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EPOXY ACIDS FROM OLEIC AND ELAIDIC ACIDS[1]

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RECEIVED NOVEMBER 5, 1929 PUBLISHED MARCH 6, 1930

The present work was undertaken to throw light on the effect of a long aliphatic chain on the reactivity of the ethylene oxide grouping. It also offered an opportunity to compare a pair of epoxides which were geometrical isomers.[2]

By the carefully controlled action of chlorine on solutions of the potassium salts containing potassium carbonate, relatively pure chlorohydrins (IIa, b) of oleic acid and of elaidic acid were obtained, though neither could be made to solidify.[3] The chlorohydrins, heated with alcoholic alkali, gave the epoxides (IVa, b), together with considerable amounts of unsaturated material which interfered seriously with the isolation of the desired products. The oleic acid chlorohydrin thus formed 45% (theoretical) of the epoxide, of which only a third could be isolated; the elaidic acid derivative yielded 75%, of which two-thirds could be separated. Both epoxides melted at 53.8.[4]

Our experience confirms the results of Albitzki, that both the chlorohydrin and the epoxide derived from oleic acid give on alkaline hydrolysis only the low-melting 9,10-dihydroxystearic acid. The corresponding derivatives from elaidic acid gave only the high-melting dihydroxy acid. It appears, however, that the epoxides are formed with such relative ease that with *these particular compounds* the hydrolysis of the chlorohydrins by alkali must take place almost exclusively by way of the epoxides.

While these epoxides react with water in the presence of alkali or of dilute acids only after hours of boiling, they add hydrogen chloride or sulfuric acid rather readily in ether solution at room temperature. When 0.1 N hydrogen chloride in dry ether was used, the reaction with elaidic acid epoxide was 90% complete after one hour at 20°; the oleic acid epoxide disappeared 3 or 4 times as rapidly. The products were chlorohydrins, each of which with alkali regenerated the same epoxide from which it had been formed. They were, however, readily obtained as solids, and appear to differ from the chlorohydrins formed by the addition of HOCl to the unsaturated

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[1] This material is taken from a thesis to be presented by Thomas C. Poulter to the Ogden Graduate School of Science in partial fulfilment of the requirements for the degree of Doctor of Philosophy. The work was completed in 1926.

[2] Kuhn and Ebel, *Ber.*, **58**, 919 (1925), have described the epoxides of maleic and fumaric acids. Their paper leaves us with no desire at present to try to distribute the labels *cis* and *trans* among the substances to be described by us.

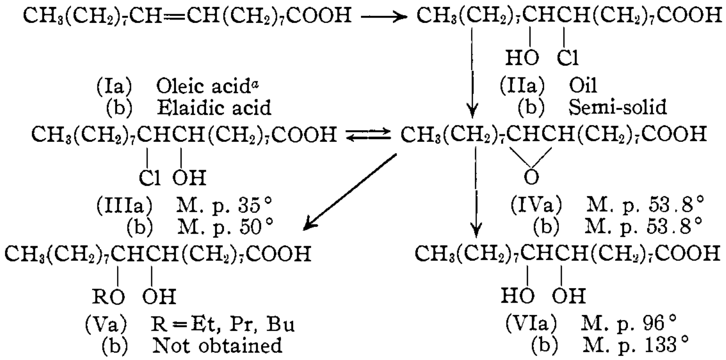
[3] Albitzki, *J. prakt. Chem.*, **61**, 65 (1900), describes oleic acid chlorohydrin as an oil, and elaidic chlorohydrin as a solid, m. p. 44–55°.

[4] Albitzki, Ref. 3, describes them as an oil, and a solid of m. p. 57–60, respectively.

acids. The latter (IIa, b) are presumably 9-chloro-10-hydroxystearic acids. It is considered probable that the products obtained from the epoxides and hydrogen chloride are the isomeric 9-hydroxy-10-chlorostearic acids (IVa, b). The suggested relationships are indicated in Table I.

TABLE I

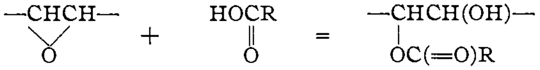
RELATIONSHIPS AND PROPERTIES OF CERTAIN COMPOUNDS



[a] No attempt is made to indicate steric relationships. The derivatives designated "a" and "b" are those obtained by the process indicated from oleic acid and elaidic acid, respectively.

