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ORGANIC REACTIONS IN STRONG ALKALIS—II[1]

FISSION OF DI-ETHYLENIC AND ACETYLENIC ACIDS

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Abstract—Linoleic and stearolic acid give myristic acid, together with small amounts of palmitic acid, on treatment with molten potassium hydroxide. These, and similar reactions of other acetylenic acids, are discussed.

As a continuation of the studies on mono-ethylenic acids described in the previous paper,[1] the alkali fusion of representative acids of the diene and acetylene series was examined.

The isomerization of linoleic acid (I) in hot dilute alkalis to a mixture of octadeca-9:11- and octadeca-10:12-dienoic acids (II; $n = 4$ and 5) is well known, and forms the basis of a widely used method of fat analysis.[2–5] Under the more drastic conditions of alkali fusion the conjugated dienes, which are doubtless formed initially, can then react further both by polymerization[6] and by fission. The latter process, by analogy with the conversion of oleic into palmitic acid (IV),[1] might be expected to give myristic acid (III) with loss of four carbon atoms. Kirschenbauer[7] has stated that such a transformation occurs during the alkali fusion of mixtures of fatty acids containing linoleic acid, but no experimental data have been published. From methyl linoleate Toyama and Iwata[8] obtained a solid product which they believed to consist mainly of palmitic acid and conjugated isomers of linoleic acid.

$$\text{I}\quad CH_3\cdot(CH_2)_4\cdot CH{:}CH\cdot CH_2\cdot CH{:}CH\cdot(CH_2)_7\cdot CO_2H \rightarrow$$

$$\text{II}\quad CH_3\cdot(CH_2)_n\cdot CH{:}CH\cdot CH{:}CH\cdot(CH_2)_{12-n}\cdot CO_2H \rightarrow$$

$$\underset{\text{III}}{CH_3\cdot(CH_2)_{12}\cdot CO_2H} + \underset{\text{IV}}{CH_3\cdot(CH_2)_{14}\cdot CO_2H} + CH_3\cdot CO_2H$$

In our experience alkali fusion of linoleic acid gave mainly myristic acid (60 per cent) together with small amounts of palmitic acid (ca. 5 per cent). (The starting material contained only traces of oleic acid, and therefore the possibility that the palmitic acid observed was an artefact can be excluded.) Acetic acid, but no butyric, was also detected. The reaction was more rapid than that of oleic acid, but the yield of fission product was lower owing to the simultaneous occurrence of decomposition and polymerization.

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[1] Part I: R. G. Ackman, Sir Patrick Linstead, B. J. Wakefield and B. C. L. Weedon, *Tetrahedron* **8**, 221 (1960).

[2] A. W. Ralston, *Fatty Acids and their Derivatives*. John Wiley, New York (1948).

[3] P. L. Nichols, S. F. Herb and R. W. Riemenschneider, *J. Amer. Chem. Soc.* **73**, 247 (1951).

[4] J. E. Jackson, R. F. Paschke, W. Tolberg, H. M. Boyd and D. H. Wheeler, *J. Amer. Oil Chem. Soc.* **29**, 229 (1952).

[5] J. J. A. Blekkingh, H. J. J. Janssen and J. G. Keppler, *Rec. Trav. Chim.* **76**, 42 (1957).

[6] cf. R. F. Paschke, J. E. Jackson and D. H. Wheeler, *Industr. Engng. Chem.* **44**, 1113 (1952).

[7] H. G. Kirschenbauer, U.S.P. 2682549; *Chem. Abstr.* **48**, 11819 (1954).

[8] Y. Toyama and Y. Iwata, *Res. Rept. Nagoya Ind. Sci. Res. Inst.* No. 8, 48 (1955); *Chem. Abstr.* **50**, 12814 (1956); *J. Amer. Oil Chem. Soc.* **33**, 375 (1956).

