the fast-moving *diastereoisomer* (IIIa), which was further purified by distillation (bath temp. 100 °C; 0.05 mmHg), n_D^{25} 1.4443; R_F 0.42 (Found: C, 68.8; H, 11.5%); t_R[b] (180 °C) 12 min 12 s; $\nu_{max.}$[b] 3 630, 3 505, 1 725, and 1 040 cm^{-1}; τ 5.89 (2 H, q, *J* 7 Hz, O·C*H*$_2$Me), 6.28—6.58br (1 H, absorption C*H*·OH), 7.68br (1 H, s, OH), 8.33—9.25 (18 H, m, 2 × C$_4$H$_9$), 8.75 (3 H, t, *J* 7 Hz, O·CH$_2$·C*H*$_3$), and 8.95 (3 H, s, CMe).

Use of dimethylformamide, lutidine, tetrahydrofuran, t-butyl alcohol, or ethylene glycol in place of methanol, or the use of potassium in place of sodium borohydride, did not change the proportions of the two diastereoisomers appreciably. Attempted reduction of the carbonyl group with aluminium isopropoxide was not successful.

Conversion of the Hydroxy-ester (IIIa) *into the* β-*Lactone* (VIIa).—The hydroxy-ester (IIIa) (0.267 g) was added to ethanol (3 ml) and aqueous sodium hydroxide (2.5N; 3.5 ml); the mixture was heated on a steam-bath for 3 h and evaporated under reduced pressure, and the residue was dissolved in water and washed with ether. The aqueous solution was acidified and extracted with ether, and the ethereal solution was washed with water, dried ($MgSO_4$), and evaporated. Anhydrous sodium carbonate (1.07 g) and pentane (10 ml) were added to the residue (0.194 g) and the resulting mixture was stirred and treated with a solution of methanesulphonyl chloride (0.62 g) in

pentane (5 ml). Stirring was continued for 30 h at room temperature, the excess of methanesulphonyl chloride was decomposed with water, and the mixture was extracted twice with pentane. The combined extracts were washed with water, dried ($MgSO_4$), and evaporated. Distillation (bath temp. 120°; 0.05 mmHg) of the residue (0.166 g) gave the *2-butyl-2-methylheptan-3-olide* (VIIa) (0.108 g), n_D^{25} 1.4377 (Found: C, 72.5; H, 11.0. $C_{12}H_{22}O_2$ requires C, 72.2; H, 11.2%); t_R^b (147 °C) 33 min 48 s; $\nu_{max.}^b$ 1 825, 1 085, 945, and 845 cm^{-1}; τ 5.93 (1 H, t, *J* 6 Hz, CH·O), 8.00—9.30 (18 H, m, 2 × C_4H_9), and 8.65 (3 H, s, CMe).

Conversion of the Hydroxy-ester (IIa) *into the* β-*Lactone* (VIa).—The hydroxy-ester (IIa) (0.251 g), ethanol (2.5 ml), aqueous sodium hydroxide (2.5N; 2.5 ml), and methanesulphonyl chloride (1.615 g), treated as described for the preparation of the β-lactone (IIIa), gave, after distillation (bath temp. 120 °C; 0.5 mmHg), the *2-butyl-2-methylheptan-3-olide* (VIa) (0.117 g), n_D^{25} 1.4377 (Found: C, 72.2; H, 11.0%); t_R^b (147 °C) 35 min 54 s; $\nu_{max.}^b$ 1 820, 1 070, 945, 860, and 840 cm^{-1}; τ 5.87 (1 H, t, *J* 6.5 Hz, CH·O), 8.00—9.33 (18 H, m, 2 × C_4H_9), and 8.80 (3 H, s, CMe).

