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# ORGANIC REACTIONS IN STRONG ALKALIS—III*

## FISSION OF KETO- AND HYDROXY-ACIDS

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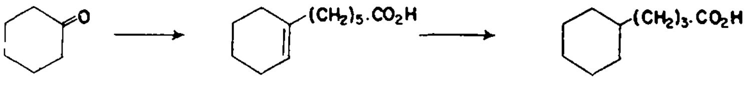
**Abstract**—Studies with suitable fatty acid derivatives have clarified many of the reactions of alcohols and ketones in concentrated alkalis.

Secondary alcohols are dehydrogenated to ketones which then yield acids by hydrolysis of the C—C bonds adjacent to the carbonyl group. Various side reactions are reported and discussed.

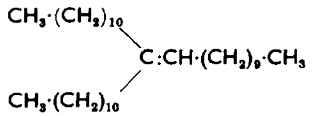
A mechanism is proposed for the fission of ricinoleic acid in concentrated alkalis.

A VARIETY of reactions has been reported for aliphatic and alicyclic ketones on alkali fusion. With camphor and fenchone Wallach noted the formation of acids by hydrolysis of a carbon-carbon bond adjacent to the carbonyl group.[1] A similar reaction with acetone, leading to acetic acid and methane, was subsequently described by Fry and Schulze.[2] With other ketones products have been isolated which suggest that alternative processes can accompany, or even largely replace, simple hydrolysis. Thus cyclohexanone, and its 2-allyl derivative, can give mainly 6-cyclohexenylhexanoic acid (I), or, by a further reaction of the Varrentrapp type, 4-cyclohexylbutyric acid (II),[3,4] and fission of laurone (III, n = 10) to lauric acid (IV, n = 10) is accompanied by the formation of an olefin, probably (V).[5] A similar reaction is possibly involved in the conversion of isophorone into an acid regarded as VI.[6] The claim that palmitic acid (IV, n = 14) as well as stearic acid (IV, n = 16) is produced from stearone (III, n = 16) implies a further mode of reaction,[7] unless the former product is regarded as an artefact.

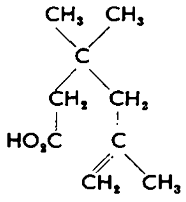


I II

III $CH_3\cdot(CH_2)_n\cdot CO\cdot(CH_2)_n\cdot CH_3 \longrightarrow CH_3\cdot(CH_2)_n\cdot CO_2H$ IV

V


$$\begin{array}{l} CH_3\cdot(CH_2)_{10} \\ \qquad\qquad\qquad C{:}CH\cdot(CH_2)_9\cdot CH_3 \\ CH_3\cdot(CH_2)_{10} \end{array}$$



VI

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* Part II: *Tetrahedron* **8,** 239 (1960).

[1] O. Wallach and M. Behnke, *Liebigs Ann.* **369,** 98 (1909); cf. 8.

[2] H. S. Fry and E. L. Schulze, *J. Amer. Chem. Soc.* **48,** 958 (1926).

[3] T. L. Cairns, R. M. Joyce and R. S. Schreiber, *J. Amer. Chem. Soc.* **70,** 1689 (1948).

[4] E. L. Pelton, C. J. Starnes and S. A. Shrader, *J. Amer. Chem. Soc.* **72,** 2039 (1950).

[5] K. Takeshita, *J. Chem. Soc. Japan* **55,** 223, 279 (1952); *Chem. Abstr.* **48,** 7545 (1954); **47,** 12228 (1953).

[6] H. Finch, K. E. Furman and S. A. Ballard, *J. Amer. Chem. Soc.* **73,** 4299 (1951).

[7] K. Takeshita, *J. Chem. Soc. Japan* **56,** 28 (1953); *Chem. Abstr.* **48,** 7545 (1954).

Under suitable conditions secondary alcohols can give products very similar to those obtained with the corresponding ketones. Thus borneol, like camphor, gives a mixture of campholic and isocampholic acid on alkali fusion.[8] Cyclohexanol can be substituted for cyclohexanone in the reactions cited above,[4] and the fission of 4-alkylcyclohexanols has been used to prepare 4-alkylhexanoic acids.[9] An unexpected variety of products has, however, been reported from the fission of 12-hydroxystearic (dihydroricinoleic) acid; in addition to dodecanedioic, heptanoic and undecanoic acids, which might be anticipated by analogy with the fission of ketones, undecanedioic, hexanoic, decanoic and stearic acid have been claimed.[10–13] The formation of hexanoic acid from 9:10:12-trihydroxystearic acid is also surprising.[14] Such reports, if valid, would indicate a novel oxidative fission. However evidence for the identity of many of the products is lacking, and some of the starting materials are known to have been impure.

To obtain further information on the behaviour of ketones and alcohols under strongly alkaline conditions, the alkali fusion of a number of keto- and hydroxy-acids has now been studied. These starting materials were chosen to ensure the introduction of the functional groups under investigation into the reaction medium, and because the products are readily analysed chromatographically.

On treatment of 12-ketostearic acid (VII, n = 5, m = 10) with molten potassium hydroxide at 300 and 360° in an inert atmosphere, the principal products, formed in approximately equimolar amounts, were heptanoic, undecanoic and dodecanedioic acid (Table 1) (traces of hexane were also detected). These may be attributed to an

$$CH_3\cdot(CH_2)_n\cdot CO\cdot(CH_2)_m\cdot CO_2H \qquad \text{VII}$$

TABLE 1. ALKALI FUSION OF 12-OXO- AND HYDROXY-OCTADECANOIC ACID
(1 hr; yield of acidic products in moles)

| | | Keto-acid | | | | Hydroxy-acid | | |
|---|---|---|---|---|---|---|---|---|
| | | 300° | 300° | 360° | 360° | 300° | 300° | 300° |
| Mono-carboxylic acids | n-$C_5$ | 0·05 | 0·06 | 0·05 | 0·06 | 0·06 | 0·07 | 0·03 |
| | n-$C_7$ | 0·38 | 0·33 | 0·39 | 0·36 | 0·29 | 0·32 | 0·27 |
| | n-$C_{11}$ | 0·26 | 0·25 | 0·25 | 0·27 | 0·28 | 0·17 | 0·19 |
| | "10-Me-$C_{16}$" | *a* | *a* | 0·05 | 0·08 | *a* | *a* | *a* |
| High b.p. acids[b] | | 0·20 | 0·20 | 0·12 | 0·12 | 0·21 | 0·17 | 0·18 |
| Di-carboxylic acids | n-$C_{10}$ | 0·07 | 0·06 | 0·10 | 0·10 | 0·05 | 0·09 | 0·08 |
| | n-$_{12}$ | 0·31 | 0·32 | 0·31 | 0·31 | 0·26 | 0·34 | 0·32 |

[a] 12-Methyloctadecenoic acids detected qualitatively.
[b] Approximate value, estimated by difference.