Information on the course of the fission reaction was sought by examination of the products formed under different conditions (Table 1). Although the competing reactions complicate the detailed interpretation of the results, a number of general conclusions can be drawn. By gas–liquid chromatography of their methyl esters, and those of the mono-carboxylic acids formed on oxidation, all products of incomplete reaction were found to contain myristic, palmitic and unsaturated C_{18}-acids. The loss of unsaturation, as shown by the iodine values of the products, was greater than could be accounted for by the amount of myristic acid detected; this discrepancy can be attributed to polymerization and other side reactions. Those products which retained large amounts of unsaturated acids exhibited light absorption maxima at ca. 230 mμ with intensities indicating that most of the residual unsaturation was present as conjugated dienes (cf. 3, 4). From the relative intensities of the infra-red light absorption maxima in the 10·0–10·6 μ region it was concluded that the dienes were predominantly the *trans*:*trans* isomers, with some *cis*:*trans* forms, and that small amounts of unconjugated (*trans*-) double bonds were also present (cf. 4). Oxidation gave mixtures in which the C_6 to C_{16} mono-carboxylic acids and the C_3 to C_{11} dicarboxylic acids were detected, indicating that the diene system had migrated in both directions

TABLE 1. ALKALI FUSION OF LINOLEIC ACID (30 min)

		245°[a]	280°[b]	300°	360°[c]
I.V. of product		115	66	16	8
Apparent loss of octadecadienoic acids[d]		38	66	92	97
Ultra-violet light absorption[e]		231(640)	230(310)	240(36)	—
Relative proportions (%) of C_{18} and lower acids	C_{18}	72	15	1·0	0
	C_{16}	3	5	12·4	6·7
	C_{14}	25	79	82·8	91·3
	C_{12}	0	1	1·4	1·9
Yield of myristic acid (mol %)		—	44	54	60
Proportion (%) of C_{16} : C_{14} acids before (and after) ozonolysis		12(25)	6(23)	15(16)	7(6)

[a] Ozonolysis of the product gave the C_{11} to C_4 dicarboxylic acids in >1·2, 5·1, 17·0, 2·2, 1·6, 1·4, 1·9 and 7·5 mol % overall yield respectively from linoleic acid (total yield based on residual octadecadienoic acids, ca. 60%), and the C_5 to C_{16} monocarboxylic acids.

[b] Ozonolysis of the product gave the C_{10} to C_5 dicarboxylic acids in 3·1, 4·1, 1·0, 1·7, 2·0 and 3·1 mol % overall yield respectively from linoleic acid and the C_6 to C_{16} monocarboxylic acids.

[c] 60 min.

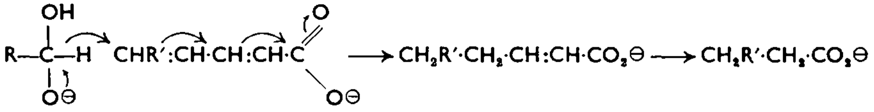
[d] Calculated from I.V. of product without allowance for the formation of unsaturated polymers.

[e] λ_{max} in mμ; $E^{1\%}_{1\,cm}$ in parentheses.

along the chain. Although unconjugated isomers of linoleic acid are not produced under mild conditions,[5] the initial rearrangement to conjugated dienes in molten alkali (involving proton removal at position 11) is apparently accompanied by the formation of some octadeca-8:12- and octadeca-9:13-dienoic acids (by proton removal at the less reactive positions 8 and 13), since oxidation of the product from the mildest alkali fusion studied gave unusually large amounts of succinic acid.

The formation of myristic acid can be attributed both to fission of a 2:4-dienoate (VI), resulting from migration of the diene system into conjugation with the carboxylate group, and to successive fissions of 2-enoate intermediates arising from the conjugation of individual double bonds with the oxygen function.

The various steps proposed above are explicable by obvious extensions of the mechanisms discussed in the previous paper[1] for the reaction of mono-ethylenic acids. It was suggested there that fission involved a hydride ion transfer from an intermediate of the type V. In the reaction now under consideration it seems plausible that a 2:4-dienoate (VI) can act as an acceptor in such a transfer. Under the conditions employed, the resulting octadecenoate would rapidly give a mixture of isomers, consisting mainly of the $\alpha\beta$- and $\beta\gamma$-compounds, and then undergo fission.[1] The formation of palmitic acid from linoleic acid can be satisfactorily explained in this way. Evidence for the presence of the octadec-2- and octadec-3-enoate intermediates in the products of incomplete reaction was provided by ozonolysis. This gave additional quantities of palmitic acid (relative to myristic acid), and small amounts of pentadecanoic acid (absent from the fusion products themselves). Lower homologous acids from C_6 to C_{13} were produced simultaneously from the various unsaturated acids, and their polymers, also present.



