The Chemistry of Terpenes. Part XVIII.[1] Synthesis of Methyl (−)-*cis*-Chrysanthemate and of a Methyl (+)-*cis*-Homochrysanthemate from (+)-Car-3- and -2-ene

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Methyl (−)-*cis*-chrysanthemate (7) has been synthesised from methyl (+)-*cis*-2,2-dimethyl-3-(2-oxopropyl)-cyclopropanecarboxylate (12) obtained in a series of steps from (+)-car-3-ene. Methyl (+)-*cis*-homochrysanthemate [methyl (+)-*cis*-2,2-dimethyl-3-(3-methylbut-2-enyl)cyclopropanecarboxylate] (16) was prepared from methyl (+)-*cis*-2,2-dimethyl-3-(3-oxobutyl)cyclopropanecarboxylate (14) obtained from (+)-car-2-ene. (+)-4α-Tosyloxymethylcar-2-ene (5) is reduced with lithium aluminium hydride to a mixture of (+)-4α-methylcar-2-ene (4) and (+)-1,4,4-trimethyl-*cis*-*transoid*-1,3-*cis*-tricyclo[5.1.0.0.^{3,5}]octane (21).

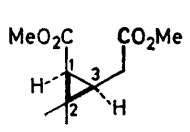
In Part XVII [1] we described a synthesis of dimethyl (+)-*cis*-homocaronate (1) starting from (+)-4α-acetoxymethylcar-2-ene (2), formed by Prins reaction of (+)-car-3-ene (6). One of the intermediates in this synthesis was methyl (+)-*cis*-2,2-dimethyl-3-(2-methylene-3-oxobutyl)cyclopropanecarboxylate (8). We now describe a synthesis of methyl (−)-*cis*-chrysanthemate (7) starting from (8).

Hydrogenation of (8) over palladised charcoal gives methyl (+)-*cis*-2,2-dimethyl-3-(2-methyl-3-oxobutyl)-cyclopropanecarboxylate (9), revealed by g.l.c. and n.m.r. as an equimolar pair of epimers about the new chiral centre. Baeyer–Villiger oxidation of the ketone (9) with *m*-chloroperbenzoic acid gives methyl (+)-*cis*-3-(2-acetoxypropyl)-2,2-dimethylcyclopropanecarboxylate (10), as a mixture of epimers. Alkaline hydrolysis of the acetate (10) and re-esterification of the product with diazomethane gives the 3-(2-hydroxypropyl)-ester (11) as an epimeric mixture, and oxidation of the alcohol (11) with Jones reagent is rapid, yielding the 3-(2-oxopropyl)-ester (12). Reaction of (12) with methylmagnesium iodide and dehydration of the alcoholic product (13) gives methyl (−)-*cis*-chrysanthemate (7) identical in spectra and g.l.c. with the methyl ester derived from an authentic specimen of the racemic acid, kindly supplied by Professor L. Crombie.

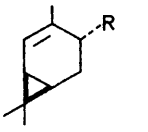
Ozonolysis of (+)-car-2-ene (3) in methanol followed by oxidative work-up with hydrogen peroxide, and esterification of the acidic product, gives the keto-ester (14). This may also be obtained [1] from (+)-4α-acetoxymethylcar-2-ene (2). Reaction of the keto-ester (14) with methylmagnesium iodide affords the 3-(3-methyl-

[1] Part XVII, W. Cocker, H. St. J. Lauder, and P. V. R. Shannon, *J.C.S. Perkin I*, 1974, 194.

3-hydroxybutyl)-ester (15). Its spectra were in accordance with its structure. The tertiary alcohol (15) was

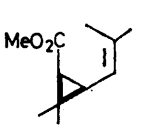


(1)

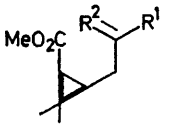


(2) R = CH_2OAc
(3) R = H
(4) R = Me
(5) R = CH_2OTs

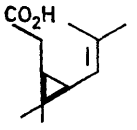
(6)



(7)



