Tetrahedron, 1960, Vol. 8, pp. 221 to 238. Pergamon Press Ltd. Printed in Northern Ireland

ORGANIC REACTIONS IN STRONG ALKALIS—I

FISSION OF ETHYLENIC ACIDS (THE VARRENTRAPP REACTION)

R. G. Ackman, Sir Patrick Linstead, B. J. Wakefield and
B. C. L. Weedon
Department of Chemistry, Imperial College of Science and Technology, London

(*Received* 11 *July* 1959)

Abstract—On treatment with molten potassium hydroxide, ethylenic acids are converted initially into a mixture of isomers, by reversible migration of the double bond in both directions along the chain, and finally into a saturated acid, with two fewer carbon atoms than the starting material, and acetic acid in high yield. A number of minor side-reactions also occur.

The mechanisms of these processes are discussed.

Numerous studies have been made on the behaviour of organic compounds in strongly alkaline media, but many of the reactions involved are still only poorly understood. Furthermore the extensive literature on the subject contains many conflicting and unexpected reports. A general study of organic reactions in strong alkalis was therefore initiated in 1953, and the results will be given in this series of papers,

Our first objective is to examine the behaviour of the main aliphatic functional groups in concentrated alkali hydroxides. For this purpose the fatty acids and their derivatives afford an ideal series of compounds; they enable the grouping under investigation to be readily introduced into the reaction medium, and give rise to products which are conveniently analysed chromatographically. During previous investigations with these compounds suitable techniques for analysis of the starting materials and products were often not available, and, in consequence, many misleading claims have been made. A preliminary account of our own studies has already been given.[1] In this paper we are concerned mainly with the fission of olefinic acids in molten alkalis.

In 1840 Varrentrapp[2] heated oleic acid (I) with molten potassium hydroxide and obtained palmitic acid, acetic acid and hydrogen. For many years oleic acid was formulated, largely on this evidence, as octadec-2-enoic acid, and the nature of the transformation involved in the Varrentrapp reaction was not fully appreciated until the advent of reliable degradative procedures enabled the correct structure of oleic acid to be deduced.[3] Other similar fatty acids which have been converted by alkali

$$CH_3{\cdot}(CH_2)_7{\cdot}CH\overset{cis}{:}CH{\cdot}(CH_2)_7{\cdot}CO_2H \longrightarrow CH_3{\cdot}(CH_2)_{14}{\cdot}CO_2H + CH_3{\cdot}CO_2H + H_2$$

II 

---

[1] *Chem. & Ind.* 402 (1958).

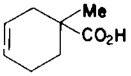
[2] F. Varrentrapp, *Liebigs Ann.* 35, 196 (1840).

[3] cf. T. P. Hilditch, *The Chemical Constitution of Natural Fats.* Chapman and Hall, London (1947) F. D. Gunstone, *Chem. & Ind.* 250 (1955).

fusion* into saturated acids containing two fewer carbon atoms include elaidic,[2] erucic,[4] brassidic,[5] and undecylenic acid,[6] and thus the reaction is clearly general for both *cis* and *trans* ethylenic fatty acids. An interesting variant is the formation of pimelic acid from cyclohex-3-ene-carboxylic acid (II),[7,8] the loss of two carbon atoms being avoided with this cyclic starting material.

Although almost quantitative yields were claimed by some early investigators,[9,10] these were not achieved by many subsequent workers who often failed to appreciate the importance of carrying out the reaction in an inert atmosphere. We find that when this precaution is taken yields of about 80 per cent are readily obtained, but that yields drop to 50 per cent or less when no attempt is made to exclude air.

The mechanism of the Varrentrapp reaction has been the subject of much speculation. Although Chuit *et al.*[11] interpreted their results with undecylenic acid as indicating fission of the double bond at positions remote from the carboxyl group, most authors have argued that the double bond, or some group derived from it, first migrates into the $\alpha\beta$ position and then undergoes fission.[8,10,12] Strong support for this view is provided by the observation that neither 1-methylcyclohex-3-ene-1-carboxylic acid (III),[7] nor 3:3-dimethylnon-8-en-1-oic acid (IV),[13] in which the α and β positions respectively are blocked, exhibit the normal Varrentrapp reaction. However $\alpha\beta$-unsaturated acids (e.g. V, $n = 2$,[14] 4,[14] 8[15] and 14;[16] cyclohex-1-enylcarboxylic acid[7,17]) are readily split under similar conditions.



III

$$CH_2{:}CH.(CH_2)_4.CMe_2.CH_2.CO_2H$$

IV

$$\text{V} \quad CH_3{\cdot}(CH_2)_n{\cdot}CH{:}CH{\cdot}CO_2H \longrightarrow CH_3{\cdot}(CH_2)_n{\cdot}CO_2H + CH_3{\cdot}CO_2H$$

Moreover Hunter and Popják[14] have demonstrated that hex-2-enoic and oct-2-enoic acid give acetic acid and either butyric or hexanoic acid in roughly equivalent amounts. A similar relationship between the two main fission products has now been established for the non-conjugated acid, undec-10-enoic acid.

Hydroxy-, keto- and dihydroxy-acids[6,10,18] have been postulated as intermediates in the migration stage of the Varrentrapp reaction, but their participation is excluded

---

* In this series "alkali fusion" will refer to a reaction with an alkali metal hydroxide in which the reagent is liquid at the reaction temperature but solid at room temperature.

[4] A. Fitz, *Ber. Dtsch. Chem. Ges.* **4**, 442 (1871).

[5] G. Goldschmidt, *Jahresbericht* 522 (1877).

[6] F. Becker, *Ber. Dtsch. Chem. Ges.* **11**, 1412 (1878); F. Krafft. *Ibid.* **15**, 1687 (1882); I. Jegorow, *J. Russ. Phys. Chem. Soc.* **46**, 975 (1914); *Chem. Zentr.* **I**, 934 (1915); R. Shagalova, *Masloboino Zhirovoe Delo* **11**, 452 (1935); *Chem. Abstr.* **30**, 1026 (1936).

[7] H. J. Pistor and H. Plieninger, *Liebigs Ann.* **562**, 239 (1949).

[8] F. X. Werber, J. E. Jansen and T. L. Gresham, *J. Amer. Chem. Soc.* **74**, 532 (1952).

[9] W. L. Carpenter, *J. Soc. Chem. Ind.* **2**, 98 (1883).

[10] F. G. Edmed, *J. Chem. Soc.* **73**, 627 (1898).

[11] P. Chuit, F. Boelsing, J. Hausser and G. Malet, *Helv. Chim. Acta* **9**, 1074 (1926); **10**, 113 (1927).

[12] M. Saytzeff, C. Saytzeff and A. Saytzeff, *J. Prakt. Chem.* **37**, 269 (1888).

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

[14] G. Hunter and G. Popják, *Biochem. J.* **50**, 163 (1951).

[15] C. H. Kao and S.-Y. Ma, *J. Chem. Soc.* 2046 (1931).

[16] G. Ponzio, *Gazzetta* **34**, 77 (1904).

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

[18] G. Wagner, *Ber. Dtsch. Chem. Ges.* **21**, 3347 (1888).

by alkali fusions of authentic compounds of these types.[1,19,20] A prototropic mechanism was first advanced by Farmer[21] in 1942, and receives support from the work of Lüttringhaus[22,23] and Pines[24] on the metallation of simple olefins. With the reservation that proton removal and proton return may be either consecutive or concerted processes, the mechanism may be represented in the following way.

$$\text{—CH:CH·CH}_2\text{—} \overset{\ominus\text{OH}}{\rightleftarrows} \text{—CH:CH·}\overset{\ominus}{\text{CH}}\text{—} \longleftrightarrow \text{—}\overset{\ominus}{\text{CH}}\text{·CH:CH—} \overset{\ominus\text{OH}}{\rightleftarrows} \text{—CH}_2\text{·CH:CH—}$$

By a sequence of such transformations the double bond might be expected to migrate into all available positions, though no true equilibria would be established owing to the removal by fission of the $\alpha\beta$-isomer. However Farmer reported that on treatment of oleic acid with molten alkali the double bond migrated solely towards the acid function, and attributed this rather surprising result to the inductive effect of the carboxylate group. Considering that a chain of seven carbon atoms originally separates the two functional groups, such an explanation cannot now be accepted. We have therefore studied the migration of double bonds under the conditions of the Varrentrapp reaction.

