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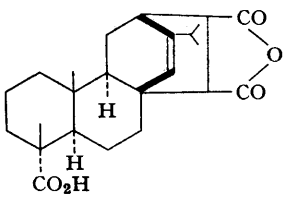
1056. *Terpenes. Part XIII.* The Oxidative Decarboxylation of Maleopimaric and Fumaropimaric Acids.*[1]

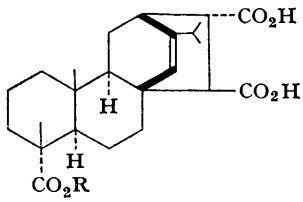
By L. H. ZALKOW and D. R. BRANNON.

Maleopimaric acid (I) was oxidatively decarboxylated by lead tetra-acetate in pyridine to give the mixture of dienes (IV), whereas fumaropimaric acid (IIa) under the same conditions gave olefins (VII) and (VIII). Olefin (VII), on further treatment with lead tetra-acetate, gave cyclopropyl lactone (XVII) in addition to (VIII). Methyl fumaropimarate (IIb) reacted with lead tetra-acetate to give the cyclopropyl lactone (XI) as the major product. All the aforementioned products are presumed to arise through a carbonium-ion mechanism.

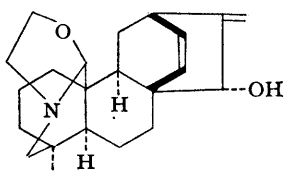
MALEOPIMARIC acid[2] (I) and fumaropimaric acid[2] (IIa) have been studied in our laboratory over several years because of their close skeletal relationship to the diterpenoid alkaloids such as atisine (III). We have previously reported the conversion of these substances into the C_{20} diterpenoid skeleton of atisine.[3,4] One of the important phases in these synthetic studies has involved the removal of the D-ring carboxyl groups by use of oxidative decarboxylation. In this communication, we report some of our previously unpublished results involving oxidative decarboxylation of these acids.[5]



(I)



(II) a: R = H
b: R = CH_3



(III)

Treatment of maleopimaric acid (I) with lead tetra-acetate in pyridine at 50° resulted in the vigorous evolution of carbon dioxide with concomitant formation of the diene mixture (IV), in which the nuclear magnetic resonance (n.m.r.) spectrum and vapour-phase chromatogram indicated the presence of 50% of the $\Delta^{4(18)}$-isomer, 35% of the $\Delta^{4(5)}$-isomer, and 15% of the Δ^{3}-isomer. The diene (IV) was converted into its dimethyl ester with methanolic diazomethane and readily absorbed a molar equivalent of hydrogen in the presence of platinum oxide catalyst to give the Δ^{13}-ene. The double bond at C-13 was not hydrogenated under these conditions as was evident from the n.m.r. spectrum; the 10-methyl group appeared at τ 9·46, showing the characteristic shielding by the double bond[6] at C-13, and the C-14 proton appeared at τ 4·52.

* Part XII, Girotra and Zalkow, *Tetrahedron*, 1965, **21**, 101.

[1] Presented in part before the Combined Southwest–Southeast Region Meeting of the American Chemical Society, New Orleans, La., December 7—9, 1961.

[2] Maleopimaric acid and fumaropimaric acid are trivial names used to refer to the Diels–Alder adducts obtained from abietic acid (or laevopimaric acid) and maleic anhydride and fumaric acid, respectively. See Halbrook and Lawrence, *J. Amer. Chem. Soc.*, 1958, **80**, 368.

[3] Zalkow and Girotra, *J. Org. Chem.*, 1963, **28**, 2037.

[4] Zalkow and Girotra, *J. Org. Chem.*, 1964, **29**, 1299

[5] For a study of the oxidation of fumaropimaric acid with alkaline permanganate see Zalkow and Brannon, *J. Org. Chem.*, 1964, **29**, 1296.

[6] Zalkow and Girotra, *J. Org. Chem.*, 1963, **28**, 2033.

