of poly(methyl acrylate) ( $\{\eta\} = 0.60, 0.25 \text{ g./100 ml. in acetone}$ ) in 100 ml. of N-methylmorpholine. After addition, the mixture was stirred under reflux for an additional 3 hr. Then, while still hot, a solution of 30 g. of potassium sodium tartrate in 150 ml. of water was added, dropwise, and very cautiously, until the excess hydride had been decomposed. Following addition of all the tartrate solution, the mixture was stirred hot for an additional hour and allowed to cool.

The filtered solution was evaporated to dryness on a steam bath under vacuum, leaving a soft residue. This was stirred with a mixture of 90 ml. of methanol and 10 ml. of water for 3 hr. Most of the solid dissolved, giving a viscous sclution. Some granular powder remained and was centrifuged off. The polymer was precipitated in acetone. The purification process was repeated, giving 5 g. (85%) of a tough resin after vacuum drying over phosphorus pentoxide.

Anal. Calcd. for C<sub>3</sub>H<sub>6</sub>O: C, 62.2; H, 10.3; methoxyl, 0. Found: C, 61.9; H, 10.3; methoxyl, <1; ash, 0.3;  $\{\eta\} = 0.76$ .

Reduction of poly(methyl acrylate), acetylation with acetic anhydride and hydrolysis. Preparation of poly(allyl acetate). Method C. A solution of 8.6 g. (0.1 mole) of poly(methyl acrylate) in 100 ml. of tetrahydrofuran was added, dropwise, under nitrogen, to a refluxing solution of 3.8 g. (0.1 mole) of lithium aluminum hydride in 200 ml. of tetrahydrofuran over a period of 1 hr. Following addition, the mixture was refluxed and stirred for an additional 2 hr., then cooled.

Acetic anhydride (250 ml.) was added, dropwise, to the mixture, cautiously at first, until all the excess lithium aluminum hydride had reacted. The mixture was then heated slowly with stirring, and the tetrahydrofuran was allowed to distill until the internal temperature reached  $110^{\circ}$ . The mixture became exceedingly thick. After stirring at  $110^{\circ}$  for 1 hr., the mixture became much more fluid and a fine, white precipitate was left. Heating was continued for a total of 3 hr.

The cooled mixture was filtered, the filter cake being washed with acetone. The combined washings were evaporated to dryness on a steam bath under vacuum. The residue, after solution in acetone, was precipitated in ether. This procedure was repeated twice to give an analytical sample; yield, 7 g. of a soft polymer which hardened somewhat on vacuum drying.

Anal. Calcd. for  $C_5H_8O_2$ : C, 60.0; H, 8.0; acetyl, 43. Found: C, 60.0; H, 7.9; acetyl, 41.4; methoxyl, >2; ash, 0.1. Reduction of poly(methyl acrylate), followed by reaction with isopropenyl acetate. Method D. A solution of 8.6 g. of poly-(methyl acrylate) in 100 ml. of diethyleneglycol dimethyl ether was added, dropwise, under nitrogen, with heating over a period of 1 hr. to a stirred solution of 3.8 g. (0.1 mole)of lithium aluminum hydride in 100 ml. of diethyleneglycol dimethyl ether. Following addition, the mixture was heated and stirred at 110° for 3 hr.

Isopropenyl acetate (100 g.) was then added, dropwise, with stirring. Fellowing addition, the temperature was raised to 135° for 2 hr., 20 ml. of material being allowed to distill. The mixture was then cooled and decomposed by the addition of a solution of 20 g. of sodium potassium tartrate in 100 ml. of water. After the stirred mixture had been heated to boiling and allowed to cool, the mixture was centrifuged. The supernatant liquid was evaporated to dryness on a steam bath under vacuum, dissclved in a mixture of acetone, and methanol, and precipitated in ether, giving 5 g. of a soft, amber solid after drying.

Anal. Calcd. for  $C_5H_{10}O_2$ : C, 60.0; H, 8.0; acetyl, 43. Found: C, 56.1; H, 8.1; acetyl, 44.4.

Hydrolysis of this product gave 2.3 g. of a tan solid.

Anal. Calcd. for C<sub>3</sub>H<sub>6</sub>O: C, 62.2; H, 10.3. Found: C, 61.2; H, 10.1; acetyl, 0.5.