(8) R^1 = Ac, R^2 = CH_2
(9) R^1 = Me, R^2 = Ac,H
(10) R^1 = Me, R^2 = OAc,H
(11) R^1 = Me, R^2 = OH,H
(12) R^1 = Me, R^2 = O
(13) R^1 = Me, R^2 = Me,OH
(14) R^1 = H, R^2 = Ac,H
(15) R^1 = H, R^2 = Me_2COH,H
(16) R^1 = H, R^2 = CMe_2
(17) R^1 = H, R^2 = $MeC{=}CH_2$,H
(18) R^1 = H, R^2 = Me_2CH,H
(19) R^1 = Me, R^2 = COEt,H



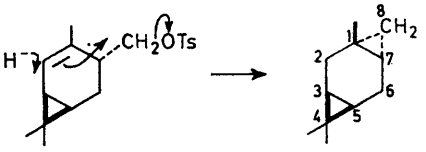
(20)

dehydrated with several reagents, *viz.*, potassium hydrogen sulphate, phosphoryl chloride, thionyl chloride, triphenylphosphine, and toluene-*p*-sulphonic acid. All gave mixtures of methyl (+)-*cis*-homochrysanthemate (16) and its double bond isomer, methyl *cis*-2,2-dimethyl-3-(3-methylbut-3-enyl)cyclopropanecarboxylate (17), but the latter was not isolated in a pure state. Toluene-*p*-sulphonic acid in refluxing xylene initially gives the methylene compound (17) in larger yield, but with time the composition of the mixture of products becomes rich (75%) in the isopropylidene isomer (16).

The field ionisation mass spectrum of the mixture of (16) and (17) shows a single molecular ion at *m/e* 196. The i.r. spectrum shows peaks at 876 cm^{-1} ($CH_2{=}CR^1R^2$) and 840 cm^{-1} ($R^1R^2C{=}CHR^3$), its n.m.r. spectrum shows a singlet at τ 5·42 ($CH_2{=}$) and a triplet at 4·99 ($CH_2CH{=}$), and hydrogenation gives a single product. Thus the initial, kinetically favoured product is (17) which isomerises to an equilibrium mixture in which the more stable compound (16) predominates. In the analogous dehydration of (13), the cyclopropane system greatly enhances the stability of the product (7) to the virtual exclusion of the isopropenyl isomer. The synthesis of the isomeric *cis*-homochrysanthemic acid (20) has been described [2] previously. Hydrogenation of the mixture of unsaturated esters (16) and (17) gives the single 3-(3-methylbutyl)-ester (18).

In an alternative method of preparing the keto-ester (9) we required (+)-4α-methylcar-2-ene (4), for which (+)-4α-tosyloxymethylcar-2-ene (5) seemed to be a useful precursor. However, reduction of the latter with lithium aluminium hydride gave a complex mixture in which the required hydrocarbon (4) and the tricyclic compound (21) were present in equal quantities. Both hydrocarbons had short retention times on g.l.c., but their preparative separation was effected on a 5% silver nitrate–silica column, the unsaturated hydrocarbon (4) being the more strongly adsorbed on silica and less strongly on g.l.c.

The tricyclic hydrocarbon (21) has a sharp, carene-like odour. Its n.m.r. spectrum is interesting because of the upfield chemical shift of the cyclopropane protons. These five protons are found in the region τ 9·4—9·85. By comparison with the n.m.r. spectrum of (−)-*cis*-carane,[3] we suggest that the signals given by the tricyclic hydrocarbon (21) at τ 9·0 and 9·04 are derived from the geminal methyl groups and the signal at τ 9·21 is from the 1β-methyl group. The formation of the additional cyclopropane system is not without precedent. Thus, for example,[4] cholest-5-en-3β-yl tosylate gives 3,5-cyclocholestane as well as cholest-5-ene. We can express our reaction in the following way:



(5) (21)

Ozonolysis in methanol of the mixture of (4) and (21) and oxidative work-up, followed by re-esterification of the acidic product, gives the keto-esters (9) and (12), the latter being isolated by preparative g.l.c. Its formation is probably the result of a Baeyer–Villiger reaction with (9) followed by hydrolysis and oxidation.

Methylation of the mixed epimeric keto-esters (9) in a solution of sodamide in liquid ammonia gave the 3-(2-methyl-3-oxopentyl)-ester (19) as a mixture of epimers about the chiral centre of the side-chain. Its spectra were in accord with its structure.

