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ORGANIC REACTIONS IN STRONG ALKALIS—IV

REARRANGEMENT AND FISSION OF ACIDS WITH α-GLYCOL AND OTHER VICINAL OXYGEN FUNCTIONS

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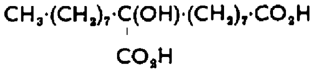
Abstract—On treatment with strong alkalis, 9,10-dihydroxystearic acid, and the corresponding hydroxy-keto and diketo acids, give α-octyl-α-hydroxysebacic acid in high yield by a benzilic acid type of rearrangement. Under more vigorous conditions 9-oxoheptadecanoic acid is formed, which then hydrolyzes to give octanoic, nonanoic and azelaic acids as the main products.

10,11-Dihydroxyundecanoic, 9,10,12-trihydroxyoctadecanoic and aleuritic acids undergo analogous fission reactions on alkali fusion.

IN the preceding paper[1] we described the reactions of monohydroxy fatty acids in concentrated alkalis. We are concerned here with the behaviour of some dihydroxy-derivatives of unsaturated fatty acids, and related compounds containing vicinal oxygen functions.

In 1914 Le Sueur and Withers[2] reported that treatment of (erythro-) 9,10-dihydroxystearic acid (I) with concentrated potassium hydroxide at 200–250° gave 65 per cent of α-hydroxy-α-octylsebacic acid (II) and, by further reaction of the latter with alkali, ca. 2 per cent of 9-oxoheptadecanoic acid (III). At higher temperatures (up to 275°) some nonanoic and azelaic acid were formed. Analogous results were also obtained with 13,14-dihydroxybehenic acid. These careful studies seem to have been overlooked by most subsequent workers who have simply reported that alkaline fission of 9,10-dihydroxystearic acid gives nonanoic and azelaic acid.[3–6] Eckert[3] claimed that the yields were improved by the addition of potassium chlorate to the

$$\mathrm{CH_3\cdot(CH_2)_7\cdot CH(OH)\cdot CH(OH)\cdot(CH_2)_7\cdot CO_2H} \qquad \mathrm{I}$$



$$\mathrm{CH_3\cdot(CH_2)_7\cdot \underset{\displaystyle CO_2H}{\underset{|}{C}}(OH)\cdot(CH_2)_7\cdot CO_2H} \qquad \mathrm{II}$$

$$\mathrm{CH_3\cdot(CH_2)_7\cdot CO\cdot(CH_2)_7\cdot CO_2H} \qquad \mathrm{III}$$

$$\mathrm{CH_3\cdot(CH_2)_4\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot CH(OH)\cdot CH(OH)\cdot(CH_2)_7\cdot CO_2H} \qquad \mathrm{IV}$$

$$\mathrm{CH_3\cdot CH_2\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot CH(OH)\cdot CH(OH)\cdot CH_2\cdot CH(OH)\cdot CH(OH)\cdot(CH_2)_7\cdot CO_2H} \qquad \mathrm{V}$$

$$\mathrm{CH_3\cdot(CH_2)_7\cdot CO\cdot CO\cdot(CH_2)_7\cdot CO_2H} \qquad \mathrm{VI}$$

$$\mathrm{CH_3\cdot(CH_2)_7\cdot CO\cdot CH(OH)\cdot(CH_2)_7\cdot CO_2H} \qquad \mathrm{VIIa}$$

$$\mathrm{CH_3\cdot(CH_2)_7\cdot CH(OH)\cdot CO\cdot(CH_2)_7\cdot CO_2H} \qquad \mathrm{VIIb}$$

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[1] R. A. Dytham and B. C. L. Weedon, *Tetrahedron* **8**, 246 (1960).

[2] H. R. Le Sueur and J. C. Withers, *J. Chem. Soc.* **105**, 2801 (1914); cf. H. R. Le Sueur, *Ibid.* **79**, 1313 (1901).

[3] A. Eckert, *Monats.* **38**, 1 (1917).

