[CONTRIBUTION FROM THE SOUTHERN REGIONAL RESEARCH LABORATORY[1]]

HYDROXYSTEARIC ACIDS. I. THE CATALYTIC HYDROGENATION OF THE 9,10-EPOXYSTEARATES[2]

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The lithium salt of 12-hydroxystearic acid is an important ingredient of high quality specialty greases. At present, this salt is derived entirely from hydrogenated castor oil. Because of the increased demand for castor oil fatty acids in the production of other derivatives, such as plasticizers, lubricants, surface coatings, etc., the preparation of supplementary materials from oils of domestic origin is highly desirable. Epoxystearic acids (1) can be readily prepared from oils of domestic origin and therefore, the possibility of reducing these acids to the corresponding monohydroxystearic acids was investigated.

Reference to the literature revealed that the catalytic hydrogenation of epoxystearic acid has received very little attention and no information is available regarding the mechanism of this reduction. Pigulevskii and Rubashko (2) reported the hydrogenation of ethyl *cis*-9,10-epoxystearate to the 10-hydroxystearate in alcohol solution using palladium-black catalyst. According to Ross, *et al.* (3) methyl *cis*-9,10-epoxystearate can be hydrogenated with Raney nickel in ethanol neutral to phenolphthalein to yield a mixture of 9- and 10-hydroxystearates in which they found 85% or more of the 10-isomer. Other workers have encountered considerable difficulty in the hydrogenation of long chain epoxy compounds. Thus, Newman, *et al.* (4) were unsuccessful in hydrogenating 1,2-epoxydecane in absolute ethanol with platinic oxide (Adams' catalyst) or with Raney nickel under ordinary conditions at room temperature, although they did succeed in reducing it to decanol with Raney nickel at a temperature of 150°. In no case previously described does the hydrogenation of the oxirane group proceed with the same degree of ease as does the hydrogenation of the ethylenic linkage.

In this laboratory repeated attempts to effect the hydrogenation of various samples of the methyl 9,10-epoxystearates in alkaline ethanolic solution using either electrolytic nickel or Raney nickel catalyst prepared by the method described in Organic Syntheses (5) were unsuccessful[3]. Attempts to hydrogenate the epoxy compounds with Raney nickel (5) in the absence of solvent under various conditions of temperature (25–200°) and pressure (1–15 atmospheres) were also unsuccessful. Various solvents including acetic acid and petroleum ether also failed to promote the hydrogenation of these compounds when Raney nickel was used as the catalyst. However, it was found that 9,10-epoxystearates

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[1] One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture.

[2] Presented at the Southwide Chemical Conference, Auburn, Alabama.

[3] Ross and co-workers employed a Raney nickel specially prepared at a low temperature by the method described by Pavlic and Adkins (6), according to a private communication from J. Ross, July 31, 1951.

can be hydrogenated at room temperature and atmospheric pressure in the presence of palladium-carbon. In alcohol solution the reduction takes place slowly even in the presence of large amounts of catalyst, but when glacial acetic acid is the solvent the hydrogenation proceeds quite rapidly.

The use of acetic acid as the solvent and palladium-carbon as the catalyst for this hydrogenation presents several advantages. The epoxidation of oleic acid is usually carried out in glacial acetic acid and the hydrogenation can then be carried out without isolating the epoxide. Furthermore, the catalyst can be reused many times before reactivation is necessary. Another advantage lies in the fact that apparently only one isomer, namely 10-hydroxystearic acid, is formed during the course of the hydrogenation. The by-products of the reaction contain small amounts of hydroxyacetoxystearic acids. There is some evidence for the attendant formation of carbonyl-containing compounds.[4] However, hydrogenation in ethanol solution does not appear to lead to the formation of keto compounds. The formation of the acetoxy compounds might be expected from the observations of Findley and coworkers (1) who found that glacial acetic acid opens the oxirane ring at the rate of about 1% per hour at room temperatures.