Oleic acid was heated with potassium hydroxide at 300° (bath temp) for various times insufficient to cause complete reaction, and the products examined (Table 1). The loss of unsaturated acid was calculated from the iodine value of the product, and the amount of palmitic acid formed was determined by gas–liquid chromatography after esterification with methanol. The good agreement between the two values showed that saturated intermediates did not accumulate during the reaction, and that the products consisted mainly of palmitic acid and mixtures of octadecenoic acids.

Information on the nature of the residual octadecenoic acids was obtained by careful ozonolysis of the fusion products, and analysis of the resulting dicarboxylic acids by paper chromatography; an octadec-n-enoic acid thus yielded a C_n-diacid. To minimize side reactions (see p. 236) the oxidations were not carried to completion, but the relative amounts of the diacids reflected the proportions of the original octadecenoic acids. The monocarboxylic acids obtained on ozonolysis of the 30 and 120 min fusion products were examined by gas-liquid chromatography of their methyl esters, and shown to contain the C_7 to C_{10} acids in roughly the same relative proportions as the complementary dicarboxylic acids. These results demonstrated the formation of all isomeric octadecenoic acids from Δ^4 to Δ^{12} (others were doubtless formed but were not detected by the analytical procedure used, see p. 236). It is clear that, contrary to Farmer's claim, *the double bond migrates initially almost equally in both directions*, and that the carboxylate group exercises no directing influence during the early stages of the reaction. Since these findings, the formation of small amounts of both octadec-8- and octadec-10-enoic acids on alkali fusion of oleic acid at 280°–300° has been reported by Blekkingh *et al.*[25]

Infra-red spectrophotometry of the fusion products showed that the proportion of the residual octadecenoic acids with the *trans* configuration rose with the time of

---

[19] A. Eckert, *Monat.* **38**, 1 (1917).

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

[21] E. H. Farmer, *Trans. Faraday Soc.* **38**, 356 (1942).

[22] A. Lüttringhaus, G. Wagner-v. Sääf, E. Sucker and G. Borth, *Liebigs Ann.* **557**, 52 (1947).

[23] cf. H. Gilman and R. L. Bebb, *J. Amer. Chem. Soc.* **61**, 109 (1939).

[24] H. Pines, J. Vesely and V. N. Ipatieff, *J. Amer. Chem. Soc.* **77**, 347 (1955).

[25] J. J. A. Blekkingh, H. J. J. Janssen and J. G. Keppler, *Rec. Trav. Chim.* **76**, 35 (1957).

reaction from 0 to ca. 65 per cent. The latter value agrees well with that found in the equilibrium between oleic and elaidic acids.[3] One fusion product was separated by the lead salt procedure[26] into solid and liquid fractions, the former composed mainly of the saturated and *trans*-acids, and the latter mainly of the *cis*-acids. The solid and liquid fractions contained 60 and 40 per cent respectively of the total unsaturation, and both were shown by oxidation to contain all octadecenoic acids from Δ^6 to Δ^{11} in about the same proportions. As the lead salt technique gives somewhat low values for *trans*-acids in multicomponent mixtures,[27] it may be concluded that each octadecenoic acid formed by double bond migration is an equilibrium mixture of *cis* and *trans* forms. The presence of octadec-*trans*-9-enoic acid indicates reformation of the Δ^9-acid, by further rearrangement of the other isomers. All these findings are consistent with the prototropic mechanism envisaged for the isomerization stage of the Varrentrapp reaction.

TABLE 1. ALKALI FUSION OF OLEIC ACID AT 300° (BATH TEMP)

		30 min	60 min	90 min	120 min
I.V. of product		87·8	79·8	71·5	61·4
octadecenoic acids lost (mol %)[a]		3	12	22	34
palmitic acid formed (mol %)		~3	15	27	35
trans-octadecenoic acids (mol %)[b]		46	59	63	67
Yield (mol %) of diacids from ozonolysis of fusion product[b,c]	C_{12}	—	—	—	(0.4)
	C_{11}	(0·8)	(0·9)	(0·9)	(1·6)
	C_{10}	13·1	9·9	8·3	4·3
	C_9	42·6	15·0	6·1	7·9
	C_8	11·7	7·9	6·5	8·1
	C_7	2·3	2·2	3·7	3·1
	C_6	1·4	1·4	3·9	2·1
	C_5	[0·3]	1·1	2·4	1·2
	C_4	[0·7]	1·5	3·4	2·7
	Total	72·9	39·9	35·2	31·4

[a] Calculated from I.V. of product without allowance for the formation of unsaturated polymers.
[b] Based on residual octadecenoic acids.
[c] Figures in parentheses ( ) probably indicate too low, and those in brackets [ ], too high, a value for the corresponding ethylenic acid (see p. 237)

In another series of experiments oleic acid was heated with molten potassium hydroxide at temperatures ranging from 260° to 380°. The results (Table 2) were generally similar to those already described. At 260° very little fission occurred, even after reaction for 5 hr.

In both the time and temperature studies, the yield of dicarboxylic acids obtained

---

[26] L. V. Cocks, B. C. Christian and G. Harding, *Analyst* **56**, 368 (1931).
[27] F. L. Jackson and J. E. Callen, *J. Amer. Oil Chem. Soc.* **28**, 61 (1951).

on oxidation dropped markedly with diminution in the iodine value of the fusion product. Spectroscopic examination of these products showed no significant amounts of the $\alpha\beta$-unsaturated acid (the formation of octadec-2-enoic acid on heating oleic acid with aqueous alkali in oxygen has been reported,[28] though the evidence is not conclusive). The absence of any substantial amount of the $\beta\gamma$-isomer was established by ozonolysis, and gas–liquid chromatography of the methyl esters of the resulting acids, which revealed only traces of methyl pentadecanoate. Since ozonolysis of authentic mixtures of palmitic acid with small amounts of oleic acid gave satisfactory results, the low yields referred to above indicate that compounds other than the Δ^2 to Δ^{12} octadecenoic acids account for much of the residual unsaturation in products of low iodine value. These compounds may include octadecenoic acids with double bonds in positions remote from the carboxyl group, and unsaturated polymers formed by intermolecular addition reactions (see below).

TABLE 2. ALKALI FUSION OF OLEIC ACID AT VARIOUS TEMPERATURES
(30 min unless stated otherwise)

		260°	280°	300°	260°*	320°	360°	380°	360°†
I.V. of product		87·8	87·8	87·8	87·0	62·3	21·0	10·2	5·8
octadecenoic acids lost (mol %)[a]				3		33	78	88	94
palmitic acid formed (mol %)				~3		~40			
trans-octadecenoic acids (mol %)[b]		2	17	46		56			
Yield (mol %) of diacids from ozonolysis of fusion product[b, c]	C_{12}	—	—	—	—	(0·7)	(0·4)	(0·06)	5·5
	C_{11}	—	—	(0·8)	(0·5)	(1·8)	(8·7)	(1·3)	5·5
	C_{10}	—	6·8	13·1	6·4	18·7	7·7	3·1	3·8
	C_9	55·3	41·9	42·6	42·3	24·7	6·7	2·3	1·9
	C_8	1·9	6·2	11·7	9·9	15·0	4·7	0·43	—
	C_7	1·8	1·0	2·3	3·0	2·8	1·4	0·08	—
	C_6	[0·5]	[0·5]	1·4	[0·4]	1·4	0·6	0·06	—
	C_5	[0·8]	[0·3]	[0·3]	[0·5]	1·0	0·3	0·04	—
	C_4	[1·3]	[0·5]	[0·7]	[0·8]	1·0	—	0·09	—
	Total	61·6	57·2	72·9	65·0	67·1	30·5	7·5	16·7

[a,b,c] See footnotes to Table 1.
* Reaction time 300 min
† Reaction time 60 min

Another feature of the above results is that, although the distribution of the double bond along the chain became more uniform as the reaction proceeded, no large amount of the Δ^2 to Δ^7 octadecenoic acids was ever detected. (Jegorow's[6] claim to have isolated octadec-5-enoic acid after heating oleic acid with concentrated aqueous alkali could not be confirmed.) It therefore seemed desirable to study the fusion of ethylenic acids with the double bond originally in such positions.