[4] R. L. Logan, U.S.P. 2,625,558.

[5] T. Asahara and M. Tomita, *J. Oil Chem. Soc. Japan* **2**, 105 (1953); *Chem. Abstr.* **48**, 11341 (1954).

[6] cf. R. Kadesch, *J. Amer. Oil Chem. Soc.* **31**, 568 (1954).

reaction mixture, and that similar degradations of 9,10,12,13-tetra- (IV) and 9,10,12,13,15,16-hexa-hydroxystearic acid (V), derived from linoleic and linolenic acids, gave azelaic, acetic and either hexanoic or propionic acid respectively. According to Logan,[4] alkaline fission of (threo-) 9,10-dihydroxystearic acid with 70 per cent sodium hydroxide also yields nonanol and an ω-hydroxy-acid, presumably 10-hydroxynonanoic acid, though no information on the properties of the product, or its isolation, have been given.

In the present studies alkali fusion of both erythro- and threo- 9,10-dihydroxystearic acid at 300–360° gave almost identical mixtures of acids (Table 1). In agreement with earlier reports the dicarboxylic acids consisted very largely of azelaic, but, surprisingly, the mono-carboxylic acids contained almost as much octanoic as nonanoic acid. Repetition of the reaction at 260–270° gave, in addition to the above fission products, 9-oxoheptadecanoic acid (III) in yields up to 30 per cent. At still lower temperatures (230–240°), α-hydroxy-α-octylsebacic acid (II) was obtained in yields up to 90 per cent together with traces of nonanoic and azelaic acid. Alkali fusion of the keto-acid at 300° gave the mixture of acids expected by analogy with 10- and 12- ketostearic acid (Part III),[1] the principal products being azelaic, by hydrolysis of the 9,10 bond, and both octanoic and nonanoic acid by fission of the 8,9-bond (Table 1). Considered in conjunction with the results of Le Sueur and Withers, the above transformations, and the close similarity between the final products from 9-oxoheptadecanoic acid and those from the dihydroxystearic acids, clearly indicate that fission of the latter proceeds by the successive formation of the hydroxy-dicarboxylic acid (II) and the keto-acid (III).

TABLE 1. ALKALI FUSION OF 9,10-DIHYDROXYOCTADECANOIC AND RELATED ACIDS

(1 hr; yield of acidic products in moles)

Acidic products		Threo-dihydroxy acid			Erythro-dihydroxy acid	Hydroxy-keto acids	9-Oxoheptadecanoic acid	
		300°	300°	360°	360°	300°	300°	300°
Mono-carboxylic acids	n-C_7	0·06	0·12	0·06	0·04	0·06	0·06	0·10
	n-C_8	0·26	0·20	0·22	0·22	0·20	0·19	0·26
	n-C_9	0·34	0·30	0·33	0·29	0·30	0·40	0·40
	"Me-C_{15}"[a]	0·03	0·03	0·05	0·04	0·06	0·04	—
	"Me-C_{17}"[a]	trace	trace	—	—	—	0·04	0·05
High b.p. acids[b]		0·20	0·18	0·18	0·27	0·17	0·17	0·10
Di-carboxylic acids	n-C_7	0·03	0·03	0·05	0·03	0·04	0·04	0·03
	n-C_9	0·34	0·33	0·40	0·34	0·41	0·38	0·41

[a] "Me-C_{15}" signifies 7-methylpentadecanoic acid and "Me-C_{17}" a mixture of 9-methylheptadecenoic acids. These products are formulated by analogy with those from other keto-acids (Part III).

[b] Approximate value estimated by difference.

In 1922 Nicolet and Jurist[7] demonstrated that 9,10-diketostearic acid (VI) underwent a benzilic acid rearrangement on treatment with molten alkali to give

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[7] B. H. Nicolet and A. E. Jurist, *J. Amer. Chem. Soc.* **44**, 1136 (1922).

