Synthetic Studies on Terpenoids. Part XVII.[1] Synthetic Approaches to Hirsutic Acid

By **Tarun K. Sarkar**, Department of Organic Chemistry, Indian Association for the Cultivation of Science, Jadavpur, Calcutta-32, India

Stereoselective syntheses of some potential intermediates for hirsutic acid (6β,6aβ-epoxy-2,3,3aα,3b,4,5,6,6a,7,7aα-decahydro-5β-hydroxy-2β,3bβ-dimethyl-4-methylene-1*H*-cyclopenta[*a*]pentalene-2-carboxylic acid) (I), *viz.* methyl 3-methyl-6-oxo-*cis*-bicyclo[3.3.0]octane-3-carboxylate (XVa and b), methyl 1,2,3,3aα,8,8aα-hexahydro-6-methoxy-2β-methylcyclopent[*a*]indene-2-carboxylate (XXV), and methyl 1,2,3,3aα,8,8aα-hexahydro-6-methoxy-2β-methoxycarbonylmethylcyclopent[*a*]indene-2-carboxylate (XXIX) are reported.

THE structural and stereochemical elucidation of hirsutic acid (I),[2] a mould metabolite with an unusual[3] tricyclo[6.3.0.0^{2,6}]undecane skeleton, was elegantly accomplished by Scott and his co-workers.[4] Current interest[5,6] in developing synthetic approaches to (I) has prompted us to report our results. The difficulty in producing the *gem*-methyl-carboxy function at C-2 in the proper stereoselective fashion was experienced by others[5,6] and it became necessary in their synthetic operations to separate the pair of epimeric compounds: the present study has developed a new synthetic route involving total stereochemical control at each of the three asymmetric centres, *viz.* C-2, C-3a and C-7a of (I) in a closely related derivative (XXIX). Although (XXIX) was obtained stereoselectively, it could not be converted into (XXV).

Two distinct approaches to (I) can be envisaged. The 'AB + C sequence' necessitates creation of a bicyclo[3.3.0]octane precursor comprising rings A and B of (I) with suitable substituents for elaboration to the tricarbocyclic system. This approach has been recognised by others.[5,6] In the alternative 'ABC approach,' appropriately substituted hexahydrocyclopent[a]indenes might be suitable, as the aryl ring may be subsequently converted into the terminal ring C of (I).

We decided first to attempt the synthesis of the pentalene derivative (XVa). This requires formation of a *cis* ring junction [through hydrogenation of (X)[7]] and provision of the correct configuration of substituents at C-2 (for which little precedent is available). The keto-ester (II) was converted into (III) *via* the pyrrolidine enamine procedure. Selective hydrolysis followed by reduction of the carbonyl group with sodium-amalgam afforded (IV). Consideration of steric factors suggested that cyclization of (IV) with polyphosphoric acid (PPA)[8] would lead to (X). In fact, (IV) afforded (XI) with complete elimination of the methoxycarbonyl function. Such elimination of alkoxycarbonyl groups in PPA cyclization has been noted in the corresponding cyclohexane series.[9,10] The hydroxy-group in (IV) is suitably disposed to produce a transient β-lactone which suffers spontaneous decarboxylation or alternatively the same hydroxy-group may help in formation of a carbonium ion β to the ester function, which facilitates its extrusion through fragmentation processes. It is obvious that a structural variant of (IV) in which the hydroxy-group is located γ to the ester function would undergo the desired reaction to furnish (X). Accordingly (VIII) was prepared in a manner analogous to (IV). The keto-ester (V) was converted into (VI) *via* the pyrrolidine enamine procedure. During this reaction a fair amount of a high boiling material, evidently the bis-condensed product, was also isolated but not investigated further. The formation of (VII) was expected to be minimal on steric grounds.[5a] Partial hydrolysis of (VI) followed by reduction of the carbonyl group with sodium borohydride furnished (VIII). Cyclization of (VIII) with PPA at 70° afforded (XIIa) as expected. The n.m.r. spectrum agreed with the structure, and this was confirmed through oxidation of (XIIa) with ruthenium tetroxide.[11] The acid obtained was heated at 180° and then esterified to the expected triester (XIV). Had the cyclization product been a structural isomer (XIIb), this sequence of reactions would have produced a diester. The ethyl ester (XIIa) was next saponified and converted into the methyl ester (X). Any trace of the isomeric bicyclo[3.3.0]-octenone (XIII) that might have been formed from (VII) would suffer hydrolysis, decarboxylation, and consequent elimination by this process. Compound (X) exhibited a sharp singlet at δ 1·4 (Me) and another at δ 3·73 (CO_2Me). Catalytic hydrogenation of (X) furnished a mixture of (XVa and b) in a ratio of 62·5 : 37·5 (as calculated from the n.m.r. methyl signals). Separation of these epimers in appreciable quantities through

[1] Part XVI, D. Mukherjee, S. K. Mukhopadhyay, K. K. Mahalanabis, A. Das Gupta, and P. C. Dutta, *J.C.S. Perkin I*, 1973, 2083.

[2] N. G. Heatley, M. A. Jennings, and H. W. Florey, *Brit. J. Exp. Pathology*, 1947, **28**, 35.

[3] T. Takita, K. Macda, and H. Umezawa, *Tetrahedron Letters*, 1971, 1955.

[4] F. W. Comer, F. McCapra, I. H. Qureshi, and A. I. Scott, *Tetrahedron*, 1967, **23**, 4761.

[5] (*a*) P. T. Lansbury, N. Y. Wang, and J. E. Rhodes, *Tetrahedron Letters*, 1971, 1829; (*b*) P. T. Lansbury and N. Nazarenko, *ibid.*, 1971, 1833; (*c*) P. T. Lansbury, N. Y. Wang, and J. E. Rhodes, *ibid.*, 1972, 2053.

[6] F. Sakan, H. Hashimoto, A. Icchihara, H. Shirahama, and T. Matsumoto, *Tetrahedron Letters*, 1971, 3703.

[7] (*a*) J. W. Barrett and R. P. Linstead, *J. Chem. Soc.*, 1936, 611; (*b*) A. C. Cope and W. R. Schmitz, *J. Amer. Chem. Soc.*, 1950, **72**, 3056; (*c*) P. E. Eaton, R. H. Mueller, *ibid.*, 1972, **94**, 1014; (*d*) G. Stork and F. H. Clarke, *ibid.*, 1961, **83**, 3114.

[8] S. B. Kulkarni and S. Dev, *Tetrahedron*, 1968, **24**, 553.