The hydrogenation of either the *cis*- or *trans*-epoxystearic acid resulted in the formation of the same product but the *trans*-isomer hydrogenated at a much slower rate. This parallels the work of King (7) who demonstrated that *trans*-9,10-epoxystearic acid is much more stable in glacial acetic acid than is the *cis*-isomer. The extreme selectivity of this hydrogenation in producing 10-hydroxystearic acid led us to investigate some of the factors that might affect the course of the reaction and in an effort to determine the mechanism for the hydrogenation, the following observations were made:

(a) Epoxystearic acid could not be hydrogenated in either neutral solvents such as petroleum ether or *n*-butyl propionate, or in petroleum ether containing 1% sulfuric acid.

(b) Hydrogenation could be effected in the following solvents, arranged in their order of increasing observed rate of hydrogenation: *n*-butyl propionate containing 1% sulfuric acid, ethanol, petroleum ether containing 1% acetic acid, anhydrous propionic acid, and glacial acetic acid.

(c) The rate of hydrogenation was unaffected by the presence of light, peroxides such as peracetic acid or free radical acceptors such as hydroquinone.

(d) Hydroxyacetoxystearic acid does not absorb hydrogen in glacial acetic acid solution under the conditions used.

These observations may be interpreted as follows:

(a) It is evident that hydroxyacetoxystearic acid is not an intermediate in this reaction, although it is formed as a side reaction product.

(b) The fact that the epoxy compound hydrogenates only in the presence of a weak acid (in the Lewis sense) or in a solvent undergoing hydrolysis to produce a weak acid suggests that hydrogen ions catalyze the reaction. This is borne out by the slow rate of hydrogenation in ethanol as contrasted to the rapid hydrogenation in acetic acid.

[4] Private communication from D. Swern, December 18, 1952.

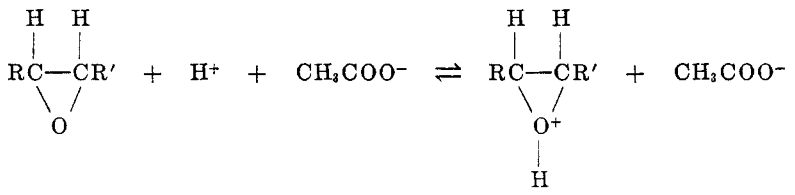
(c) Since free radical initiators and acceptors are without effect the hydrogenation does not proceed by a free radical mechanism and since hydrogen ions catalyze the reaction an ionic mechanism is indicated.

(d) The most probable ionic intermediate would be an oxonium type ion inasmuch as the oxirane group with two pairs of unshared electrons would favor the attraction of a proton. In this connection it is noteworthy that Alexander (8) also considered the possibility of the existence of a similar oxonium type ion to account for certain observations made relating to the hydrolysis of epoxy compounds.

(e) The fact that strong acids as such do not catalyze the reaction while weak acids do suggests that the anion of a weak acid which does not add rapidly stabilizes the transitory existence of the oxonium type ion allowing hydrogenation to proceed whereas the presence of an anion of a strong acid results in an addition reaction, thereby excluding the possibility of hydrogenation.

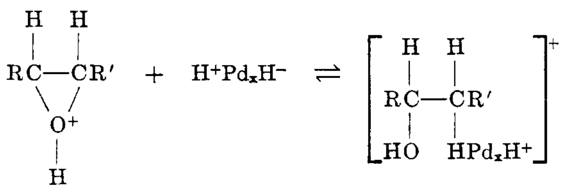
(f) The fact that 10-hydroxystearic acid is produced to the exclusion of the 9-isomer indicates that there is a strong directional force within the molecule which favors the rupture of the ninth carbon-oxygen bond. Consideration of the geometrical configuration of the molecule as well as its infrared spectra (9) suggests that the folding back (field effect) of the carboxyl group would cause the ninth carbon atom to be slightly positive with respect to the tenth carbon atom. Yet the relative non-selectivity of other addition reactions of epoxystearic acid indicates that the field effect in itself is not sufficient to account for the high selectivity encountered in the hydrogenation reaction. Therefore the electrophilic nature of the —COO— group must also exert its influence on the activated hydrogen on the catalyst surface, so orienting the respective ions that a hydride ion is exclusively directed toward the more positive ninth carbon atom resulting in the selective rupture of the ninth carbon-oxygen bond.