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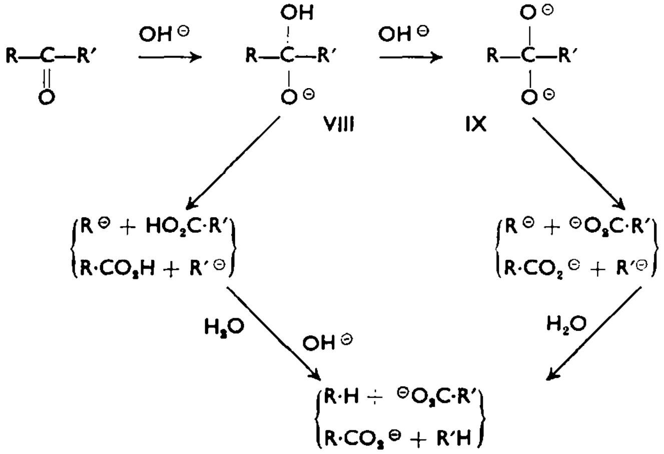
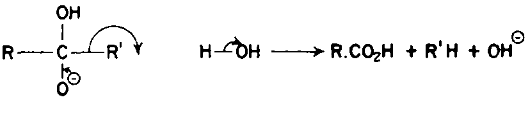
[8] M. Guerbet, *C.R. Acad. Sci., Paris* **148**, 720 (1909); *Bull. Soc. Chim. Fr.* **5**, 420 (1909).
[9] E. L. Pelton and A. A. Holzschuh, U.S. Pat. 2531363; *Chem. Abstr.* **45**, 2969 (1951).
[10] L. A. Mikeska, U.S. Pat. 2614122; *Chem. Abstr.* **47**, 5431 (1953).
[11] M. Kobayashi, *J. Oil Chem. Soc. Japan* **2**, 183 (1953); *Chem. Abstr.* **48**, 9718 (1954).
[12] R. L. Logan, U.S. Pat. 2777865; *Chem. Abstr.* **51**, 14296 (1957).
[13] T. R. Steadman and J. O. H. Peterson, *Industr. Engng. Chem.* **50**, 59 (1958).
[14] R. L. Logan, U.S. Pat. 2625558; *Chem. Abstr.* **47**, 10551 (1953).

initial attack of the carbonyl group by hydroxyl ion to give either VIII or IX, followed by equal fission of the 11:12 and 12:13 bonds (Scheme 1).



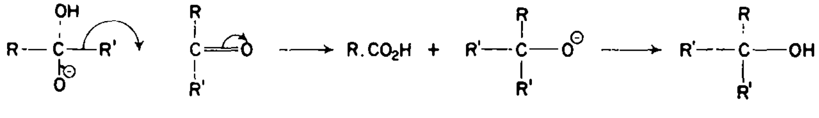
Scheme I

It seems unlikely that the carbanions indicated in the above scheme have a free existence;[15] they are probably transferred directly to an acceptor such as water (e.g. Scheme 2).



Scheme 2

However, the yield of undecanoic acid was always lower than that of heptanoic and dodecanedioic acid, and no large amount of hexane was ever obtained. An alternative acceptor, presumably the ketone itself,[5] must therefore play a rôle (e.g. Scheme 3).



Scheme 3

Partial dehydration of tertiary alcohols formed in this way, followed by isomerization of the resulting olefins and fission reactions of the Varrentrapp type, would then account for the complex mixture of high boiling acids observed in the products. [The transformations, referred to above, leading to V and VI may also be simply explained along similar lines.] Evidence for side reactions of these types was provided by studies on 10-keto-stearic acid (see below).

Two minor by-products from the alkali fusion of 12-keto-stearic acid were valeric and sebacic acid. These cannot be attributed to further reaction of heptanoic and

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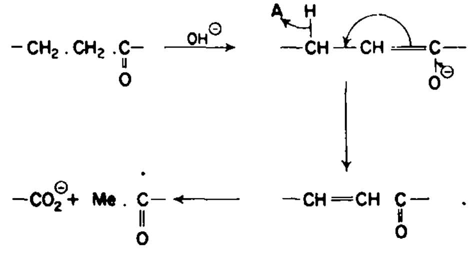
[15] H. M. Walborsky and F. J. Impastato, *Chem. & Ind.* 1690 (1958).

dodecanedioic acid (cf. conversion of decanoic into octanoic acid, Part I), since no degradation of the undecanoic acid to nonanoic acid was detected. It is conceivable that an initial dehydrogenation of the ketone, similar to, but occurring more rapidly than, that postulated for acids led to a mixture of αβ-unsaturated ketones which then underwent fission to give the observed by-products (Scheme 4). The detection of traces of a simple ketone (semicarbazone), which did not separate from an authentic specimen of octan-2-one in a mixed gas-liquid chromatogram, lends support to this view. (The reported formation of palmitic acid from stearone[7] may have been due, at least partially, to a similar process.) Another by-product observed was formulated as 10-methylpalmitic acid from the chromatographic behaviour of its methyl ester, and by analogy with products from 10-oxo-octadecanoic and 5-oxoheptadecanoic acids.



Scheme 4

Alkali fusion of 10-ketostearic acid (VII, n = 7, m = 8) gave results very similar to those obtained with the 12-keto-isomer. In addition to the expected acids (Table 2), octane was also isolated in low yield and identified by a mixed gas-liquid chromatogram with an authentic specimen. The fortuitous circumstance that fission of the 9:10 bond can give 2 moles of nonanoic acid accounts for the high yield of the latter

TABLE 2. ALKALI FUSION OF 10-OXO- AND HYDROXY-OCTADECANOIC ACID
(1 hr; yield of acidic products in moles)

| | | Keto-acid | | | | Hydroxy-acid | |
|---|---|---|---|---|---|---|---|
| | | 300° | 300° | 360° | 360°[a] | 300° | 360° |
| Mono-carboxylic acids | n-$C_7$ | 0·07 | 0·11 | 0·05 | 0·11 | 0·07 | 0·06 |
| | n-$C_9$ | 0·42 | 0·30 | 0·42 | 0·42 | 0·41 | 0·34 |
| | "8-Me-$C_{16}$" | 0·02 | 0·02 | 0·07 | 0·07 | 0·01 | 0·01 |
| | "10-Me-oleics" | 0·04 | 0·05 | — | — | 0·05 | — |
| High b.p. acids[b] | | 0·24 | 0·30 | 0·12 | 0·22 | 0·13 | 0·22 |
| Di-carboxylic acids | n-$C_8$ | 0·04 | 0·07 | 0·07 | 0·10 | 0·05 | 0·04 |
| | n-$C_{10}$ | 0·30 | 0·33 | 0·31 | 0·29 | 0·31 | 0·23 |

[a] Using 20 parts by weight of potassium hydroxide instead of 3.
[b] Approximate value, estimated by difference.

compared with sebacic acid. That there is no selective fission of the 9:10 bond in a 10-keto-acid was confirmed with 10-oxoheptadecanoic acid (III, n = 6, m = 8). This gave octanoic and sebacic acids in equal amounts; the yield of nonanoic acid formed simultaneously was, as expected, lower (Table 3).