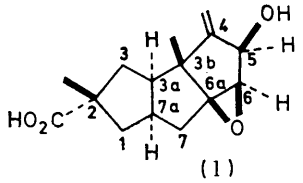
[9] J. A. Barltrop and A. C. Day, *J. Chem. Soc.*, 1959, 671.

[10] U. R. Ghatak, J. Chakravarty, and A. K. Banerjee, *Tetrahedron Letters*, 1965, 3145.

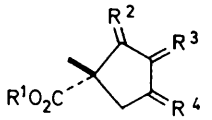
[11] D. M. Piatok, H. B. Bhat, and E. Caspi, *J. Org. Chem.*, 1969, **34**, 112.

column chromatography or preparative g.l.c. proved difficult, so the 'AB + C approach' was abandoned and the alternative approach to (I) was undertaken.

First a model study was undertaken to examine the feasibility of forming the ring system (XXII), which



(I)



(II) $R^1 = Me, R^2 = O, R^3 = H_2, R^4 = H_2$

(III) $R^1 = Me, R^2 = O, R^3 = \langle^{H}_{[CH_2]_2CO_2Me}, R^4 = H_2$

(IV) $R^1 = Me, R^2 = \langle^{H}_{OH}, R^3 = \langle^{H}_{[CH_2]_2CO_2H}, R^4 = H_2$

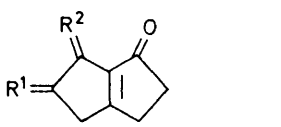
(V) $R^1 = Et, R^2 = H_2, R^3 = O, R^4 = H_2$

(VI) $R^1 = Et, R^2 = H_2, R^3 = O, R^4 = \langle^{H}_{[CH_2]_2CO_2Et}$

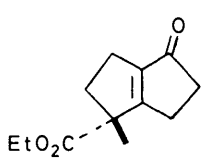
(VII) $R^1 = Et, R^2 = \langle^{H}_{[CH_2]_2CO_2Et}, R^3 = O, R^4 = H_2$

(VIII) $R^1 = Et, R^2 = H_2, R^3 = \langle^{H}_{OH}, R^4 = \langle^{H}_{[CH_2]_2CO_2H}$

(IX) $R^1 = Me, R^2 = H_2, R^3 = O, R^4 = H_2$



(X) $R^1 = \langle^{Me}_{CO_2Me}, R^2 = H_2$

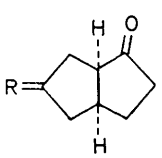


(XIII)

(XI) $R^1 = \langle^{Me}_{H}, R^2 = H_2$

(XIIa) $R^1 = \langle^{Me}_{CO_2Et}, R^2 = H_2$

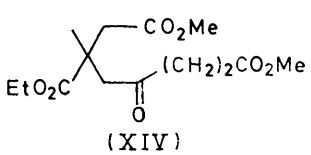
(XIIb) $R^1 = H_2, R^2 = \langle^{Me}_{CO_2Et}$



(XVa) $R = \langle^{Me}_{CO_2Me}$

(XVb) $R = \langle^{Me}_{CO_2Me}$

(XVI) $R = \langle^{Me}_{H}$



(XIV)

has a relatively high degree of strain. Cyclopentanone was converted into (XVIII) through (XVII). Initial attempts to cyclise (XVIII) with a catalytic amount of toluene-*p*-sulphonic acid in boiling benzene were unsuccessful. Cyclodehydration with PPA followed by chromatography furnished a crystalline solid (XXI) in *ca.* 11% yield and an oily material, which was a complex mixture as evident from g.l.c. Compound (XXI) absorbed in the u.v. at 264 nm (log ε 4·2) and upon storage turned into a gummy yellow oil with $\lambda_{max.}$ 266, 270, and 274 nm.[12,13] Catalytic hydrogenation of (XXI) afforded (XXIV). Since hydrogenation is rapid, the A/B junction in (XXIV) must be *cis*.[13,14] We now present additional evidence for its stereostructure and suggest a W-conformation[15,16] (XXXII) for the molecule on the basis of its n.m.r. spectrum. The benzylic proton at C-3a occurs as a triplet of doublets centred at δ 3·53 ($J_{3\beta,3a\alpha} = J_{3a\alpha,8a\alpha}$ 8 Hz, $J_{3\alpha,3a\alpha}$ 3 Hz). The pair of doublets at δ 2·59 ($J_{8\alpha,8\beta}$ 15 Hz, $J_{8\alpha,8a\alpha}$ 2·4 Hz) is due to H-8α and that at δ 3·16 ($J_{8\alpha,8\beta}$ 15 Hz, $J_{8\beta,8a\alpha}$ 8 Hz) is attributed to H-8β. Incidentally, all these data rule out any bridged structure for (XXIV). Birch reduction of (XXIV) followed by hydrolysis of the resulting enol ether afforded (XXXIII) which upon oxidation furnished an acid that revealed two strong bands in the i.r. at 1735 (five membered ketone) and 1710 cm^{-1} (acid). The corresponding methyl ester (XXXIV) showed a strong band at 1740 in addition to 1730 cm^{-1} (ester).

We next proceeded to synthesize (XXII). Accordingly, the keto-ester (IX) was converted into the keto-acid (XIX). Formation of this is rationalized in terms of a δ-lactone formed according to the mechanism of the Stobbé condensation. The possibility of any C-2 alkylated product was remote as the reaction was carried out under equilibrating conditions. Catalytic hydrogenation of (XIX) followed by esterification afforded (XX) which was cyclodehydrated with PPA to (XXII) in about 12% yield. Catalytic hydrogenation of (XXII) furnished a 55 : 45 mixture of (XXVI) and (XXV) respectively, as revealed from n.m.r. and g.l.c. analyses. Alkaline hydrolysis followed by fractional crystallization of the resulting acid mixture afforded (XXVIII) and (XXVII) separately, and these acids were reconverted into their respective methyl esters (XXVI) and (XXV).

The configurational assignment of these epimeric acids is based on a detailed analysis of the n.m.r. spectra of (XXV), (XXVI), and the product from catalytic hydrogenation of (XXII) (which is an almost equimolar mixture of C-2 epimers and thereby offers a comparison of the spectra of these epimers taken under identical conditions). The ester methyl signal of (XXV) occurs at δ 3·6 while it is shifted upfield to δ 3·35 in (XXVI) by long-range shielding from the benzene ring. In the spectrum of the mixture, the $W_{\frac{1}{2}}$ value of the peak due to the C-2 methyl group at δ 1·21 corresponding to

[12] J. Chakravarty and U. R. Ghatak, *Indian J. Chem.*, 1969, **7**, 215.