Thermal Decomposition of the β-*Lactone* (VIa).—A solution of the β-lactone (VIa) (0.0419 g) in collidine (5 ml) was heated to reflux during 10 min and refluxed for 1 h, cooled, poured into ice (30 g) and concentrated hydrochloric acid (15 ml), and extracted with pentane. The extract was washed successively with dilute hydrochloric acid, aqueous sodium hydrogen carbonate, and water, dried ($MgSO_4$), and evaporated. Distillation (bath temp. 90—118 °C; 23 mmHg) of the residue (0.0332 g) gave (Z)-*5-methyldec-5-ene* (VIIIa) (0.0189 g, 58%) (Found: C, 85.3; H, 14.2. $C_{12}H_{22}$ requires C, 85.6; H, 14.4%); t_R^b (92 °C) 4 min 54 s; $\nu_{max.}^b$ 1 655, 1 610, and 830 cm^{-1}; τ 4.93 (1 H, t, *J* 7 Hz, CH_2·C*H*:C), 7.82—8.28 (4 H, m, CH_2·C:C·CH_2), 8.43 (3 H, s, C:C·CH_3), 8.50—8.90 (8 H, m, 2 × CH_2·CH_2·CH_2·C:C), and 9.11 (6 H, t, *J* 7 Hz, 2 × $C_3H_6CH_3$).

Thermal Decomposition of the β-*Lactone* (VIIa).—A solution of the β-lactone (VIIa) (0.0416 g) in collidine (5 ml), treated as described for the β-lactone (VIa), gave (E)-*5-methyldec-5-ene* (0.0198 g, 61%) (Found: C, 85.25; H, 14.4%); t_R^b (92 °C) 4 min 18 s (this material contained at least 95% *cis*-form); $\nu_{max.}^b$ 1 665, 1 605, 860, and 840 cm^{-1}; τ 4.94 (1 H, t, *J* 7 Hz, C:C*H*·CH_2), 7.80—8.25 (4 H, m, CH_2·C:C·CH_2), 8.35 (3 H, s, C:CMe), 8.50—8.90 (8 H, m, 2 × CH_2·CH_2·CH_2·C:C), and 9.10 (6 H, t, *J* 7 Hz, 2 × Me).

Conversion of the Hydroxy-ester (IIIa) *into* (E)-*5-Methyldec-5-ene* (IXa).—The hydroxy-ester (IIIa) (0.1098 g) was converted into the crude β-lactone (VIIa) (0.070 g) by the procedure described above. A solution of this crude lactone (0.070 g) in collidine (6 ml) on thermal decomposition and work-up as described above gave a residue (0.0589 g) which on distillation (bath temp. 120—130 °C; 70 mmHg) gave the *E*-olefin (IXa) (0.0297 g) in an overall yield of 43% based on the hydroxy-ester. This product was 90% pure *E*-form as shown by g.l.c.

Conversion of the Hydroxy-ester (IIa) *into* (Z)-*5-Methyldec-5-ene* (VIIIa).—The hydroxy-ester (IIa) (0.123 g) was similarly converted into the *Z*-olefin (VIIIa). The overall yield was 43.5% and the product was 99% pure *Z*-isomer (by g.l.c.).

Methyl 3-Oxoheptanoate.—This *ester* was prepared essentially by the general procedure of Stallberg-Stenhagen [19] except for the use of sodium hydride instead of granulated sodium; b.p. 45.5—47° at 0.2 mmHg, n_D^{25} 1.4283 (Found: C, 60.6; H, 8.9. $C_8H_{14}O_3$ requires C, 60.7; H, 8.9%); t_R^a (140 °C) 1 min 36 s.

Methyl 2-Butyl-3-oxoheptanoate.—The *butyl derivative* was prepared in 63% yield from methyl 3-oxoheptanoate and butyl bromide as described for the ethyl ester; b.p. 75—78° at 0.1 mmHg, n_D^{24} 1.4346 (Found: C, 67.1; H, 10.3. $C_{12}H_{22}O_3$ requires C, 67.25; H, 10.35%), t_R^a (142 °C) 7 min 12 s.