TABLE 3. ALKALI FUSION OF 10-OXOHEPTADECANOIC ACID
(1 hr; yield of main acidic products in moles)

| | | 300° | 300° | 300°[a] |
|---|---|---|---|---|
| Mono-carboxylic acids | n-$C_6$ | 0·06 | 0·09 | 0·08 |
| | n-$C_7$ | 0·01 | — | 0·02 |
| | n-$C_8$ | 0·26 | 0·30 | 0·29 |
| | n-$C_9$ | 0·16 | 0·13 | 0·18 |
| | "10-Me—$C_{17}$ (unsatd.)" | 0·06 | 0·05 | 0·06 |
| High b.p. acids[b] | | 0·35 | 0·32 | 0·21 |
| Di-carboxylic acids | n-$C_8$ | 0·03 | 0·05 | 0·05 |
| | n-$C_{10}$ | 0·26 | 0·30 | 0·25 |

[a] Using 20 parts by weight of potassium hydroxide instead of 3.
[b] Approximate value, estimated by difference.

Chromatography of the methyl esters of the product obtained on alkali fusion of 10-ketostearic acid at 300° gave a band with a retention volume slightly greater than that of methyl palmitate, and two others both with retention volumes slightly greater than that of methyl oleate. Similar examination of the product from a reaction at 360° indicated that the acids responsible for the last two bands had been converted, under the more drastic conditions, into that giving rise to the first. Ozonolysis of the lower temperature product destroyed the acids similar to oleic and gave a mixture which was shown chromatographically to contain decan-2-one (semicarbazone), octanoic acid, azelaic acid and (probably) 10-oxoundecanoic acid. The unsaturated acids are therefore regarded as 10-methyloctadecenoic acids (mainly $\Delta^9$ and $\Delta^{10}$ isomers), and the acid similar to palmitic as 8-methylpalmitic acid arising from further reactions of the Varrentrapp type. The initial production of the methyloctadecenoic acids may be attributed to the following sequence of reactions: (i) formation of decan-2-one and 10-oxoundecanoic acid as in Scheme 4, (ii) conversion of these ketones into 10-hydroxy-10-methyloctadecanoic acid by reactions similar to those in Scheme 3, and (iii) dehydration. Ozonolysis also gave di-n-octyl ketone and 10-ketostearic acid. These latter degradation products, together with octanoic and azelaic acid already mentioned, indicate the formation (during alkali fusion) of branched chain olefins by reactions similar to those just discussed, but in which the original keto-acid serves as both donor and acceptor of carbanions (Scheme 3).

As expected by analogy with 10-keto-stearic acid, alkali fusion (300°/1 hr) of the symmetrical nonadeca-10-onedioic acid X gave mainly sebacic (0·60–0·76 mole) and nonanoic acid (0·42–0·57 mole)

$$HO_2C{\cdot}(CH_2)_8{\cdot}CO{\cdot}(CH_2)_8{\cdot}CO_2H \qquad X$$

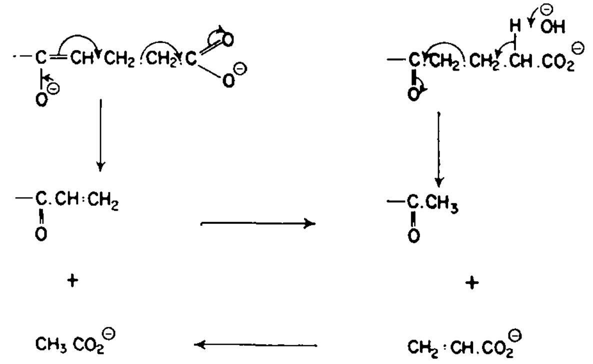
The alkali fusion of 5-oxoheptadecanoic acid (VII, n = 11, m = 3) proved somewhat anomalous (Table 4). Though tridecanoic acid was formed in good yield, only

TABLE 4. ALKALI FUSION OF 5-OXOHEPTADECANOIC ACID
(1 hr; yield of acidic products in moles)

| | 300° | 300° | 300°[a] | 300° | 300° |
|---|---|---|---|---|---|
| $C_2$[b] | | | | 0·26 | 0·40 |
| n-$C_4$ | | | | 0·07 | 0·10 |
| n-$C_{11}$ | 0·04 | 0·02 | 0·02 | 0·02 | 0·02 |
| n-$C_{13}$ | 0·20 | 0·25 | 0·34 | 0·23 | 0·26 |
| n-$C_{15}$ | 0·05 | 0·08 | 0·04 | 0·03 | 0·03 |
| "3-Me—$C_{15}$" | 0·06 | 0·15 | 0·07 | 0·07 | 0·07 |
| High b.p. acids[c] | 0·23 | 0·28 | 0·16 | 0·28 | 0·22 |

[a] Using 20 parts by weight of potassium hydroxide instead of 3.
[b] *p*-Bromophenacyl ester, m.p. and mixed m.p. 83°.
[c] Approximate value, estimated by difference.

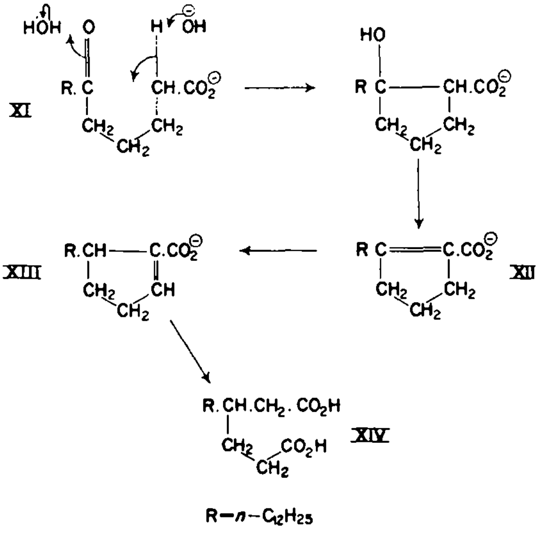
small amounts of butyric and glutaric were obtained. This suppression of the usual reactions suggests that fission of a 5-keto-acid occurs mainly by alternative routes involving reactions of the "retro-Michael" type (Scheme 5).



Scheme 5

The resulting methyl ketone may then undergo "normal fission", or attack by a carbanion leading eventually to a 3-methyl acid and other products. It is consistent with this interpretation that 5-oxoheptadecanoic acid gave unusually high yields of acetic acid (25–40 per cent; cf. 10 per cent from 10-ketostearic acid) and an acid, the methyl ester of which did not separate from an authentic specimen of methyl 3-methylpentadecanoate in a mixed chromatogram. Another by-product detected was tentatively identified as pentadecanoic acid from the retention volume of its methyl ester and its resistance to ozonolysis. Its formation may be attributed to reduction of the keto-acid to the corresponding hydroxy acid, by aldehydes formed in the fission of $\alpha\beta$-unsaturated ketone and acid intermediates (cf. the reduction of ketones by primary alcohols discussed below), followed by dehydration and a Varrentrapp fission of the resulting unsaturated acid. The formation of pentadecanoic acid can thus be regarded as a further consequence of the greater importance with 5-keto-acids of reactions giving aldehydes or other hydride ion donors.