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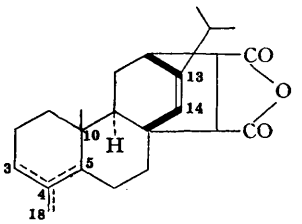
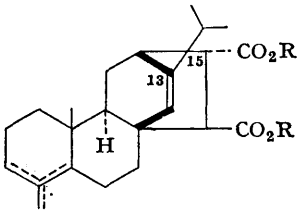
Under similar conditions fumaropimaric acid (IIa) reacted with lead tetra-acetate to give compound (VIIa) as the major product, with some of the triene (VIII). When compound (VIIa) was resubmitted to oxidative decarboxylation, the triene was obtained in 25% yield and a lactone later identified as compound (XVII) was obtained in 65% yield.

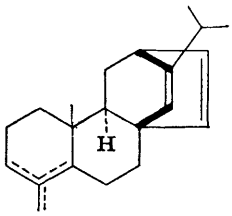
Alkaline treatment of compound (IV) also gave compound (VIIa). The double bond in the A ring and the double bond at C-15 in compound (VIII) were readily hydrogenated with platinum oxide catalyst in acetic acid to give the Δ^{13}-olefin. The C-13 double bond in this compound was ultimately reduced with platinum oxide catalyst in ethanol–acetic acid and a hydrogen pressure of 40 lb./sq. in. to give the saturated hydrocarbon, the n.m.r. spectrum of which showed no olefinic protons and the 10-methyl group gave a signal at τ 9·20.



(IV)

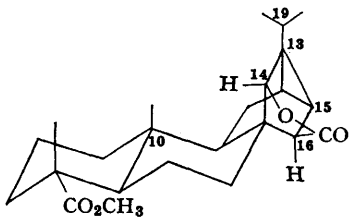


(VII) a: R = H
b: R = CH_3

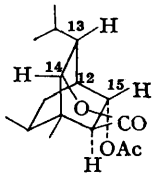


(VIII)

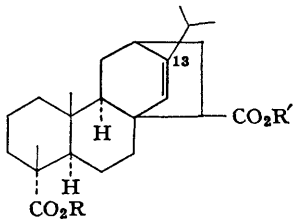
The reaction of methyl fumaropimarate (IIb) with lead tetra-acetate in pyridine gave unexpected results. Chromatography of the crude reaction product on alumina gave as the major product a crystalline compound (m. p. 177—178°) which has been assigned structure (XI) on the basis of the following evidence. The infrared spectrum showed the ester carbonyl band at 1730 cm.$^{-1}$ and in addition a sharp band appeared at 1775 cm.$^{-1}$ which was assigned to a γ-lactone. The n.m.r. spectrum showed a signal at τ 5·5 arising from the C-14 proton[5,7] and no olefinic protons appeared to be present; the 10-methyl group showed no unusual shielding and the isopropyl methyl groups appeared in the region τ 8·90—9·10, showing the absence of a $\Delta^{13(19)}$ double bond. When an attempt was made to hydrogenate (XI) with a small amount of platinum oxide catalyst (4%) in acetic acid, no hydrogen was absorbed but



(XI)



(XII)



(XIII) a: R = H, R′ = CH_3
b: R = R′ = CH_3
c: R = R′ = H

instead compound (XII) was isolated; its infrared spectrum showed the presence of carbonyl bands at 1775 cm.$^{-1}$ (γ-lactone) and 1735 cm.$^{-1}$, whereas its n.m.r. spectrum showed the 15-acetoxyl signal at τ 7·95, the C-14 proton as a singlet at τ 5·25 and the C-15 proton as a doublet ($J_{12,15}$ = 4 c./sec.) centred at τ 5·06. An inspection of Dreiding models indicates that in (XII) the dihedral angle between the C-13 and C-14 protons is ~ 90° and a coupling

[7] Zalkow, Ford, and Kutney, *J. Org. Chem.*, 1962, **27**, 3535.