V VI

$$\mathrm{R{-}C(OH)(O^{\ominus}){-}H\quad CHR'{:}CH{\cdot}CH{:}CH{\cdot}CO_2^{\ominus} \longrightarrow CH_2R'{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CO_2^{\ominus} \longrightarrow CH_2R'{\cdot}CH_2{\cdot}CO_2^{\ominus}}$$

The reaction products of low iodine value had ultra-violet light absorption maxima at different wavelengths from those of conjugated isomers of linoleic acid, and it is probable that polymers accounted for much of the residual unsaturation. These products also contained small amounts (ca. 1–2%) of lauric acid (a degradation product of myristic acid) and traces of the C_6 to C_{11} and the C_{13} monobasic acids. These latter impurities can be attributed to oxidations of the type discussed in Part III. The occurrence of other side reactions was not investigated.

In agreement with the above conclusion, alkali fusion of sorbic acid (VI, R′ = Me) gave acetic acid (1·6 moles) and 2·5 per cent of butyric acid (*p*-bromophenacyl ester). Recently Lukeš and Hofman[9] reported that alkali fusion of 6:6-diallylhexanoic acid (VII) gave di-n-propylacetic acid (VIII) and acetic acid.

$$\underset{\mathrm{VII}}{\mathrm{(CH_2{:}CH{\cdot}CH_2)_2CH{\cdot}(CH_2)_4{\cdot}CO_2H}} \longrightarrow \underset{\mathrm{VIII}}{\mathrm{(CH_3{\cdot}CH_2{\cdot}CH_2)_2CH{\cdot}CO_2H}}$$

That alkali fusion of the acetylenic analogues of unsaturated fatty acids also leads to saturated products with loss of four carbon atoms was demonstrated by Marasse[10]

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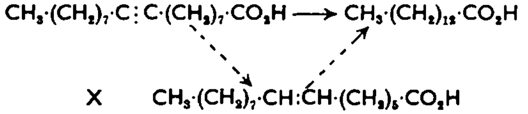
[9] R. Lukeš and J. Hofman, *Chem. Listy* **52**, 1747 (1958).

[10] S. Marasse, *Ber. Dtsch. Chem. Ges.* **2**, 359 (1869).

and Bodenstein.[11] The conversion of stearolic acid (IX) into myristic (III) and acetic acid was believed to proceed by the initial formation of hexadec-6-enoic acid (X). However fission of an intermediate of this type would not occur rapidly under the conditions employed (210–300°; cf. fission of oleic and petroselinic acid[1]). Moreover the extensive studies which have since been carried out on the prototropic rearrangements of acetylenes make such a reaction sequence extremely improbable. In alkaline solution hex-4-ynoic (XI, R = Me) and pent-4-ynoic acid (XI, R = H) isomerize to sorbic (XII, R = Me) and penta-2:4-dienoic acid (XII, R = H) respectively, and other ω-acetylenic acids (XIII) are converted into their methylacetylenyl analogues (XIV).[12–14] All these rearrangements are believed to involve allenic intermediates and buta-2:3-dienoic acid has been isolated as the initial product from the reaction of but-3-ynoic acid (XIII, $n = 1$).[14] It might therefore be expected that, on alkali fusion of an acetylenic acid, the triple bond would migrate along the carbon chain by a sequence of reversible acetylene–allene–acetylene rearrangements which may be represented:

IX  III

X

$$CH_3{\cdot}(CH_2)_7{\cdot}C{:}C{\cdot}(CH_2)_7{\cdot}CO_2H \longrightarrow CH_3{\cdot}(CH_2)_{12}{\cdot}CO_2H$$

$$CH_3{\cdot}(CH_2)_7{\cdot}CH{:}CH{\cdot}(CH_2)_5{\cdot}CO_2H$$

$$\text{XI}\quad R{\cdot}C{:}C{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H \longrightarrow R{\cdot}CH{:}CH{\cdot}CH{:}CH{\cdot}CO_2H \quad \text{XII}$$

$$\text{XIII}\quad HC{:}C{\cdot}(CH_2)_n{\cdot}CO_2H \longrightarrow Me{\cdot}C{:}C{\cdot}(CH_2)_{n-1}{\cdot}CO_2H \quad \text{XIV}$$

$$—C{:}C{\cdot}CH_2— \rightleftharpoons —CH{:}C{:}CH— \rightleftharpoons —CH_2{\cdot}C{:}C—$$

On reaching the Δ^4 position, formation of a 2:4-dienoate, an intermediate of the type postulated in the reaction of linoleic acid, would then precede fission. Our findings agree well with these expectations.