α-hydroxy-α-octylsebacic acid (II), and suggested that the diketo-acid is an intermediate in the conversion of 9,10-dihydroxystearic acid into the same product (II). Since it has recently been demonstrated (Part III)[1] that mono-hydroxy acids are smoothly converted into keto-acids in molten alkali, a dehydrogenation of 9,10-dihydroxystearic acid to give successively the corresponding α-hydroxy-ketones and α-diketone, or related ionic species, seems plausible. Although Nicolet and Jurist[7] obtained α-hydroxy-α-octylsebacic acid in only 12 per cent yield from 9,10-diketostearic acid, repetition of their experiment (in an inert atmosphere) raised the yield to 70 per cent; small amounts (4 per cent) of nonanoic and azelaic acid were also detected.*

As expected, alkali fusion of an authentic mixture of 9-hydroxy-10-oxo- and 10-hydroxy-9-oxo-octadecanoic acids (VIIa and b) at 300° gave a product very similar in composition to that obtained from the corresponding dihydroxy acids under similar conditions. At 230° the main product (52 per cent), as from the dihydroxy-acids, was α-hydroxy-α-octylsebacic acid (II); small amounts (12 per cent) of nonanoic and azelaic acid, and traces (2 per cent) of octanoic acid, were also detected. Hilditch and Plimmer[8] have previously demonstrated the fission of the mixture of hydroxy-oxo-octadecanoic acids to nonanoic and azelaic acid in 50 per cent alcoholic alkali at 50°. We find that, at slightly higher temperatures (ca. 80°), α-hydroxy-α-octylsebacic acid is also produced.

As mentioned above, small amounts of nonanoic and azelaic acid are formed from the dihydroxy-, hydroxy-keto-, and diketo-stearic acids under conditions which favour the production of α-hydroxy-α-octylsebacic acid. It is noteworthy that octanoic acid is either absent from the products, or obtained in much smaller amounts than nonanoic and azelaic acid. This indicates that (in an inert atmosphere) octanoic acid is formed by conversion of α-hydroxy-α-octylsebacic acid into 9-oxoheptadecanoic acid, and subsequent hydrolysis, but that, under conditions too mild for the breakdown of the α-hydroxy-diacid, nonanoic and azelaic acid are still formed by fission of the hydroxy-keto- and diketo-stearic acids, and dehydrogenation of the initially formed alcohols or aldehydes. Such dehydrogenations are believed to involve hydride ion transfers, and it has been shown that ketones can act as acceptors in these reactions (cf. Part III). This suggests an obvious explanation for the reported formation of dihydroxystearic acid as a by-product during the reaction of the hydroxy-keto-[8] and the diketo-stearic acids[7] with alkalis.

Treatment of threo-9,10-dihydroxyoctadecanoic acid under conditions similar to those stated by Logan[4] to give nonanol and an "ω-hydroxy acid" gave α-hydroxy-α-octylsebacic acid (II) in 60 per cent yield. Repetition of the reaction in an atmosphere of oxygen (claimed[4] to favour the formation of alcohols) gave a small amount of a volatile product whose three main components were identified as n-nonanol, n-nonanal, and n-octanol by mixed gas-liquid chromatograms with authentic specimens; both octanoic and suberic acid were also detected in addition to the usual fission products. The use of an oxygen atmosphere thus appears to promote oxidation of the dihydroxystearic acid, but other reactions (probably involving oxidative cleavage of ketones,[9] or oxygenation of carbanion intermediates[1]) clearly intrude.

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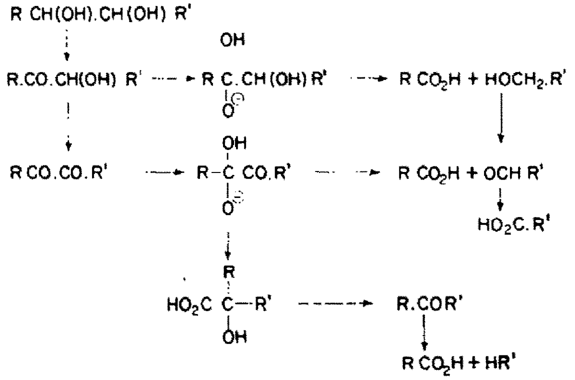
* Dr. J. F. McGhie has kindly informed us of results obtained in his laboratory which are in good agreement with ours. We are also indebted to him for samples of both the hydroxy-keto and diketo acids.