Further departures from the general pattern of ketone fission must be expected with appropriately substituted compounds. Alkali fusion of 6-ketostearic acid XI gave only small amounts of tridecanoic and adipic acid, by fission of the 5:6 and 6:7 bonds respectively (Scheme 1). The main products isolated were an $\alpha\beta$-unsaturated acid, which was shown to be the cyclopentenyl derivative XII by ozonolysis to 5-ketoheptadecanoic acid, and a saturated $C_{18}$-dicarboxylic acid, which was shown to be $\beta$-dodecyladipic acid XIV by comparison with a sample synthesised unambiguously. On further reaction with molten alkali XII was converted into XIV in 50 per cent yield. The initial production of the cyclopentenyl acid may be attributed (Scheme 6) to our intramolecular reaction of the aldol or Claisen type, followed by dehydration of the resulting $\beta$-hydroxy-acid (cf. conversion of 2-hydroxycyclohexanecarboxylic acid into cyclohexenecarboxylic acid[16]). The isolation of an $\alpha\beta$-unsaturated acid from an alkali fusion was unexpected, but is no doubt associated with the fact that direct fission of XII merely regenerates 6-ketostearic acid. Isomerization of XII to XIII, by a prototropic migration of the double bond, followed by a fission of the Varrentrapp type, accounts satisfactorily for the formation of XIV (cf. isomerization and fission of octadec-2-enoic acid, Part I, and the conversion of cyclohexenecarboxylic acid into pimelic acid[16]).



Scheme 6

On prolonged reaction in molten alkali, XIV was converted into a mixture of acids, probably branched chain $C_{17}$-acids.

Attention was next directed to the reaction of hydroxy-acids. Alkali fusion of 12-hydroxystearic acid (XV, n = 5, m = 10) gave, in very similar yields, the same products as 12-ketostearic acid (Table 1). Undecanedioic acid, reported by some previous authors as the principal product,[12,13] was not detected, nor were hexanoic, decanoic or stearic acid (cf. 10–13). However, when the reaction was carried out in

$$CH_3\cdot(CH_2)_n\cdot CHOH\cdot(CH_2)_m\cdot CO_2H \qquad XV$$

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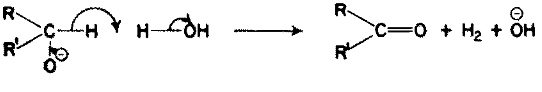
[16] H. J. Pistor and H. Plieninger, *Liebigs Ann.* **562**, 239 (1949); F. X. Werber, J. E. Jansen and T. L. Gresham, *J. Amer. Chem. Soc.* **74**, 532 (1952).

an atmosphere of oxygen, all n-monocarboxylic acids from $C_5$ to $C_{11}$ and all n-dicarboxylic acids from $C_8$ to $C_{12}$ were detected in small amounts. Oxygenation of the intermediate carbanions, and subsequent dehydrogenation (see below), probably accounts for the production of the lower homologues of the main products obtained from fusions in an inert atmosphere. Such side reactions cannot predominate over the reactions discussed previously for the formation of acids, and cannot therefore be invoked to justify the anomalous reports to which reference has already been made.



Scheme 7

The products from the alkali fusion of 10-hydroxystearic acid (XV, n = 7, m = 8) were also the same as those from the corresponding keto-acid (Table 2), and alkali fusion of 6-hydroxystearic acid, (XV, n = 11, m = 4) gave both XII and XIV. This close similarity between the products from the hydroxy- and keto-acids, particularly in the 6-oxygenated series, implied that reaction of the hydroxy compounds involved an initial dehydrogenation to give the corresponding ketones. The formation of camphor during the fission of borneol with molten alkali was reported by Guerbet,[8] but the significance of this observation does not seem to have been appreciated. A recent study of the alkaline fission of 12-hydroxy- and 12-keto-stearic acid afforded no evidence of such a conversion.[13] However, it has now been shown that treatment of 12- and 10-hydroxystearic acid with either molten alkali at 200–260°, or with 30 per cent aqueous potassium hydroxide at 300° gives the corresponding keto-acids and hydrogen (Table 5). These reactions occur in both metal and glass vessels; the

TABLE 5. DEHYDROGENATION OF 10- AND 12-HYDROXY-OCTADECANOIC ACID

| Apparatus | | Alkali[a] | Temp. | Time | Yield of ketone (%) | |
|---|---|---|---|---|---|---|
| | | | | | Spectral[b] | Isolated |
| 12-Hydroxy-acid | glass | KOH-NaOH | 200–210° | 1 hr | 41 | — |
| | glass | KOH-NaOH-CdO | 200–210° | 1 hr | 66 | — |
| | copper | KOH-NaOH | 200–210° | 1 hr | 36 | — |
| | nickel | KOH-NaOH | 200–210° | 1 hr | 25 | — |
| | nickel | KOH-NaOH-CdO | 200–210° | 1 hr | 60 | 35 |
| | nickel | KOH-NaOH | 250–260° | 1 hr | 45 | 30[d] |
| | steel[c] | 30% KOH | 360° | 2 hr | 80 | 60 |
| | steel[c] | 30% KOH-CdO | 300° | 2 hr | 90 | 76 |
| | steel[c] | 60% KOH-CdO | 300° | 1 hr | 71 | 45 |
| 10-Hydroxy-acid | nickel | KOH-NaOH | 240–250° | 1 hr | 45 | 30[d] |
| | nickel | KOH-NaOH-CdO | 250–260° | 1 hr | 41 | 30[d] |

[a] KOH-NaOH represents a 1 : 1 mixture of the two alkalis which form a low melting eutectic; cadmium oxide (ca. 10% by weight of the acid used) was added where indicated.

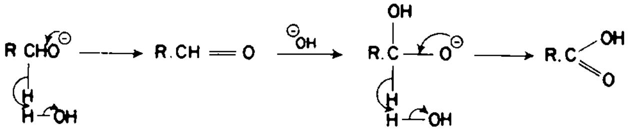
[b] Estimated from the intensity of the carbonyl absorption at 1715 $cm^{-1}$ after esterification of the product.

[c] Autoclave.

[d] Products formed by fission of the ketone were also detected.

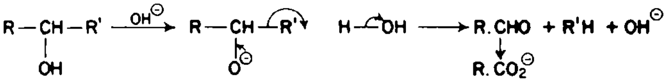
addition of cadmium oxide (claimed to promote the dehydrogenation of primary alcohols and the fission of ricinoleic and dihydroricinoleic acid[13,17]) seemed to favour keto-acid formation, but the number of experiments performed do not warrant a generalisation at this stage.

The dehydrogenation of secondary alcohols to ketones is depicted in Scheme 7. The well known dehydrogenation of primary alcohols to carboxylates on alkali fusion, first observed by Dumas and Stass,[18] may be represented similarly (Scheme 8).



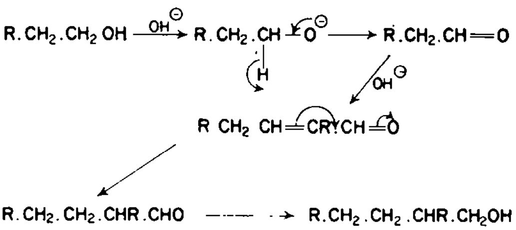
Scheme 8

Though reactions of secondary alcohols in strong alkalis have now been shown to involve dehydrogenation to the corresponding ketones, the possibility cannot be excluded of simultaneous fission by a mechanism of the type shown in Scheme 9. With *β*-hydroxy-acids such a pathway even seems to be preferred (Part I).