Methyl 2-Butyl-2-methyl-3-oxoheptanoate (XV).—The *methyl derivative* was prepared in 79% yield as described for the ethyl ester; b.p. 74—78° at 0.75 mmHg, n_D^{25} 1.4370 (Found: C, 68.2; H, 10.5. $C_{13}H_{24}O_3$ requires C, 68.4; H, 10.6%); t_R^a (148 °C) 5 min 12 s.

Methyl 2-Butyl-3-hydroxy-2-methylheptanoates (XVI) *and* (XVII).—The oxo-ester (XV) (3.45 g) in methanol (100 ml) was stirred with sodium borohydride (0.94 g) at room temperature for 8 h and the solvent was evaporated off under reduced pressure. The residue was dissolved in water, acidified, and extracted with ether. The extract was washed with water, dried ($MgSO_4$), and evaporated. The residue (3.41 g) on distillation (bath temp. 120 °C; 10^{-2} mmHg) gave a mixture of the hydroxy-esters (XVI) and (XVII) (Found: C, 67.7; H, 11.3. Calc. for $C_{13}H_{26}O_3$: C, 67.8; H, 11.4%).

Methyl 2-Butyl-3-mesyloxy-2-methylheptanoates (XVIII) *and* (XIX).—Methanesulphonyl chloride (0.205 g) was added to a solution of the mixture of hydroxy-esters (XVI) and (XVII) (0.174 g) in pyridine (3 ml). The resulting solution was kept at room temperature for 24 h, poured into ice and concentrated hydrochloric acid, and extracted twice with ether. The combined extracts were washed successively with aqueous sodium hydrogen carbonate and water, dried ($MgSO_4$), and evaporated. Column chromatography [Fluorisil; butane–ether (14 : 1)] of the residue gave a mixture of the mesylates (XVIII) and (XIX) (0.2276 g) (Found: C, 55.0; H, 9.2; S, 10.5. Calc. for $C_{14}H_{28}O_5S$: C, 54.5; H, 9.15; S, 10.4%); $\nu_{max.}^b$ 1 755, 1 275, and 900 cm^{-1}.

Reaction of the Methyl 2-Butyl-3-mesyloxy-2-methylheptanoates (XVIII) *and* (XIX) *with Lithium Iodide in Collidine*.—A mixture of the mesylates (XVIII) and (XIX) (0.226 g), lithium iodide (0.667 g), and collidine (10 ml) was refluxed under nitrogen for 8 h, cooled, poured into ice and concentrated hydrochloric acid (20 ml), and extracted twice with pentane. The combined extracts were washed successively with N-sodium hydroxide (5 × 4 ml) and water, dried ($MgSO_4$), and evaporated. The residue (0.0235 g) on distillation (bath temp. 90—120 °C; 17 mmHg) gave a mixture shown by g.l.c. and n.m.r. to contain *E*- (IXa) and *Z*- (VIIIa) 5-methyldec-5-enes.

The combined aqueous and alkaline washings were acidified and extracted with pentane. The extract was dried ($MgSO_4$) and evaporated, and the residue (0.782 g) was dissolved in ether and treated with an excess of ethereal diazomethane. The solution was dried ($MgSO_4$) and evaporated and the residue distilled (bath temp. 50—60 °C; 0.025 mmHg) to give *methyl 2-butyl-2-methylhept-3-enoate* (XXI) (0.0587 g) (Found: C, 73.8; H, 11.25. $C_{13}H_{24}O_2$ requires C, 73.5; H, 11.4%); t_R^b (125 °C) 7 min; $\nu_{max.}^a$ 1 736 and 1 667 cm^{-1}; τ 4.52 (2 H, m, HC:CH), 6.39 (3 H, s, OMe), 7.83—8.13 (2 H, m, CH_2·C:C), and 8.30—9.11 (17 H, m).