[8] T. P. Hilditch and H. Plimmer, *J. Chem. Soc.* 204 (1942); cf. R. S. Morrell and E. O. Phillips, *J. Soc. Chem. Ind.* 57, 245 (1938).

[9] W. von E. Doering and R. M. Haines, *J. Amer. Chem. Soc.* 76, 482 (1954).

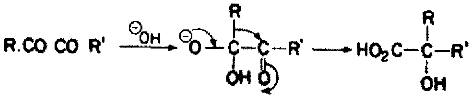
The principal reactions discussed above are summarized in Scheme 1. The mechanisms of the dehydrogenations and hydrolyses are doubtless similar to those



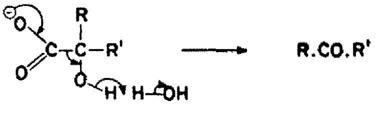
[R and R' represent the two different end groups, viz. $CH_3.(CH_2)_7$ or $(CH_2)_7.CO_2H$.]

Scheme I.

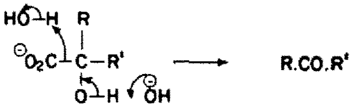
of simple hydroxy and keto compounds (Part III). The formation of α-hydroxy-α-octylsebacic acid from 9,10-diketostearic acid may be regarded as a rearrangement of the benzilic acid type (Scheme 2). The conversion of the hydroxy-octylsebacic acid into 9-oxoheptadecanoic acid involves fission of a carbon–carbon bond; carbon dioxide or a carbonate (e.g. Scheme 3) or a formate (Scheme 4) may be the other product formed initially in this process.



Scheme 2.



Scheme 3.



Scheme 4.

As reported by Logan,[4] alkaline fission of 10,11-dihydroxyundecanoic acid (VIII) gave sebacic acid (90 per cent); small amounts of suberic (2 per cent) and nonanoic acid (5 per cent) were also detected.

$$HOCH_2{\cdot}CH(OH){\cdot}(CH_2)_8{\cdot}CO_2H \rightarrow HO_2C{\cdot}(CH_2)_8{\cdot}CO_2H \qquad \text{(VIII)}$$

Logan also reported[4] that alkali fusion of 9,10,12-trihydroxystearic acid (IX), derived from ricinoleic acid, gave a mixture of azelaic acid, sebacic acid and what appeared to be hexanoic acid with small amounts of nonanoic acid. Repetition of this reaction during the present studies gave no hexanoic or sebacic acids, though heptanoic, octanoic and azelaic acids were obtained (Table 2), as expected by analogy with the fission products of 12-hydroxy-[1] and 9,10-dihydroxy-stearic acids. However, compared with the fission of the latter acid, the formation of azelaic acid was strongly favoured at the expense of octanoic acid. This difference is not surprising. In view of the oxygen function at $C_{(12)}$, the reaction of 9,10,12-trihydroxystearic acid doubtless involves β-hydroxy-ketone (e.g. X) or β-diketone intermediates. It is therefore to be expected that fission at positions corresponding to the 10,11 and 11,12 bonds in the starting material will predominate. Initial dehydrogenation of the $C_{(12)}$ hydroxyl group, and fission to give an intermediate of type XI and octan-2-one, would also favour the formation of azelaic acid. A neutral product formed during treatment of 9,10,12-trihydroxystearic acid with strong alkalis was shown chromatographically to contain octan-2-ol and small amounts of octan-2-one. Since the mixture had only weak optical activity, and the $C_{(12)}$ centre in the starting material was that known to be asymmetric in ricinoleic acid, it can be concluded that the octan-2-ol was formed mainly by reduction of octan-2-one produced initially, and not by direct fission. This is consistent with a dehydrogenation of the $C_{(12)}$ hydroxyl group prior to fission.