---

[28] W. Treibs and M. Rothe, *Chem. Ber.* **84**, 370 (1951).

The results (Table 3) from the alkali fusion of petroselinic acid (VI) under a variety of conditions resembled those obtained with oleic acid. The monocarboxylic acids obtained on ozonolysis of the fusion products were those to be expected from analyses of the complementary dicarboxylic acids, and the relative proportions were similar. Double bond migration occurred in both directions; in one experiment (300°/1 hr) nearly all the residual unsaturation detected was in positions further from the carboxylate group than the original Δ^6 position. However, even before any appreciable fission had occurred, there was more migration towards, than away from, the acid function.

TABLE 3. ALKALI FUSION OF PETROSELINIC ACID

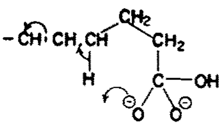
		250°/30 min	280°/30 min	300°/30 min	300°/60 min	360°/30 min
I.V. of product		86·2	56·5	32·0	18·2	2
octadecenoic acids lost (mol %)[a]		3	39	66	81	98
palmitic acid formed (mol %)		~1		58	84	
trans-octadecenoic acids (mol %)[b]		10	24	69		
Yield (mol %) of diacids from ozonolysis of fusion product[b]	C_{11}	—	—	—	—	
	C_{10}	—	—	—	0·9	
	C_9	—	—	0·3	1·5	
	C_8	—	—	4·2	8·9	
	C_7	2·3	4·0	8·6	19·5	
	C_6	67·3	45·3	27·8	2·0	
	C_5	3·0	11·1	3·4	—	
	C_4	3·6	4·5	1·6	—	
	Total	76·2	64·9	45·9	32·8	

[a,b] See footnotes to Table 1.

$$CH_3{\cdot}(CH_2)_{10}{\cdot}\overset{cis}{CH{:}CH}{\cdot}(CH_2)_4{\cdot}CO_2H \qquad CH_3{\cdot}(CH_2)_{14}{\cdot}\overset{trans}{CH{:}CH}{\cdot}CO_2H$$

VI VII

A direct comparison (Table 4) of the behaviour of oleic, petroselinic and αβ-oleic (VII) acids under the same conditions showed that the rate of reaction increased with the proximity of the original double bond to the carboxyl group. It is conceivable that double bonds in the Δ^4 and Δ^5 positions, and perhaps, to a lesser extent, even



VIII

those at Δ^6 and Δ^7, react faster than those in the Δ^9 and more remote positions due to the operation of an intramolecular mechanism. This may be represented for the Δ^5-isomer by VIII.

Similar proposals have been made by Jones *et al.*[29] to account for the more rapid isomerization in concentrated alkalis of pent-4-ynoic and hex-5-ynoic acid compared with higher ω-acetylenic acids. It has previously been reported that Δ^4-ethylenic acids are hardly affected by treatment with alkali, in marked contrast to the Δ^2 and Δ^3 isomers which undergo rapid equilibration;[30] the conditions (30 per cent KOH/100°) were, however, far less drastic than those used in the present studies.

TABLE 4. ALKALI FUSION OF OCTADECENOIC ACIDS (300° bath temp/30 min)

		$\Delta^{9:10}$	$\Delta^{6:7}$	$\Delta^{2:3}$
I.V. of product		87·8	32·0	13·1
octadecenoic acid lost (mol %)[a]		3	66	87
trans-octadecenoic acids[b]		46	69	
Yield (mol %) of diacids from ozonolysis of fusion product[b, c]	C_{11}	(0·8)	—	—
	C_{10}	13·1	—	—
	C_9	42·6	0·3	—
	C_8	11·7	4·2	—
	C_7	2·3	8·6	—
	C_6	1·4	27·8	—
	C_5	[0·3]	3·4	—
	C_4	[0·7]	1·6	3·0
	Total	72·9	45·9	

[a, b, c] See footnotes to Table 1.

When octadec-2-enoic acid was heated with potassium hydroxide at 300° for 30 min, fission was incomplete (Table 4). The composition of the residual (13 per cent) octadecenoic acids was estimated as 85 per cent of the Δ^2-isomer (determined by ultra-violet light absorption), 12 per cent of the Δ^3-isomer (determined by ozonolysis and analysis of the resulting acids by gas–liquid chromatography of their methyl esters), and 3 per cent of the Δ^4-isomer (determined by oxidation to succinic acid). The rapid equilibration of $\alpha\beta$- and $\beta\gamma$-ethylenic acids in alkalis is well known,[30,31] but the formation of some Δ^4-isomer from octadec-2-enoic acid is interesting. Crossley and Hilditch[32] reported that, when heated with potassium hydroxide in glycol at 170–180°, deca-2:4-dienoic acid appeared to give mainly the $\Delta^{4,6}$- and

---

[29] E. R. H. Jones, G. H. Whitham and M. C. Whiting, *J. Chem. Soc.* 3201 (1954).

[30] A. A. Goldberg and R. P. Linstead, *J. Chem. Soc.* 2343 (1928); R. P. Linstead and E. G. Noble, *Ibid.* 614 (1934).

[31] J. Cason and G. Sumrell, *J. Org. Chem.* **16**, 1181 (1951); J. Cason, N. L. Allinger and G. Sumrell, *Ibid.* **18**, 850 (1953).

[32] A. Crossley and T. P. Hilditch, *J. Chem. Soc.* 4613 (1952).

$\Delta^{5,7}$-isomers, and a thermal rearrangement of 5-methyltridec-2-enoic acid to the Δ^4-isomer has been claimed by Cason *et al.*[33]

The interconversion of Δ^2- and Δ^3-isomers in molten alkalis was more conveniently demonstrated with non-2-enoic acid. After brief treatment with potassium hydroxide (ca. 280°/3 min) a mixture containing ca. 70 per cent of the Δ^2-isomer and ca. 20 per cent of the Δ^3-isomer was recovered (cf. 74 per cent $\alpha\beta$- and 26 per cent $\beta\gamma$-isomer from equilibration of hex-2-enoic acid in aqueous potassium hydroxide[30]). Under more drastic conditions (300°/5 min), heptanoic acid was produced.

TABLE 5. ALKALI FUSION OF UNDEC-10-ENOIC ACID

		250°/60 min*	300°/30 min	300°/60 min	300°/90 min	360°/60 min
I.V. of product		132	127·7	70·3	43·3	<1
undecenoic acids lost (mol %)[a]		—	8	50	70	99
trans-undecenoic acids (mol %)[d]		68				
Yield (mol %) of diacids from ozonolysis of fusion product[b]	C_{10}	5	4·1	1·9	1·8	
	C_9	48	17·0	14·5	20·3	
	C_8	15	13·3	10·0	15·3	
	C_7	2	7·2	8·6	8·1	
	C_6	—	5·3	6·1	6·0	
	C_5	—	2·8	3·1	2·4	
	C_4	—	4·2	3·8	1·4	
	Total	70·0	53·9	48·0	55·3	

* Dicarboxylic acids from ozonolysis of fusion products were analysed by G.L.C. of their methyl esters.
[a,b] See footnotes to Table 1.
[d] Based on undecenoic acids other than Δ^{10}

Both Jegorow[6] and Eckert[19] demonstrated that undec-10-enoic acid could be converted by treatment with concentrated alkalis into a product consisting mainly of the Δ^9-isomer. Later Chuit *et al.*[11] stated that alkali fusion of undec-10-enoic acid gave not only nonanoic acid, as reported by Becker,[6] but also small amounts of the next four lower homologues. They concluded that the Δ^9-isomer and, subsequently, small amounts of other isomers were first formed by rearrangement, and that fission of the double bond in the various positions then gave the observed products. An initial rapid migration of the double bond into the penultimate position is to be expected, as di-alkylated ethylenes are thermodynamically more stable than their mono-substituted isomers, but we believe the conclusions of the Swiss authors concerning fission to be incorrect. Examination of the products from various alkali fusions of undec-10-enoic acid (Table 5) indicated that the double bond migrated rapidly away from the terminal position, and then along the chain. (After the completion of this investigation Lüttringhaus and Reif[34] reported the migration of the double bond as