An analytical method for the determination of the epoxides in mixtures was based on the reaction with hydrogen chloride in ether just described. By using a standard acid solution, allowing the reaction to go to completion and then determining the total acidity of the final solution, it was possible to determine the amount of hydrogen chloride which had disappeared in the reaction, and therefore the amount of epoxide initially present. Results consistent within 1% or less were readily obtained, and as neither the chlorohydrins nor the dihydroxystearic acids interfered, this method was very useful in following the reactions to be reported below.

Prolonged heating of the dry epoxides at 100–150° causes a reaction which leads in some hours to the complete destruction of the epoxide grouping, and simultaneously to the disappearance of much of the free carboxyl. After the epoxide has all reacted, the free carboxyl, now reduced to 25–50% of the initial value, remains constant on further heating. The chief reaction is thus apparently an addition of carboxyl at the epoxide group (probably, in general, of a different molecule) with the final formation of products of rather high and variable molecular weight. Here again the



$$-\underset{\diagdown\,O\,\diagup}{CHCH}- \quad + \quad \underset{\overset{\|}{O}}{HOCR} \quad = \quad -\underset{\overset{|}{OC(=O)R}}{CH}CH(OH)-$$

oleic acid epoxide reacts considerably more rapidly than its isomer. It is evident that other reactions also take place at the same time, since the carboxyl group does not disappear sufficiently completely to account for more than 50–75% of the epoxide disappearing.

At higher temperatures a different change becomes more prominent. Even on rapid distillation of small quantities at 10 mm., most of the epoxide does not distil unchanged. On slower distillation, or at higher temperatures, it disappears completely, giving a considerable quantity of 10-ketostearic acid, and usually a somewhat larger quantity of an unsaturated material which is presumably an hydroxyoleic acid of unknown constitution. Under parallel conditions the elaidic acid epoxide decomposes less rapidly, and gives a somewhat larger yield of the keto acid. The two 9,10-dihydroxystearic acids decompose much less readily on distillation than do the epoxides, but yield (at the higher temperatures required for their decomposition) the same ketostearic acid and presumably the same unsaturated hydroxy acid.

There are thus essentially three reactions of thermal decomposition of these epoxides: (A) hydroxy ester formation; (B) unsaturated hydroxy acid formation, which may possibly proceed through A, and (C) rearrangement to ketostearic acid.

When the epoxide of oleic acid is allowed to stand for two days in absolute alcohol containing 1% of concentrated sulfuric acid and the product then saponified, an ethoxyhydroxystearic acid (m. p. 87°) is formed. The corresponding *n*-propyl and *n*-butyl derivatives melt at 87–88° and 90°. The same process applied to elaidic acid epoxide yielded only dihydroxystearic acid, indicating that the sulfuric acid had added to the epoxide group, but that alcoholysis of the product had not taken place.

Esters of the epoxy acids themselves were not readily attainable by standard methods. The silver salts reacted extremely sluggishly with methyl iodide, and hydrogen chloride or sulfuric acid in alcohol attacked the epoxide group rapidly. The methyl esters were easily obtained in excellent yields when phosphorus pentoxide was added to the cooled solution of the epoxide in absolute methanol, and the product, after an hour, poured into water.

Experimental Part

9-Chloro-10-hydroxystearic Acids (IIa, b).—A 2% solution of potassium oleate (or elaidate) containing 4% of potassium carbonate was cooled below 10° and stirred while chlorine was passed in until the iodine number[5] was less than 1.0. Excess hypochlorite was destroyed with sodium thiosulfate before acidification. Oleic acid chlorohydrin was a viscous oil.

Anal. (Carius). Calcd. for $C_{18}H_{35}O_3Cl$: Cl, 10.6. Found: Cl, 10.23.

Elaidic acid chlorohydrin was a semi-solid, but could not be crystallized.

Oleic Acid Epoxide (IVa).—The chlorohydrin was refluxed for two hours with

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[5] The Wijs iodine numbers of the chlorohydrins, the epoxides and the dihydroxystearic acids here discussed were negligible.

excess of molar sodium ethylate in 95% alcohol. The solution was then poured into 10 volumes of cold water, the acid liberated with hydrochloric acid and crystallized from methanol. It melts at 53.8°; samples have been kept for four years practically unchanged; on the other hand, certain other samples have become salve-like and developed a rancid odor in less than a year.

Anal. (Titration). Calcd. for $C_{18}H_{34}O_3$: equiv. wt., 298.3. Found: 296, 300.

The yield of pure product was about 15%. The oily residue contained 35–40% of epoxide which we could not isolate. This oil also contained (in various preparations) 1–3% of chlorine and had an iodine number of 10–25.