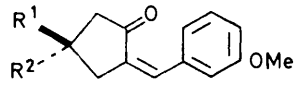
[13] A. C. Gray and A. Hart, *J. Amer. Chem. Soc.*, 1968, **96**, 2569.

[14] (*a*) G. R. Clemo, L. H. Grove, L. Mundy, and G. A. Swan, *J. Chem. Soc.*, 1951, 863; (*b*) D. McIntyre, G. R. Proctor and L. Rees, *ibid.*, 1966, 985.

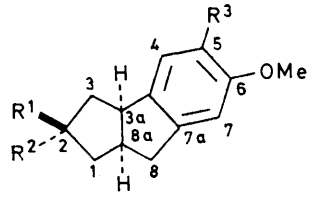
[15] I. Tabushi, K. Fujita, and R. Oda, *J. Org. Chem.*, 1970, **35**, 2383.

[16] I. Tabushi, T. Okada, and R. Oda, *Tetrahedron Letters*, 1969, 1605.

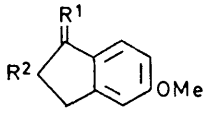
(XXVI) is 2 Hz whereas that of the corresponding peak at δ 1·15 corresponding to the epimer (XXV) is 1·2 Hz, indicating 4 σ-bond coupling between the axial methyl protons and the axial 1β- and 3β-protons in (XXVI). Such coupling has been reported in analogous bicyclo-[3.3.0]octane systems.[6] These results once again indicate the W-conformation [*cf.* (XXXII)] of the bicyclo-[3.3.0]octane system in hexahydrocyclopent[*a*]indenes.



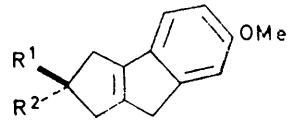
(XXVII) $R^1 = H, R^2 = H$
(XXVIII) Dihydro, $R^1 = H, R^2 = H$
(XXIX) $R^1 = Me, R^2 = CO_2H$
(XXX) Dihydro, $R^1 = Me, R^2 = CO_2Me$



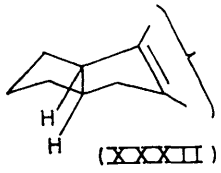
(XXXIV) $R^1 = H, R^2 = H, R^3 = H$
(XXXV) $R^1 = Me, R^2 = CO_2Me, R^3 = H$
(XXXVI) $R^1 = CO_2Me, R^2 = Me, R^3 = H$
(XXXVII) $R^1 = Me, R^2 = CO_2H, R^3 = H$
(XXXVIII) $R^1 = CO_2H, R^2 = Me, R^3 = H$
(XXXIX) $R^1 = CH_2CO_2Me, R^2 = CO_2Me, R^3 = H$
(XXXX) $R^1 = CH_2CO_2H, R^2 = CO_2Me, R^3 = H$
(XXXXI) $R^1 = CH_2CO_2H, R^2 = CO_2Me, R^3 = Br$



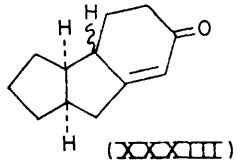
(XXXXV) $R^1 = O, R^2 = CH(CO_2Et)_2$
(XXXXVI) $R^1 = O, R^2 = CH_2CO_2Me$
(XXXXVII) $R^1 = C<^{H}_{CO_2Me}, R^2 = CH_2CO_2H$



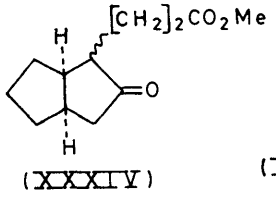
(XXXI) $R^1 = H, R^2 = H$
(XXXII) $R^1 = Me, R^2 = CO_2Me$
(XXXIII) $R^1 = Me, R^2 = CO_2H$



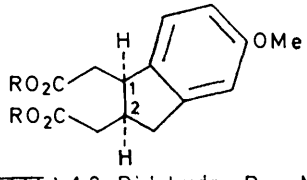
(XXXXII)



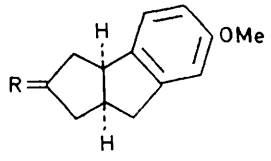
(XXXXIII)



(XXXXIV)



(XXXXVIII) 1,2-Didehydro, R = Me
(XXXXIX) R = Me
(XL) R = H



(XLI) R = O
(XLII) $R = C<^{CN}_{CO_2Et}$

With the two epimeric acids in hand, we investigated the course of metal–ammonia reduction of the styrenoid double bond in (XXII). Such reactions generally proceed with some stereospecificity and moreover it has been shown in a number of related hydrofluorene [17] and hydrophenanthrene [18] ring systems that a carboxy-group, if present in the vicinity of a styrenoid bond, plays a significant role in directing the stereochemical consequences in such reductions. The ester (XXII) was hydrolysed, and reduction of (XXIII) with lithium in liquid ammonia afforded a crystalline solid which had a wide melting point range, and was not characterized further as the reaction was evidently non-stereoselective.

The synthetic route adumbrated for (XXV) proved difficult to pursue because of the low yield in the cyclodehydration step and the lack of stereoselectivity at C-2. A comprehensive scheme was next taken up to synthesize (XXV) *via* (XLI). The ketone (XLI) was prepared stereo-selectively [12,19] and in a satisfactory yield starting from (XXXVI). The keto-ester (XXXVI), prepared from (XXXV),[20] on Reformatsky reaction with methyl bromoacetate afforded (XXXVIII) and a half-ester (XXXVII). The diester (XXXVIII) was hydrogenated to (XXXIX), which upon Dieckmann condensation followed by hydrolysis and decarboxylation of the resulting β-keto-ester furnished the desired ketone (XLI). According to Linstead [21] the A/B ring junction in (XLI) must be *cis*; this suggests that the stereochemistry of the diester is as shown in (XXXIX). The diester (XXXIX) was hydrolysed to the crystalline diacid (XL) and this on pyrolysis

[17] U. R. Ghatak, J. Chakravarty, A. K. Banerjee, and N. R. Chatterjee, *Chem. Comm.*, 1967, 217.
[18] U. R. Ghatak, N. R. Chatterjee, A. K. Banerjee, and R. E. Moore, *J. Org. Chem.*, 1969, **34**, 3739.
[19] L. H. Grove and G. A. Swan, *J. Chem. Soc.*, 1951, 867.
[20] D. Mukherjee, *Indian J. Chem.*, 1971, **9**, 628.
[21] R. P. Linstead and E. M. Meade, *J. Chem. Soc.*, 1934, 935.

with barium hydroxide gave the same tricyclic ketone (XLI). Catalytic hydrogenation of (XXXVII) in the presence of perchloric acid, followed by esterification afforded the same diester (XXXIX) since its hydrolysis furnished the diacid (XL).