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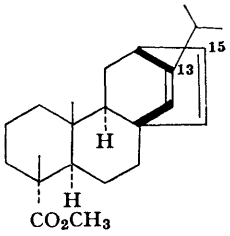
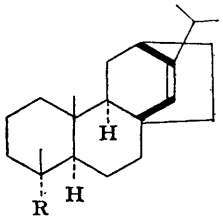
constant of ~0 c./sec. for the C-14 proton is therefore to be expected. Assignment of the acetoxy-group at C-15 to an α-configuration is also consistent with the observed coupling of the C-15 proton with the C-12 bridgehead proton.

When the hydrogenation of compound (XI) was attempted with a large amount of platinum oxide catalyst (35%), one molar equivalent of hydrogen was absorbed and product (XIIIa) was isolated; its infrared and n.m.r. spectra clearly showed that it was an acid ester; in addition, the n.m.r. spectrum showed the olefinic C-14 proton in the usual place, and the shielding effect of the C-13 double bond on the 10-methyl group was apparent.

In the oxidation of methyl fumaropimarate (IIb) with lead tetra-acetate the expected product (XIV) was also obtained, but in low yield. As before, the C-15 double bond was more readily reduced than the C-13 double bond, to give compound (XV), which was ultimately

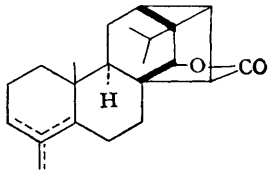


(XIV)



(XV) R = CO_2CH_3

(XVI) R = CH_3



(XVII)

converted into the hydrocarbon (XVI). When compound (IIb) was subjected to Kolbe electrolysis, compound (XI) was again produced but compound (XIV) was absent.

The lactone obtained in the oxidative decarboxylation of compound (VIIa) was assigned structure (XVII) because of the similarity of its i.r. and n.m.r. spectra with those of compound (XI). In the reaction of compound (IIa) with lead tetra-acetate the more polar fractions obtained in the chromatography of the crude product showed absorption bands in the infrared at 1775 cm.$^{-1}$, presumably due to the presence of compound (XI).

Detailed studies of oxidative decarboxylation with tetravalent lead compounds have been reported only since 1953.[8–11] Mosher and Kehr[12] first postulated a mechanism which involved carbonium ions, and recent workers[13] have offered evidence for such intermediates.

The production of A-ring olefins, (IV) and (VII), as described above, is consistent with the formation of intermediate carbonium ions at C-4. A similar case was recently reported by Büchi *et al.*[14]

The formation of the C-15 double bonds of compounds (VIII) and (XIV) provides additional examples of oxidative bisdecarboxylation and a number of related cases can be found in the literature.[10,15] It is clear, however, that in these examples a cyclic intermediate involving the two carboxyl groups cannot be involved. It is interesting that in the reaction of maleopimaric acid with lead tetra-acetate the anhydride moiety in ring D was not removed. Grovenstein *et al.*[16] made a similar observation. The most likely explanation may be that in these substances the anhydride groups attached to the six-membered rings are not readily opened and thus are unaffected by lead tetra-acetate. Since maleopimaric acid is readily converted into fumaropimaric acid by alkali, the lack of reactivity of the anhydride moiety

[8] Doering, Farber, and Sayigh, *J. Amer. Chem. Soc.*, 1952, **74**, 4370.
[9] Doering and Finkelstein, *J. Org. Chem.*, 1958, **23**, 141.
[10] Grob, Ohta, Renk, and Weiss, *Helv. Chim. Acta*, 1958, **41**, 1191.
[11] Grob, Ohta, and Weiss, *Angew. Chem.*, 1958, **70**, 343.
[12] Mosher and Kehr, *J. Amer. Chem. Soc.*, 1953, **75**, 3172.
[13] Corey and Casanova, *J. Amer. Chem. Soc.*, 1963, **85**, 165.
[14] Büchi, Erickson, and Wakabayashi, *J. Amer. Chem. Soc.*, 1961, **83**, 927.
[15] Sauers, *J. Amer. Chem. Soc.*, 1959, **81**, 4873.
[16] Grovenstein, Rao, and Taylor, *J. Amer. Chem. Soc.*, 1961, **83**, 1705.