Elaidic Acid Epoxide (IVb).—The chorohydrin of elaidic acid was treated as described above. This epoxide also melts at 53.8°, but a mixture of the two epoxides melts at 45–47°. The yield was 45–50% and the oily residue still contained about 50% of epoxide.

Anal. (Titration). Calcd. for $C_{18}H_{34}O_3$: equiv. wt., 298.3. Found: 297, 300.

Both epoxides were more than 99% pure, as determined by their absorption of hydrogen chloride.

Action of Peracids on Oleic and Elaidic Acids.—In the hope of obtaining the desired epoxides more directly, the action of perbenzoic acid in chloroform,[6] on oleic and elaidic acids was tried. In each case the dihydroxystearic acid to be expected from the hydrolysis of the epoxide (m. p. 96 and 133°, respectively) was the only solid product isolated. Peracetic acid[7] gave entirely similar results.

9-Hydroxy-10-chlorostearic Acids (IIIa, b).—Oleic acid epoxide was dissolved in at least twice the calculated volume of a solution of hydrogen chloride (*ca.* 0.2 *N*) in dry ether. After an hour at room temperature, the excess hydrogen chloride was removed by washing the ether solution with water. Evaporation of the ether gave the hydroxychlorostearic acid as an oil which after several days solidified; m. p. 35°. By the same process elaidic acid epoxide gave an isomeric hydroxychlorostearic acid; m. p. 50°.

Anal. Calcd. for $C_{18}H_{35}O_3Cl$: equiv. wt., 334.7; Cl, 10.59. Found for acid of m. p. 35°: equiv. wt., 335.7; Cl, 10.2. Found for acid of m. p. 50°: equiv. wt., 336; Cl, 10.8.

Each of the 9-hydroxy-10-chlorostearic acids regenerates, when warmed with alcoholic alkali, the same epoxide from which it was made.

Methyl Esters of the Two Epoxides.—The silver salts of the epoxy acids reacted extremely slowly with alkyl iodides. On the other hand, attempts to catalyze esterification with hydrochloric or sulfuric acid led to rapid destruction of the epoxide ring.

TABLE II

PROPERTIES AND ANALYSES OF METHYL ESTERS

		Equivalent weight by saponification		
Methyl ester of	M. p., °C.	Formula	Calcd.	Found
Oleic acid epoxide	18	$C_{19}H_{36}O_3$	312	313.7
Elaidic acid epoxide	25	$C_{19}H_{36}O_3$	312	312.6
9,10-Dihydroxystearic acid (m. p. 96°)	63	$C_{19}H_{38}O_4$	330	331.3
9,10-Dihydroxystearic acid (m. p. 133°)	97	$C_{19}H_{38}O_4$	330	330.9
10-Ketostearic acid	43	$C_{19}H_{36}O_3$	312	311.1

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[6] Pigolevskii and Petrov, *J. Russ. Phys.-Chem. Soc.*, **58**, 1062–1066 (1926); *C. A.*, **22**, 943 (1928), obtained among other products the epoxide of oleic acid by the use of benzoyl peroxide (?) in ether.

[7] Hilditch and Lea, *J. Chem. Soc.*, 1576–1583 (1928), found no indication of epoxide formation by hydrogen peroxide in acetic acid with methyl oleate or elaidate.

Phosphoric acid seems not to behave in this manner. To 2 g. of the organic acid in 75 cc. of absolute methanol, 2 g. of phosphorus pentoxide was added and the mixture cooled and shaken until solution was complete. After an hour it was poured into 10 volumes of cold water, and the ester separated by filtration or, if liquid, by extraction with ether. The yields were very good. Table II gives the melting points and equivalent weights by saponification of a number of esters thus obtained. All were recrystallized from methanol and each regenerated the original acid when saponified.

Alcoholysis of Oleic Acid Epoxide. Monoalkyl Ethers of (Low Melting) 9,10-Dihydroxystearic Acid.—Oleic acid epoxide was dissolved in 25 parts of absolute ethanol containing 1% of sulfuric acid and allowed to stand for two days. The solution was poured into excess aqueous alkali and heated to saponify the ester formed, allowing the alcohol to evaporate. When the cooled solution was poured into an excess of dilute hydrochloric acid, the acid separated and was recrystallized from ether. Analogous products were obtained by the use of absolute propyl and *n*-butyl alcohols. The melting points and titrations are given in Table III.