With the tricyclic ketone available, we next followed the route developed in this laboratory [22] for stereoselective introduction of the *gem*-methyl-carboxy function at C-2 in (XLI). Condensation of (XLI) with ethyl cyanoacetate afforded (XLII) which on subsequent addition of hydrocyanic acid followed by hydrolysis and esterification furnished the desired stereoisomer (XXIX) only. Such high stereoselectivity in the addition of hydrocyanic acid may be rationalized in terms of a W-conformation of the substrate which favours axial attack since both steric and stereoelectronic factors reinforce each other in this conformation. The n.m.r. spectrum of (XXIX) displays two sharp signals at δ 3·63 and 3·75 assigned to the respective primary and tertiary ester functions. The band at δ 3·63 disappears in the half ester (XXX). When the silver salt of (XXX) was subjected to the usual Hunsdiecker reaction, a bromo-compound was obtained to which structure (XXXI) has been assigned from n.m.r. spectrum. This reveals the absence of *ortho*-coupling in the downfield region. The bromo-compound (XXXI) was reconverted into (XXX) by catalytic hydrogenation in presence of triethylamine. As other methods [23,24] also failed, it may be necessary to modify ring C suitably before effecting the above degradation for introducing the *gem*-methyl-carboxy residue.

EXPERIMENTAL

M.p.s were taken for samples in open capillary tubes in a sulphuric acid bath. U.v. spectra were recorded with a Beckman DU spectrophotometer for solutions in 95% ethanol. I.r. spectra were taken with a Perkin-Elmer model 21 instrument. N.m.r. spectra were recorded on either Varian A-60 or T-60 or HA-100 instruments with tetramethylsilane as internal standard. T.l.c. plates were coated (0·2 mm thickness) with silica gel G (200 mesh). Gas chromatography was carried out by using Varian Aerograph model 1868–4. Light petroleum refers to the fraction of b.p. 60—80°.

Methyl 3-(2-*Methoxycarbonylethyl*)-1-*methyl*-2-*oxocyclopentanecarboxylate* (III).—A mixture of methyl 1-methyl-2-oxocyclopentane carboxylate (II) (30 g), pyrrolidine (30 ml), toluene-*p*-sulphonic acid (100 mg), and benzene (150 ml) was refluxed under nitrogen for 8 h. The crude enamine ($\nu_{max.}$ 1622 and 1730 cm^{-1}) was dried at 120° and 9 mmHg for 1 h and dissolved in dry dioxan (150 ml), and methyl acrylate (48 g) was added and the mixture refluxed under nitrogen for 14 h. Water (48 ml) was then added and refluxing continued for a further 3 h. The product on distillation afforded a forerun of unchanged keto-ester (II) (8 g) followed by the *diester* (III) (22 g, 47%), b.p. 115—117° at 0·1 mmHg (Found: C, 59·4; H, 7·5. $C_{12}H_{18}O_5$ requires C, 59·4; H, 7·4%).

7-*Methylbicyclo*[3.3.0]*oct*-1(5)-*en*-2-*one* (XI).—A mixture of the keto-ester (III) (12·1 g), methanol (66·5 ml), water (3·5 ml), and potassium hydroxide (3·5 g) was left at room temperature for 16 h and then refluxed for 1 h to afford the half-ester (6·55 g). The half-ester (11 g) was dissolved in sodium hydrogen carbonate solution (100 ml; 7%) and a slow stream of carbon dioxide was bubbled through it. Sodium amalgam (250 g; 4%) was introduced with stirring during 4 h, dilute hydrochloric acid (70 ml; 6N) being added after the addition of 3/4 of the amalgam. The mixture was left overnight and then filtered. The filtrate on acidification afforded the hydroxy-acid (IV) as a pale yellow viscous oil (9·2 g), $\nu_{max.}$ ($CHCl_3$) 1735 cm^{-1} in the presence of a few drops of triethylamine. The foregoing hydroxy-acid (3 g) was added to PPA [from phosphorus pentoxide (18·5 g) and orthophosphoric acid (8·2 ml; 85%)], at 60° and the mixture stirred for 2·5 h to afford the ketone (XI) as a pale yellow oil (0·4 g, 22%), b.p. 68° at 0·1 mmHg (bath), $\lambda_{max.}$ 238 nm (log ε 4·04), $\nu_{max.}$ 1640 and 1700 cm^{-1}; 2,4-*dinitrophenylhydrazone*, m.p. 197—198·5° (from benzene–methanol) (Found: C, 56·6; H, 5·1. $C_{15}H_{16}N_4O_4$ requires C, 56·9; H, 5·1%).

7-*Methyl*-cis-*bicyclo*[3.3.0]*octan*-2-*one* (XVI).—The unsaturated ketone (XI) (0·6 g) in ethanol (30 ml) was hydrogenated over palladium–charcoal (50 mg; 10%) to afford the ketone (XVI) as a light yellow oil (0·4 g, 66%), b.p. 88—90° at 1 mmHg (bath), $\nu_{max.}$ 1740 cm^{-1}, δ 1·0 (*J* 6 Hz); 2,4-*dinitrophenylhydrazone*, m.p. 145—147° (from methanol) (Found: C, 56·8; H, 5·8. $C_{15}H_{18}N_4O_4$ requires C, 56·6; H, 5·7%).

Ethyl 4-(2-*Ethoxycarbonylethyl*)-1-*methyl*-2-*oxocyclopentanecarboxylate* (VI).—The crude, dried enamine ($\nu_{max.}$ 1625 and 1725 cm^{-1}), prepared from ethyl 1-methyl-3-oxocyclopentanecarboxylate (V) (20 g) and pyrrolidine (17 g), was refluxed under nitrogen with ethyl acrylate (36 g) in dioxan (100 ml) for 7 h. Addition of water (30 ml) and refluxing for another 2·5 h finally afforded the *diester* (VI) (13 g, 41%), b.p. 130—140° at 0·2 mmHg (Found: C, 62·1; H, 8·1. $C_{14}H_{22}O_5$ requires C, 62·2; H, 8·2%), and a higher boiling product (5 g), b.p. 160—170° at 0·2 mmHg (Found: C, 61·8; H, 8·3. Calc. for $C_{19}H_{30}O_7$: C, 61·6; H, 8·1%).