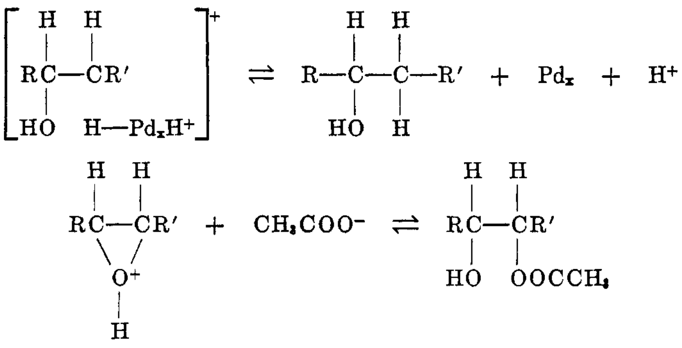
On the basis of the above observations and interpretations the following mechanism is proposed:



$$Pd_x + H_2 \rightleftharpoons H^+Pd_xH^-$$

in which Pd_x represents the activated catalyst surface.





$$\left[\begin{array}{ll} \mathrm{H} & \mathrm{H} \\ | & | \\ \mathrm{RC}- & \mathrm{CR'} \\ | & \\ \mathrm{HO} & \mathrm{H{-}Pd_xH^+} \end{array}\right]^+ \rightleftharpoons \begin{array}{lll} & \mathrm{H} & \mathrm{H} \\ & | & | \\ \mathrm{R}- & \mathrm{C}- & \mathrm{C}-\mathrm{R'} \\ & | & | \\ & \mathrm{HO} & \mathrm{H} \end{array} + Pd_x + H^+$$

$$\begin{array}{ll} \mathrm{H} & \mathrm{H} \\ | & | \\ \mathrm{RC}- & \mathrm{CR'} \\ \backslash & / \\ \mathrm{O^+} & \\ | & \\ \mathrm{H} & \end{array} + CH_3COO^- \rightleftharpoons \begin{array}{ll} \mathrm{H} & \mathrm{H} \\ | & | \\ \mathrm{RC}- & \mathrm{CR'} \\ | & | \\ \mathrm{HO} & \mathrm{OOCCH_3} \end{array}$$

$$H^+ + CH_3COO^- \rightleftharpoons CH_3COOH$$

where R represents $CH_3(CH_2)_7$— and R′ represents —$(CH_2)_7COOH$.

EXPERIMENTAL

MONOHYDROXYLATION OF OLEIC ACID

cis-9,10-Epoxystearic acid. Oleic acid (99%, 83 g.) (iodine value, 89.0) was epoxidized (1) by dropwise addition to 100 ml. of anhydrous peracetic acid solution (25.0% peracetic acid) maintained at 20–25°. On completion of the reaction the mixture was poured into 300 ml. of cold water and the crystals were filtered off and dried. This product crystallized from Skellysolve B[5] (3 ml./gram) at 0°, gave 65 g. of *cis*-9,10-epoxystearic acid melting at 59.0°. Mixture melting point with a sample of authentic *cis*-9,10-epoxystearic acid, 59°.

Anal. Calc'd: Oxirane oxygen, 5.36; Neut. equiv., 298.

Found: Oxirane oxygen, 4.95; Neut. equiv., 297.