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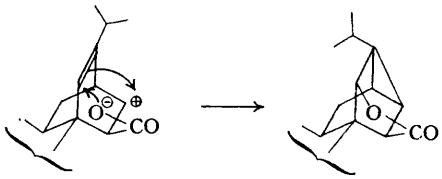
in the first acid is no serious disadvantage if oxidative bisdecarboxylation is desired. The rearrangement required in the formation of compounds (XI) and (XVII) is particularly suggestive of a carbonium-ion mechanism and could arise as shown:



There are two related cases of oxidative decarboxylation with concomitant lactone formation.[17,18] LeBel and Huber[19] recently reported the isolation of tricyclo[2,2,2,$0^{2,6}$]-octan-3-yl acetate in the reaction of *exo*-5-carboxybicyclo[2,2,2]oct-2-ene with lead tetra-acetate in acetic acid in the presence of excess of potassium acetate. Again, these products are most readily explained as arising *via* carbonium-ion intermediates.

In the compounds studied in this investigation the ease of loss of carboxyl groups appears to be 4 > *exo*-15 > *endo*-16. That the 4-carboxyl group should be lost most readily is compatible with the known stability of carbonium ions (3° > 2°) and loss of the *exo*-15-carboxyl group in preference to the *endo*-16-carboxyl group in compounds (VIIa) and (IIb), to give compounds (XVII) and (XI), respectively, may be due to the operation of a concerted mechanism as illustrated above.

Experimental

A Fisher–Johns apparatus was used for the determination of melting points (uncorrected). Analyses were performed by Midwest Microlab, Inc., Indianapolis, Indiana. Infrared and n.m.r. spectra were recorded with Beckman IR-5 and Varian A-60 n.m.r. spectrometers, the latter with tetramethylsilane as internal standard (τ 10). Gas chromatographs were run at the indicated temperature with a column (0·125 in. × 60 in.) of 5% silicone–gum rubber (SE-30) on diatomaceous silica (acid-washed chromosorb W), a hydrogen flame detector, and nitrogen (28 c.c./min.) as carrier gas.

Oxidative Decarboxylation of Maleopimaric Acid (I). *Preparation and Reduction of Mixture* (IV).—Maleopimaric acid[7] (10 g.) was dissolved in dry pyridine (75 c.c.). Dry lead tetra-acetate (11·06 g.) was added to the solution at 50° under a nitrogen atmosphere with stirring. An immediate exothermic reaction ensued with vigorous evolution of carbon dioxide, and the colour of the solution changed from orange to red and, finally, brown. When the evolution of carbon dioxide subsided, more dry lead tetra-acetate (5·53 g.) was added, but no further reaction was observed. The entire reaction was complete in < 5 min. The dark brown solution was cooled and filtered, and the filtrate concentrated with a rotary evaporator. Cold 5% hydrochloric acid solution (300 c.c.) was added to the gummy residue and the resulting solution extracted with 4 × 100 c.c. quantities of ether. Concentration of the combined dried ether extracts gave a crude non-crystalline product (7·35 g.).

Chromatography of crude product (4 g.) on Merck acid-washed alumina (200 g.; activity I) gave amorphous material (IV) (3·9 g.), m. p. 66—68°, in the ether eluent. Gas chromatography at 280° showed two peaks with retention times of 150 and 158 sec. in a ratio of 18 (Δ^3-isomer) to 82 ($\Delta^{4(5)}$- and $\Delta^{4(18)}$-isomers), respectively; $\nu_{max.}$ (KBr) 1845, 1780, 1645, 880, and 855 cm.$^{-1}$. The n.m.r. spectrum (in CCl_4) showed the C_{10}-methyl groups of the mixture at τ 9·55 (0·45 protons, Δ^3-isomer), τ 9·46 (1·05 protons, $\Delta^{4(5)}$-isomer), and τ 9·25 (1·50 protons, $\Delta^{4(18)}$-isomer), the olefinic protons at τ 5·50 (0·50 protons, $\Delta^{4(18)}$-isomer), τ 5·28 (0·50 protons, $\Delta^{4(18)}$-isomer), τ 4·72 (0·15 protons, $\Delta^{4(5)}$-isomer).