Ethyl 3-*Methyl*-6-*oxobicyclo*[3.3.0]*oct*-1(5)-*ene*-3-*carboxylate* (XIIa).—The keto-ester (VI) was saponified partially to a half-ester. To the half-ester (18·6 g) in water (63·4 ml) containing sodium hydrogen carbonate (7·7 g), sodium borohydride (2·03 g) was added in small lots with stirring. The mixture was stirred at room temperature for 12 h, acidified with dilute hydrochloric acid to pH 2, and worked up to afford a yellow viscous oil (VIII) (14·8 g). To PPA [from phosphorus pentoxide (18·5 g) and orthophosphoric acid (7·5 ml)] at 70 ± 1° was added the above hydroxy-acid (3 g) and the mixture was stirred for 3 h. It afforded the *keto-ester* (XIIa) as a pale yellow oil (0·95 g, 37%), b.p. 100—105° at 0·2 mmHg (bath), $\lambda_{max.}$ 240 nm (log ε 4·04), $\nu_{max.}$ 1640, 1695, and 1720 cm^{-1} (Found: C, 68·8; H, 7·6. $C_{12}H_{16}O_3$ requires C, 69·2; H, 7·7%); 2,4-*dinitrophenylhydrazone*, m.p. 108—109° (from ethanol) (Found: C, 55·6; H, 5·3. $C_{18}H_{20}N_4O_6$ requires C, 55·6; H, 5·2%).

Dimethyl 3-*Ethoxycarbonyl*-3-*methyl*-5-*oxo*-*octanedioate* (XIV).—A solution of the keto-ester (XIIa) (0·5 g) in

[22] U. R. Ghatak, N. N. Saha, and P. C. Dutta, *J. Amer. Chem. Soc.*, 1957, **79**, 4487.

[23] (*a*) J. A. Davis, J. Herynk, S. Carroll, J. Bunds, and D. Johnson, *J. Org. Chem.*, 1965, **30**, 415; (*b*) N. J. Bunce, *ibid.*, 1972, **37**, 664; (*c*) J. Cason and D. M. Walba, *ibid.*, p. 669.

[24] R. R. Sauers, K. W. Kelly, and B. R. Bickles, *J. Org. Chem.*, 1972, **37**, 537.

acetone (25 ml) was added dropwise during 45 min to the yellow ruthenium tetroxide solution [generated by stirring ruthenium dioxide (50 mg) suspended in acetone (25 ml) with sodium periodate (200 mg) in water (4 ml)]. As the mixture turned from yellow to black during the addition, portions of a periodate solution prepared by dissolving sodium metaperiodate (3 g) in water (15 ml) and adding an equal volume of acetone were introduced. After stirring for 4 h at room temperature, isopropyl alcohol (4 ml) was added. The solid material was separated, and the filtrate was concentrated and worked up to afford an acidic material, $\nu_{max.}$ 1720br cm^{-1}. This was heated at 180° for 15 min, cooled, and esterified (diazomethane) to afford the triester (XIV) as a thick oil (0·3 g, 41%), b.p. 140—145° at 0·2 mmHg (bath) (Found: C, 55·7; H, 7·4. $C_{14}H_{22}O_7$ requires C, 55·6; H, 7·3%).

Methyl 3-*Methyl*-6-*oxobicyclo*[3.3.0.]*oct*-1(5)-*ene*-3-*carboxylate* (X).—The keto-ester (XIIa) (2·3 g) was refluxed with methanolic potassium hydroxide solution (20 ml; 10%) for 3 h under nitrogen. On working up, the acidic product was esterified (diazomethane) to afford the *diester* (X) (1·2 g, 56%), b.p. 100° at 0·2 mmHg (bath), $\lambda_{max.}$ 238 nm (log ε 4·08), $\nu_{max.}$ 1645, 1700, and 1735 cm^{-1} (Found: C, 67·6; H, 7·1. $C_{11}H_{14}O_3$ requires C, 68·0; H, 7·2%).

Methyl 3-*Methyl*-6-*oxo*-cis-*bicyclo*[3.3.0]*octane*-3-*carboxylate* (XVa *and* b).—The keto-ester (X) (0·55 g) in ethanol (15 ml) was hydrogenated over palladium–charcoal (100 mg; 5%) to furnish the epimeric *keto-esters* (XVa and b) as a mobile oil (0·45 g, 80%), b.p. 110° at 0·2 mmHg (bath), $\nu_{max.}$ 1740 cm^{-1}, δ 1·24, 1·27, 3·62, and 3·65 (each 3H, s) (Found: C, 67·0; H, 8·0. $C_{11}H_{16}O_3$ requires C, 67·3; H, 8·2%).

2-(m-*Methoxybenzylidene*)*cyclopentanone* (XVII).—A mixture of cyclopentanone (2·1 g), *m*-methoxybenzaldehyde (2·6 g), and potassium hydroxide (1·2 g) in water (30 ml) was stirred vigorously at 100° for 45 min. It afforded the ketone (XVII) as a pale yellow oil (2·65 g, 52%), b.p. 160° at 0·6 mmHg, which solidified on cooling, as yellow *needles*, m.p. 58—59° (from light petroleum), $\lambda_{max.}$ 245 (log ε 3·6) and 300 nm (4·2) (Found: C, 77·0; H, 7·0. $C_{13}H_{14}O_2$ requires C, 77·2; H, 6·9%).

2-(m-*Methoxybenzyl*)*cyclopentanone* (XVIII).—The benzylidene compound (XVII) (9·8 g) in ethanol (40 ml) was hydrogenated over palladium–charcoal (150 mg; 10%). The product in acetone (40 ml) was oxidized with Jones reagent to afford the ketone (XVIII) as an oil (7·2 g, 73%), b.p. 140—145° at 0·8 mmHg, $\nu_{max.}$ 1745 cm^{-1} (Found: C, 76·3; H, 7·6. $C_{13}H_{16}O_2$ requires C, 76·4; H, 7·9%).

6-*Methoxy*-1,2,3,8-*tetrahydrocyclopent*[a]*indene* (XXI).—To PPA [from phosphorus pentoxide (75 g) and orthophosphoric acid (30 ml; 85%)] maintained at 55—56°, the ketone (XVIII) (10 g) was added and the mixture stirred for 2 min. The resulting product (4·1 g), b.p. 100—120° at 0·3 mmHg, was chromatographed over neutral activated alumina (135 g). Elution with light petroleum furnished an oil (1·6 g) ($\nu_{max.}$ 1580 and 1610 cm^{-1}) followed by the *cyclopent*[a]*indene* (XXI) as a crystalline material (0·86 g). Elution with benzene–light petroleum (1 : 9) afforded further quantity of the same solid (0·17 g), m.p. 50—50·5° (from ethanol–light petroleum), t.l.c. single spot (benzene–light petroleum, 1 : 3) (Found: C, 83·6; H, 7·4. $C_{13}H_{14}O$ requires C, 83·8; H, 7·5%).