In many cases the molecular ions (see Experimental section) of the cyclopropane compounds described were measured by field ionisation mass spectrometry, no molecular ion being obtained by the electron impact technique. The comparison of field ionisation and electron impact mass spectra of these and related carane derivatives will be described elsewhere.

EXPERIMENTAL

I.r. spectra were measured as liquid films, and n.m.r. spectra at 60 or 100 MHz in CCl_4 unless otherwise stated.

[2] L. Crombie, J. Crossley, and D. A. Mitchard, *J. Chem. Soc.*, 1963, 4957; T. Sasaki, S. Eguchi, M. Ohno, and T. Oyobe, *Bull. Chem. Soc. Japan*, 1969, **42**, 3582.

[3] W. Cocker, P. V. R. Shannon, and P. A. Staniland, *J. Chem. Soc.* (*C*), 1966, 41.

[4] H. Schmidt and P. Karrer, *Helv. Chim. Acta*, 1949, **32**, 1371.

Optical rotations were measured in $CHCl_3$. Analytical g.l.c. was carried out on a 2 m × 3 mm 20% Carbowax 20M on Chromosorb W column at 150°, N_2 pressure 33 lb in^{-2} and preparative g.l.c. on a 3 m 20% Carbowax on Chromosorb W column at 158°, N_2 pressure 40 lb in^{-2}. Mass spectra were measured on a Varian CH5 spectrometer using a field ion source supplied by Varian Associates. With the exceptions of compounds (4), (7), (19), and (21) the M^+ peaks reported were measured under field ionisation conditions. Additional i.r. and mass spectral data, where marked with an obelus (†), are available in Supplementary Publication No. SUP 21213 (3 pp.).*

Methyl (−)-cis-*Chrysanthemate* [*Methyl* 2,2-*Dimethyl*-3-(2-*methylprop*-1-*enyl*)*cyclopropanecarboxylate*] (7).—*Methyl* (+)-cis-2,2-*dimethyl*-3-(2-*methyl*-3-*oxobutyl*)*cyclopropanecarboxylate* (9). Methyl (+)-*cis*-2,2-dimethyl-3-(2-methylene-3-oxobutyl)cyclopropanecarboxylate (8) [1] (2·5 g) in ethyl acetate (20 ml) was stirred under hydrogen with 5% palladised charcoal (150 mg). Chromatography on a silica column and elution with ether–light petroleum (1 : 6) gave the *keto-ester* (9) as a clear oil (1·6 g) which showed a double peak on g.l.c., $[\alpha]_D^{20}$ +29·3° (*c* 1·5), n_D^{20} 1·4570, $\nu_{max.}$† 1724 cm^{-1}, τ (60 MHz) 8·98 (3H, d, *J* 7 Hz, *Me*CH), 8·63 (1H, d, *J* 8 Hz, 1-H), 8·83 and 8·87 (6H, 2s, Me_2C), 8·5—9·1 (1H, m, 3-H), 8·2 (2H, m, CH_2), 7·99 (3H, s, MeCO), 7·75 (1H, m, C*H*Me), and 6·48 (3H, s, CO_2Me), *m/e* 212 (M^+) (Found: C, 68·2; H, 9·7. $C_{12}H_{20}O_3$ requires C, 67·9; H, 9·5%).

Methyl (+)-cis-3-(2-*acetoxypropyl*)-2,2-*dimethylcyclopropanecarboxylate* (10). The keto-ester (9) (1·3 g) was refluxed for 6 h in methylene chloride (15 ml) with *m*-chloroperbenzoic acid (1·5 g). Usual work-up followed by chromatography on silica and elution with ether–light petroleum (1 : 3) gave the required *acetate* (10) as an oil (0·87 g), b.p. 83° at 0·1 mmHg, showing a double peak on g.l.c., $[\alpha]_D^{21}$ +19·1° (*c* 1·2), n_D^{20} 1·4476, $\nu_{max.}$† 1727 (ester) and 1243 cm^{-1} (acetate), τ (60 MHz) (CCl_4) 9·82 (9H, complex m, Me_2C and *Me*CH), 8·5—9·1 (2H, m, 1- and 3-H), 8·16 (2H, m, *J* 6 Hz, CH_2), 8·04 (3H, s, MeCO), 6·43 (3H, s, CO_2Me), and 5·15 (1H, m, *J* 6 Hz, C*H*Me), τ (C_6D_6) 9·08 and 8·77 (6H, 2s, Me_2C), 8·8—9·2 (1H, m, 3-H), 8·89 (3H, 2d, each *J* 6 Hz, *Me*CH), 8·57 (1H, d, *J* 8 Hz, 1-H), 8·24 (3H, s, MeCO), 8·03 (2H, m, CH_2), 6·57 (3H, s, CO_2Me), and 4·88 (1H, m, C*H*Me), *m/e* 228 (M^+) (Found: C, 63·0; H, 9·1. $C_{12}H_{20}O_4$ requires C, 63·1; H, 8·8%).