---

[33] J. Cason, N. L. Allinger and C. F. Allen, *J. Org. Chem.* **18**, 857 (1953).
[34] A. Lüttringhaus and W. Reif, *Liebigs Ann.* **618**, 221 (1958).

far as the Δ^6 position on heating undec-10-enoic acid with methanolic alkalis, an 82 per cent conversion into the Δ^9-isomer being achieved under some conditions. Their conclusions concerning the course of the Varrentrapp reaction are in many respects similar to ours.) The di-substituted double bonds formed by rearrangement were shown (infra-red spectra) to be equilibrium mixtures of the *cis* and *trans* forms. The greater reactivity of undec-10-enoic acid compared with oleic acid (cf. Tables 1 and 5) may be partly due to the absence of any stable double bond position more remote than Δ^9 from the carboxylic group. Complete reaction of undec-10-enoic acid gave nonanoic acid in 80 per cent yield; only traces of lower homologues were observed (cf. Chuit *et al.*[11]), and these probably arose from side reactions of the types discussed later.

All the information presented above is consistent with the view that *alkaline fission of an ethylenic acid occurs by reversible migration of the double bond along the chain until it reaches the αβ-position, where it undergoes irreversible fission.* There is as yet no evidence to suggest that either inter- or intramolecular hydrogen transfer leads to an αβ-ethylenic acid more directly. Both processes are unlikely. Moreover the former would result in equimolecular amounts of two saturated acids, one containing the same number of carbon atoms as the starting material and the other four fewer (cf. Part II); such products are not observed to any significant extent in Varrentrapp reactions.

Considering now the fission of the αβ-ethylenic acids (IX), it seems most likely that this involves an initial nucleophilic attack by hydroxyl ions to give a β-hydroxy-acid (X). The formation of β-hydroxy-acids during the alkaline equilibration of αβ- and βγ-ethylenic acids has been reported.[35–37] Such hydrations are reversible; when heated with alkali, crotonic acid gives β-hydroxybutyric acid,[38] and the latter yields crotonic acid together with small amounts of vinylacetic acid.[36] The conversion of 2-hydroxycyclohexane-1-carboxylic acid into cyclohexene-1-carboxylic acid in concentrated alkalis has also been described.[7,8] Although β-hydroxy-acids have not been isolated from alkali fusions of ethylenic acids, this is probably due to their ease of fission. Alkali fusion of β-hydroxystearic and β-hydroxybutyric acid gave palmitic acid and (1·9 moles) acetic acid respectively.

There are two plausible mechanisms for the breakdown of a β-hydroxy-acid. Either dehydrogenation occurs ("route A"), followed by normal "acid fission" of the resulting β-keto-acid (XI), or fission by a reaction of the "retro-aldol" or "retro-Claisen" type gives acetate and an aldehyde (XII), which is then converted into the corresponding acid ("route B"). The dehydrogenation in alkalis of other hydroxy-acids to keto-acids has recently been demonstrated,[20] but alkali fusion of 3-oxobutyric acid, 3-oxodecanoic acid and methyl 3-oxo-octadecanoate gave neutral by-products which were not observed during Varrentrapp reactions (the formation of small amounts of cyclohexanone during the conversion of cyclohexenecarboxylic acids into pimelic acid has been noted,[8] but may have resulted from pyrolysis of the main product, sodium pimelate). Such by-products were produced in the alkali fusion of dec-2-ynoic acid where there is good reason to believe that a β-keto-acid is implicated (Part II). The view that decarboxylation of a β-keto-acid first formed gave a ketone which then

---

[35] R. Fittig and J. G. Spenzer, *Liebigs Ann.* **283**, 66, 80 (1894).

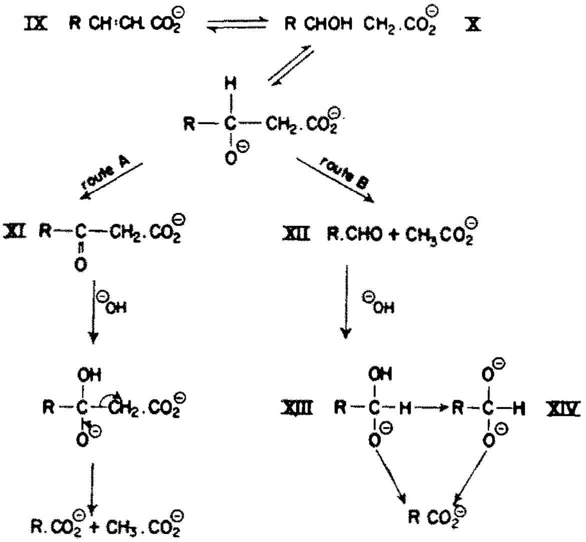
[36] F. Fichter and F. Sonneborn, *Ber. Dtsch. Chem. Ges.* **35**, 938 (1902).

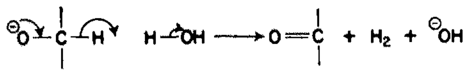
[37] D. J. G. Ives and R. H. Kerlogue, *J. Chem. Soc.* 1362 (1940).

[38] L. N. Owen, private communication.

underwent fission is incompatible with the formation of a long chain fatty acid and acetic acid in approximately equimolar proportions.

With regard to "route B", it is known that aldehydes are readily converted by concentrated alkalis into acids.[39] The reaction may be represented as an attack by hydroxyl ion to give either XIII or, by analogy with the Cannizzaro reaction,[40] the double charged species XIV, followed by transfer of a hydride ion to some acceptor. If the latter is water, then hydrogen is formed simultaneously and hydroxyl ion regenerated:





$$^{\ominus}O-\overset{|}{\underset{|}{C}}-H \quad H-OH \longrightarrow O=\overset{|}{\underset{|}{C}} + H_2 + {}^{\ominus}OH$$

Similar transformations are probably involved in the conversion of primary alcohols into acids[44] on treatment with concentrated alkalis, and in related processes.

Attempts to demonstrate the formation of aldehydes during the alkali fission of ethylenic or β-hydroxy-acids have so far met with little success. No acetaldehyde (or acetone) could be entrained in a steam of nitrogen during the alkali fusion of crotonic and β-hydroxybutyric acid (acetoacetic and 3-oxononanoic acid gave small amounts of acetone and nonan-2-one respectively). However treatment of both acids with hot 40 per cent potassium hydroxide gave traces of acetaldehyde (acetoacetic and 3-oxononanoic acid again gave acetone and nonan-2-one respectively), and the fission of β-alkyl-$\alpha\beta$-ethylenic acids and β-alkyl-β-hydroxy acids to ketones under similar conditions is well authenticated.[41,42] The recent report that distillation of ethyl 2-methyl-2-benzyl-3-hydroxypentanoate in the presence of traces of alkali gives

---

[39] H. S. Fry and E. L. Schulze, *J. Amer. Chem. Soc.* **48**, 958 (1926); G. H. Hargreaves and L. N. Owen, *J. Chem. Soc.* 753 (1947).

[40] L. P. Hammett, *Physical Organic Chemistry*. McGraw-Hill, New York (1940).

[41] R. P. Linstead, *J. Chem. Soc.* 362 (1927).

[42] M. M. Schemjakin and I. A. Redkin, *J. Gen. Chem. U.S.S.R.* **11**, 1163 (1941).

propionaldehyde and ethyl 2-benzylpropionate is also relevant.[43] Although not conclusive, these considerations favour "route B" for the fission of β-hydroxy-acids.