Reduction of poly(butyl  $\alpha$ -acetoxyacrylate) with lithium borohydride. Method E. A solution of 9.3 g. (0.05 mole) of poly(butyl  $\alpha$ -acetoxyacrylate) in 100 ml. of diethyleneglycol dimethyl ether was added dropwise over a period of 1 hr. to a stirred solution of 2.5 g. of lithium borohydride in 200 ml. of diethyleneglycol dimethyl ether kept at 100° under nitrogen. Following addition, the mixture was heated to 115° for an additional 2 hr., then allowed to cool to room temperature.

The reaction mixture was then poured slowly into 1 l. of water containing 50 ml. of acetic acid, giving a clear solution which was dialyzed overnight. The undialyzed material was filtered, then evaporated to dryness on a steam bath under vacuum. The residue was dissolved in 20 ml. of distilled water giving a clear viscous solution which was precipitated into acetone to give a white powder. The product was vacuum dried; yield, 3.3 g., soluble in water, but insoluble in methanol, acetone and ether.

Anal. Calcd. for C<sub>3</sub>H<sub>6</sub>O<sub>2</sub>: C, 48.8; H, 8.1. Found: C, 49.2, 49.4; H, 7.5, 7.7; N, 0.12.

ROCHESTER, N. Y.

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF THE ARMOUR INDUSTRIAL CHEMICAL COMPANY]

# Phase Properties of Mixtures of 9- and 10-Oxo-octadecanoic Acids and of 9- and 10-Hydroxyoctadecanoic Acids<sup>1</sup>

### C. C. COCHRANE AND H. J. HARWOOD<sup>2</sup>

## Received July 19, 1960

Pure homolog-free samples of 9- and 10-oxo- and the corresponding hydroxyoctadecanoic acids have been prepared and phase diagrams for mixtures of the isomers have been established. That for the oxo acids is a simple eutectic system; that for the hydroxy acids shows compound formation at a 1:1 ratio of the components. On the basis of these diagrams the identity of various preparations of the four compounds reported in the literature is discussed. Evidence for preferential reactivity at the 9- or 10-position of the eighteen-carbon fatty-acid molecule which is based upon conclusions regarding the identity of the oxo or hydroxy acids is invalidated.

A number of reports in the literature present evidence for a directive influence during reactions of unsaturated or epoxy eighteen-carbon fatty acids which results in preferential reactivity at the 9or 10-position of the molecule. For the most part, this evidence is based on isolation of a preponderance of a substance identified as 9- or 10-oxoor 10-hydroxyoctadecanoic acid.

<sup>(1)</sup> Presented in part before the Division of Organic Chemistry at the 138th Meeting of the American Chemical Society, New York, September, 1960.

<sup>(2)</sup> Address communications to this author.

april 1961

In an investigation of the constitution of stearolic (9-octadecynoic) acid, Baruch<sup>a</sup> produced an oxooctadecanoic acid melting at 76°. Through the Beckmann rearrangement of the oxime of this oxo acid, substances identified as nonanoic acid. octylamine, decanedioic acid, and 9-aminononanoic acid were isolated. Baruch concluded therefrom that only 10-oxo-octadecanoic acid was produced by the hydration of stearolic acid. Robinson and Robinson<sup>4</sup> repeated this work and obtained, after recrystallization of the sodium salt, oxo-octadecanoic acid freezing at 70.90°. In order to estimate the composition of this product, which was assumed to be a mixture of the 9- and 10-isomers, these authors synthesized the pure oxo acids and determined the freezing points of synthetic mixtures. On the basis of the partial phase diagram, the original product was estimated to contain 42.4% of the 9-isomer. The apparent difference in reactivity at the 9- and 10-positions was ascribed to the inductive influence of the carboxyl group. Myddleton, Bercham, and Barrett<sup>5</sup> also produced an oxo-octadecanoic acid through the reaction of stearolic acid with mercuric acetate. This oxo acid, purified according to the procedure of Robinson and Robinson, melted at 76°. It was believed to be 10-oxo-octadecanoic acid.

In a review of earlier work on the sulfation of oleic (9-octadecenoic) acid, Tomecko and Adams<sup>6</sup> reached the conclusion that a major product after hydrolysis of the sulfate is 10-hydroxyoctadecanoic acid. This conclusion was based on melting-point data obtained with mixtures of pure synthetic positional isomers and on the fact that the melting point of the hydroxy acid obtained by sulfation of oleic acid was in the range of 80-85° in most cases.