Methyl (+)-cis-3-(2-*hydroxypropyl*)-2,2-*dimethylcyclopropanecarboxylate* (11). The acetate (10) (0·66 g) in methanol (20 ml) was treated with 10% aqueous potassium hydroxide solution (4 ml) and set aside overnight, and the acid product treated with ethereal diazomethane. The oil produced (0·48) was chromatographed on silica and eluted with ether–light petroleum (1 : 3) giving the hydroxy-ester (11) as a viscous oil (0·31 g), b.p. 94—97° at 0·05 mmHg, $[\alpha]_D^{20}$ +6·25° (*c* 0·9), $\nu_{max.}$† 3365 (OH) and 1722 cm^{-1} (CO_2Me), τ (60 MHz) (CCl_4) 8·6—9·3 (2H, m, 1- and 3-H), 8·88 (3H, d, *J* 6 Hz, *Me*CH), 8·83 (6H, s, Me_2C), 8·34 (2H, m, *J* 6 Hz, CH_2), 7·53 (1H, s, OH), 6·43 (3H, s, CO_2Me), and 6·35 (1H, m, C*H*OH), τ (C_6D_6) 8·5—9·25 (2H, m, 1- and 3-H), 9·1 and 8·77 (6H, 2s, Me_2C), 8·93 (3H, d, *J* 6 Hz, *Me*CHOH), 8·23 (1H, s, OH), 8·18 (2H, t, *J* 6 Hz, CH_2), 6·64 (3H, s, CO_2Me), and 6·32 (1H, m, C*H*OH).

Methyl (+)-cis-2,2-*dimethyl*-3-(2-*oxopropyl*)*cyclopropanecarboxylate* (12). The alcohol (11) (0·31 g) in acetone (5 ml) was treated dropwise with a solution of Jones reagent [5] until a pale orange colour persisted. Usual work-up and chromatography on a silica column [ether–light petroleum (1 : 12)], gave the *ketone* (12) as an oil (0·16 g), $[\alpha]_D^{20}$ +38·2° (*c* 1·6), n_D^{20} 1·4523, $\nu_{max.}$† 1723 cm^{-1} (ester and ketone), τ (60 MHz) 8·4—9·3 (2H, m, 1- and 3-H), 8·79 and 8·89 (6H, 2s, Me_2C), 7·94 (3H, s, MeCO), 7·23 (2H, d, *J* 5 Hz, CH_2CO), and 6·43 (3H, s, CO_2Me), *m/e* 184 (M^+) (Found: C, 65·1; H, 9·0. $C_{10}H_{16}O_3$ requires C, 65·2; H, 8·75%).