TABLE 2. ALKALI FUSION OF 9,10,12-TRIHYDROXYOCTADECANOIC ACID
(1 hr; yield of C_9 and lower acids in moles)

Acidic products		300°	300°
Mono-carboxylic acids	n-C_7	0·25	0·32
	n-C_8	0·08	0·12
	n-C_9	0·04	0·04
Di-carboxylic acids	n-C_8	0·13	0·11
	n-C_9	0·47	0·46

$$CH_3{\cdot}(CH_2)_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CH(OH){\cdot}CH(OH){\cdot}(CH_2)_7{\cdot}CO_2H \tag{IX}$$

$$\downarrow$$

$$CH_3{\cdot}(CH_2)_6{\cdot}CO_2H + HO_2C{\cdot}(CH_2)_7{\cdot}CO_2H$$

$$CH_3{\cdot}(CH_2)_5{\cdot}CH(OH){\cdot}CH_2{\cdot}CO{\cdot}(CH_2)_7{\cdot}CO_2H \tag{X}$$

$$OCH{\cdot}CH(OH){\cdot}(CH_2)_7{\cdot}CO_2H \tag{XI}$$

Two other products, nonanoic and suberic acid, were detected chromatographically after alkali fusion of 9,10,12-trihydroxystearic acid (IX). The former is conceivably an artefact (resulting from contamination of the starting material with 9,10-dihydroxystearic acid) but may arise by dehydration of a β-hydroxy-ketone (e.g. X), reduction of the resulting $\alpha\beta$-unsaturated ketone (cf. reduction of $\alpha\beta$-unsaturated acids,[10]) and fission. Several tentative explanations can be advanced for

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[10] R. G. Ackman, R. P. Linstead, B. J. Wakefield and B. C. L. Weedon, *Tetrahedron* **8**, 221 (1960); R. G. Achman, R. A. Dytham, B. J. Wakefield and B. C. L. Weedon, *Tetrahedron* **8**, 239 (1960).

the production of suberic acid. Perhaps the most plausible at present is the formation of an $\alpha\beta$-unsaturated aldehyde or acid from an intermediate of the type XI, and subsequent fission.

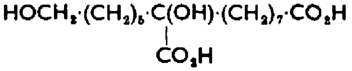
Some preliminary studies have also been made on the alkali fusion of the natural trihydroxy-acid, (β-) aleuritic acid (XII). In addition to a (threo) α-glycol system, this starting material has a primary alcohol grouping which can undergo dehydrogenation in strong alkalis to give a carboxyl function.[1] At 300° hexanoic, octanoic, pimelic and azelaic acids, the expected fission products, were formed in approximately equimolecular amounts (Table 3). However a branched chain or cyclic dicarboxylic acid of higher molecular weight was formed simultaneously in yields up to 40 per cent. The structure of this acid has not yet been determined. From reactions at 250° two products were isolated in poor yield and tentatively formulated as XIII and XIV by analogy with intermediates derived from 9,10-dihydroxystearic acid.

TABLE 3. ALKALI FUSION OF 9,10,16-TRIHYDROXYHEXADECANOIC ACID
(1 hr; yield of C_9 and lower acids in moles)

Acidic products		300°	300°	300°	300°	300°[a]
Mono-carboxylic acids	n-C_6	0·16	0·23	0·14	0·19	0·22
	n-C_8	0·18	0·23	0·13	0·16	0·20
Di-carboxylic acids	n-C_7	0·17	0·22	0·15	0·16	0·22
	n-C_9	0·15	0·24	0·14	0·17	0·23

[a] Reaction time 2·5 hr.

$$HOCH_2\cdot(CH_2)_5\cdot CH(OH)\cdot CH(OH)\cdot(CH_2)_7\cdot CO_2H \qquad \text{XII}$$



$$HOCH_2\cdot(CH_2)_5\cdot\underset{\displaystyle CO_2H}{\underset{|}{C}}(OH)\cdot(CH_2)_7\cdot CO_2H \qquad \text{XIII}$$

$$HO_2C\cdot(CH_2)_5\cdot CO\cdot(CH_2)_7\cdot CO_2H \qquad \text{XIV}$$

EXPERIMENTAL

The general procedures and analytical methods were those indicated in Part III.