Alkali fusion of stearolic acid gave myristic acid (57 per cent) containing a small amount of a C_{16}-acid. This by-product was not destroyed by oxidation, and was therefore palmitic acid and not the hexadec-6-enoic acid reported by Bodenstein. As was to be expected if a common intermediate is involved, the proportion of palmitic to myristic acid was very similar to that obtained from the fission of linoleic acid under comparable conditions. Comparison of the loss of unsaturation, determined by the hydrogen numbers of the products, with the amounts of myristic acid formed, again showed that appreciable polymerization had occurred. Spectral examination of products of incomplete reaction revealed bands (230 mμ, 10·03, 10·15, 10·36 and 10·55 μ) indicating the presence of small amounts (<5 per cent) of conjugated dienes and unconjugated double bonds; a very weak band (5·09 μ) possibly due to traces of allenes was also observed. The residual C_{18}-acids were therefore mainly acetylenic, in accord with previous findings on the equilibria between acetylenes and allenes.[15] The dicarboxylic acids detected after oxidation demonstrated that the triple bond, like the double bond in ethylenic acids, migrates in both directions by a sequence of reversible rearrangements before fission occurs.

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[11] M. Bodenstein, *Ber. Dtsch. Chem. Ges.* **27**, 3397 (1894).

[12] F. Krafft, *Ber. Dtsch. Chem. Ges.* **29**, 2232 (1896).

[13] E. Stenhagen, *Arkiv Kemi* **1**, 99 (1949).

[14] G. Eglinton, E. R. H. Jones, G. H. Mansfield and M. C. Whiting, *J. Chem. Soc.* 3197 (1954); E. R. H. Jones, G. H. Whitham and M. C. Whiting, *Ibid.* 3201 (1954).

[15] T. L. Jacobs, R. Akawie and R. G. Cooper, *J. Amer. Chem. Soc.* **73**, 1273 (1951).

TABLE 2. ALKALI FUSION OF STEAROLIC ACID

		245°/90 min[a]	300°/30 min	360°/30 min	360°/60 min
Relative proportions (%) of C_{18} and lower acids	C_{18}	73	4	—	2
	C_{16}	1·4	10	6	8
	C_{14}	25·6	86	91	89
	C_{12}	0	0	2	1
Yield of myristic acid (mol %)		19	—	51	~55

[a] Ozonolysis gave the C_{12} to C_4 dicarboxylic acids in 0·4, 1·9, 6·4, 13·9, 5·9, 1·4, 1·3, 0·6 and 1·0 mol % yield from stearolic acid (total yield of dicarboxylic acids based on the residual octadecynoic acids, ca. 50 %). The methyl esters of the fusion product had λ_{max} 210 and 233 mμ, $E^{1\%}_{1cm}$ 50 and 80 respectively; hydrogenation number 211, equivalent to an I.V. of 120.

TABLE 3. ALKALI FUSION OF UNDEC-10-YNOIC ACID

		220°/30 min[a]	280°/15 min[b]	300°/60 min	300°/60 min	300°/60 min
Wt. ratio of alkali : acid		3 : 1	3 : 1	3 : 1	20 : 1	70 : 1
Relative proportions (%) of C_{11} and lower acids	C_{11}	99	87	0	0	0
	C_9	trace	trace	29	21	17
	C_7	1	13	71	79	83
Yield of heptanoic acid (mol %)		—	—	26	22	12
Yield of nonanoic acid (mol %)		—	—	9	5	2
Proportion (%) of C_9 : C_7 acids		—	—	35	23	17

[a] In a mixture (1 : 1) of NaOH and KOH. Hydrogenation no. of product = 168.