Hydrogenation of cis-9,10-epoxystearic acid. A mixture of 30 g. of *cis*-9,10-epoxystearic acid, 3.0 g. of 10% palladium-carbon catalyst, and 60 ml. of glacial acetic acid was shaken with hydrogen (initial pressure, 28 pounds) in a Parr hydrogenation apparatus[5] at room temperature. The reduction (100% absorption) was completed in about 45 minutes. No further absorption occurred on continued shaking. The catalyst was filtered off and the filtrate was poured into 300 ml. of cold water. The aqueous mixture was extracted with two 75-ml. portions of ethyl ether. After washing the ether solution free of acetic acid, drying over sodium sulfate, and removing the ether under reduced pressure there was obtained 28 g. of crude hydroxystearic acid, melting point, 74°.

Anal. Calc'd: Hydroxyl oxygen, 5.33; Oxirane oxygen, 0.00; Neut. equiv., 300.

Found: Hydroxyl oxygen, 4.73; Oxirane oxygen, 0.05; Neut. equiv., 298.

10-Ketostearic acid. A 10-g. sample of this crude hydroxystearic acid (not recrystallized) was oxidized with a solution of 7.50 g. of CrO_3 in 40 ml. of acetic acid and 5 ml. of water, stirring for one hour at 30–35° and two hours at room temperature. The oxidation mixture was then poured into 300 ml. of cold water and the crystals were filtered off and dried. This product was fractionally crystallized from an acetone-Skellysolve B mixture (1:2). Altogether 8 g. of 10-ketostearic acid, m.p. 71°, were collected as fine needles and no 9-ketostearic acid was found. Reworking of the 2 g. of material recovered from the mother liquors also failed to give any indication of the presence of the 9-keto acid which crystallizes as lustrous plates and melts at 81.5° (3). The semicarbazone of the 10-ketostearic acid was prepared and when recrystallized from alcohol it melted at 100–101°.

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[5] The mention of this and other commercial products does not imply endorsement or recommendation by the Department of Agriculture over others having similar properties but are mentioned as a part of the exact experimental conditions used in the work being reported.

Anal. Calc'd for $C_{19}H_{37}N_3O_3$: N, 11.83. Found: N, 11.8.

Ross, *et al.* (3) reported that the semicarbazone of 10-ketostearic acid melts at 101–103°.

10-Hydroxystearic acid. The remainder of the crude hydroxystearic acid, which contained about 5% hydroxy-acetoxy stearic acid as impurity, was successively recrystallized from ethanol, Skellysolve F, and methanol; it then melted at 80°. Tomecko and Adams (10) report the melting point for 10-hydroxystearic acid as 81–82°.

The hydrazide was prepared by the method of Kyame, *et al.* (11). After crystallization from ethanol it melted at 112°.

Anal. Calc'd for $C_{18}H_{38}N_2O_2$: N, 8.91. Found: N, 8.89.

MONOHYDROXYLATION OF METHYL OLEATE

Methyl cis-9,10-epoxystearate. Methyl oleate (98%, 97 g.) (iodine value, 84.1) was exoxidized with 100 ml. of 27.3% anhydrous peracetic acid solution according to the method described by Findley, *et al.* (1). After crystallization from acetone (4 ml./gram) at −20° there was obtained 66 grams of methyl *cis*-9,10-epoxystearate.

Anal. Oxirane oxygen: Calc'd, 5.12. Found: 4.79.

TABLE I

COMPARISON OF RATE OF HYDROGENATION OF METHYL *cis*-9,10-EPOXYSTEARATE IN VARIOUS SOLVENTS[a]

SOLVENT	CALC'D H_2 ABSORPTION, ML. AT STP[b]	H_2 ABSORBED BY SAMPLE, ML. AT STP	H_2 ABSORBED AFTER 5 MIN. (ML.)	TIME FOR COMPLETE HYDROGENATION[c]
Acetic acid	21.4	22.4	22.4	5 min.
Propionic acid	21.4	22.9	21.9	7 min.
Absolute ethanol	21.4	20.8	1.2	6.5 hours
n-Butyl propionate plus 1% H_2SO_4	21.4	22.6	1.0	11 hours (app.)