TABLE III

PROPERTIES AND ANALYSES OF 9,10-ALKOXY-HYDROXYSTEARIC ACIDS

Monoalkyl ether	M. p., °C.	Formula	Equiv. wt. by titration Calcd.	Found
(a) Ethyl	87	$C_{20}H_{40}O_4$	344	340
(b) *n*-Propyl	87–88	$C_{21}H_{42}O_4$	358	351
(c) *n*-Butyl	90	$C_{22}H_{44}O_4$	372	366

Mixtures of a and b, a and c, and b and c, all melted at about 85°.

Attempts to apply the same procedure to elaidic acid epoxide gave in every case only the dihydroxystearic acid of m. p. 133°. Under somewhat more severe conditions, the alcoholysis might be successful.

Quantitative Determination of the Epoxides.—The absorption of hydrogen chloride by the epoxides in dry ether has been discussed. An analytical method was based on this reaction.

A 0.1–0.2 *N* solution of hydrogen chloride in dry ether was prepared and standardized. The sample of epoxide was dissolved in a measured volume of this solution containing at least twice the amount of hydrogen chloride theoretically necessary, allowed to stand for two hours at room temperature in a stoppered flask, then poured into neutralized alcohol and titrated with standard potassium hydroxide solution, using phenolphthalein. The alkali equivalent of the fatty acid used must be separately determined on another sample. The acid which disappears in the reaction (hydrogen chloride) is reported as moles of epoxide. The dihydroxystearic acids and 10-ketostearic acid do not interfere. Results within 1% could be obtained with known mixtures.

This method was used to determine the epoxides in the various experiments to be reported on the (approximate) rates of reaction of these substances.

Relative Reactivities of the Two Epoxides toward Hydrogen Chloride.—Appropriate titrations showed that in 0.1 *N* ethereal hydrogen chloride at 20°, elaidic acid epoxide reacted to the extent of 90% in one hour. The oleic acid epoxide reacted at least three times as rapidly.

Relative Rates of Hydrolysis to Dihydroxystearic Acids.—On boiling with 1% aqueous hydrochloric or sulfuric acid, the epoxides of oleic and elaidic acids gave the dihydroxystearic acids (m. p. 96 and 133°, respectively). The oleic epoxide reacted decidedly the more rapidly, but the hydrolysis requires many hours even in this case.

The comparison in alkaline solution is more significant, as the question of solubility does not here arise. A 2% solution of the epoxide in 2 *N* potassium hydroxide was heated at 100° and the unaltered epoxide determined from time to time by the method described. Hydrolysis took place at the rates of about 11 and 3.5% an hour for the oleic and elaidic acid epoxides, respectively.

Reactions of the Dry Epoxides

Effect of Heating at 114 and 150°.—At either temperature, the dry epoxides decomposed over a period of some hours. At intervals samples were titrated for unchanged epoxide and for free acid. As usual the elaidic acid epoxide proved to be the more stable. The results are given in Table IV; their interpretation has already been discussed. Attention is called to the fact that, after the disappearance of the epoxide, acidity remains constant.

TABLE IV

RESULTS OF HEATING THE EPOXIDES

Time, hrs.	Temp., °C.	Oleic acid epoxide		Elaidic acid epoxide	
		Epoxide, %	Free acid, %	Epoxide, %	Free acid, %
0	114	100	100	100	100
1	114	40	66	83	94
3	114	13	55	70	86
8	114	0	50	35	71
17	114	0	50	8	56
22	114			0	53
40	114			0	53
0	150	100	100	100	100
1	150	24	37	50	78
2	150	10	26	25	64
3	150	4	24	9	56
4	150	0	23	0	53
5	150	0	23	0	53

Effect of Higher Temperatures.—On distillation, even at 10 mm. (*ca.* 290°) and in small quantities, the epoxy acids are largely decomposed. A 4-g. sample of oleic acid epoxide thus distilled (during about ten minutes) gave a product with an iodine number of 62, containing only 17% of epoxide and some 10-ketostearic acid. Under as nearly parallel conditions as possible, the distillate from elaidic acid epoxide had an iodine number of 10, contained 40% of unchanged epoxide, and a somewhat larger proportion of ketostearic acid than in the former case.

Summary

1. The epoxides of oleic and elaidic acids have been obtained in crystalline form.
2. The splitting of the epoxide ring by hydrogen chloride, water and alcohol has been investigated.
3. Three directions in which these epoxy acids decompose on heating have been discussed.
4. In all the reactions considered, the oleic acid epoxide is the less stable, and reacts in general from two to four times as rapidly as does its isomer.
5. A method for the quantitative determination of these epoxides has been described.

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