5-Methylhex-5-en-2-one. This was prepared according to the described method; [11] b.p. 151°, n_D^{25} 1.4284; semi-

[19] S. Stallberg-Stenhagen, *Arkiv Kem. Min. Geol.*, 1945, **20**, 1.

carbazone, m.p. 136—137° (lit.,[11] b.p. 147—150°, n_D^{25} 1.4278; semicarbazone, m.p. 137—138°); t_R[b] (92 °C) 9 min 6 s; $\nu_{max.}$[a] 1 755 and 1 655 cm^{-1}; τ 5.35 (2 H, s, C:CH$_2$), 7.32—7.48 (4 H, m, CO·CH$_2$·CH$_2$·C:C), 7.92 (3 H, s, COMe), and 8.28 (3 H, s, C:CMe).

Ethyl 6-Methyl-3-oxohept-6-enoate.—The described[11] method gave a mixture of products from which the title compound was obtained (43%) by fractional distillation; $\nu_{max.}$[a] 1 745, 1 725, 1 650, 1 060, and 900 cm^{-1} τ 5.33br (2 H, s, C:CH$_2$), 5.88 (2 H, q, *J* 7 Hz, O·C*H*$_2$·CH$_3$), 6.68 (2 H, s, CO·CH$_2$·CO), 7.21—7.80 (4 H, m, CH$_2$·CH$_2$), 8.27 (3 H, s, C:CMe), and 8.73 (3 H, t, *J* 7 Hz, O·CH$_2$·C*H*$_3$).

Ethyl 2-(6-Benzyloxyhex-3-ynyl)-6-methyl-3-oxohept-6-enoate.—Ethyl 6-methyl-3-oxohept-6-enoate (1.193 g) was added in 10 min to a stirred (nitrogen atmosphere) solution of sodium (0.15 g) in magnesium methoxide-dried ethanol (4 ml); the solution was refluxed for a few minutes and treated with sodium iodide (0.10 g). 6-Benzyloxy-1-bromohex-3-yne (1.838 g)* was then added dropwise in 15 min to the refluxing solution and the refluxing was continued for a further 64 h. Ethanol (2 ml) was evaporated off under reduced pressure and the residue was refluxed for a further 3 h, cooled, acidified with acetic acid (0.5 ml), diluted with water, and extracted twice with ether. The combined extracts were washed successively with aqueous sodium carbonate and water, dried (MgSO$_4$), and evaporated. The residue, after removal of low boiling materials by distillation (bath temp. 120 °C; 2 × 10^{-4} mmHg) was purified by column chromatography [Fluorisil; pentane–ether (4 : 1)] to give the *product* (1.311 g, 52%), n_D^{24} 1.5055 (Found: C, 74.3; H, 7.9. C$_{23}$H$_{30}$O$_4$ requires C, 74.55; H, 8.15%); $\nu_{max.}$[a] 1 750, 1 725, 1 035, 740, and 695 cm^{-1}; τ 2.85 (5 H, s, Ph), 5.43br (2 H, s, C:CH$_2$), 5.60 (2 H, s, O·C*H*$_2$Ph), 5.94 (2 H, q, *J* 7 Hz, O·C*H*$_2$·CH$_3$), 6.57 (3 H, t, *J* 7 Hz, O·C*H*$_2$·CH$_2$ and CO·C*H*·CH$_2$), 7.38—8.30 (10 H, m, CH$_2$·C:C·CH$_2$·CH$_2$·C and CO·CH$_2$·CH$_2$), 8.36 (3 H, s, C:C·CH$_3$), and 8.82 (3 H, t, *J* 7 Hz, O·CH$_2$·C*H*$_3$).