The olefin mixture (IV) (210 mg.) in methanol was converted into its corresponding dimethyl ester by the addition of an ethereal solution of diazomethane. After being dried ($MgSO_4$) the solvent was removed and the residue chromatographed on Merck acid-washed alumina

[17] Kitahonoki and Takano, *Tetrahedron Letters*, 1963, 1597.
[18] McCoy and Zagalo, *J. Org. Chem.*, 1960, **25**, 824.
[19] LeBel and Huber, *J. Amer. Chem. Soc.*, 1963, **85**, 3195.

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(15 g.; activity I). The dimethyl ester (170 mg.) was obtained from the ether–benzene (2:3) eluent. Two recrystallizations from light petroleum (fraction b. p. 30—60°) gave the analytical sample, m. p. 122—123°, $\nu_{max.}$ (KBr) 1745, 1725, 1645, and 880 cm.$^{-1}$ (Found: C, 75·0; H, 9·2. Calc. for $C_{25}H_{36}O_4$: C, 75·0; H, 9·1%).

A solution of olefin mixture (IV) (446 mg.) in acetic acid (15 c.c.) in the presence of platinum oxide (47 mg.) readily absorbed a molar equivalent of hydrogen, and further hydrogen uptake then ceased. After removal of the acetic acid with a rotary evaporator, the residue was distributed between sodium hydrogen carbonate solution and ether. The ether layer was dried ($MgSO_4$) and concentrated to give amorphous material (432 mg.), m. p. 53—55°, $\nu_{max.}$ (film) 1845 and 1789 cm.$^{-1}$, τ 9·48 (C_{10}-methyl), τ 4·58 (C_{14}-proton) (Found: C, 77·2; H, 8·7. Calc. for $C_{23}H_{32}O_3$: C, 77·5; H, 9·0%).

Oxidative Decarboxylation of Fumaropimaric Acid (IIa). *Preparation of Compounds* (VII) *and* (VIII).—By the procedure described above, compound (IIa)[2] (10 g.) was treated with lead tetra-acetate (12 g.) in dry pyridine (100 c.c.) to give non-crystalline product (7·88 g.), which was directly esterified with ethereal diazomethane. Gas chromatography at 280° showed that the esterified product contained the three major components, (VIIb), (VIII), and starting material, in the ratio 3·5:1:1·5. Chromatography on 130 g. of Merck acid-washed alumina (activity I) gave (VIII) (1·6 g.), $\nu_{max.}$ (film) 1642, 880, and 705 cm.$^{-1}$; n_D^{25} 1·5360; b. p. 75—77°/0·1 mm. (Found: C, 89·5; H, 10·4. $C_{21}H_{30}$ requires C, 89·3; H, 10·7%) in the petroleum ether eluent. The n.m.r. spectrum of (VIII) was similar to that of (IV) but, in addition, showed the C-15 and C-16 protons as the AB part of an ABX system in the region τ 4·16—3·66.

The ether–benzene (1:4) eluent from the chromatography of the esterified crude product yielded (VIIb) (4·8 g.), b. p. 153—155°/0·1 mm.; $\nu_{max.}$ (film) 1730, 1645, and 880 cm.$^{-1}$ (Found: C, 75·2; H, 9·1. Calc. for $C_{25}H_{36}O_4$: C, 75·0; H, 9·1%). The n.m.r. spectrum of (VIIb) was similar to that of (IV). Further elution (ether–benzene 1:1) gave unchanged (IIb) (1·1 g.) and finally elution with ether gave material whose infrared spectrum showed absorption at 1775 cm.$^{-1}$ (γ-lactone).