Scheme 9

Though not examined in the present studies, reference must also be made to another reaction of alcohols under strongly alkaline conditions. Guerbet demonstrated that both primary and secondary alcohols, when heated with their alkali metal alcoholates under essentially anhydrous conditions, yield "dimeric" alcohols and higher condensation products.[19] These reactions may be regarded as involving an aldol condensation, and hydride ion transfers from either the alcoholate, or a derived aldehyde, to the



Scheme 10

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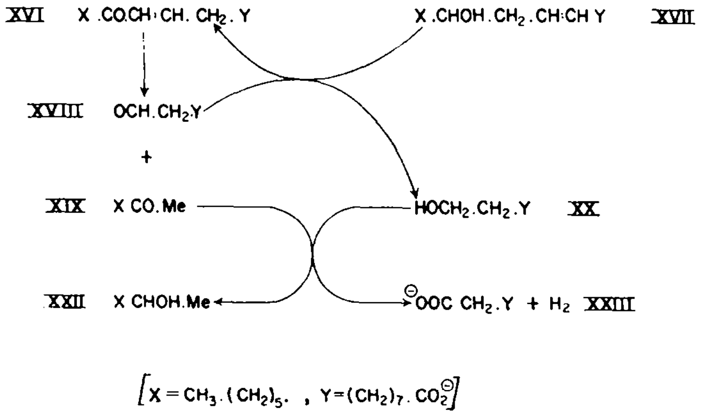
[17] H. P. Chitwood, U.S. Pat. 2384817; *Chem. Abstr.* **40**, 354 (1946); Brit. Pat. 601, 817; *Chem. Abstr.* **42**, 7325 (1948); W. Stein, Brit. Pat. 698154; *Chem. Abstr.* **48**, 6147 (1954); U.S. Pat. 2696501; *Chem. Abstr.* **49**, 2760 (1955).

[18] J. Dumas and J. S. Stass, *Liebigs Ann.* **35**, 129 (1840); cf. M. Guerbet, *Bull. Soc. Chim. Fr.* **11**, 164 (1912); E. E. Reid, H. Worthington and A. W. Larchar, *J. Amer. Chem. Soc.* **61**, 99 (1939).

[19] M. Guerbet, *Ann. Chim. Phys.* **27**, 67 (1902); *Bull. Soc. Chim. Fr.* **11**, 279 (1912); cf. C. Weizmann and S. F. Garrard, *J. Chem. Soc.* **117**, 324 (1920); C. Weizmann, M. Sulzbacher and E. Bergmann, *Ibid.* 772 (1947); W. Markownikow and P. Zubow, *Ber. Dtsch. Chem. Ges.* **34**, 3246 (1901); J. Bolle and L. Bourgeois, *Mém. Serv. Chim. État* **41**, 87 (1957); E. G. E. Hawkins and W. E. Nelson, *J. Chem. Soc.* 4704 (1954).

$\alpha\beta$-unsaturated carbonyl compound and its dihydroderivative (e.g. Scheme 10; cf.[20-22]). With primary alcohols the Guerbet reaction is frequently accompanied, or followed, by a dehydrogenation of the Dumas-Stass type.[19,23]

The results presented above throw new light on the course of the industrially important fission of ricinoleic acid (XVII) in concentrated alkalis.[24,25] It is well known that octan-2-one (XIX) and 10-hydroxydecanoic acid (XX) are the principal products formed at ca. 200°, but that mainly octan-2-ol (XXII) sebacic acid (XXIII) and hydrogen are obtained at temperatures above 240° (Scheme 11). The formation of the low temperature products is understandable if it is assumed that ricinoleic acid, like 12-hydroxystearic acid, first undergoes dehydrogenation. Isomerization of the resulting $\beta\gamma$-unsaturated ketone into the $\alpha\beta$-isomer (XVI), followed by a fission of the "retro-aldol" type, would then give octan-2-one (XIX) and the aldehydo-acid (XVIII) (cf.[26]). The isolation of the hydroxy-acid (XX) rather than XVIII may be attributed to the latter's acting as a hydride ion acceptor in the initial dehydrogenation (cf. Cannizzaro and Guerbet reactions in which hydride ions are also transferred to aldehydes). Preliminary experiments indicate that addition of the aldehydo-acid[25] (XVIII) to the reaction mixture enables the fission of ricinoleic acid to be carried out at temperatures ca. 20–30° lower than those required in the absence of this or another initiator, and that the formation of octan-2-ol is appreciably reduced in such "promoted' reactions.



Scheme 11

Hargreaves and Owen[25] have demonstrated that the products from the high temperature fission of ricinoleic acid are formed by further interaction of the low temperature products, and have cited many other examples of the reduction of ketones to secondary alcohols by treatment with primary alcohols and alkali. Such

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[20] W. Hückel and H. Naab, *Ber. Dtsch. Chem. Ges.* **64**, 2137 (1931).

[21] C. Weizmann, E. Bergmann and L. Haskelberg, *Chem. Industr.* **56**, 589 (1937); C. Weizmann, E. Bergmann and M. Sulzbacher, *J. Org. Chem.* **15**, 54 (1950).

[22] A. Lüttringhaus, *Angew. Chem.* **62**, 87 (1950); **63**, 244 (1951).

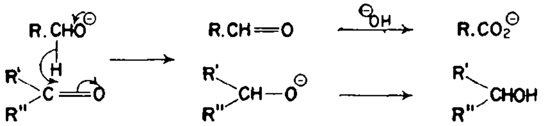
[23] B. W. Howk, U.S. Pat. 2293649; *Chem. Abstr.* **37**, 978 (1943).

[24] M. J. Bouis, *C.R. Acad. Sci., Paris* **33**, 141 (1851); **41**, 603 (1859).

[25] G. H. Hargreaves and L. N. Owen, *J. Chem. Soc.* 753 (1947).

[26] G. W. Ellis, *J. Chem. Soc.* 9 (1950).

hydrogen transfers indicate that ketones can compete efficiently with water as hydride ion acceptors from the intermediates involved in the Dumas–Stass dehydrogenation of primary alcohols to carboxylates (e.g. Scheme 12). The products of both low and high temperature fission of ricinoleic acid can therefore be readily explained in terms of the present concepts.