Ethyl 2-(6-Benzyloxyhex-3-ynyl)-2,6-dimethyl-3-oxohept-6-enoate (Ib).—Ethyl 2-(6-benzyloxyhex-3-ynyl)-6-methyl-3-oxohept-6-enoate (2.240 g) was added dropwise in 30 min to a stirred suspension of sodium hydride (obtained by washing 0.265 g of a 54.7% emulsion with pentane) in a 1 : 1 mixture (8 ml) of benzene and dimethylformamide and stirring was continued for a further 20 min. Methyl iodide (1.57 g) was added to the stirred mixture and stirring was continued first at 50 °C for 1 h and then at room temperature overnight. The resulting neutral mixture was diluted with water and extracted with ether. The extract was washed with water, dried (MgSO$_4$), and evaporated under reduced pressure. Column chromatography [Fluorisil; pentane–ether (4 : 1)] of the residue (1.754 g) gave the pure *ester* (Ib) (1.564 g), 67%), $n_D^{26.5}$ 1.5034 (Found: C, 74.7; H, 8.3. C$_{24}$H$_{32}$O$_4$ requires C, 74.95; H, 8.4%); $\nu_{max.}$[a] 1 745, 1 710, 740, and 700 cm^{-1}; τ 2.78 (5 H, s, Ph), 5.37br (2 H, s, C:CH$_2$), 5.54 (2 H, s, O·C*H*$_2$Ph), 5.86 (2 H, q, *J* 7 Hz, O·C*H*$_2$·CH$_3$), 6.53 (2 H, t, *J* 7 Hz, O·C*H*$_2$·CH$_2$), 7.33—8.05 (10 H, m, CH$_2$·C:C·CH$_2$·CH$_2$ and CO·CH$_2$·CH$_2$·C:C), 8.30 (3 H, s, C:CMe), 8.72 (3 H, s, CMe), and 8.74 (3 H, t, *J* 7 Hz, O·CH$_2$·C*H*$_3$).

Ethyl 2-(6-Benzyloxyhex-3-ynyl)-3-hydroxy-2,6-dimethylhept-6-enoates (IIb) *and* (IIIb).—A solution of the oxo-ester (Ib) (1.504 g) in methanol (40 ml) was stirred with sodium borohydride (0.302 g) for 3 h. More borohydride (0.50 g) was then added and the stirring continued for a further 3 h. Methanol was evaporated off under reduced pressure. The residue was dissolved in water, acidified, and extracted with ether. The extract was dried (MgSO$_4$) and evaporated to give a mixture (t.l.c., n.m.r.) of diastereoisomeric hydroxy-esters (1.47 g). Repeated preparative t.l.c. [silica; pentane–ether (4 : 1) or C$_6$H$_6$–EtOAc (19 : 1)] gave (i) the faster-moving *hydroxy-ester* (IIIb), n_D^{24} 1.5086 (Found: C, 74.4; H, 8.7. C$_{24}$H$_{34}$O$_4$ requires C, 74.55; H, 8.85%); $\nu_{max.}$[b] 3 550, 1 730, 1 720, 1 648, 965, 885, and 860 cm^{-1}; τ 2.73 (5 H, s, Ph), 5.30br (2 H, s, C:CH$_2$), 5.50 (2 H, s, O·C*H*$_2$Ph), 5.87 (2 H, q, *J* 7 Hz, O·C*H*$_2$·CH$_3$), 6.17—6.70br (1 H, C*H*OH), 6.51 (2 H, t, *J* 7 Hz, O·C*H*$_2$·CH$_2$), 7.50—8.53 (11 H, m, CH$_2$·C:C·CH$_2$·CH$_2$, C:C·CH$_2$·CH$_2$, and OH), 8.28 (3 H, s, C:CMe), 8.75 (3 H, t, *J* 7 Hz, O·CH$_2$·C*H*$_3$), and 8.92 (3 H, s, CMe); and (ii) the slower-moving *hydroxy-ester* (IIb), n_D^{24} 1.5076 (Found: C, 74.3; H, 8.8. C$_{24}$H$_{34}$O$_4$ requires C, 74.55; H, 8.85%); $\nu_{max.}$[b] 3 540, 1 736, 1 710, 1 648, 883, and 695 cm^{-1}; τ 2.70 (5 H, s, Ph), 5.27br (2 H, s, C:CH$_2$), 5.48 (2 H, s, O·C*H*$_2$Ph), 5.83 (2 H, q, *J* 7 Hz, O·C*H*$_2$·CH$_3$), 6.27—6.64br (1 H, O·C*H*), 6.49 (2 H, t, *J* 7 Hz, O·C*H*$_2$·CH$_2$), 7.48—8.55 (11 H, m, CH$_2$·C:C·CH$_2$·CH$_2$, C:C·CH$_2$·CH$_2$, and OH), 8.27 (3 H, s, C:C·CH$_3$), 8.72 (3 H, t, *J* 7 Hz, O·CH$_2$·C*H*$_3$), and 8.90 (3 H, s, CMe).