The diester (VIIb) was also obtained from (IV) as follows. Anhydride (IV) (200 mg.) was refluxed in methanol (0·5 c.c.) and 10% aqueous potassium hydroxide (5 c.c.) for 9 hr. After cooling, the solution was acidified with dilute hydrochloric acid and the precipitate esterified with excess of ethereal diazomethane. The crude esterified product was chromatographed on Merck acid-washed alumina (9 g.; activity III), whereupon (VIIb) (90 mg.) was obtained from the benzene eluent. The diester so obtained was identical in all respects with that obtained as described above.

Oxidative Decarboxylation of Compound (VIIa.) *Preparation of* (VIII) *and* (XVII).—The diester (VIIb) was hydrolysed by refluxing in 10% aqueous potassium hydroxide for 3 hr. Acidification of the solution with dilute hydrochloric acid and removal of the precipitate gave the diacid (VIIa), m. p. 140—143°; $\nu_{max.}$ (KBr) 2850—3100, 1715, 1645, and 880 cm.$^{-1}$.

The diacid (VIIa) (2·50 g.) was decarboxylated as previously described to give a crude viscous product to which ether was added to give a 65% yield of lactone (XVII), which, on recrystallization from acetic acid, had m. p. 310—313°; $\nu_{max.}$ (KBr) 1775 cm.$^{-1}$ (Found: C, 74·4; H, 8·4. Calc. for $C_{22}H_{30}O_2,CH_3{\cdot}CO_2H$: C, 74·6; H, 8·9%). Chromatography of the remaining crude product, after the removal of (XVII), on Merck acid-washed alumina (activity III) gave a 25% yield of (VIII) in the petroleum (b. p. 30—60°) eluent. The material (VIII) thus obtained was identical in infrared and n.m.r. spectra with (VIII) obtained previously.

Hydrogenation of Compound (VIII).—When compound (VIII) (300 mg.) in 20 c.c. of acetic acid was hydrogenated at room temperature and atmospheric pressure in the presence of platinum oxide (38 mg.), 2 molar equiv. of hydrogen were absorbed within 2·5 hr., after which all hydrogen uptake ceased. After removal of the catalyst by filtration, aqueous sodium hydrogen carbonate solution (100 c.c.) was added to the filtrate, which was then extracted with ether. Evaporation of the ether extract, after drying ($MgSO_4$), gave the Δ^{13}-ene (254 mg.), b. p. 65—70°/0·1 mm., n_D^{25} 1·5208, $\nu_{max.}$ (film) 2950 and 1640 cm.$^{-1}$; n.m.r. (CCl_4): τ 9·47(C_{10}-methyl), τ 4·55 (C_{14}-proton). When this was further hydrogenated in acetic acid–ethanol at 40 lb./sq. in. and room temperature in the presence of platinum oxide for 12 hr., one molar equiv. of hydrogen was absorbed to give the hydrocarbon, b. p. 70—72°/0·1 mm., n_D^{25} 1·5165; $\nu_{max.}$ (film) 1640 and 1380 cm.$^{-1}$ (Found: C, 87·6; H, 12·4. Calc. for $C_{21}H_{46}$: C, 87·4; H, 12·6%).

Oxidative Decarboxylation of Methyl Dihydrogen Fumaropimarate (IIb). *Preparation of Compounds* (XI) *and* (XIV).—The material (IIb) (10 g.) was added to dry pyridine (80 c.c.) in a