Erythro-9,10-dihydroxyoctadecanoic acid[10] was prepared by permanganate oxidation of oleic acid.[11] Threo-9,10-dihydroxyoctadecanoic and 10,11-dihydroxyundecanoic acid were prepared by performic acid hydroxylation of oleic and undec-10-enoic acid respectively.[12] 9,10,12-Trihydroxyoctadecanoic acid was prepared by peracetic acid hydroxylation of methyl ricinoleate and subsequent hydrolysis.[13] The 9,10-dioxooctadecanoic acid was prepared by oxidation of the corresponding dihydroxy-acid with N-bromosuccinimide;[14,15] its methyl ester had no infra-red light absorption attributable to hydroxyl groups. The mixture of 9-hydroxy-10-oxo- and 10-hydroxy-9-oxo-octadecanoic acids was prepared by reduction of the diketo-acid with zinc and acetic acid;[14,15] the esters of the mixture of hydroxy-keto acids had ν_{max} 3470 (OH), 1735 (CO_2Me) and 1715 cm^{-1} (CO).

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[11] G. M. Robinson and R. Robinson, *J. Chem. Soc.* 177 (1925).

[12] D. Swern, G. N. Billen, T. W. Findley and J. T. Scanlan, *J. Amer. Chem. Soc.* **67**, 1786 (1945).

[13] J. T. Scanlan and D. Swern, *J. Amer. Chem. Soc.* **62**, 2309 (1940).

[14] J. F. McGhie, unpublished results.

[15] J. F. McGhie, *Chem. & Ind.* 578 (1954).

Natural (β-) aleuritic acid (kindly supplied by Messrs. Boake Roberts and Co. Ltd.) was crystallized from aqueous methanol and had m.p. 100–101° (lit,[16] m.p. 100°).

α-Hydroxy-α-octylsebacic Acid

(a) *From threo-9,10-dihydroxyoctadecanoic acid*

(i). The dihydroxy-acid (3·5 g) and a finely powdered mixture of potassium and sodium hydroxides (1 : 1, 10 g) were heated for 1 hr at 230–240° (bath temp). The mixture was cooled and dissolved in water. The solution was acidified, and the product was isolated with ether in the usual way. Crystallization from chloroform-light petroleum (b.p. 40–60°) gave α-hydroxy-α-octylsebacic acid (3·3 g), m.p. 110–111° (lit,[3] m.p. 111°) (Found: C, 65·55; H, 10·55. Calc. for $C_{18}H_{34}O_5$: C, 65·4; H, 10·35%). Permanganate oxidation[2] gave 9-oxoheptadecanoic acid, m.p. 79·5–80·5° (lit,[3] m.p. 78·5°); methyl ester, m.p. 43–44° (lit, m.p. 44°), undepressed on admixture with the specimen described below.

In other reactions of the dihydroxy-acid with molten alkalis at temperatures ranging from 200–260°, the yield of hydroxy-diacid varied from 40–80%.

(ii). The dihydroxy-acid (4·6 g) was heated with a solution of potassium hydroxide (12 g) in water (20 cc) in a nitrogen filled stainless steel autoclave at 300° for 2 hr. When the autoclave was opened, after it had been cooled, hydrogen was released. Isolation of the acidic product (4·5 g) and fractional crystallization from aqueous methanol and chloroform-light petroleum (b.p. 40–60°) gave α-hydroxy-α-octylsebacic acid (1·75 g, 40%), m.p. 110–111°.