Conversion of the Hydroxy-ester (IIIb) *into the β-Lactone* (VIIb).—A solution of the hydroxy-ester (IIIb) (0.0856 g) in ethanol (2 ml) and aqueous sodium hydroxide (2.5N; 2 ml) was refluxed on a steam-bath for 90 min. Ethanol was removed under reduced pressure and the residue was dissolved in water and washed with ether. The aqueous solution was cooled, acidified, and extracted with ether. The ethereal solution was dried (MgSO$_4$) and evaporated and the residue (0.0742 g) was treated with pentane (20 ml) and anhydrous sodium carbonate (0.786 g); the mixture was stirred at room temperature for 24 h. Water was added and the pentane layer was separated. The aqueous layer was extracted with ether and the combined ether and pentane extracts were dried (MgSO$_4$) and evaporated. The residue (0.702 g), purified by preparative t.l.c. [silica gel; benzene–ethyl acetate (9 : 1)] to give the 2-(6-*benzyloxyhex-3-ynyl*)-2,6-*dimethylhept-6-en-3-olide* (VIIb) (0.0355 g), n_D^{25} 1.5122 (Found: C, 77.5; H, 8.25. C$_{22}$H$_{28}$O$_3$ requires C, 77.6; H, 8.3%); $\nu_{max.}$[b] 1 827, 1 649, 890, 850, and 695 cm^{-1}; τ 2.71 (5 H, s, Ph), 5.24br (2 H, s, C:CH$_2$), 5.50 (2 H, s, O·C*H*$_2$Ph), 5.91 (1 H, t, *J* 6.5 Hz, CH·O·CO), 6.51 (2 H, t, *J* 7 Hz, O·C*H*$_2$·CH$_2$), 7.45—8.40 (10 H, m, CH$_2$·C:C·CH$_2$·CH$_2$ and CH$_2$·CH$_2$·C:C), 8.25 (3 H, s, C:CMe), and 8.61 (3 H, s, CMe).

Conversion of the Hydroxy-ester (IIb) *into the β-Lactone* (VIb).—The hydroxy-ester (IIb) (0.0835 g) was converted into the β-*lactone* (VIb) (0.029 g) as described for the ester (IIIb); n_D^{25} 1.5133 (Found: C, 77.8; H, 8.25%); $\nu_{max.}$[b] 1 827, 1 647, 890, 840, and 675 cm^{-1}; τ 2.70 (5 H, s, Ph), 5.24br (2 H, s, C:CH$_2$), 5.49 (2 H, s, O·C*H*$_2$Ph), 5.61 (1 H, t, *J* 5 Hz, CO·O·CH), 6.51 (2 H, t, *J* 7 Hz, O·C*H*$_2$·CH$_2$), 7.45—8.30 (10 H, m, CH$_2$·C:C·CH$_2$·CH$_2$ and CH$_2$·CH$_2$·C:C), 8.25 (3 H, s, C:CMe), and 8.75 (3 H, s, CMe).

Thermal Decomposition of the β-Lactone (VIIb).—A solution of the lactone (VIIb) (0.0355 g) in collidine (5 ml) was refluxed (under nitrogen) for 1 h, cooled, poured into an excess of ice and concentrated hydrochloric acid (15 ml), and extracted twice with ether. The combined extracts were washed with water, dried (MgSO$_4$), and evaporated, and the residue (0.0298 g) was distilled (bath temp. 130 °C;

* We thank Dr. W. R. Bartlett for providing this compound.