Through catalytic hydrogenation of methyl 9,10epoxyoctadecanoate followed by chromic oxide oxidation of the resulting hydroxy acid, Ross, Gebhart, and Gerecht<sup>7</sup> obtained a major amount of an oxo acid melting at 71° and a small amount of an oxo acid melting at 81.5°. The 71° compound yielded decanedioic acid upon Beckmann rearrangement of the oxime and was identified as 10-oxooctadecanoic acid. The 81.5° compound was believed to be the 9-isomer. By the same process, Mack and Bickford<sup>8</sup> obtained only the 71° compound; no product melting at 81.5° was isolated. These authors concluded that a strong directional force favors rupture of the C—O bond at the 9position. Jungermann and Spoerri<sup>9</sup> produced a mixture of chlorohydrins by hydrochlorination of methyl 9,10-epoxyoctadecanoate. Fractional crystallization yielded chlorohydroxyoctadecanoates in a 3:1 ratio. These were converted to oxo acids by removal of chlorine with zinc amalgam and oxidation of the hydroxyl group with chromic oxide. There were obtained a compound melting at 72° described as 10-oxo-octadecanoic acid and one melting at 80° said to be 9-oxo-octadecanoic acid. The apparent preponderance of the 10-isomer was attributed to an inductive effect during reaction of the epoxide with hydrogen chloride.

Other work in the same general area of chemistry has shown no evidence of directive influences. Rockett<sup>10</sup> obtained formoxyoctadecanoic acid through the reaction of oleic acid with formic and perchloric acids. Conversion to the hydroxy acid followed by oxidation with chromic oxide yielded the oxo acid. This was converted to the oxime which then was subjected to the Beckmann rearrangement. Elution chromatography showed equal amounts of azelaic (nonanedioic) and sebacic (decanedioic) acids. No evidence for inductive or field effects during formoxylation was found. Fore and Bickford<sup>11</sup> hydrogenated both cis-9,10-epoxyoctadecanol and its actate, oxidized the resulting hydroxy compounds to oxo acids, converted these to the oximes, and through the Beckmann rearrangement obtained mixtures of dibasic acids which were resolved chromatographically. Here again the evidence showed no directive influence.

The contradictory nature of the literature reviewed above, discrepancies in reported melting points of compounds assumed to be pure,<sup>12</sup> and complete disregard of phase properties of the mixtures which might result from the various reactions discussed lead to the work which is presented here. Binary mixtures of fatty acids or derivatives of fatty acids generally form eutectics or minimummelting mixtures.13 Frequently, evidence of compound formation also exists, usually as an incongruent melting point in the phase diagram. On theoretical grounds, it is not possible to effect total separation of the components of such systems by fractional crystallization. In order to clarify the several points in question, high-purity samples of 9- and 10-oxo-octadecanoic acids and DL-9- and pL-10-hydroxyoctadecanoic acids were synthesized and phase diagrams of the two sets of positional isomers were established.

<sup>(3)</sup> J. Baruch, Ber. 27, 172 (1894).

<sup>(4)</sup> G. M. Robinson and R. Robinson, J. Chem. Soc., 2204 (1926).

<sup>(5)</sup> W. W. Myddleton, R. G. Bercham, and A. W. Barrett, J. Am. Chem. Soc., 49, 2264 (1927).

<sup>(6)</sup> C. G. Tomecko and R. Adams, J. Am. Chem. Soc., 49, 522 (1927).

<sup>(7)</sup> J. Ross, A. I. Gebhart, and J. F. Gerecht, J. Am. Chem. Soc., 71, 282 (1949).

<sup>(8)</sup> C. H. Mack and W. G. Bickford, J. Org. Chem., 18, 686 (1953).

<sup>(9)</sup> E. Jungermann and P. E. Spoerri, J. Am. Chem. Soc., 75, 4704 (1953).

<sup>(10)</sup> J. Rockett, J. Am. Chem. Soc., 78, 3191 (1956).

<sup>(11)</sup> S. P. Fore and W. G. Bickford, J. Org. Chem., 24, 620 (1959).

<sup>(12)</sup> T. F. Grey, J. F. McGhie, and W. A. Ross, J. Chem. Soc., 1502 (1960).

<sup>(13)</sup> A. E. Bailey, *Melting and Solidification of Fats*, Interscience Publishers, Inc., New York, 1950, Chapter IV.

### EXPERIMENTAL

*Materials.* Dimethyl azelate, dimethyl sebacate, heptylmalonic, and octylmalonic esters were fractionated on a Podbielniak column and those fractions that contained only one component, as indicated by gas chromatographic analysis, were retained. Heptylmalonic acid, m.p. 96–97°, <sup>14</sup> and octylmalonic acid, m.p. 113–114°, were obtained by hydrolysis of the corresponding homolog-free esters.<sup>15</sup>

Methyl hydrogen azelate and sebacate, prepared by the Organic Syntheses method,<sup>16</sup> were converted by reaction with thionyl chloride to 8-carbomethoxyoctanoyl chloride, b.p. 95–99° (0.15 mm.), and 9-carbomethoxynonanoyl chloride, b.p. 117–122° (0.6 mm.).