(b) *From 9-hydroxy-10-oxo- and 10-hydroxy-9-oxo-octadecanoic acids*

(i). The hydroxy-keto acids (1·03 g) and a finely powdered mixture of potassium and sodium hydroxides (1 : 1, 5 g) were heated at 230° for 30 min. The crude product (1·04 g) was isolated and shown (G.L.C. of methyl esters) to contain octanoic, nonanoic and azelaic acids in 1, 5 and 7% yields respectively. Crystallization of the crude product from chloroform-light petroleum (b.p. 40–60°) gave α-hydroxy-α-octylsebacic acid (0·49 g, 52%), m.p. and mixed m.p. 111°.

(ii). A solution of the hydroxy-keto acids (0·76 g) in 50% ethanolic potassium hydroxide (50 cc) was heated under reflux for 10 hr and then concentrated (to 20 cc) and diluted with water (50 cc). The solution was acidified with 2 N sulphuric acid, and steam distilled. From the distillate an acidic fraction (48 mg) was isolated which was shown (G.L.C. of methyl esters) to consist of octanoic (9%) and nonanoic acids (91%). The residual oil, involatile in steam, was separated, washed with hot water, dried (in ether) and crystallized from ethyl acetate to give α-hydroxy-α-octylsebacic acid (0·16 g), m.p. and mixed m.p. 111°. Azelaic acid (60 mg) was detected in the aqueous mother liquors.

(iii). A solution of the hydroxy-keto acids (1·7 g) in 10% potassium hydroxide (100 cc), and then water (20 cc), were added successively over 1½ hr to a stirred mixture of potassium hydroxide (5 g) and water (5 cc) in a copper vessel at 250°. The aqueous distillate was collected and extracted with ether. Evaporation of the extract left a residue (50 mg) which was shown by gas–liquid chromatography to contain nonanol (60%) and nonanal (40%). From the reaction vessel, α-hydroxy-α-octylsebacic acid (0·5 g), m.p. and mixed m.p. 111°, was isolated in the usual way.

(c) *From 9,10-dioxo-octadecanoic acid*

The diketo-acid (1·02 g), a finely powdered mixture of potassium and sodium hydroxides (1 : 1, 4 g), and a few drops of water, were heated at 160° for 15 min. The mixture was cooled, dissolved in water, and acidified. Steam distillation gave nonanoic acid (4%) which was identified by gas–liquid chromatography of its methyl ester. The residual oil, involatile in steam, was separated, washed with hot water, dried (in ether), and crystallized from chloroform–light petroleum (b.p. 40–60°) to give α-hydroxy-α-octylsebacic acid (0·75 g), m.p. and mixed m.p. 110–111°. Azelaic acid (4%) was detected in the aqueous mother liquors.

9-Oxoheptadecanoic Acid

(a) *From erythro-9,10-dihydroxyoctadecanoic acid*

The dihydroxy acid (2·3 g) and potassium hydroxide (7 g) were heated at 260–270° for 1 hr. The mixture was cooled, dissolved in water, and the solution was acidified. Isolation of the product by

[16] H. Hunsdiecker, *Ber. Dtsch. Chem. Ges.* 77, 185 (1944).

extraction with light petroleum (b.p. 40–60°) and then with ether, and crystallization from light petroleum (b.p. 40–60°) or aqueous methanol, gave 9-oxoheptadecanoic acid (0·57 g), m.p. 79·5–80·5° (lit,[2] m.p. 78·5°) (Found: C, 72·4; H, 11·65. Calc. for $C_{17}H_{32}O_3$: C, 71·8; H, 11·3%). Esterification ($MeOH–H_2SO_4$) gave the methyl ester, m.p. 43–44° (lit,[2] m.p. 44°); ν_{max} 1715 (C=O) and 1735 cm^{-1} (CO_2Me). A mixed m.p. with the ester of a specimen of 9-oxoheptadecanoic acid prepared by the method of Le Sueur and Withers[2] showed no depression.