2.5×10^{-3} mmHg) to give (E)-12-*benzyloxy*-2,6-*dimethyldodeca*-1,5-*dien*-9-*yne* (IXb); t_R[a] (204 °C) 16 min 36 s (Found: C, 84.4; H, 9.4. $C_{21}H_{28}O$ requires C, 85.1; H, 9.5%); $\nu_{max.}$[b] 1 646, 885, and 695 cm^{-1}; τ 2.74 (5 H, s, Ph), 4.82 (1 H, t, J 6.5 Hz, C:C*H*·CH_2), 5.31br (2 H, s, C:CH_2), 5.52 (2 H, s, O·CH_2Ph), 6.51 (2 H, t, J 7 Hz, O·CH_2·CH_2), 7.48—7.97 (10 H, m, CH_2·C:C·CH_2·CH_2 and H_2C·CH_2·C:C), and 8.30 (6 H, s, 2 × :CMe).

Thermolysis of the β-*Lactone* (VIb).—The lactone (VIb) (0.0291 g) was treated as described for the lactone (VIIb) to give the *Z-olefin* (VIIIb) (0.0240 g), which was purified by distillation (bath temp. 130 °C; 1.5 mmHg); purity 96% (g.l.c.), t_R[a] (204 °C) 17 min 54 s; $\nu_{max.}$[b] 1 646, 885, and 685 cm^{-1}; τ 2.73 (5 H, s, Ph), 4.83 (1 H, t, J 6 Hz, C:C*H*·CH_2), 5.32br (2 H, s, C:CH_2), 5.52 (2 H, s, O·CH_2Ph), 6.51 (2 H, t, J 7 Hz, O·CH_2·CH_2), 7.49—7.07 (10 H, m, CH_2·C:CH_2·CH_2 and CH_2·CH_2·C:C), 8.29 (3 H, s, C:CMe), and 8.39 (3 H, s, C:CMe).

Conversion of the Hydroxy-ester (IIb) *into the Z-Olefin* (VIIIb).—The ester (IIb) (0.636 g) was hydrolysed with aqueous sodium hydroxide (2.5N; 2 ml) in ethanol (2 ml) as described above to give the corresponding hydroxy-acid (0.0454 g), which was converted (without purification) as above with sodium carbonate (0.560 g), pentane (15 ml), and methanesulphonyl chloride (0.365 g) into the β-lactone (VIb) (0.0416 g). This crude lactone, when refluxed in collidine, gave the (crude) *Z*-olefin (VIIIb) (0.0351 g), which on distillation (bath temp. 150 °C; 20 mmHg) gave a mixture (0.0147 g) of *E*- and *Z*-olefins in the ratio 9 : 91 (g.l.c.).

Conversion of the Hydroxy-ester (IIIb) *into the* E-*Olefin* (IXb).—The ester (IIIb) (0.0503 g) was hydrolysed as described for the ester (IIb) to the (crude) hydroxy-acid (0.0436 g), which was in turn converted with sodium carbonate (0.550 g), pentane (15 ml), and methanesulphonyl chloride (0.420 g) into the lactone (VIIb) (0.0376 g). This (crude) lactone when refluxed in collidine for 90 min gave the *E*-olefin (IXb) (0.0151 g) after distillation (bath temp. 130 °C; 5 mmHg). The olefin was at least 92% *E*-isomer as indicated by g.l.c.

This problem was suggested by Professor W. S. Johnson, and the experimental work was carried out during the stay of one of us (M. U. S. S.) at Stanford University, California. We are grateful to Professor Johnson for advice, encouragement, and hospitality. The work was supported in part by the U.S. Public Health Service and the National Science Foundation. One of us (M. U. S. S.) thanks the U.S.E.F. in Sri Lanka for a Fulbright Senior Fellowship and the Council of the University of Sri Lanka for study leave.

[5/576 *Received*, 24*th March*, 1975]