Methyl (−)-cis-*chrysanthemate* (7). A Grignard reagent prepared from freshly distilled methyl iodide (0·25 ml), magnesium (19 mg), and ether (1 ml) was added to a stirred solution of the keto-ester (12) (112 mg) in ether (4 ml), kept under nitrogen. The solution was refluxed for 1 h, and worked up in the usual way giving the alcohol (13) (74 mg), which gave a single major peak on g.l.c. Without further purification it was refluxed for 2 h with toluene-*p*-sulphonic acid (3 mg) in xylene (1 ml), the reaction being monitored by g.l.c. Initially two dehydration products were formed, but later methyl (−)-*cis*-chrysanthemate (7) was the only product. Chromatography on a silica column and elution with 1·5% ether in light petroleum gave the ester, $[\alpha]_D^{20}$ −41·5° (*c* 0·65) (*cf.* ref. 6 for $[\alpha]_D$ of the acid), τ (100 MHz) 8·79 and 8·80 (6H, s, with shoulder, Me_2C), 8·41 (1H, partly obscured d, *J* 8 Hz, 1-H), 8·25 and 8·33 (6H, 2d, *J* 1·2 Hz, Me_2C=), 6·42 (3H, s, CO_2Me), and 4·70 (1H, d, *J* 8 Hz, HC=), *m/e* 182 (M^+) and 123 (100%, $M^+ - CO_2Me$). Its g.l.c.–mass spectral and n.m.r. data [7] were identical with those of a specimen of the methyl ester prepared from authentic (±)-*cis*-chrysanthemic acid.

Methyl (+)-cis-*Homochrysanthemate* [*Methyl* (+)-cis-2,2-*Dimethyl*-3-(3-*methylbut*-2-*enyl*)*cyclopropanecarboxylate*] (16).—*Methyl* (+)-cis-3-(3-*hydroxy*-3-*methylbutyl*)-2,2-*dimethylcyclopropanecarboxylate* (15). (+)-Car-2-ene (3) (6 g) was ozonised at −65° in methanol (40 ml) until (1·5 h) the solution was blue. The product was added over 1 h to a stirred solution of hydrogen peroxide (30%; 25 ml) and sodium hydroxide (30%; 25 ml), and refluxed for 1 h. Water was added, methanol was removed under reduced pressure, and the residue was extracted with ether. The alkaline solution was acidified, extracted with ether, the dried extract was treated with ethereal diazomethane, and the product was eluted from a silica column with ether–light petroleum (1 : 6) giving methyl (+)-*cis*-2,2-dimethyl-3-(3-oxobutyl)cyclopropanecarboxylate (14) (4·4 g), identical with a sample prepared from (+)-4α-acetoxymethylcar-2-ene (2).[1]

The keto-ester (14) (2·3 g) was treated, as described above for (12), with a Grignard solution prepared from methyl iodide (1·5 ml) and magnesium (0·35 g) in ether (2 ml). Elution of the product from a silica column with ether–light petroleum (1 : 5) gave the hydroxy-ester (15) (1·5 g) as a viscous oil, b.p. 120° at 0·1 mmHg, $[\alpha]_D^{20}$ +33·7° (*c* 1·8), $\nu_{max.}$† 3380 (OH) and 1728 cm^{-1} (ester), τ (60 MHz) 8·8—9·3 (2H, m, 1- and 3-H), 9·02 and 8·9 (12H, 2s, Me_2C and Me_2COH), 8·3—8·8 (4H, m, $[CH_2]_2$), 8·22 (1H, s, OH), and 6·56 (3H, s, CO_2Me), *m/e* 214 (M^+).

Methyl (+)-cis-*Homochrysanthemate* (16). The tertiary alcohol (15) (1·2 g) was refluxed in xylene (9 ml) for 4 h

* For details of Supplementary Publications, see Notice to Authors No. 7 in *J.C.S. Perkin I*, 1973, Index issue.

[5] A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 1953, 2548.

[6] I. G. M. Campbell and S. H. Harper, *J. Sci. Food Agric.*, 1952, **3**, 189.

[7] A. F. Bramwell, L. Crombie, P. Hemesley, G. Pattenden, M. Elliott, and N. F. Janes, *Tetrahedron*, 1969, **25**, 1727.

with toluene-*p*-sulphonic acid (5 mg) giving two products in a 3 : 1 ratio (g.l.c.). Chromatography on a 2% silver nitrate–silica column, and elution with 1% ether in light petroleum gave *methyl* (+)-cis-*homochrysanthemate* (16) as an oil (210 mg), b.p. 48° at 0·7 mmHg, $[\alpha]_D^{21}$ +27·7° (*c* 1·6), n_D^{20} 1·4599, $\nu_{max.}$† 1726 (ester) and 840 cm^{-1} (>C=CH), τ (60 MHz) 8·5—9·1 (2H, m, 1- and 3-H), 8·86 and 8·80 (6H, 2s, Me_2C), 8·34 and 8·40 (6H, 2s, Me_2C=), 7·73 (2H, t, *J* 7 Hz, CH_2), 6·43 (3H, s, CO_2Me), and 4·99 (1H, t, *J* 7 Hz, CH=), *m/e* 196 (M^+) (Found: C, 73·1; H, 10·4. $C_{12}H_{20}O_2$ requires C, 73·4; H, 10·3%). The minor product (17) was not further investigated.