Scheme 12

One feature of the above proposals deserves further comment. It will be noted that the low temperature products are regarded as being formed by conversion of a secondary alcohol and an aldehyde into a ketone and a primary alcohol respectively, and the high temperature products by a subsequent reduction of a ketone by a primary alcohol. This apparent contradiction is resolved by the reasonable assumption that a hydrogen transfer of the type shown in Scheme 13 is reversible (cf. Meerwein–Ponndorf and Oppenauer reactions):

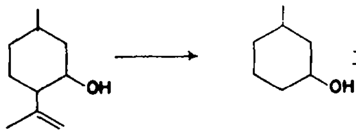
$$R{\cdot}CH_2OH + R'R''C{=}O \overset{\ominus OH}{\rightleftharpoons} R{\cdot}CHO + R'R''CHOH$$

Scheme 13

In most examples, equilibrium is disturbed by the (non-reversible) conversion of aldehyde into carboxylate, and the formation of secondary alcohol is therefore favoured. In the initial stage of the ricinoleic acid reaction, however, the ketone formed is unsaturated and hence destroyed by fission; the reaction therefore proceeds in the reverse direction with reduction of the aldehyde. The ability of secondary alcohols to reduce aldehydes under appropriate alkaline conditions is also implicit in the observation of Doering and Aschner[27] that (—)-active amyl alcohol is racemized in the presence of both alkalis and ketones, but not of alkalis alone. This result is attributed to dehydrogenation, and reformation, of the primary alcohol by reactions of the type generalized in Scheme 13, and racemization of the intermediate aldehyde.[27]

The mechanisms proposed in this paper can obviously be extended to embrace the fission not only of other $\beta\gamma$-unsaturated alcohols, e.g. of isopulegol (XXIV) to

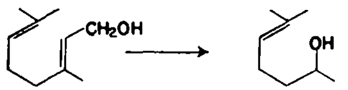
XXIV



XXV

XXVI $HOCH_2{\cdot}CH_2.CH{:}CH.(CH_2)_2.CH_2OH \rightarrow HO_2C.CH_3 + HO_2C.(CH_2)_3.CO_2H$

XXVII



XXVIII

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[27] W. von E. Doering and T. C. Aschner, *J. Amer. Chem. Soc.* **71**, 839 (1949); **75**, 393 (1953).

3-methylcyclohexanol (XXV),[28] and of hept-3-ene-1:7-diol (XXVI) to glutaric and acetic acids,[29] but also of allylic alcohols,[30] e.g. of geraniol (XXVII) to methylheptenol (XXVIII).[31]

The behaviour of systems with two vicinal oxygen functions will be considered in Part IV.

## EXPERIMENTAL

The general procedures and analytical methods used were those described in Part I, except that both mono- and dicarboxylic acids were analysed by gas-liquid chromatography (G.L.C.) of their methyl esters. The sources of starting materials not mentioned in Part I are indicated below:

*Keto-acids.* 6- and 10-Oxo-octadecanoic acid were prepared by the method of Bergstrom *et al.*[32] 5- and 10-Oxoheptadecanoic acid were prepared similarly (ca. 60%) and had m.p. 84·5–86° (Found: C, 71·8; H, 11·3. $C_{17}H_{32}O_3$ requires: C, 71·8; H, 11·35%), and 77·8–78·5° respectively (Found: C, 71·95; H, 11·15%). 12-Oxo-octadecanoic acid was prepared by oxidation of methyl 12-hydroxyoctadecanoate in benzene with chromic acid in aqueous acetic acid (cf.[33]), and hydrolysis of the product; the keto-acid had m.p. 80·0–81·4° (lit.[32] m.p. 81·5–82°). Nonadec-10-onedioic acid was prepared by the method of Blomquist *et al.*[34]

*Hydroxy-acids.* Potassium borohydride (5·0 g) in 2% KOH (50 cc) was added over 30 min to a stirred solution of 10-oxo-octadecanoic acid (15 g) in 10% KOH (150 cc) at 100°. The mixture was stirred at 100° for a further 2 hr. Isolation of the product, and crystallization from methanol, gave 10-hydroxyoctadecanoic acid (12 g), m.p. 79–80° (lit.[32] m.p. 79·2–79·5°); the infra-red spectrum of the methyl ester showed no ketone absorption. 6-Hydroxyoctadecanoic acid was prepared similarly in 70% yield and had m.p. 81·8–82·6° (lit.[32] m.p. 82·0–82·4°).

Ricinoleic acid was prepared from castor oil (B.P. grade), via the barium salt (cf.[35]), and had m.p. 2–3°, $n_D^{24}$ 1·4735 (Found: I.V. 84. Calc: I.V. 85·5). Esterification (MeOH–HCl) gave the methyl ester, b.p. 188–190°/2 mm, $n_D^{20}$ 1·4633 (lit.[36] b.p. 185°/2 mm, $n_D^{20}$ 1·4628); $\nu_{max}$ 3460 (—OH) and 1736 cm$^{-1}$ (—$CO_2Me$), bands due to conjugated dienes were absent. Catalytic reduction of methyl ricinoleate (50 g) in methanol (200 cc) over W-6 Raney nickel at 160°/150 atm, and crystallization from the same solvent, gave methyl 12-hydroxyoctadecanoate (37·5 g), m.p. 56–57° (lit.[37] m.p. 57–58° for the optically active form). Hydrolysis with hot 10% KOH, and crystallization from alcohol, gave (84%) 12-hydroxyoctadecanoic acid, m.p. 80–81·5° (lit.[37] m.p. 80·5–81° for the optically active form).

*Alkali fusions.* Unless otherwise stated, these were performed as described in Part I. The temperatures quoted are bath temperatures. The reaction products were cooled and dissolved in water. The clear solutions were acidified with hydrochloric acid, and the resulting mixtures extracted with light petroleum (b.p. 40–60°). Any insoluble acids (mainly dicarboxylic) were filtered off and washed with light petroleum. The petroleum solutions were combined, washed with water, dried ($Na_2SO_4$) and evaporated at ca. 40° under reduced pressure until the weights of the residues (mainly monocarboxylic acids) were constant. The aqueous solutions were extracted with ether, evaporated to dryness, and the residues extracted thoroughly with ether (Soxhlet). The ethereal solutions were combined with the petroleum insoluble acids and evaporated until the weights of the residues (mainly di-carboxylic acids) were constant. The products were either analysed by G.L.C. of their methyl esters (see Tables), or purified as indicated in the examples given below:

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[28] *Ber. Schimmel*, p. 91. Oct. (1913).

[29] F. Runge, R. Hueter and H. -D. Wulf, *Chem. Ber.* **87**, 1430 (1954).

[30] G. H. Hargreaves and L. N. Owen, *J. Chem. Soc.* 756 (1947).

[31] P. Barbier, *C.R. Acad. Sci., Paris* **126**, 1423 (1898); F. Tiemann, *Ber. Dtsch. Chem. Ges.* **31**, 2989 (1898); J. Doeuvre, *Bull. Soc. Chim. Fr.* **45**, 351 (1929).

[32] S. Bergstrom, G. Aulin-Erdtman, B. Rolander, E. Stenhagen and S. Ostling, *Acta Chem. Scand.* **6**, 1157 (1952); cf. J. Cason, *Chem. Rev.* **40**, 15 (1947).

[33] O. Grummitt and K. G. Siedschlag, *J. Amer. Oil Chem. Soc.* **26**, 690 (1949).

[34] A. T. Blomquist, J. R. Johnson, L. I. Duiguid, J. K. Shillington and R. D. Spenser, *J. Amer. Chem. Soc.* **74**, 4203 (1952).

[35] I. V. Gulbenkian and J. H. Skellon, *J. Appl. Chem.* **9**, 224 (1959).

[36] J. B. Brown and N. D. Green, *J. Amer. Chem. Soc.* **62**, 738 (1940).

[37] F. Strauss, H. Heinze and L. Salzmann, *Ber. Dtsch. Chem. Ges.* **66B**, 631 (1933).