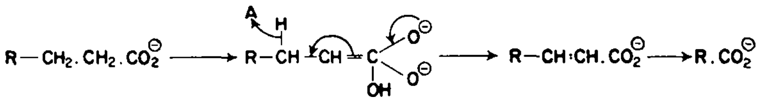
The overall yields of the saturated fatty acids formed on substantially complete reaction of the various ethylenic acids studied are summarized in Table 6 (acetic acid was not normally isolated). Small amounts of by-products were also detected, and their formation deserves comment.

TABLE 6. OVERALL YIELDS OF FISSION PRODUCTS

Starting material	Reaction conditions	Principal product	
		Acid	Yield (%)
Oleic	360°/60 min	palmitic	80–85
Petroselinic	360°/30 min	palmitic	78
αβ-Oleic	360°/60 min	palmitic	83
Undec-10-enoic	360°/30 min	nonanoic	80
Non-2-enoic	300°/5 min	heptanoic	~80

Even after prolonged fusion with alkali the product from oleic acid was not fully saturated. The residual unsaturated acids (ca. 5 mol %) were probably composed mainly of isomers in which the double bond had migrated into positions remote from the carboxyl group, and of unsaturated polymers. These by-products were less in evidence with alkali fusions of petroselinic and αβ-oleic acid.

A commonly encountered impurity (ca. 2–3 mol %) in the fusion products was the saturated acid with two carbon atoms fewer than the main product. Direct experiment with palmitic and capric acid showed that these impurities were formed by further reaction of the main products. Under more drastic conditions than those used in the present studies, γ-alkyl acids have been degraded to α-alkyl acids.[46] Pending a detailed examination of reactions of this type, they are tentatively regarded as proceeding by an initial slow dehydrogenation, involving the transfer of a hydride ion to an acceptor (A), followed by a rapid fission of the resulting αβ-ethylenic acid:



The first of these steps may well be reversible under suitable conditions. Thus it is conceivable that the 2-enoate intermediates in the fission of ethylenic acids might act as an acceptor of hydride ions, e.g. from XIII or XIV, leading to the saturated analogue of the starting material. The oleic acid fusion products contained traces (≯1 %) of stearic acid, and Werber *et al.*[8] obtained 2–3 % cyclohexanecarboxylic acid from the

---

[43] J. R. Hanley, H. S. Killam, R. D. Lanyon, S. MacKenzie, *J. Org. Chem.* **23**, 1461 (1958).

[44] J. Dumas and J. S. Stass, *Liebigs Ann.* **35**, 129 (1840); M. M. Guerbet, *Bull. Soc. Chim. Fr.* **11**, 164 (1912).,

[45] M. M. Guerbet, *Ann. Chim. Phys.* **27**, 67 (1902).

[46] E. L. Pelton and A. A. Holzschuh, U.S. Pat. 2425343, 2531363.

alkaline fission of cyclohexenecarboxylic acids. The formation of 5–10 per cent of octanoic acid in the alkali fusion of oct-2-enoic acid was noted by Hunter and Popják;[14] their starting material was contaminated with neopentyl alcohol which probably served as the hydrogen donor. Hydrogen transfers of the type under consideration appear to assume greater importance in the fission of diene and acetylenic acids (Part II).

Another possible side-reaction is the addition of a carbanion to a 2-enoate intermediate, in a reaction of the Michael type, to give products which can then undergo further transformations. The production of high boiling acids was observed in many alkali fusions, but these products were not investigated further.

Other materials detected chromatographically or spectrally in fusion products were traces of saturated acids, with three and five carbon atoms less than the starting material, dicarboxylic acids (azelaic and sebacic from oleic; sebacic and lower homologues from undec-10-enoic), and hydroxy-acids. Though not normally prominent, it is possible that side reactions leading to such by-products become significant under modified conditions. Thus Treibs and Rothe[47] have claimed that heating oleic acid with aqueous alkali in oxygen gave 9:10-dihydroxystearic acid and sebacic acid, and that undec-10-enoic acid under similar conditions gave azelaic acid. Again Jegerow[6] reported isolating 5- (or 6-) hydroxystearic acid after heating oleic acid with aqueous potassium hydroxide; the structure of his product is, however, doubtful as its m.p. was lower than those subsequently reported for the authentic hydroxystearic acids.[48]

Finally we wish to emphasize that, despite the variety of side reactions that have been observed, the products of Varrentrapp reactions carried out under favourable conditions can be readily purified by standard procedures.

EXPERIMENTAL

(M.p.s were determined on samples in capillary tubes.)

Analytical methods

Iodine values were determined by the method of Benham and Klee[49] using samples of 0·1–0·3 g. Authentic specimens of oleic, elaidic, petroselinic, octadec-2-enoic and undecylenic acid gave values within ±0·5 of the theoretical; methyl octadec-*trans*-10: *trans*-12-dienoate within ±2; β-elaeostearic and sorbic acid gave 90 and 60% respectively of the calculated values; palmitic and 10-hydroxystearic acid under similar conditions gave apparent iodine values of <0·2 and ca.1–3 respectively.

Infra-red light absorption spectra were determined on a Grubb–Parsons D.B. spectrometer. The proportions of (unconjugated) *cis* and *trans* ethylenic acids were determined by the intensity of the absorption maximum at 10·36 μ shown by the methyl esters in carbon disulphide solution (cf. [50]).

Ultra-violet light absorption spectra were determined on a Unicam Quartz Spectrophotometer, using ethanolic solutions. Estimations of the amounts of αβ-unsaturated acids were made from the intensity of absorption at 209 mμ of the derived methyl esters, correction being made for the background absorption by non-conjugated isomers and saturated esters (cf. [51]).

Acetic acid was estimated by steam distillation and titration, or, more accurately, by azeotropic distillation with benzene.[52] Other mono-acids were analysed by gas–liquid chromatography (G.L.C.) of their methyl esters in nitrogen, generally on silicone or Apiezon columns using a positive inlet pressure and either a katharometer or thermistor detector; adjacent members of the homologous

---

[47] W. Treibs and M. Rothe, *Chem. Ber.* **84**, 370 (1951).

[48] S. Bergstrom, *Acta Chem. Scand.* **6**, 1157 (1952).

[49] G. H. Benham and L. Klee, *J. Amer. Oil Chem. Soc.* **27**, 127 (1950).

[50] O. D. Shreve, M. R. Heether, H. B. Knight and D. Swern, *Analyt. Chem.* **22**, 1261 (1950).

[51] J. Cason and G. Sumrell, *J. Org. Chem.* **16**, 1181 (1951).

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

series up to methyl stearate were readily separated. Quantitative analyses were made either by the "normalization procedure" or by means of an "internal standard" (e.g. methyl caprate or myristate); "correction factors" for different components of a mixture were determined with authentic mixtures of approximately the same composition.[53]

Dicarboxylic acids were analysed by paper chromatography in an all-glass cabinet (Shandon) maintained at constant temperature by immersion in a bin of sawdust. The paper (Whatman No 1) was irrigated with aqueous ammoniacal ethanol, and the spots were subsequently developed by spraying firstly with bromo-cresol green and then with lead acetate.[54] Good separations of dicarboxylic-acids from C_3 to C_{12} were achieved. Identifications were made by mixed chromatograms on the same sheet. Quantitative analyses were made by comparison chromatograms of the unknown and authentic mixtures. Model experiments showed that the linear relationship between spot area and log. (moles of acid), previously established for the lower aliphatic mono-carboxylic acids,[55] also applied to the dicarboxylic acids from C_4 to C_{11} with an accuracy of $\pm 5\%$ provided that (i) all spots were on the same sheet, (ii) the solution of acids applied to the paper was allowed to spread freely, and not evaporated during application, (iii) the concentration of each component in the solution was $>0{\cdot}05$ M, and (iv) the amounts of the acid in the spots being compared did not differ by a factor of >ca. 1·3. To conform with these requirements the sample was often separated in such a way as to concentrate the minor components, and the fractions analysed separately (see under "Oxidation" below). Components applied to the paper in solution $<0{\cdot}05$ M gave spots of different colours on development. Visual comparison of these spots with those obtained on the same sheet with equal volumes of standard solutions allowed quantitative estimates to be made with an accuracy of ± 10–15%.[56] It is possible that the dicarboxylic acids could be more conveniently analysed by G.L.C. of their methyl esters, a technique which has been developed since most of the above analyses were carried out.[57]

Starting materials

Commercial potassium hydroxide pellets ($\nless 84{\cdot}5\%$ KOH) were used in all alkali fusions.