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nitrogen atmosphere, the temperature of the solution raised to 50°, and dry lead tetra-acetate (14·23 g.) added in one portion. Within 3 min. carbon dioxide evolution ceased and the solution, which had become black, was filtered, the filtrate being concentrated with a rotary evaporator. Dilute hydrochloric acid (5%, 500 c.c.) was added to the concentrate and the aqueous solution was exhaustively extracted with ether. After being dried ($MgSO_4$), the ether extract was evaporated to yield crude non-crystalline product (7·85 g.), which, after chromatography on Merck acid-washed alumina (500 g.; activity III) gave compound (XIV) (1·22 g.) in the ether–benzene (1:9) eluent as a viscous oil, b. p. 140°/0·1 mm., n_D^{25} 1·5163; $\nu_{max.}$ (film) 1730, 1645, and 705 cm.$^{-1}$ (Found: C, 80·4; H, 10·0. Calc. for $C_{23}H_{34}O_2$: C, 80·6; H, 10·0%). This showed a single peak at 230° with a retention time of 115 sec. in its gas chromatogram. The n.m.r. spectrum in carbon tetrachloride showed the C-14 proton as a singlet at τ 4·58 and the C-15 and C-16 protons as the AB portion of an ABX system in the region τ 4·16—3·72 (see analysis of dihydro-derivative below). Further elution with ether–benzene (1:1) gave lactone (XI) (4·3 g.) which after two recrystallizations from acetic acid had m. p. 177—178°; $\nu_{max.}$ (KBr) 1775 and 1730 cm.$^{-1}$ (Found: C, 74·3; H, 8·8. Calc. for $C_{24}H_{34}O_4$: C, 74·6; H, 8·9%).

Hydrogenation of Compound (XIV). *Preparation of Compound* (XV).—When the diene (XIV) (116 mg.) was hydrogenated in acetic acid (15 c.c.) with platinum oxide catalyst (26 mg.) at atmospheric pressure and room temperature, one molar equiv. of hydrogen was rapidly absorbed. After the usual work-up the olefin (XV) (110 mg.) was obtained, b. p. 140°/0·1 mm., n_D^{25} 1·5163; $\nu_{max.}$ (KBr) 1740, 1645, and 1245 cm.$^{-1}$ (Found: C, 80·0; H, 10·6. Calc. for $C_{23}H_{36}O_2$: C, 80·2; H, 10·5%). The n.m.r. spectrum (CCl_4) showed indications at τ 9·42 (C_{10}-methyl), τ 4·61 (C_{14}-proton).

Conversion of the Olefin (XV) *into* (XVI).—The olefin (XV) (5·86 g.) in anhydrous ether (30 c.c.) was added, with stirring, to a solution of lithium aluminium hydride (0·68 g.) in ether (100 c.c.), and the entire solution was refluxed for 3 hr. After the usual work-up, the corresponding alcohol(4·54 g.) [$\nu_{max.}$ (film) 3410 cm.$^{-1}$] was obtained, and was transformed into its toluene-*p*-sulphonate. The tosylate (3·34 g.) was directly reduced by refluxing with lithium aluminium hydride (0·42 g.) in dioxan (50 c.c.) for 17 hr. to give a colourless liquid (2·15 g.) which was chromatographed on Merck acid-washed alumina (120 g.; activity I). The petroleum (b. p. 30—60°) eluent gave compound (XVI), b. p. 70°/0·1 mm., n_D^{25} 1·5133, $\nu_{max.}$ (film) 2925 and 1460 cm.$^{-1}$ (Found: C, 87·6; H, 12·2. Calc. for $C_{22}H_{36}$: 87·9; H, 12·1%). The ether–benzene (1:1) eluent gave the starting alcohol (1·51 g.). The yield of compound (XVI) was greatly improved as follows.[3] The alcohol (1 g.) obtained by reduction of compound (XV) with lithium aluminium hydride–pyridine (10 c.c.) was added to a solution of chromic anhydride (0·5 g.) in pyridine (10 c.c.) and after stirring at room temperature for 3 hr. the solution was poured into ice–water (100 c.c.). The aqueous solution was extracted with ether and after being washed and dried the ether extract was evaporated to give the crude aldehyde (0·88 g.), $\nu_{max.}$ (film) 2680 and 1725 cm.$^{-1}$, which was directly reduced as follows. The aldehyde (0·88 g.) was refluxed with potassium hydroxide (1·5 g.), hydrazine (2 c.c.), and diethylene glycol (10 c.c.) for 3 hr., and the solution distilled, removing water and hydrazine, until the temperature reached 240°, when hydrazine (1·5 c.c.) was again added and refluxing continued for an additional 10 hr. The solution was then poured into water and the aqueous solution extracted with ether. After being washed with water, the ether extract was dried ($MgSO_4$) and evaporated to give crude product (720 mg.), which gave compound (XVI) (520 mg.) after chromatographing on alumina.

