612. *Synthetic Long-chain Aliphatic Compounds. Part VI.* Some Anomalous Reductions of 9-Keto-10-methoxyoctadecanoic Acid.*†

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IN Part II of this series (Bowman, *J.*, 1950, 177) we examined the reduction of 13-keto-14-methoxydocosanoic acid † (I; $n = 11$) by sodium and alcohol and by zinc and acid, and the products were thought to be 13- (II; $n = 11$) and 14-hydroxydocosanoic (III; $n = 11$) acids, respectively. Confirmation of these conclusions was not possible, however, for both the

$$CH_3\cdot[CH_2]_7\cdot CH(OMe)\cdot CO\cdot[CH_2]_n\cdot CO_2H \quad \text{(I.)}$$

$$\text{Na–EtOH}\downarrow \qquad\qquad \text{Zn}\downarrow$$

$$\text{(II.)}\ CH_3\cdot[CH_2]_8\cdot CH(OH)\cdot[CH_2]_n\cdot CO_2H \qquad CH_3\cdot[CH_2]_7\cdot CH(OH)\cdot[CH_2]_{n+1}\cdot CO_2H\ \text{(III.)}$$

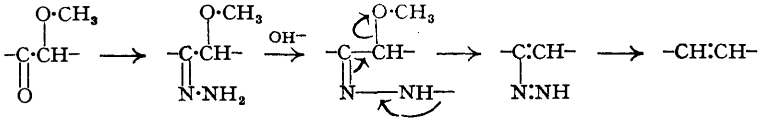
hydroxy-acids were new, and only one of the corresponding keto-acids was known. We have now examined similar reductions of the corresponding octadecanoic acid (I; $n = 7$) (Part III; *J.*, 1951, 1079) in the hope of confirming the above results, since both of the expected hydroxy-acids had been prepared previously.

With sodium and alcohol, the acid (I; $n = 7$) did, in fact, yield the expected hydroxy-acid (II; $n = 7$), identified by oxidation to the corresponding keto-acid. On the other hand, with zinc under Clemmensen conditions, a mixture of hydroxy-acids was obtained but reduction with zinc and hydrochloric–acetic acids yielded an apparently pure hydroxy-acid, m. p. 81—82°, oxidised to a keto-acid, m. p. 84°. This m. p. agrees with that previously reported for 10-keto-octadecanoic acid, but various m. p.s between 80° and 85° have been reported for the expected hydroxy-acid (III; $n = 7$); Tomecko and Adams (*J. Amer. Chem. Soc.*, 1927, **49**, 523) recorded m. p. 81—82° and Robinson and Robinson (*J.*, 1925, **127**, 175) gave m. p. 84·5°. There is still, therefore, some ambiguity regarding the reduction with zinc and this can only be resolved by synthesis.

We have also examined the reduction of the methyl ester of the acid (I; $n = 7$) by Huang-Minlon's modification (*J. Amer. Chem. Soc.*, 1946, **68**, 2487) of the Wolff–Kishner method. As far as we are aware, no example of the reduction of an acyloin ether has been reported. Examples of the reduction of acyloins by the Wolff–Kishner method have been mainly confined to the sterol series (Barton, Holness, and Klyne, *J.*, 1949, 2456, and references cited therein) and have been shown to give the fully reduced compound (IV) or, in some cases, the corresponding unsaturated compound (V). Kishner (*J. Russ. Phys. Chem. Soc.*, 1913, **45**, 973) described the reduction of 2-hydroxy-3-keto-2 : 6-dimethyloctane to 2 : 6-dimethyloct-2-ene.

$$\underset{\text{(IV.)}}{R\cdot CH_2\cdot CH_2\cdot R'} \longleftarrow R\cdot CH(OH)\cdot CO\cdot R' \longrightarrow \underset{\text{(V.)}}{R\cdot CH{:}CH\cdot R'}$$

The product obtained from the methyl ester of (I; $n = 7$) was found to contain 75% of olefinic acids (by iodine value), and stearic, elaidic, and oleic acids were isolated by fractional crystallisation. A possible mechanism for the formation of olefin is as follows (Barton *et al.*, *loc. cit.*; Seibert, *Ber.*, 1947, **80**, 494) :



EXPERIMENTAL.