Nitrogen was freed from oxygen and dried.

All saturated mono-carboxylic acids were purified by fractional distillation of their methyl esters, and/or by crystallization, until G.L.C. of their methyl esters indicated purities $>99{\cdot}5\%$. Dicarboxylic acids were purified by fractional crystallization, and gave only one spot on a paper chromatogram.

The origin and properties of the unsaturated acids are indicated below:

Oleic acid. Olive oil (3·8 kg, B.P. grade) was hydrolysed,[58] and the fatty acids obtained were slowly cooled to 15°. The solid which separated was removed by centrifugation, and the residual liquid acids were purified firstly by means of their urea complexes,[59] and then by distillation of their methyl esters (prepared with MeOH–H_2SO_4) at 2·5 mm through a Stedman column (60 × 2 cm). Collection of the C_{18} fraction, hydrolysis and low temperature crystallization from acetone,[60] then gave oleic acid (265 g), m.p. 13·25–13·40°, n_D^{20} 1·4597 (Smith[60] gives m.p. 13·36° for the α-form, and Craig[61] gives n_D^{20} 1·4597) (Found: I.V., 89·4. Calc: I.V., 89·9). Spectrometric analyses (kindly carried out by the Paint Research Laboratory, Teddington) showed the linoleic acid content to be $<0{\cdot}5\%$. The methyl ester exhibited no light absorption maxima at 10·36 μ (absence of *trans*-—CH:CH—) or 233 mμ (absence of conjugated diene), and gave one band on gas–liquid chromatography.

Ozonolysis, and chromatographic analysis of the resulting acids, revealed no mono- or di-acids greater than C_9 (absence of positional isomers of oleic acid cf. [62]); the detection of traces (ca. 0·1%) of hexanoic and stearic acid suggests that the oleic acid contained traces of linoleic and stearic acid.

---

[53] A. I. M. Keulemans and C. G. Verver, *Gas Chromatography*. Reinhold, New York (1957).

[54] R. I. Chaftel, R. Munier and M. Marcheboeuf, *Bull. Soc. Chim. Biol.* **34**, 380 (1952); cf. H. Kalbe, *Z. Physiol. Chem.* **297**, 19 (1954).

[55] R. L. Reid and M. Lederer, *Biochem. J.* **50**, 60 (1952).

[56] R. J. Block, R. LeStrange and G. Zweig, *Paper Chromatography*. Academic Press, New York (1952).

[57] cf. A. T. James and J. Webb, *Biochem. J.* **66**, 515 (1957).

[58] H. B. Knight, E. F. Jordan, E. T. Roe and D. Swern, *Biochem. Prep.* **2**, 100 (1952).

[59] D. Swern and W. E. Parker, *J. Amer. Oil Chem. Soc.* **29**, 614 (1952).

[60] J. C. Smith, *J. Chem. Soc.* 974 (1939).

[61] B. M. Craig, *Canad. J. Chem.* **31**, 499 (1953).

[62] R. R. Allen and A. A. Kiess, *J. Amer. Oil Chem. Soc.* **32**, 400 (1955).

Elaidic acid. This was prepared by treating oleic acid with oxides of nitrogen.[63] It had m.p. 44·4–44·9° corr (lit.[64] m.p. 43–45°) (Found: I.V. 89·5. Calc.: 89·9). Ozonolysis gave no acids greater than C_9 (absence of positional isomers).

Using the above procedure no positional isomers could be detected even in the crude reaction mixture. However the widely used Bertram method,[65] involving stereomutation with catalytic amounts of selenium, was found to give up to 10% of positional isomers (Δ^8 and Δ^{10} with smaller amounts of Δ^7 and Δ^{12}) depending on the extent of the reaction and the purity of the selenium.

Petroselinic acid (cf.[66]). Hydrolysis of the seed oil (480 g) of *Ammi visnaga* (kindly supplied by Dr. J. H. Skellon), fractional distillation (Stedman, 60 × 2 cm) at 2 mm of the methyl esters of the resulting acids, and hydrolysis of the C_{18} fraction gave a mixture of acids. Separation of the solid and liquid acids by the lead salt technique,[3] and crystallization of the former from acetone, gave petroselinic acid (30 g), m.p. 29·5–29·7° (lit.[64] m.p. 30°) (Found: C, 76·6; H, 12·25%; I.V., 89·2. Calc. for $C_{18}H_{34}O_2$: C, 76·55; H, 12·15%; I.V., 89·9). It showed no infra-red light absorption at 10·36 μ (absence of *trans* —CH:CH—). Ozonolysis led to no mono-acids greater than C_{12} and no di-acids greater than C_6 (absence of positional isomers).

Octadec-2-enoic acid. This acid was prepared in 14% yield from stearic acid by Myers' method.[67] It had m.p. 58·0–58·5° corr (lit.[67] m.p. 58°) (Found: C, 76·6; H, 12·25%; I.V., 89·8. Calc. for $C_{18}H_{34}O_2$: C, 76·55; H, 12·15%; I.V., 89·9).

Esterification (CH_2N_2 or MeOH–H_2SO_4) gave the methyl ester, m.p. 34·4–35·2° (lit.[68] m.p. 34–35°) (Found: I.V., 86·0. Calc.: 85·6): λ_{max} (EtOH), 209 mμ (ε 14,500); λ_{max} (CS_2) 10·25 μ (ε 96·5) (conjug *trans* —CH:CH—).

Non-2-enoic acid. This acid, prepared by condensing heptaldehyde with malonic acid,[69] had b.p. 135–137°/5·5 mm, n_D^{22} 1·4598 (lit.[64] gives b.p. 130–132°/2 mm, n_D^{23} 1·4598). Esterification (MeOH–H_2SO_4) gave the methyl ester, b.p. 145°/85 mm, n_D^{23} 1·4443, end absorption at 209 mμ (ε, 9600), λ_{max} (liq film) 6·10 (conjugated CO_2Me) and 10·28 μ (conjugated *trans* —CH:CH—), which gave one peak on gas–liquid chromatography (on silicone the $R_{F'}$ was greater than that of other methylnonenoates and methyl nonanoate).

Undec-10-enoic acid. Commercial undecylenic acid (St. Just) was fractionally distilled (Stedman, 60 × 2 cm) at 7 mm, and then crystallized from light petroleum (b.p. 40–60°). The product had m.p. 25·1–25·4°, n_D^{25} 1·4471 (Ashton and Smith[70] give m.p. 25·5°; Jordan and Swern[71] give m.p. 24·3–24·5°) (Found: I.V., 137·4. Calc.: 137·5). The methyl ester (prepared with CH_2N_2) had no absorption at 10·36 μ (absence of *trans* —CH:CH—), and gave one band on gas–liquid chromatography.

Dodec-11-enoic acid. This acid was prepared by homologation of undec-10-enoic acid (cf. 72). It had m.p. 19·4–19·5°, n_D^{20} 1·4512 (lit.[72] m.p. 19·50°, n_D^{20} 1·4511) (Found: I.V., 126·0. Calc. 127·0). Infra-red and oxidation studies indicated the presence of ca. 1% of an isomeric acid.

Methyl 3-oxo-octadecanoate and 3-hydroxyoctadecanoic acid. The former was prepared from pure palmitic acid by Ställberg-Stenhagen's method[73] and had m.p. 49·6–50·0° (lit.[73] 48·7–49·2°) (Found: C, 73·1; H, 11·7. Calc. for $C_{19}H_{36}O_3$: C, 73·05; H, 11·6%). Reduction by Skogh's method,[74] and hydrolysis, gave 3-hydroxyoctadecanoic acid, m.p. 90·0–90·5° (lit.[74] 89·5–90·0°).

3-Hydroxybutyric acid. Reduction[75] of ethyl acetoacetate gave ethyl 3-hydroxybutyrate,

---

[63] C. H. Mack and W. G. Bickford, *J. Org. Chem.* **18**, 686 (1953).