[a] All hydrogenations were carried out in an analytical hydrogenator (12) using approximately the same degree of agitation. [b] In all runs, the weight of the sample was 0.3 g., the weight of palladium-carbon catalyst 0.3 g., and the volume of solvent 20 ml. [c] The rate of hydrogenation was unaffected by the addition of either peracetic acid or hydraquinone.

Hydrogenation of methyl cis-9,10-epoxystearate. The comparison of the rate of hydrogenation in various solvents is given in Table I. A mixture of 44 g. of methyl *cis*-9,10-epoxystearate, 4.0 g. of 10% palladium-carbon catalyst, and 133 ml. of glacial acetic acid was shaken with hydrogen in the usual way. Hydrogenation was completed in about two hours, after which the catalyst was removed by filtration and the filtrate was reserved for the experiments described below.

10-Ketostearic acid. To a 130-ml. portion of the filtrate (containing 33 g. of reaction product; *ca.* 30 g. of hydroxy ester) there was slowly added with stirring a solution of 7.96 g. of chromic oxide in 48 ml. of 90% acetic acid. After three hours the oxidation mixture was poured into one liter of cold water and extracted with three 300-ml. portions of Skellysolve F. The solution was freed from acetic acid by washing with 5% sodium hydroxide solution followed by water and finally was dried over sodium sulfate. Evaporation of the solvent yielded 25.2 g. of oxidation products from which 21.5 g. of crude keto acids was obtained on saponification. When 20 g. of the crude keto acids was dissolved in 200 ml. of an acetone-Skellysolve B mixture (1:2) and allowed to crystallize at room temperature, 3.5 g. of fine needles was collected and was twice recrystallized from Skellysolve B, yielding 3.0 g. of keto-acid melting at 72°. This was identified as 10-ketostearic acid through its semicarbazone, melting point 100°. All of the mother liquors from the crystallizations of the keto-acid were combined and after standing at 0° overnight 12 g. of product melting at 70° was filtered off. This was also identified as 10-ketostearic acid through its semicarbazone. The filtrate was evaporated to dryness and the residue was redissolved in 50 ml. of the acetone-petroleum ether mixture and again cooled to 0°. There was thus obtained 2 g. of impure 10-ketostearic acid, m.p. 67°. The filtrate was evaporated to dryness and the residue (1 g.) was converted to the semicarbazone. After recrystallization this melted at 100°. A mixture melting point with an authentic sample of the semicarbazone of 10-ketostearic acid showed no depression. 9-Ketostearic acid, m.p. 81.5°, forms a semicarbazone which melts at 118–120° (3).

Since no keto-acid melting higher than 72° was encountered and since none of the fractions produced a semicarbazone melting in the region of 118°, there is no indication of the presence of 9-hydroxystearic ester in the hydrogenation mixture.

10-Hydroxystearic acid. The remainder of the filtrate from the hydrogenation of 44 g. of methyl *cis*-9,10-epoxystearate was poured into water, extracted with Skellysolve F, washed free of acetic acid with dilute alkali followed by several water washings, and finally dried over sodium sulfate. After removal of the solvent, the esters were saponified with alcoholic KOH and the acids were recovered and dried in the usual manner. This product, after recrystallization, as previously described, melted at 80°. A mixture melting point with an authentic sample of 10-hydroxystearic acid showed no depression.

MONOHYDROXYLATION OF METHYL *trans*-9,10-EPOXYSTEARATE

Methyl elaidate. Methyl oleate (120 g.), 30 ml. of 15% sodium nitrite solution, and 30 ml. of 6 *N* nitric acid solution were shaken together in a separatory-funnel for 10 minutes. After diluting with water and extracting with ether, 112 g. of elaidinized ester was recovered. Analysis using an infrared spectrophotometer indicated 67% methyl elaidate. After four recrystallizations from acetone (10 ml./g) at −40°, 56 g. of 95% methyl elaidate were obtained.

Methyl trans-9,10-epoxystearate. Methyl elaidate (56 g.), was epoxidized in the usual manner and after purification yielded 42 g. of methyl *trans*-9,10-epoxystearate.