(b) *From threo*-9,10-*dihydroxyoctadecanoic acid*

The dihydroxy acid (1·2 g) and potassium hydroxide (6 g) in water (10 cc) were heated in a nitrogen filled stainless steel autoclave at 340° for 2 hr. When the autoclave was opened, after it had been cooled, hydrogen was released. Isolation of the acidic product (1.05 g) in the usual way, and crystallization from aqueous methanol, gave 9-oxoheptadecanoic acid (0·14 g, 12%), m.p. and mixed m.p. 79–80°.

Alkali fusion of 10,11-*dihydroxyundecanoic acid*

The dihydroxy-acid (3.3 g) and potassium hydroxide (9 g) were heated at 300° for 1 hr. The mixture was cooled rapidly and dissolved in water (300 cc). The solution was acidified (evolution of CO_2) and the acidic product (3·1 g), m.p. 125–127° isolated with ether. Analysis (G.L.C. of methyl esters) revealed sebacic acid (ca. 95%), nonanoic acid (ca. 5%) and suberic acid (trace). One crystallization of a portion (0·56 g) of the crude product from water gave sebacic acid (0·50 g), m.p. and mixed m.p. 133–134°.

Alkaline fission of 9,10,12-*trihydroxyoctadecanoic acid*

(i) The trihydroxy-acid (1·28 g) and potassium hydroxide (5·2 g) were heated at 300° in a stream of nitrogen for 1 hr. The neutral product formed a fine cloud in the nitrogen stream from the reaction vessel, and collected partially in a cold (0°) trap inserted in the gas stream. Isolation with ether gave an oil (65 mg); analysis by gas–liquid chromatography on "Reoplex 400" (poly-ethylene adipate) at 130° indicated a composition 94% octan-2-ol and 6% octan-2-one; mixed chromatograms with authentic specimens showed no separation. Isolation of the acidic products in the usual way, and fractional crystallization of the dicarboxylic acid fraction from water, gave azelaic acid, m.p. and mixed m.p. 105–106°.

(ii) A solution of the trihydroxy-acid (6·4 g) in 30% potassium hydroxide (50 cc) was added with stirring over 90 min to potassium hydroxide (10 g) in a copper vessel at 300°. The steam distillate from the reaction vessel was condensed and the neutral product (0·8 g) isolated with ether; analysis by gas–liquid chromatography as described above indicated a composition 79% octan-2-ol and 21% octan-2-one; mixed chromatograms with authentic specimens showed no separation. After distillation, the mixture had $[\alpha]_D^{24} = +0·13°$ in ethanol (active octan-2-ol has $[\alpha]_D^{17}$ 9·9°). Isolation of the acidic products gave mixtures similar to those from normal alkali fusions at 300° (Table 2).

Alkali fusion of aleuritic acid

The crude acid product from an alkali fusion of aleuritic acid at 250° for 1 hr was triturated with ether. The solid was collected, crystallized from ether–light petroleum (b.p. 40–60°), and then from aqueous methanol, giving *pentadecan-7-one-*1,15-*dioic acid* as plates, m.p. 103–104° (Found: C, 63·3; H, 9·1; O, 28·05. $C_{17}H_{26}O_4$ requires: C, 62·9; H, 9·15; O, 27·95%.) A mixed m.p. with aleuritic acid showed a marked depression. The methyl ester of the product had ν_{max} 1715 and 1735 cm^{-1}; the intensities of the bands were those expected for a keto-diester.

In another experiment fractional precipitation of the acidic product in ether with light petroleum (b.p. 40–60°) gave a solid. Crystallization from chloroform–methanol, and finally from water gave plates, m.p. 143–144° (Found: C, 60·75; H, 9·6; equiv., 147. $C_{16}H_{30}O_6$ require: C, 60·4; H, 9·5%; equiv. 153).

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