6-*Methoxy*-cis-1,2,3,3a,8,8a-*hexahydrocyclopent*[a]*indene* (XXIV).—Compound (XXI) (0·2 g) in ethanol (15 ml) was hydrogenated over palladium–charcoal (50 mg; 10%). The oily product was chromatographed over neutral activated alumina (8 g) and upon elution with light petroleum furnished the *cyclopent*[a]*indene* (XXIV) (0·18 g, 89%), b.p. 80—85° at 0·05 mmHg (bath) (Found: C, 82·7; H, 8·5. $C_{13}H_{16}O$ requires C, 82·9; H, 8·5%).

cis-2,3,3a,3b,4,5,8,8a-*Octahydrocyclopent*[a]*inden*-6(1H)-*one* (XXXIII).—To a solution of lithium (0·8 g) in liquid ammonia (100 ml), (XXIV) (1·3 g) in ether (40 ml) was added during 2 min and the mixture was stirred for 8 min. Ethanol was added dropwise and the product worked up. The enol ether in ethanol (17 ml) was left overnight under nitrogen with hydrochloric acid (12 ml; 6N) and finally refluxed for 2 h to afford the *ketone* (XXXIII) as a very pale yellow oil (0·82 g, 67%), b.p. 85—95° at 0·1 mmHg (bath), $\lambda_{max.}$ 232 nm (log ε 4·1), $\nu_{max.}$ 1680 and 1720vw cm^{-1} (Found: C, 81·7; H, 9·3. $C_{12}H_{16}O$ requires C, 81·7; H, 9·1%); 2,4-*dinitrophenylhydrazone*, m.p. 163° (from benzene–ethanol) (Found: C, 60·7; H, 5·8. $C_{18}H_{20}N_4O_4$ requires C, 60·6; H, 5·6%).

Methyl 3-*Oxo*-cis-*bicyclo*[3.3.0]*octane*-2-*propionate* (XXXIV).—The ketone (XXXIII) (0·5 g) was treated with ruthenium tetroxide in acetone solution following an analogous method as described for (XIIa). The crude acid (0·41 g) was esterified (diazomethane) to afford the *keto-ester* (XXXIV) (0·33 g, 55%), b.p. 95—100° at 0·05 mmHg (bath) (Found: C, 68·7; H, 8·9. $C_{12}H_{18}O_3$ requires C, 68·5; H, 8·6%); 2,4-*dinitrophenylhydrazone*, m.p. 102—103° (from methanol) (Found: C, 55·4; H, 5·9. $C_{18}H_{22}N_4O_6$ requires C, 55·3; H, 5·7%).

3-(m-*Methoxybenzylidene*)-1-*methyl*-4-*oxocyclopentanecarboxylic Acid* (XIX).—Methyl 1-methyl-3-oxocyclopentanecarboxylate (IX) (12·48 g) and *m*-methoxybenzaldehyde (10·88 g) were condensed in aqueous potassium hydroxide solution (120 ml; 4%) as described for (XVII). The resulting acidic material was crystallised from ethyl acetate–petroleum (40—60°) to furnish the *keto-acid* (XIX) (4·3 g), m.p. 127·5°, $\lambda_{max.}$ 242 (log ε 3·87) and 295 nm (4·37), $\nu_{max.}$ 1630 and 1715 cm^{-1} (Found: C, 69·0; H, 6·4. $C_{15}H_{16}O_4$ requires C, 69·2; H, 6·2%). The mother liquor was concentrated and distilled to afford 1-methyl-3-oxocyclopentanecarboxylic acid (4·6 g), b.p. 120—130° at 0·3 mmHg, and a high boiling fraction, b.p. 180—200° at 0·3 mmHg, which on crystallisation furnished an additional crop of (XIX) (3·9 g). The total yield of (XIX) on the basis of consumed (IX) was 60%.

Methyl 3-(m-*Methoxybenzyl*)-1-*methyl*-4-*oxocyclopentanecarboxylate* (XX).—The acid (XIX) (5 g) in ethyl acetate (45 ml) was hydrogenated over palladium–charcoal (200 mg; 10%) and the product was esterified (diazomethane) to afford the *keto-ester* (XX) (4·6 g, 87%), b.p. 178—180° at 0·6 mmHg, $\nu_{max.}$ 1610 and 1740 cm^{-1} (Found: C, 69·2; H, 7·3. $C_{16}H_{20}O_4$ requires C, 69·5; H, 7·3%).

Methyl 6-*Methoxy*-2-*methyl*-1,2,3,8-*tetrahydrocyclopent*[a]*indene*-2-*carboxylate* (XXII).—To PPA [from phosphorus pentoxide (175 g) and orthophosphoric acid (72·5 ml; 85%)], was added (XX) (10 g) in benzene (12 ml) and the mixture was stirred for 1·75 h. It afforded a pale yellow solid (2·2 g), b.p. 185—190° at 0·3 mmHg (bath) which upon crystallisation from methanol furnished the *ester* (XXII) (1·1 g, 12%), m.p. 88·5—89·5°, $\lambda_{max.}$ 264 nm (log ε 4·2), δ 1·45 (3H, s, Me), 3·73 (3H, s, CO_2Me), 3·81 (3H, s, OMe), and 6·4—7·1 (3H, m, ArH), t.l.c. single spot (chloroform–benzene, 1 : 1) (Found: C, 74·6; H, 7·3. $C_{16}H_{18}O_3$ requires C, 74·4; H, 7·0%).

6-*Methoxy*-2-*methyl*-1,2,3,8-*tetrahydrocyclopent*[a]*indene*-

2-*carboxylic Acid* (XXIII).—The ester (XXII) (0·2 g) was refluxed under nitrogen for 5h with methanolic potassium hydroxide solution (5 ml; 10%) to afford the *acid* (XXIII) (0·15 g, 79%), m.p. 150—153° (from ethyl acetate–light petroleum), $\lambda_{max.}$ 265 nm (log ε 4·24), δ 1·5 (3H, s, Me), 3·79 (3H, s, OMe), 7 (3 H, m, ArH), and 10·75 (1H, s, CO_2H) (Found: C, 73·5; H, 6·4. $C_{15}H_{16}O_3$ requires C, 73·7; H, 6·6%).