Anal. Oxirane oxygen: Calc'd, 5.12. Found: 4.79.

This product also therefore contained about 93.6% epoxide.

Hydrogenation of methyl trans-9,10-epoxystearate. Methyl *trans*-9,10-epoxystearate (33 g.) was mixed with 100 ml. of glacial acetic acid and 3 g. of palladium-carbon catalyst, placed in the Parr hydrogenation apparatus,[5] and hydrogenated as previously described. This particular preparation required 48 hours for complete hydrogenation. The catalyst was removed by filtration and the filtrate was used in the following experiments.

10-Ketostearic acid. An aliquot of the filtrate containing 29 g. of crude hydroxystearate was removed and oxidized with chromic oxide in acetic acid as described above. This ester was saponified and the resulting acids (16 g.) were fractionally crystallized from an acetone-petroleum ether mixture, yielding 13 g. of pure 10-ketostearic acid, m.p. 71°. This acid was identical with that produced from the reduction and oxidation of the *cis*-epoxy compound, as shown by the mixture melting points of the acids as well as the mixture melting points of their semicarbazones. The semicarbazone of this 10-keto acid was analyzed.

Anal. Calc'd for $C_{19}H_{37}N_3O_3$: N, 11.83. Found: N, 11.8.

10-Hydroxystearic acid. The remaining portion of the above hydrogenation mixture (containing 4 g. of hydroxy ester) was freed from solvent and saponified, yielding 3 g. of free acids. This was crystallized from petroleum ether and yielded fine needles melting at 80°, which did not lower the melting point of an authentic sample of 10-hydroxystearic acid.

MONOHYDROXYLATION OF ELAIDIC ACID

10-Hydroxystearic acid. Pure *trans*-9,10-epoxystearic acid (0.1360 g., m.p. 55°), 0.1 gram of 10% palladium-carbon catalyst, and 25 ml. of glacial acetic acid were hydrogenated in an analytical hydrogenator (12) at 25°. In 30 minutes 10.36 ml. of hydrogen at STP was absorbed; calculated hydrogen absorption for 1 mole of hydrogen per mole of epoxide 10.30 ml. After removing the catalyst and the acetic acid, the product was crystallized from dilute methanol. It then melted at 80°, and did not lower the melting point of an authentic sample of 10-hydroxystearic acid.

ATTEMPTED HYDROGENATION OF HYDROXYACETOXYSTEARIC ACID

cis-9,10-Epoxystearic acid (15 g., m.p. 59°) was refluxed with 103 ml. of glacial acetic acid for three hours. One-third of the solution was removed and the hydroxyacetoxystearic acid was recovered and purified, m.p. 81°.

Anal. Neut. equiv.: Calc'd, 358. Found, 360.

The remaining two-thirds of the above solution was mixed with 5 g. of palladium-carbon catalyst and shaken with hydrogen in a Parr hydrogenation apparatus (initial hydrogen pressure, 10 pounds) for 16 hours. No hydrogen was absorbed during this time. The catalyst and the acetic acid were removed. The recovered product (neut. equiv. 364) melted at 80.5° and did not depress the melting point of the original hydroxyacetoxystearic acid.

SUMMARY

1. A method for the catalytic hydrogenation of *cis*- and *trans*-9,10-epoxystearic acids and their methyl esters to their monohydroxy derivatives in glacial acetic acid using palladium-carbon catalyst has been described.

2. The position of the resultant hydroxyl group was established by conversion to the corresponding keto acid.

3. Hydrogenation in the presence of palladium-carbon and glacial acetic acid is highly selective and leads to the formation of the 10-hydroxy compound to the exclusion of the 9-isomer. Approximately 5% of the hydroxyacetoxy compound is formed as the result of a side reaction between the solvent and the epoxy compound.

4. The reaction mechanism has been studied and the observations made support the concept that the hydrogenation of the epoxy compound proceeds through an oxonium type ion intermediate.

NEW ORLEANS 19, LA.

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