Methyl (+)-cis-2,2-*Dimethyl*-3-(3-*methylbutyl*)*cyclopropanecarboxylate* (18).—The mixture of isomers (16) and (17) (0·1 g), derived from the previous experiment, was hydrogenated in ethyl acetate (7 ml) over 5% palladised charcoal (22 mg), giving the *ester* (18) as an oil (87 mg), b.p. 45° at 0·05 mmHg, $[\alpha]_D^{20}$ +38·2° (*c* 0·8), n_D^{20} 1·4366, $\nu_{max.}$† 1725 cm^{-1} (ester), τ (60 MHz) 8·8—9·3 (1H, m, 3-H), 9·12 (6H, d, *J* 6 Hz, Me_2CH), 8·82 and 8·87 (6H, s, Me_2C), 8·67 (1H, d, *J* 8 Hz, 1-H), 8·1—8·6 (5H, m, $[CH_2]_2CH$), and 6·47 (3H, s, CO_2Me), *m/e*† 198 (M^+) (Found: C, 73·0; H, 11·8. $C_{12}H_{22}O_2$ requires C, 72·7; H, 11·2%).

(+)-4α-p-*Tosyloxymethylcar*-2-*ene* (5).—Toluene-*p*-sulphonyl chloride (15 g) was added to a cold solution of (+)-4α-hydroxymethylcar-2-ene, $[\alpha]_D^{20}$ +155° (*c* 2·3) (10 g) in pyridine (100 ml) and kept at 0° overnight. Work-up gave the *tosyl ester* (5), which was crystallised from light petroleum at −60° as rhombs, m.p. 49°, $[\alpha]_D^{20}$ +121° (*c* 1·4), $\nu_{max.}$† 1354 and 1194 cm^{-1} (SO_2O), τ (60 MHz) 8·9—9·4 (1H, m, 3-H), 8·19 and 9·0 (6H, 2s, Me_2C), 8·5—8·9 (1H, m, 1-H), 8·4 (3H, s, MeC=), 8·02 (3H, m, CH_2CH), 7·59 (3H, s, *Me*Ar), 6·18 (2H, m, CH_2OTs), 4·66 (1H, s, CH=), and 2·35 and 2·79 (4H, 2d, *J* 8 Hz, ArH) (Found: C, 67·7; H, 7·8. $C_{18}H_{24}O_3S$ requires C, 67·5; H, 7·55%).

(+)-4α-*Methylcar*-2-*ene* (4) *and* (+)-1,4,4-*Trimethyl*-cis-transoid-1,3-cis-*tricyclo*[5.1.0.$0^{3,5}$]*octane* (21).—A solution of the tosyl ester (5) (32 g) in dry ether (200 ml) was added over 3 h to an ice-cold, stirred solution of lithium aluminium hydride (3 g) in ether (25 ml) and the mixture was stirred overnight. Work-up in the usual way gave a sharp smelling oil (14·5 g) which showed two major peaks of similar intensities and a minor peak on g.l.c. All had very short retention times. Distillation gave an oil, b.p. 23° at 0·6 mmHg, which was chromatographed on a 5% silver nitrate–silica column and eluted with light petroleum. Early fractions contained (+)-1,4,4-*trimethyl*-cis-transoid-1,3-cis-*tricyclo*[5.1.0.$0^{3,5}$]*octane* (21), b.p. 65° at 12 mmHg, $[\alpha]_D^{21}$ +13·5° (*c* 1·6), n_D^{20} 1·4671, τ (100 MHz) 9·4—9·85 (5H, m, cyclopropane-H), 9·21 (3H, s, 1-Me), 9·0 and 9·04 (6H, 2s, Me_2C), 8·5—8·95 (2H, m, CH_2), and 7·9—8·3 (2H, m, CH_2), *m/e* 150 (M^+) (Found: C, 87·9; H, 11·9. $C_{11}H_{18}$ requires C, 87·9; H, 12·1%), $\nu_{max.}$†.