### *Fission of* 12-*hydroxyoctadecanoic acid*

The hydroxy acid (2·67 g) and KOH (8 g) were heated at 300° for 1 hr, and the crude products isolated by the standard procedure. Crystallization of the dicarboxylic acid fraction (0·92 g) from water gave dodecanedioic acid, m.p. and mixed m.p. 127–128° (lit.[38] m.p. 127·5–128·5°). Distillation of the esters of the mono-carboxylic acid fraction, gave (i) impure methyl heptanoate and (ii) methyl undecanoate which was converted into N-benzyl undecanoamide, m.p. and mixed m.p. 78–79°.

### *Fission of* 10-*oxo-octadecanoic acid*

The keto-acid (5 g) and KOH (15 g) were heated (in two batches) at 300–320° for 1 hr, and the product was cooled and dissolved in water (200 cc). The solution was acidified with 2 N HCl, and then steam distilled until a clear distillate was obtained. The distillate (500 cc) was neutralized with 2 N NaOH and concentrated. The residue (ca. 50 cc) was acidified and then extracted with ether. The ethereal solution was washed, dried ($Na_2SO_4$) and evaporated giving nonanoic acid (1·23 g) (*p*-bromophenacyl ester, m.p. and mixed m.p. 68–69°), which was shown to contain 8% of heptanoic acid by G.L.C. of the methyl esters.

The residue from the steam distillation was extracted (2 × 100 cc) with light petroleum (b.p. 40–60°). The extract was filtered and the insoluble solid dissolved in ether. The aqueous mother liquors were extracted (2 × 50 cc) with ether and all the ethereal solutions were combined, washed with water, dried ($Na_2SO_4$) and evaporated. The residue (1·42 g) was shown to contain 85% sebacic acid and 15% suberic acid by G.L.C. of the methyl esters. Crystallization of a portion (1·0 g) from water gave sebacic acid (0·53 g), m.p. and mixed m.p. 134°.

The light petroleum solution was dried and evaporated giving a mixture of acids (1·80 g) which was shown by G.L.C. of the methyl esters to contain 6% of nonanoic acid, 2% of 8-methylhexadecanoic acid, and 11% of 10-methyloctadecenoic acids (octanoic, azelaic and 10-oxo-octadecanoic acids were absent). A portion of the mixture (0·9 g) was ozonized in acetic acid–methyl acetate by the procedure described in Part I. After decomposition of the ozonide with hydrogen peroxide, the mixture was neutralized with aqueous potassium hydroxide. The neutral products were isolated with ether and steam distilled; extraction of the distillate with ether gave decan-2-one (G.L.C. and mixed G.L.C. with an authentic specimen), semicarbazone, m.p. and mixed m.p. 123–124° (lit [39] m.p. 125–126°). Extraction of the residues from the steam distillation with ether gave di-*n*-octyl ketone (G.L.C. and mixed G.L.C. with an authentic specimen), m.p. 46–48° undepressed on admixture with an authentic specimen, m.p. 49–50° (lit.[40] m.p. 50°).

After removal of the neutral products of ozonolysis, the alkaline solution was acidified and the acidic products extracted (2 × 100 cc) with light petroleum (b.p. 40–60°). The extract was washed with water, dried and evaporated giving a solid (0·42 g), which was esterified (MeOH–$H_2SO_4$). Analysis of the methyl esters by G.L.C. revealed 4% of methyl heptanoate, 20% of methyl octanoate, 13% methyl nonanoate, and 15% of an ester, probably methyl 10-oxoundecanoate. Crystallization of the methyl esters from aqueous methanol (charcoal) gave methyl 10-oxo-octadecanoate (0·1 g) as plates, m.p. and mixed m.p. 45–46° (lit.[32] m.p. 45·8–46·1°); $\nu_{max}$ 1733 (—$CO_2Me$) and 1706 $cm^{-1}$ (—CO—).

The aqueous mother liquors from the petroleum extraction were steam distilled (to remove acetic acid) and then extracted (2 × 100 cc) with ether. The extract was washed, dried and evaporated. The residue (0·3 g) was esterified (MeOH–$H_2SO_4$) and the resulting methyl esters were shown by G.L.C. to contain 2% of methyl pimelate, 8% of methyl suberate and 46% of methyl azelate; a band (ca. 15%), which did not separate from either methyl 10-oxoundecanoate or methyl sebacate, was also observed before, but not after, treatment of the mixture with Girard reagent P.

### *Alkali fusion of* 6-*oxo-octadecanoic acid*

(i) The keto-acid (5·2 g) and KOH (9 g) were heated at 280–300° for 2 hr and the products isolated by the standard procedure. A solution of the mono-carboxylic acid fraction (3·2 g) in light petroleum (b.p. 40–60°) (40 cc) was decolourized with charcoal and then cooled to 0°. The solid (1·6 g), m.p.

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[38] B. W. Baker, R. W. Kierstead, R. P. Linstead and B. C. L. Weedon, *J. Chem. Soc.* 1804 (1954).

[39] T. Shenton and J. C. Smith, *Chem. & Ind.* 1510 (1958).

[40] F. L. Breusch and F. Baykut, *Chem. Ber.* **86**, 684 (1953).

77–78°, which separated was collected and crystallized from aqueous alcohol to give 2-*dodecylcyclopent-1-ene carboxylic acid* (1·0 g) as plates, m.p. 82–83° (Found: C, 76·8; H, 11·65. $C_{18}H_{32}O_2$ requires: C, 77·1; H, 11·5%); $\lambda_{max}$ 233 m$\mu$, $\varepsilon = 11{,}800$; $\nu_{max}$ 1667 (conjug. $CO_2H$) and 1623 cm$^{-1}$ (conjug. C=C). On hydrogenation in acetic acid over Adams catalyst, the cyclopentenyl acid absorbed 0·92 mole of hydrogen; the product had m.p. 50·6–51·3° (Found: C, 76·7; H, 12·35. $C_{18}H_{34}O_2$ requires: C, 76·55; H, 12·15%). The cyclopentenyl acid (0·42 g) was ozonized by the procedure described in Part I. The water insoluble product was separated and extracted with light petroleum (b.p. 40–60°). The insoluble residue (0·25 g) was crystallized from aqueous methanol and gave 5-oxoheptadecanoic acid, m.p. 86·5–87·0° (Found: C, 71·75; H, 11·35; O, 16·65%; equiv., 273. Calc. for $C_{17}H_{32}O_3$: C, 71·8; H, 11·35; O, 16·9%; equiv., 284), which did not depress the m.p. of an authentic specimen.

(ii) The keto-acid (3·0 g) and KOH (9 g) were heated at 300–320° for 1 hr and the products isolated as usual. Crystallization of the petroleum insoluble acids (1·17 g) from aqueous alcohol gave *β-dodecyladipic acid* (0·7 g) as needles, m.p. 85–86° (Found: C, 68·85; H, 11·1%; equiv. 156; mol. wt. 337. $C_{18}H_{34}O_4$ requires C, 68·75; H, 10·9%; equiv. 157; mol. wt. 315). The m.p. was undepressed on admixture with an authentic specimen (see below), which had an identical infra-red light absorption spectrum. The m.p. was depressed on admixture with the starting material.