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

[65] S. H. Bertram, *Chem. Weekblad* **33**, 3 (1936); J. H. Skellon and J. W. Spence, *Chem. & Ind.* 302 (1953); D. Swern and J. T. Scanlon, *Biochem. Prep.* **3**, 118 (1953); D. K. Kolb and J. B. Brown, *J. Amer. Oil Chem. Soc.* **32**, 357 (1955).

[66] J. H. Skellon and J. W. Spence, *Chem. & Ind.* 75 (1954).

[67] G. S. Myers, *J. Amer. Chem. Soc.* **73**, 2100 (1951); cf. E. F. Jenny and C. A. Grob, *Helv. Chim. Acta* **36**, 1936 (1953).

[68] R. G. Sinclair, A. F. McKay, G. S. Myers and R. N. Jones, *J. Amer. Chem. Soc.* **74**, 2578 (1952).

[69] K. von Auwers, *Liebigs Ann.* **432**, 46 (1923); A. A. Goldberg and R. P. Linstead, *J. Chem. Soc.* 2343 (1928).

[70] R. Ashton and J. C. Smith, *J. Chem. Soc.* 435 (1934).

[71] E. F. Jordan and D. Swern, *J. Amer. Chem. Soc.* **71**, 2377 (1949).

[72] C. G. Tomecko and R. Adams, *J. Amer. Chem. Soc.* **49**, 522 (1927); J. M. Rountree and J. C. Smith, *Chem. & Ind.* 190 (1954).

[73] S. Ställberg-Stenhagen, *Arkiv. Kemi* **20A**, No. 19 (1945).

[74] M. Skogh, *Acta Chem. Scand.* **6**, 809 (1952).

[75] K. Serck-Hanssen, S. Ställberg-Stenhagen and E. Stenhagen, *Arkiv. Kemi* **5**, 203 (1953).

b.p. 87–89°/20 mm, n_D^{17} 1·4208 (lit,[75] b.p. 76–77°/15 mm, n_D^{24} 1·422), λ_{max} 5·78 μ (—CO_2Et). Alkaline hydrolysis at 20° gave the hygroscopic acid.

3-*Oxodecanoic and* 3-*oxobutyric acid.* Methyl 3-oxodecanoate was prepared from pure octanoic acid by Ställberg-Stenhagen's method[73] and had b.p. 117–120°/2 mm, $n_D^{24.5}$ 1·4371 (lit.[73] n_D^{20} 1·4393). The ester was hydrolysed at 20° with dilute potassium hydroxide.[76] The resulting solution was either treated with further potassium hydroxide to give the desired alkali concentration for fission studies, or, after neutralization of the excess alkali with dilute hydrochloric acid, freeze-dried to give the (hygroscopic) potassium salt which was used in alkali fusions. The potassium salt of 3-oxobutyric acid was similarly prepared from ethyl acetoacetate.[77]

Alkali fusions

In some preliminary studies oleic acid was heated with potassium hydroxide in an open nickel crucible at 340°. A soft tacky soap was formed. After about 15 min, this coagulated to a putty-like mass. On further heating the mass softened, and an exothermic reaction occurred with vigorous evolution of hydrogen. After the reaction had subsided, the residual dark solid was cooled. Isolation of the product gave palmitic acid in ca. 50% yield.

All subsequent fusions were carried out in a cylindrical nickel pot (internal dimensions; 5·7 × 3·4 cm) having a lid (Syndanio lined with nickel) fitted with nitrogen inlet and outlet ports, and a nickel stirrer (attached to a 50 r.p.m. shaft) and thermocouple well. The acid (usually ca. 3 g), and 3 parts by weight of potassium hydroxide, were placed in the pot which was then closed and flushed rapidly with nitrogen. The flow of nitrogen was reduced to ca. 4 ml/min, the mixture stirred, and the pot placed in a Wood's metal bath, preheated to ca. 60° above the required temperature. The bath was strongly heated with a Meker burner until the required temperature was attained (2–3 min), when the rate of heating was adjusted so that the bath temperature was constant throughout the experiment. (Separate studies showed that, for bath temperatures of 275–350°, the internal temperature of the pot rose to within ca. 15° of the bath temperature in ca. 5 min, and then remained approximately constant.) At the end of the desired reaction time, the metal bath was replaced by a water bath, thus quenching the reaction within 2–3 min. The contents of the pot were dissolved in water (150 cc/g of acid), and the solution was acidified and then extracted with light petroleum (b.p. 40–60°). The extract was dried and evaporated giving the acidic product (90–95 mol %). A portion was used for the iodine value determination and oxidation studies, and another, after esterification with methanolic sulphuric acid, for spectral studies and G.L.C. examination. Thorough extraction of the aqueous mother liquors with ether sometimes gave small amounts (<5%) of a material similar in composition to the main product, but containing traces of dicarboxylic acids.

Fusion of oleic acid with one part by weight of potassium hydroxide at 300°/30 min gave a product identical with that obtained using the standard proportion of alkali.

The majority of the results are summarized in the Tables. The following notes illustrate the characterization of some of the main fission products.

(i) Oleic acid (3·04 g) and potassium hydroxide (9·2 g) were heated at 360° for 60 min (cf. Table 2). Isolation gave a crude product (2·65 g) which was shown (G.L.C. of methyl esters) to contain ca. 5, 90 and 1 mol % of octadecenoic acids, palmitic acid and myristic acid respectively (Found: I.V., 5·8). Crystallization of the crude product from methanol gave palmitic acid, m.p. and mixed m.p. 62·5–62·8° corr.

(ii) Similarly alkali fusion of petroselinic acid (2·53 g) at 360° for 30 min (cf. Table 3) gave a crude product (2·7 g) (Found: I.V., 2·1). One crystallization from methanol gave palmitic acid, m.p. and mixed m.p. 62·0–62·5°.

(iii) Undec-10-enoic acid (2·696 g) and potassium hydroxide (8 g) were heated at 360° for 30 min. The product was cooled and dissolved in water. The solution was acidified and steam distilled, and the distillate was neutralized and evaporated. Analysis (cf. 52) of the residue by acidification with toluene-*p*-sulphonic acid and azeotropic distillation gave acetic acid (0·54 g), *p*-bromophenacyl ester, m.p. and mixed m.p. 83°. The long chain fatty acids (1·82 g) were isolated from the still residues and shown (G.L.C. of methyl esters) to contain 88% of nonanoic acid and 12% of undecenoic acids. The yields of acetic and nonanoic acid, based on the amount of undecenoic acid which underwent fission, were 67 and 74% respectively.

---

[76] cf. L. Breusch and H. Keskin, *Rev. Fac. Sci. Univ. Istanbul* **11A**, 24 (1946).

[77] cf. P. Karrer and C. H. Eugster, *Helv. Chim. Acta* **32**, 1934 (1949).

Alkali fusion of undec-10-enoic acid (21·1 g) at 360°/30 min, isolation and steam distillation of the crude product gave nonanoic acid (13·82 g, 75%) which was shown to be 99% pure. Extraction of the residues from the steam distillation gave high boiling acids (1·91 g).

(iv) Non-2-enoic acid (3·00 g) and KOH (9 g) were heated at 300° for 30 min. Isolation gave heptanoic acid; anilide, m.p. 69–70° (lit.[64] m.p. 71°).

(v) Methyl 3-oxo-octadecanoate (0·53 g) was heated with KOH (1·5 g). The bath temp was raised from 200–300° over 5 min and then kept at 300° for 30 min. Isolation gave a non-saponifiable product (0·11 g) and an acid fraction (0·24 g), which consisted mainly of palmitic acid (G.L.C. of methyl esters).

(vi) The potassium salt of 3-oxodecanoic acid (from 1·0 g of methyl ester) and KOH (3 g) were heated from 200° to 300° and kept at this temp for 1 hr. A liquid (0·10 g, 13%) which condensed in a cold trap in the nitrogen outlet line was identified as nonan-2-one (semicarbazone, m.p. and mixed m.p. 120°). Isolation of the acidic product gave octanoic acid (0·49 g, 63%); *p*-bromophenacyl ester, m.p. and mixed m.p. 66°. A trace of hexanoic acid was also detected (G.L.C. of methyl esters).