Preparation of Compound (XII).—A solution containing (XI) (3 g.) and platinum oxide (0·12 g.) in acetic acid (20 c.c.) was stirred in a hydrogen atmosphere at room temperature for 36 hr., but no hydrogen uptake was observed. The catalyst was filtered off and the acetic acid solution poured into water (200 c.c.). The aqueous solution was exhaustively extracted with ether, and the extract washed with water and dried ($MgSO_4$). Evaporation of the ether layer gave crude material (2·83 g.), which after recrystallization from carbon tetrachloride gave pure *compound* (XII) (2·50 g.), m. p. 195—196°; $\nu_{max.}$ (film) 1775, 1735, and 1300 cm.$^{-1}$ (Found: C, 70·4; H, 8·1. $C_{26}H_{38}O_6$ requires C, 70·0; H, 8·6%).

Preparation of Compound (XIII).—A solution prepared by dissolving compound (XI) (0·39 g.) in glacial acetic acid (10 c.c.) was stirred in the presence of platinum oxide (0·14 g.) in a hydrogen atmosphere; over a period of 2 hr., hydrogen (22·1 c.c.) was absorbed. The solution was worked up as above to give crude product (XIIIa) (0·37 g.), $\nu_{max.}$ (film) 2800—3100, 1740, 1715, and 1645 cm.$^{-1}$, n.m.r. (CCl_4): τ 9·40 (C_{10}-methyl), τ 6·40 (methyl ester in ring A), τ 4·66 (C_{14}-proton), τ −0·15 (carboxyl proton). Compound (XIIIa) was methylated with ethereal diazomethane

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and the product chromatographed on alumina to give, in the ether–benzene eluent (1:4), compound (XIIIb) as a viscous oil; $\nu_{max.}$ (film) 1740, 1735, and 1645 cm.$^{-1}$, n.m.r. spectrum similar to that of compound (XIIIa). Compound (XIIIb) (250 mg.) was hydrolysed by refluxing for 6 hr. with 3N-aqueous sodium hydroxide (2·5 c.c.) and methanol (1·0 c.c.). The *diacid* (XIIIc), obtained by acidification of the above solution, was twice recrystallized from carbon disulphide–ether (7:3) to give a product, m. p. 194—196°, $\nu_{max.}$ (KBr) 3100—2800, 1710—1715, and 1645 cm.$^{-1}$ (Found: C, 73·4; H, 9·3. $C_{23}H_{34}O_4$ requires C, 73·75; H, 9·15%).

Preparation of Compound (XI) *by Kolbe Electrolysis.*—The diacid (IIa) (5·0 g.) in aqueous sodium hydroxide (200 c.c., 5%) and methanol (60 c.c.) was electrolysed for 3 hr. at 2A and 22v d.c. at 23° in a cell equipped with platinum electrodes and a commutator. At the end of this period, water (700 c.c.) was added and the aqueous solution extracted with ether. The dried ether extract yielded neutral material (0·33 g.). The alkaline aqueous solution was then acidified with cold dilute hydrochloric acid and the precipitate was filtered off and dried (3·7 g.), m. p. 290—293°. The infrared spectrum and mixed melting point showed this material to be identical to starting diacid (IIa). The neutral fraction (300 mg.) was chromatographed on Merck acid-washed alumina (10 g.; activity III) and the ether–benzene (1:1) eluent yielded compound (XI) (205 mg.), identical in all respects with that obtained in the reaction of compound (IIa) with lead tetra-acetate.

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