Later fractions from the chromatograph yielded (+)-4α-*methylcar*-2-*ene* (4), b.p. 57° at 12 mmHg, $[\alpha]_D^{20}$ +182° (*c* 1·0), n_D^{20} 1·4695, $\nu_{max.}$† 1654 and 820 cm^{-1} (R_2C=CHR), τ (100 MHz), 9·0—9·4 (2H, 1- and 3-H), 9·21 (3H, s, cyclopropyl-*Me*), 8·98 (3H, d, *J* 7 Hz, *Me*CH), 8·93 (3H, s, cyclopropyl-*Me*), 8·36 (3H, s, MeC=), 8·1—8·5 (3H, m, CH_2CHMe), and 4·7 (1H, s, CH=), *m/e* 150 (M^+) (Found: C, 87·5; H, 12·2. $C_{11}H_{18}$ requires C, 87·9; H, 12·1%). The unsaturated compound (4) has the shorter retention time of the two isomers on g.l.c.

The crude mixture of (4) and (21) (2 g) in methanol (30 ml) was ozonised at −70° for 1 h, the product was slowly added to an ice-cold solution of 30% sodium hydroxide (8 ml) and 30% hydrogen peroxide (13 ml), and the mixture was then refluxed for 1 h. Work-up gave a very complex (g.l.c.) neutral fraction and an acidic fraction, the methyl ester (1·1 g) from which contained two major components (g.l.c.). The larger was the keto-ester (9) which was isolated pure by column chromatography and identified with the specimen prepared as described above. The second component was further purified by preparative g.l.c. and identified as the keto-ester (12) by comparison (g.l.c. and i.r.) with an authentic specimen.

Methyl (+)-cis-2,2-*Dimethyl*-3-(2-*methyl*-3-*oxopentyl*)*cyclopropanecarboxylate* (19).—The ketone (9) (1·3 g) in ether (7 ml) was added dropwise to a stirred solution of sodamide (275 mg) in liquid ammonia (400 ml). After 2 h, methyl iodide (3 g) in ether (10 ml) was added and the solution was left overnight to allow solvent to evaporate. Usual work-up gave a brown oil (0·97 g) consisting (g.l.c.) of starting ketone (9) and the methylated product (19). Chromatography on silica and elution with ether–light petroleum (1 : 10) gave first the *keto-ester* (19) (115 mg) as an oil, b.p. 69° at 0·05 mmHg, $[\alpha]_D^{21}$ +19·8° (*c* 1·0), n_D^{21} 1·4557, $\nu_{max.}$† 1727 cm^{-1} (ester and ketone), τ (60 MHz) (CCl_4) 9·02 (3H, t, *J* 7 Hz, *Me*CH_2), 8·96 (3H, d, *J* 7 Hz, *Me*CH), 8·83 and 8·86 (6H, 2s, Me_2C), 8·7—9·1 (1H, m, 3-H), 8·65 (1H, d, *J* 8 Hz, 1-H), 8·2 (2H, m, $CHCH_2CH$), 7·63 (2H, q, *J* 7 Hz, CH_2Me), 7·4—8·0 (1H, m, CHMe), and 6·47 (3H, s, CO_2Me), τ (C_6D_6) 8·8—9·2 (1H, m, 3-H), 9·07 and 8·82 (6H, 2s, Me_2C), 9·06 (3H, d, *J* 7 Hz, *Me*CH), 9·04 (3H, t, *J* 7 Hz, *Me*CH_2), 8·63 (1H, d, *J* 8 Hz, 1-H), 8·05—8·45 (2H, m, $CHCH_2CH$), 7·82 and 7·84 (2H, 2q, *J* 7 Hz, CH_2Me), 7·5—8·0 (1H, m, CHMe), and 6·58 (3H, s, CO_2Me), *m/e* 226 (M^+) (Found: C, 69·2; H, 10·0. $C_{13}H_{22}O_3$ requires C, 69·0; H, 9·8%). Unchanged starting material (9) was later eluted from the column.

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