Alkali fusion of the potassium salt of acetoacetic acid at 300°/1 hr gave acetone (2:4-dinitrophenylhydrazone, 5% overall; in a control experiment acetone was recovered in 50% yield).

Fissions in aqueous alkali

Solutions of the $\alpha\beta$-unsaturated, β-hydroxy, or β-oxo-acids in 40% KOH were heated at 130° in hard glass flasks. A stream of nitrogen was passed through the reaction mixture, to entrain any volatile products, and then into aqueous 2:4-dinitrophenylhydrazine sulphate, dimedone reagent, or a cold trap.

Acetaldehyde (ca. 1%) from crotonic and β-hydroxybutyric acid was identified as the 2:4-dinitrophenylhydrazone and dimedone derivative, acetone from 3-oxobutyric acid as the 2:4-dinitrophenylhydrazone, and octan-2-one from 3-oxodecanoic acid as the semicarbazone (and by G.L.C.).

Oxidations of unsaturated acids

Oxidative fission of unsaturated fatty acids, and their derivatives, is usually accompanied by undesirable side reactions (cf.[78]). After a study of various methods, the following improvement of a procedure by Klenk and Bongard[79] was adopted as the best available at the time the present work was commenced.

A stream of ozonized oxygen (3–5% O_3) was slowly bubbled through a cooled (0°) solution of the fatty acid or mixture (ca. 1 g) in glacial acetic acid (30 cc) and methyl acetate (10 cc) until ca. 20% excess of ozone had been introduced. Most of the solvent was then evaporated by warming (steam-bath) the mixture under reduced pressure in an all glass apparatus. To the residue, glacial acetic acid (40 cc) and then 30% hydrogen peroxide (5 cc, unstabilized) were added. The solution was kept at ca. 35° for 48 hr and then poured into water (200 cc). The mixture was extracted with light petroleum (b.p. 40–60°) (100 cc), and the extract washed once with warm water (20 cc). The petroleum solution was dried and evaporated. The residual mono-carboxylic acids were esterified ($MeOH-H_2SO_4$) and the methyl esters examined by G.L.C. The aqueous mother liquors and washings were combined and concentrated (to 50 cc) under reduced pressure. Water (100 cc) was added and the concentration repeated. The residual solution (50 cc) was extracted once with chloroform (50 cc), and the two phases evaporated to dryness under reduced pressure. The residues were crystallized from small volumes of water (or alcohol) and chloroform respectively, and the two mother liquors evaporated to dryness. The four fractions, comprising the dicarboxylic acids, were dissolved in ethanol, and the solutions analysed by paper chromatography. By the preliminary separation it was possible to insure that the concentrations of the minor products exceeded the limiting value of 0·05 M in the solutions being analysed, and that the concentrations of the various components in any one chromatogram did not differ by a factor of >10–20, as recommended by Bighi and Trabanelli.[80]

Oxidation of pure oleic, elaidic, petroselinic, undec-10-enoic and dodec-11-enoic acid by the above

---

[78] P. H. Begemann, J. G. Keppler and H. A. Boekenoogen, *Rec. Trav. Chim.* **69**, 439 (1950); J. G. Keppler, *Ibid.* **76**, 49 (1957).

[79] E. Klenk and W. Bongard, *Z. Physiol. Chem.* **290**, 181 (1952).

[80] C. Bighi and G. Tranbanelli, *Ann. Chim.* (*Rome*) **45**, 109 (1955).

procedure gave the products summarized in Table 7. The formation of lower homologues of the principal products was very similar in both the mono- and the di-carboxylic acid fractions. These by-products, which totalled ca. 5–7 mol %, were composed mainly of the homologues with one or two carbon atoms fewer than the principal products. The absence of any higher homologues excludes the possibility that the starting materials were contaminated with positional isomers.

The yields of dicarboxylic acids given in Tables 1–6 are uncorrected for side reactions of the above type, which affect the principal products only slightly. The general conclusions concerning the approximate proportions of isomeric ethylenic acids in fusion products are therefore valid. Only where an acid was found as a small proportion of a longer chain homologue is there reason to believe that it may be mainly an artefact, due to side reactions of the above type, rather than an oxidation product of the corresponding ethylenic acid. Values likely to be seriously affected in this way are given in the tables in brackets [ ]. Though the detection after oxidation of a small amount of a mono- or di-carboxylic acid shorter than the main product does not necessarily indicate the presence of a particular isomeric ethylenic acid, the detection of the complementary di- or mono-carboxylic acid longer than the main product provides convincing evidence. Thus after alkali fusion of oleic acid at 300°/30 min, the presence of the Δ^6, Δ^7 and Δ^8 isomers, indicated by the formation of the C_6, C_7 and C_8 dicarboxylic acids on oxidation (Table 1), is confirmed by the simultaneous formation of the C_{10}, C_{11} and C_{12} monocarboxylic acids.

TABLE 7. OXIDATION OF ETHYLENIC ACIDS
Yields of mono- (M) and di- (D) carboxylic acids in mol %

Oleic		Elaidic		Petroselinic		Undec-10-enoic	Dodec-11-enoic*
M	*D*	*M*	*D*	*M*	*D*	*D*	*D*
C_9 71·8	C_9 69·3	C_9 69·5	C_9 68·2	C_{12} 70·2	C_6 55·9	C_{10} 70·6	C_{11} 55·6
C_8 2·7	C_8 2·1	C_8 3·9	C_8 2·1	C_{11} 4·9	C_5 3·9	C_9 0·9	C_{10} 0·6
C_7 0·4	C_7 1·0	C_7 0·2	C_7 1·2	C_{10} 0·2	C_4 0·3	C_8 0·8	C_9 1·2
C_6 0·2	C_6 0·4	C_6	C_6 0·2			C_7 0·2	C_8 0·0
C_5	C_5 0·5	C_5	C_5 0·3			C_6 0·5	C_7 0·1
C_4	C_4 0·7	C_4	C_4 0·6			C_5 0·7	C_6 0·2
						C_4 1·3	C_5 0·2
							C_4 0·3
75·1	74·0	73·6	72·6	75·3	60·1	75·0	58·2

* Contains ca. 1 % of an isomer.

Another limitation of the above procedure for the analysis of complex mixtures of isomeric ethylenic acids must also be considered. The separation of the mono- and di-carboxylic acids in the oxidation products by extraction of the former with petroleum ether is unsatisfactory in the presence of long chain dicarboxylic acids;[31] thus the recovery of thapsic acid was shown to be only 50%. It is also significant that the yield of undecanedioic acid from dodec-11-enoic acid was appreciably lower than that of sebacic or azelaic acid from undec-10-enoic and oleic acid respectively (Table 7). Moreover the chromatographic procedure used in the present studies was unsuitable for the analysis of dicarboxylic acids beyond C_{12}. Any ethylenic acids with a double bond more remote than the Δ^{12} position therefore escaped detection by the above procedure, and low figures were obtained for the amounts of Δ^{11} and Δ^{12} compounds. Only some of the results with oleic acid are likely to have been influenced by these factors. Values for dicarboxylic acids which are regarded as low are quoted in Tables 1 and 2 in parentheses ( ). In one experiment on the alkali fusion of oleic acid at 360°/60 min,

---

[31] cf. V. Zbinovsky, *Analyt. Chem.* 27, 764 (1955).

the glacial acetic acid solution of the oxidation products was diluted with half the normal volume of water, and the analysis then carried out in the usual way. As expected, a big loss of the monocarboxylic acids was incurred, but the yield of the long chain dicarboxylic acids increased markedly (Table 2).

Carbon and hydrogen determinations were carried out 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.

Acknowledgements—The authors thank Mr. R. A. Dytham for assistance with some of the experiments. One of them (R. G. A.) thanks the Royal Commissioners for the Exhibition of 1851, and the National Research Council of Canada, for scholarships. Another (B. J. W.) thanks the Department of Scientific and Industrial Research for a research studentship.