1,2,3,3aα,8,8aα-*Hexahydro*-6-*methoxy*-2β-*methylcyclopent*[a]*indene*-2-*carboxylic Acid* (XXVII) *and* 1,2,3,3aα,8,8aα-*Hexahydro*-6-*methoxy*-2α-*methylcyclopent*[a]*indene*-2-*carboxylic Acid* (XXVIII).—The ester (XXII) (0·51 g) in ethanol (16 ml) was hydrogenated over palladium–charcoal (100 mg; 10%) to afford an oil (0·41 g), b.p. 130° at 0·1 mmHg (bath). This was refluxed with methanolic potassium hydroxide solution (10 ml; 10%) to furnish a pale yellow solid (0·36 g, 93%), m.p. 94—112°, which on repeated crystallisation from ethyl acetate–light petroleum afforded the *acid* (XXVII), m.p. 127—128°, δ 1·26 (3H, s, Me), 1·5 (2H, m), 2·8 (6H, m), 3·79 (3H, s, OMe), and 7·0 (3H, m, ArH) (Found: C, 73·4; H, 7·6. $C_{15}H_{18}O_3$ requires C, 73·1; H, 7·4%) and its *epimer* (XXVIII), m.p. 124—125°, δ 1·3 (3H, s, Me), 2·0 (4H, m), 3·0 (4H, m), 3·74 (3H, s, OMe), 7·0 (3H, m, ArH), and 9·66 (1H, m, CO_2H) (Found: C, 73·4; H, 7·5. $C_{15}H_{18}O_3$ requires C, 73·1; H, 7·4%).

Methyl 1,2,3,3aα,8,8aα-*Hexahydro*-6-*methoxy*-2β-*methylcyclopent*[a]*indene*-2-*carboxylate* (XXV).—A small portion of (XXVII) was esterified (diazomethane) to afford the *ester* (XXV) as an oil, b.p. 125—130° at 0·1 mmHg (bath), δ 1·15 (3H, s, Me), 1·4 (2H, m), 2·75 (6H, m), 3·6 (3H, s, CO_2Me), 3·71 (3H, s, OMe), and 6·75 (3H, m, ArH), g.l.c. (SE 30 on Varaportzo 5 ft × 1/8 in, 200°) showed a single peak, t_R 11·4 min, t.l.c. single spot (chloroform–benzene, 1 : 1), R_F 0·49 (Found: C, 73·9; H, 7·9. $C_{16}H_{20}O_3$ requires C, 73·8; H, 7·7%).

Methyl 1,2,3,3aα,8,8aα-*Hexahydro*-6-*methoxy*-2α-*methylcyclopent*[a]*indene*-2-*carboxylate* (XXVI).—A small portion of the epimeric acid (XXVIII) was esterified (diazomethane) to afford the *ester* (XXVI) as an oil (XXVI), b.p. 125—130° at 0·1 mmHg (bath), δ 1·21 (3H, s, Me), 1·9 (4H, m), 2·9 (4H, m), 3·35 (3H, s, CO_2Me), 3·68 (3H, s, OMe), and 6·75 (3H, m), g.l.c. (SE 30 on Varaportzo 5 ft × 1/8 in, 200°) showed a single peak, t_R 10·6 min, t.l.c. single spot (chloroform–benzene, 1 : 1), R_F 0·41 (Found: C, 74·0; H, 7·6. $C_{16}H_{20}O_3$ requires C, 73·8; H, 7·7%).

Methyl 5-*Methoxy*-1-*oxoindane*-2-*acetate* (XXXVI).—Diethyl 5-methoxy-1-oxoindane-2-malonate (XXXV) (65 g) was refluxed with methanolic potassium hydroxide solution (700 ml; 10%) for 1·5 h. The resulting yellow solid (56 g) was decarboxylated by heating for 0·5 h at 180° and then esterified by refluxing for 10 h with methanol (250 ml) and sulphuric acid (30 ml; conc.) to afford the *keto-ester* (XXXVI) (35 g, 74%), m.p. 85° (from ethyl acetate–light petroleum), $\lambda_{max.}$ 233 (log ε 4·24), 266 (4·27), and 286 nm (4·16), $\nu_{max.}$ 1605, 1705, and 1735 cm^{-1} (Found: C, 66·4; H, 6·1. $C_{13}H_{14}O_4$ requires C, 66·6; H, 6·0%).

5-*Methoxy*-1-*methoxycarbonylmethyleneindane*-2-*acetic Acid* (XXXVII).—A mixture of dried zinc-wool (7 g), (XXXVI) (3·8 g), and methyl bromoacetate (1 ml) in benzene (50 ml) was heated slowly in the presence of a crystal of iodine until the colour disappeared. Methyl bromoacetate (5 ml) in benzene (10 ml) was then added over 1·5 h and the mixture was heated under reflux for 3·5 h. It afforded dimethyl 6-methoxyindene-2,3-diacetate (XXXVIII) as a yellowish viscous liquid (3 g, 64%), b.p. 200—210° at 0·4 mmHg, $\lambda_{max.}$ 268 nm (log ε 4·1), $\nu_{max.}$ 1730 cm^{-1}, and the *acid* (XXXVII), m.p. 155—157° (from ethyl acetate–light petroleum), $\lambda_{max.}$ 237 (log ε 3·93), 290 (4·14), and 320 nm (4·29), $\nu_{max.}$ 1600, 1630, and 1710 cm^{-1} (when the i.r. spectrum was taken in chloroform containing a few drops of triethylamine, the band at 1710 cm^{-1} sharpened), δ 3·86 (3H, s, CO_2Me), 3·93 (3H, s, OMe), and 6·33 (1H, s, vinylic H) (Found: C, 65·4; H, 5·9. $C_{15}H_{16}O_5$ requires C, 65·2; H, 5·8%).

Methyl 5-*Methoxyindane*-cis-1,2-*diacetate* (XXXIX).—(*a*) The diester (XXXVIII) (3 g) in ethyl acetate (20 ml) was hydrogenated over palladium–charcoal (100 mg; 10%). Uptake became slow, but it was continued after the addition of a drop of perchloric acid and a fresh batch of the catalyst (50 mg) to afford the *diester* (XXXIX) as a pale yellow oil (2·5 g, 82·7%), b.p. 180—190° at 0·1 mmHg, $\nu_{max.}$ 1740 cm^{-1}.

(*b*) The acid (XXXVII) (14 g) in ethyl acetate (100 ml) was hydrogenated over palladium–charcoal (1 g; 10%) in the presence of a few drops of perchloric acid. The product was esterified (diazomethane) to furnish the *diester* (XXXIX) (12·2 g, 82%), b.p. 180—185° at 0·1 mmHg, $\nu_{max.}$ 1740 cm^{-1} (Found: C, 65·4; H, 6·8. $C_{16}H_{20}O_5$ requires C, 65·7; H, 6·9%).