[b] Ozonolysis of product (hydrog. no. = 158; λ_{max} 230 mμ, $E^{1\%}_{1cm}$ = 110) gave the C_{10} to C_3 dicarboxylic acids, and the C_5 to C_9 monocarboxylic acids (proportion of C_9 : C_7 = 16 %).

Alkali fusion of undec-10-ynoic acid (XIII, $n = 8$) was accompanied by extensive polymerization, but fission giving heptanoic acid (12–26 %) was detected (Table 3). It is of interest that the formation of the by-product with loss of only two carbon atoms was more prominent in the C_{11} than the C_{18} series. Moreover, as required by the explanation offered above for this side reaction, the proportion of nonanoic to heptanoic acid fell with increasing dilution of the reaction mixture. Undec-9-ynoic acid also gave heptanoic (20–30 %) and nonanoic acid (3–6 %) on alkali fusion (300°/30 min), but trideca-6:12-diynoic acid polymerized completely (300°/60 min). Alkali fusion (300°/30 min) of dodec-6-ynedioic acid (XV) gave suberic acid in 60 per cent yield and only 1 per cent of sebacic acid.

$$\text{XV}\quad HO_2C{\cdot}(CH_2)_4{\cdot}C\,\vdots\,C{\cdot}(CH_2)_4{\cdot}CO_2H \longrightarrow HO_2C{\cdot}(CH_2)_6{\cdot}CO_2H$$

The suppression of the side reaction in this example may be due to enhanced repulsion of the intermediates resulting from their increased negative charges.

The schemes discussed above for the fission of acetylenic fatty acids will not apply to the $\alpha\beta$- and $\beta\gamma$-acetylenic compounds. These are known to decompose in strong alkalis, probably by initial hydration to a β-keto-acid.[14] As expected, alkali fusion (300°/10 min) of dec-2-ynoic acid (XVI) gave octanoic acid in low yield, traces of hexanoic acid and nonan-2-one (semicarbazone), and much non-saponifiable high boiling material. This result lends considerable support to the view that β-keto-acids are not key intermediates in the fission stage of the Varrentrapp reaction.[1]

$$\text{XVI}\quad CH_3{\cdot}(CH_2)_6{\cdot}C\,\vdots\,C{\cdot}CO_2H \longrightarrow CH_3{\cdot}(CH_2)_6{\cdot}CO_2H$$

EXPERIMENTAL

The general methods and analytical techniques used were those described in the experimental section to Part I.[1] Acetic and butyric acid were analysed by azeotropic distillation.[16]

Starting materials

Linoleic acid. The authors thank Dr. A. H. Hosking for a generous supply of methyl linoleate which had been prepared from the α-tetrabromide of natural linoleic acid. It had $n_D^{22\cdot5}$ 1·4621; λ_{max} 228 mμ, $E_{1\,cm}^{1\%} = 42$ (ca. 3% of conjugated diene); 10·16 μ (trace of conjugated *cis*:*trans* diene); 10·36 μ (ca. 3% unconjugated *trans* double bond). Only one band was obtained on G.L.C. (silicone).

A solution of potassium hydroxide (10% excess) in methanol (10 vol) was added slowly (ca. 1 cc/10 min) to a boiling solution of methyl linoleate in methanol (15 min) in an atmosphere of nitrogen. The mixture was boiled for a further 15 min, cooled, poured into water, extracted with ether, and then acidified with 2 N H_2SO_4. Isolation of the product with ether gave linoleic acid.

Ozonolysis of linoleic acid gave mixtures of mono- and di-carboxylic acids in ca. 70% yield. The mono-carboxylic acid fraction consisted almost entirely of hexanoic acid, but contained ca. 0·2 mol % of octanoic and nonanoic acid (derived from oleic acid impurity). The dicarboxylic acid fraction consisted mainly of azelaic acid but also contained 2·2, 0·2 and 0·9 mol % of suberic, pimelic and succinic acid respectively; malonic acid was also detected qualitatively.

Stearolic acid. This was prepared from oleic acid[17] and had m.p. 47·5–48·5° (lit.[17] m.p. 46–46·5°), hydrogenation number, 142 (calc. 140). Ozonolysis gave nonanoic acid, which contained traces of octanoic and heptanoic acid (0·5 and 0·1 mol % respectively), and azelaic acid (86%) which was contaminated with 1·3, 1·4, 0·1, 0·3 and 0·4 mol % of suberic, pimelic, adipic, glutaric and succinic acid respectively.