Tridecanoic acid was detected in the petroleum soluble fraction by G.L.C. of the methyl esters. Evaporation of the aqueous mother liquors from the reaction product, and extraction with ether gave traces of adipic acid (identified by paper chromatography).

### *Alkali fusion of 6-hydroxyoctadecanoic acid*

(i) The hydroxy-acid (3·0 g) and a finely powdered mixture (1 : 1, 9 g) of sodium and potassium hydroxides were heated at 250–260° for 1 hr. Isolation of the products in the usual way gave a petroleum soluble fraction (2·4 g). Crystallization from light petroleum (b.p. 40–60°) and then from methanol (charcoal) gave 2-dodecylcyclopent-1-enecarboxylic acid (1·2 g, 50%), m.p. and mixed m.p. 82–83°.

(ii) The hydroxy-acid (2·2 g) and potassium hydroxide (6 g) were heated at 280–300° for 2 hr, and the products isolated in the usual way. Crystallization of the petroleum insoluble fraction from aqueous methanol gave a solid (0·5 g, 20%), m.p. 79–81°. Recrystallization from the same solvent gave β-dodecyladipic acid, m.p. and mixed m.p. 84·5–85·5°.

### *Fission of 2-dodecylcyclopent-1-ene carboxylic acid*

The acid (1·67 g) and KOH (5 g) were heated at 300–310° for 1 hr. Isolation of the products gave (i) recovered starting material (0·36 g), m.p. and mixed m.p. 82–83°, and (ii) β-dodecyladipic acid (0·8 g), m.p., and mixed m.p. 86°.

### *Fission of β-dodecyladipic acid*

The acid (1·7 g) and KOH (5 g) were heated at 360° for 1 hr and the products isolated in the usual way. The petroleum soluble fraction (1·3 g) was esterified (MeOH–$H_2SO_4$). Distillation gave an oil (1·0 g), b.p. 160–162°/3 mm, $n_D^{20}$ 1·4433 (Found: C, 75·55; H, 12·95%; C–Me, 2·05. Calc. for $C_{18}H_{36}O_2$: C, 76·0; H, 12·75%), which probably consisted of a mixture of methyl esters of branched chain $C_{17}$ acids; G.L.C. on Apiezon T at 240° gave two bands of comparable size and with retention volumes slightly greater than that of methyl palmitate (only one band was observed on silicone at 240°).

Alkali fusion of adipic acid under similar conditions gave valeric acid in low yield. β-Methyladipic acid gave (ca. 5–10%) an acid, the methyl ester of which did not separate from methyl 4-methylpentanoate in a mixed chromatogram on silicone.

### *Dehydrogenation of hydroxy-acids*

(i) 12-Hydroxyoctadecanoic acid (1·00 g) and KOH (0·6 g) in water (2 cc) were heated in a nitrogen filled steel autoclave at 360° for 2 hr. The autoclave was cooled and opened, releasing a combustible gas, and the contents were dissolved in water (200 cc). The solution was acidified, and the product (0·93 g) was isolated with ether and esterified (MeOH–$H_2SO_4$). The intensity of the carbonyl band at 1715 cm$^{-1}$ indicated an 80% yield of the keto-ester. Crystallization from aqueous methanol gave methyl 12-oxo-octadecanoate (0·60 g) as plates, m.p. and mixed m.p. 45–46° (lit.[32] 45·4–45·7°).

(ii) The preceding experiment was repeated, at 300° with the addition of cadmium oxide (0·1 g) to the reaction mixture, and gave methyl 12-oxo-octadecanoate (76%; spectral yield, 90%), m.p. and mixed m.p. 45–46°.

(iii) 10-Hydroxyoctadecanoic acid (1·0 g) and a finely powdered mixture (1 : 1; 3·0 g) of sodium and potassium hydroxides were heated in nitrogen in a nickel pot at 240–250° for 1 hr. Isolation of the product, esterification and crystallization from aqueous methanol gave methyl 10-oxo-octadecanoate (30%; spectral yield 45%), m.p. and mixed m.p. 45–46° (lit.[32] m.p. 45·8–46·1°).

*β-Dodecyladipic acid*

*p*-Dodecylphenol[41] (7·0 g) in alcohol (30 cc) was hydrogenated over W-6 Raney nickel at 150°/150 atmos for 6 hr. Isolation of the neutral product gave an oil (2·1 g). A portion (1·2 g) was treated with sodium dichromate (3 g) in 15% $H_2SO_4$ (20 cc) for 1 hr. Isolation of the product, and crystallization from methanol, gave 4-*dodecylcyclohexanone* (0·5 g), as plates, m.p. 42° (Found: C, 80·6; H, 12·95. $C_{18}H_{34}O$ requires: C, 81·15; H, 12·85%). The 2:4-*dinitrophenylhydrazone* crystallized from ethyl acetate and had m.p. 112–113° (Found: N, 12·65. $C_{24}H_{38}O_4N_4$ requires: N, 12·55%). Oxidation of the ketone (0·5 g) with conc. $HNO_3$ (10 cc) in the presence of ammonium vanadate (1 g) at 90° for 3 hr., isolation of the acidic product (0·4 g), and crystallization from aqueous methanol, gave *β*-dodecyladipic acid as plates, m.p. 86° (Found: C, 68·85; H. 11·1. Calc. for $C_{18}H_{34}O_4$: C, 68·75; H, 10·9%).

3-*Methylpentadecanoic acid*

Dodecanoic acid (15 g) and methyl hydrogen *β*-methylglutarate[42] (3·0 g) in methanol (100 cc) were added to sodium methoxide (from 50 mg of sodium) in methanol (200 cc), and the solution was electrolysed (2–3·5 A, 100 V) at 60° between two platinum plate electrodes (6·5 × 5 cm) until neutral (6 hr). Water (200 cc) was added and the mixture was extracted with ether. The extract was washed thoroughly with 5% KOH, dried and evaporated. The residue was treated with 10% KOH at 90° for 2 hr, and the acidic fraction isolated in the usual way. After steam distillation (to remove traces of dodecanoic acid), the crude product was esterified ($MeOH–H_2SO_4$). Distillation gave methyl 3-methylpentadecanoate (1·5 g), b.p. 128–130°/1 mm, $n_D^{27}$ 1·4380 (Found: C, 75·1; H. 12·8. Calc. for $C_{17}H_{34}O_2$: C, 75·5; H, 12·65%). Hydrolysis gave 3-methylpentadecanoic acid which crystallized from acetone in plates, m.p. 36–37·5° (lit.[43] m.p. 37·2–37·7°).

Carbon and hydrogen determinations were carried out in the microanalytical laboratory (Miss J. Cuckney), and infra-red measurements in the spectroscopic laboratory (Mr. R. L. Erskine) of this Department.

*Acknowledgements*—One of us (R. A. D.) thanks the Department of Scientific and Industrial Research for a research studentship.

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[41] N. K. Adam, W. A. Berry and H. A. Turner, *Proc. Roy. Soc.* A **117**, 539 (1927).

[42] R. P. Linstead, J. C. Lunt and B. C. L. Weedon, *J. Chem. Soc.* 3331 (1950).

[43] J. Cason, N. L. Allinger and D. E. Williams, *J. Org. Chem.* **18**, 842 (1953).