5-*Methoxyindane*-cis-1,2-*diacetic Acid* (XL).—The diester (XXXIX) (2·5 g) was refluxed with methanolic potassium hydroxide solution (25 ml; 10%) under nitrogen for 11 h to afford the *diacid* (XL) (1·5 g, 66%), m.p. 151—153·5° (from ethyl acetate–benzene), $\nu_{max.}$ 1610 and 1715 cm^{-1} (Found: C, 63·6; H, 6·1. $C_{14}H_{16}O_5$ requires C, 63·6; H, 6·1%).

3,3aα,8,8aα-*Tetrahydro*-6-*methoxycyclopent*[a]*inden*-2(1H)-*one* (XLI).—(*a*) To sodium dust (1·2 g) suspended in benzene (75 ml), was added the diester (XXXIX) (10 g) followed by dry methanol (1 ml) and the mixture was heated to reflux for 3 h under nitrogen. The product on refluxing with conc. hydrochloric acid (25 ml), glacial acetic acid (50 ml), and water (10 ml) for 6 h afforded a pale yellow oil (3·2 g), b.p. 130—140° at 0·1 mmHg. This was purified by chromatography over neutral alumina and upon elution with light petroleum afforded the *ketone* (XLI) (3·1 g, 45%), b.p. 130—135° at 0·1 mmHg, $\nu_{max.}$ 1740 cm^{-1}, δ 1·7—3·4 (8H, m), 3·71 (3H, s, OMe), 6·62 (1H, q, $J_{4,5}$ 8, $J_{5,7}$ 2 Hz, 5-H), 6·66 (1H, s, 7-H), and 6·9 (1H, d, $J_{4,5}$ 8 Hz, 4-H), t.l.c. single spot (benzene–ethyl acetate, 4 : 1 and benzene–chloroform, 1 : 1) (Found: C, 76·9; H, 7·1. $C_{13}H_{14}O_2$ requires C, 77·2; H, 6·9%); *semicarbazone*, m.p. 189—191° (decomp.) (from methanol) (Found: C, 64·6; H, 6·6. $C_{14}H_{17}N_3O_2$ requires C, 64·8; H, 6·6%).

(*b*) An intimate mixture of (XL) (0·5 g) and barium hydroxide (100 mg) was heated at 180—190° for 20 min. Low vacuum was applied and the temperature further raised to 300° when a pale yellow oil distilled over. On work-up and purification it afforded (XLI) (100 mg, 26%); semicarbazone, m.p. and mixed m.p. with the sample obtained in (*a*) 191° (decomp).

Methyl 1,2,3,3aα,8,8aα-*Hexahydro*-6-*methoxy*-2β-*methoxycarbonylmethylcyclopent*[a]*indene*-2-*carboxylate* (XXIX).—Following a standard procedure, (XLI) (2·02 g) was condensed with ethyl cyanoacetate (1·7 g) in the presence of glacial acetic acid (0·6 ml) and ammonium acetate (0·6 g) to afford the α-cyano-ester (XLII) as a viscous yellow oil (2·8 g), b.p. 220—225° at 0·05 mmHg (bath), $\lambda_{max.}$ 227 nm (log ε 4·09), $\nu_{max.}$ 1610, 1725, and 2265 cm^{-1}. This was

taken up in ethanol (13·5 ml) containing water (0·6 ml), and a solution of potassium cyanide (1·3 g) in water (7 ml) was added with stirring. The mixture was cooled, a chilled solution of hydrochloric acid (1·6 ml) in water (1·1 ml) was added and the reaction mixture was left at room temperature for 1·5 h, and then poured into water (170 ml) containing hydrochloric acid (2 ml) and worked up to afford a glassy material (2·7 g), $\nu_{max.}$ 1610, 1750, and 2280 cm^{-1}. This was refluxed with a mixture of glacial acetic acid (10 ml), conc. hydrochloric acid (20 ml), and water (6 ml) for 25 h to furnish a yellow solid (1·3 g). It was further refluxed with ethylene glycol (20 ml) containing potassium hydroxide (2 g) under nitrogen for 10 h and the diacid, m.p. 171—182°, thereby obtained was esterified (diazomethane) to furnish a yellow thick oil. On chromatography over neutral alumina using benzene–light petroleum (1 : 3) as the eluant, it afforded the *diester* (XXIX) (0·8 g, 25%), m.p. 69—71° [from ether–petroleum (40—60°)], $\nu_{max.}$ 1610 and 1730 cm^{-1} (Found: C, 67·9; H, 6·8. $C_{18}H_{22}O_5$ requires C, 67·9; H, 6·9%).

1,2,3,3aα,8,8aα-*Hexahydro-6-methoxy-2α-methoxycarbonylcyclopent*[a]*indene-2-acetic Acid* (XXX).—The diester (XXIX) (1·7 g) in methanolic potassium hydroxide solution (11 ml; 3%) was left overnight and then heated to reflux for 3 h to furnish the *acid* (XXX) (1·3 g, 80%), m.p. 133—135° (from ethyl acetate–light petroleum), δ 3·75 (3H, s, CO_2Me) and 3·8 (3H, s, OMe) (Found: C, 66·8; H, 6·5. $C_{17}H_{20}O_5$ requires C, 67·0; H, 6·6%).

5-*Bromo*-1,2,3,3aα,8,8aα-*hexahydro-6-methoxy-2α-methoxycarbonylcyclopent*[a]*indene-2-acetic Acid* (XXXI).—The dry silver salt from (XXX) (2·5 g) was suspended in carbon tetrachloride (30 ml), and bromine (0·7 ml) in carbon tetrachloride (10 ml) was added to the boiling mixture with stirring. After 2 h, it was cooled, filtered, the filtrate washed with sodium carbonate solution (5%), and the alkaline extract worked up to afford the *bromo-acid* (XXXI) (1·5 g, 48%), m.p. 164—165° (from ethyl acetate–light petroleum), δ 3·73 (3H, s, CO_2Me), 3·86 (3H, s, OMe), and 6·76 and 7·3 (each 1H, s, ArH) (Found: C, 53·1; H, 4·9. $C_{17}H_{19}BrO_5$ requires C, 53·2; H, 4·9%).

I thank Professor P. C. Dutta for his help and encouragement. Thanks are also due to Dr. U. R. Ghatak for his interest, to Dr. N. Nand, C.D.R.I., Lucknow, for n.m.r. spectra, to Mrs. C. Dutta of this laboratory for microanalyses, to Mr. A. Ghosal for u.v. spectral measurements, and the National Institute of Health, U.S.A. for financial help.

[3/893 *Received*, 30*th April*, 1973]