Reduction of 9-*Keto*-10-*methoxyoctadecanoic Acid with Sodium and Ethanol*.—The acid was obtained, without isolation, from the methyl ester (Part III). Sodium (2 g.) was added to a solution of the acid (1·8 g.) in ethanol (25 c.c.); the mixture was boiled to complete dissolution of the metal and poured into dilute sulphuric acid (200 c.c.; 1N.). The oily product, which slowly crystallised, was eventually separated by filtration and dissolved in boiling methanol (activated charcoal), and the filtered solution evaporated to dryness. Crystallisation of the residue from light petroleum (b. p.

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* Part V, preceding paper. † Geneva notation ($CO_2H = 1$) is used for long-chain acids throughout.

60—80°) furnished needles of 9-hydroxyoctadecanoic acid, m. p. 75·5° (yield of material melting at 74°; 0·4 g.) (Found: C, 71·8; H, 11·7. Calc. for $C_{18}H_{36}O_3$: C, 71·9; H, 12·1%). The methyl ester crystallised from aqueous methanol in needles, m. p. 49—50° (Found: C, 72·6; H, 12·0. Calc. for $C_{19}H_{38}O_3$: C, 72·6; H, 12·2%). Tomecko and Adams (*loc. cit.*) gave m. p.s 74—75° and 45—46°, respectively. Oxidation of the hydroxy-acid by chromic acid in acetic acid yielded 9-keto-octadecanoic acid, which separated from ethanol in colourless plates, m. p. 82°. Tomecko and Adams (*loc. cit.*) reported m. p. 82—83°.

Reduction of Methyl 9-keto-10-methoxyoctadecanoate.—(i) *With zinc.* The ester (0·6 g.) in acetic acid (10 c.c.; 70%) was boiled for 10 minutes with zinc dust (4 g.) and concentrated hydrochloric acid (0·1 c.c.). After decantation of the liquid, the zinc was extracted with boiling glacial acetic acid (2 × 10 c.c.) and the combined solutions were poured into water. The crystalline product was filtered off, boiled with excess of sodium hydroxide solution to hydrolyse some ester, and acidified. Crystallisation from aqueous ethanol yielded the product, probably 10-hydroxyoctadecanoic acid, m. p. 79—80° (0·4 g.), which recrystallised from light petroleum (b. p. 60—80°) in colourless plates, m. p. 81—82°.

Oxidation of this hydroxy-acid with chromic acid in acetic acid furnished 10-keto-octadecanoic acid, which crystallised from ethanol in plates, m. p. 82°. Robinson and Robinson (*loc. cit.*) gave m. p. 83°.

(ii) *By modified Wolff–Kishner method.* A mixture of the ester (2 g.), hydrazine hydrate (3·5 c.c.; 60%), sodium hydroxide (1 g.) in water (1·5 c.c.), and 2 : 2′-dihydroxydiethyl ether (25 c.c.) was boiled under reflux for 1½ hours. Water was then removed by distillation, and the mixture was heated at 200° (internal temp.) for 4 hours (Huang-Minlon, *loc. cit.*) and poured into excess of dilute sulphuric acid, the products being isolated with benzene. Distillation furnished a colourless oil, b. p. 180—190°/0·2 mm. (1·2 g.), which rapidly solidified and contained approx. 75% of octadecenoic acids (Found: Iodine val., 67. Calc. for $C_{18}H_{34}O_2$: Iodine val., 90).

Fractional crystallisation of the product from light petroleum (b. p. 40—60°) at low temperatures yielded stearic acid, m. p. 68—69°, and elaidic acid, m. p. 43—44°; the m. p. of each acid was undepressed by admixture with an authentic specimen. From the mother-liquors, oleic acid was isolated as the lithium salt, which was converted directly into the *p*-phenylphenacyl ester, m. p. and mixed m. p. 60—61°.

In another experiment ethylene glycol was used as solvent during the reduction; the distilled product contained approximately 78% of octadecenoic acids (Found: Iodine val., 70).

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