*Undec-*10*-ynoic acid.* This was prepared[18] from undec-10-enoic acid and had m.p. 42·7–43·0° (lit.[2] m.p. 42·7–42·9°), λ_{max} (CCl_4) 3·04 (—C≡C—H) and 4·70 μ (C≡C). Its methyl ester gave only one band on G.L.C. and had b.p. 126–130°/12 mm, n_D^{22} 1·4460, λ_{max} 3·05 and 4·70 μ.

Undec-9-ynoic acid. This was prepared[12] from undec-10-enoic acid and had m.p. 59·0–59·5° (lit.[2] m.p. 59·5°). Its methyl ester gave only one band on G.L.C. and had b.p. 173–175°/100 mm, n_D^{20} 1·4514; it exhibited no light absorption at 3·04 μ (absence of —C⋮C—H).

*Dodec-6-ynedioic and tridec-*6:12*-diynoic acid.* The samples used were those previously described.[19]

*Dec-*2*-ynoic acid.* Carboxylation of the Grignard reagent of dec-1-yne gave the acid, b.p. 116–118°/0·9 mm, n_D^{19} 1·4546 (lit.[20] b.p. 164–168°/20 mm). Its methyl ester had b.p. 125°/17 mm (lit.[17]

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[16] S. T. Schicktanz, W. I. Steele and A. C. Blaisdell, *Industr. Engng. Chem.* (*Anal.*) **12,** 320 (1940).

[17] H. Adkins and R. E. Burks, *Org. Synth.* **27,** 76 (1947).

[18] N. A. Khan, *Org. Synth.* **32,** 104 (1952); cf. L. Crombie and A. G. Jacklin, *J. Chem. Soc.* 1622 (1957).

[19] B. W. Baker, R. P. Linstead and B. C. L. Weedon, *J. Chem. Soc.* 2218 (1955).

[20] C. Moureu and R. Delange, *C. R. Acad. Sci., Paris* **136,** 552 (1903).

b.p. 133–135°/21 mm), n_D^{19} 1·4419, λ_{max} 4·45 μ (C≡C); the ultra-violet light absorption spectrum showed only end absorption, $E_{1\,cm}^{1\%}$ (208 mμ) = 300; G.L.C. indicated the presence of a trace of an impurity (<1 %).

Alkali fusions

The majority of the results are summarized in the Tables. The following examples illustrate the isolation of some main reaction products.

(i) Linoleic acid (from 3·0 g of methyl ester) and KOH (9·0 g) were heated at 360° for 30 min (cf. Table 1). The crude acid product (ca. 75 %) was isolated in the usual way[1] and had m.p. 50–51°. Crystallization from methanol gave myristic acid, m.p. and mixed m.p. 53·5–54°.

(ii) Stearolic acid (2·24 g) and KOH (7·0 g) were heated at 360° for 30 min (cf. Table 2). The crude acid product (1·54 g) was isolated and esterified (MeOH–H_2SO_4). Distillation gave a liquid, b.p. 100–110°/1 mm, which was shown by G.L.C. to contain >95 % methyl myristate. Hydrolysis gave a solid m.p. 50–51°. Crystallization from light petroleum (b.p. 40–60°) gave myristic acid, m.p. and mixed m.p., 53·7–54·2°.

(iii) Dec-6-ynedioic acid (2·9 g) and KOH (9·0 g) were heated at 330° for 30 min. The mixture was cooled and dissolved in water. The solution was acidified and extracted thoroughly with ether. The extract was evaporated, and the residue esterified (MeOH–H_2SO_4). Analysis of the product by G.L.C. revealed methyl suberate and sebacate formed in 60 % and 1 % yield respectively. Distillation gave methyl suberate, b.p. 105–110°/2 mm, which was shown by G.L.C. to contain only traces of impurities. Hydrolysis, and crystallization from water, gave suberic acid, m.p. and mixed m.p. 144°.

Hydrogen numbers were determined in the microanalytical laboratory (Miss J. Cuckney), and ultra-violet (Mrs. A. I. Boston) and infra-red measurements (Mr. R. L. Erskine) in the spectrographic laboratory of this department.

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