9- and 10-Oxo-octadecanoic acids. The procedure of Bowman and Fordham<sup>17</sup> was employed for the preparation of these keto acids. The following preparation of 10-oxo-octadecanoic acid is typical of the method.

To a solution of 109 g. of dihydropyran<sup>13</sup> in 200 ml. of dry benzene containing 2 drops of concentrated sulfuric acid, 111.1 g. of octylmalonic acid was added in portions, with stirring and cooling below 30°. When a clear solution was obtained, the reaction mixture was allowed to stand at room temperature for 0.5 hr., then stirred with 4 g. postassium hydroxide pellets for 0.5 hr. The acid-free benzene solution was decanted and the solvent and excess dihydropyran removed under vacuum below 30°.

The residual ester in 500 ml. of dry benzene was added dropwise, with cooling and stirring, to 24 g. of a 50% sodium hydride-oil suspension in 500 ml. of dry benzene. When all the hydride had reacted (about 2 hr.), 117.3 g. of 9-carbomethoxynonanoyl chloride in 300 ml. of dry benzene was added dropwise (temperature  $\sim 20^{\circ}$ ). The reaction mixture gelled near the end of the addition. After 1.5 hr. stirring at room temperature, 10 ml. of acetic acid was added and the mixture refluxed overnight to hydrolyze and decarboxylate the  $\beta$ -ketoester.

The reaction mixture was washed twice with water, the solvent removed, and low-boiling material distilled at 1 mm. (up to a bath temperature of 190°). The residue was refluxed 3 hr. in 10% methanolic potassium hydroxide and acidified with dilute hydrochloric acid, and the filtered solid was air-dried and crystallized from *n*-heptane to give 109 g. (73% yield) of 10-oxo-octadecanoic acid, m.p.  $80-81^\circ$ . Two crystallizations from acetonitrile gave m.p.  $81-82^\circ$ ; semicarbazone, from 95% alcohol, m.p. 117-118°; methyl ester, m.p.  $46-47^\circ$ .

In an analogous manner 9-oxo-octadecanoic acid, m.p.  $80-81^{\circ}$ , was prepared in 63% yield; semicarbazone, from 95% alcohol, m.p.  $110-111^{\circ}$ ; methyl ester, m.p.  $47-48^{\circ}$ .

DL-9- and DL-10-hydroxyoctadecanoic acids. The hydroxy acids were prepared by hydrogenation of methanolic solutions of methyl 9- and 10-oxo-octadecanoate in the presence of Raney nickel as described by Bergström *et al.*<sup>19</sup> DL-10-Hydroxyoctadecanoic acid, m.p. 79-80°; hydrazide, m.p. 115-116°; methyl ester, m.p. 54-55°. DL-9-Hydroxyoctadecanoic acid, m.p. 76-77°; hydrazide, m.p. 113-114°; methyl ester, m.p. 50-51.5°.

*Phase studies.* The thaw-melt method<sup>20</sup> was used for the study of phase changes. Synthetic mixtures were prepared, melted, and, when cool, ground in an agate mortar prior to

(16) S. Swann, R. Oehler and R. J. Buswell, Org. Syntheses, Coll. Vol. II, 276 (1944).

(17) R. E. Bowman and W. D. Fordham, J. Chem. Soc., 3945 (1952).

(18) Generously supplied by the Quaker Oats Company, Chicago, Ill.

(19) S. Bergström, G. Aulin-Erdtman, B. Rolander, E. Stenhagen, and S. Ostling, Acta Chem. Scand., 6, 1157 (1952).

(20) H. Rheinboldt, Ber., 74, 756 (1941); H. Lettré, H. Barnbeck, and W. Lege, Ber. 69, 1151 (1936).

use. Observations were made through an Ernst Leitz polarizing microscope fitted with an electrically heated hot stage. Temperatures were measured by means of a calibrated thermometer with 0.2° graduations. Liquidus temperatures were reproducible within less than 0.1°; solidus curves are approximations, as it is not possible to locate the solidus accurately by the thaw-melt technique. Precise temperature values are significant only in relation to other values obtained in this work; other techniques and equipment may yield values which differ by as much as 1°.

#### RESULTS AND DISCUSSION

The phase diagram for the binary system of 9oxo- and 10-oxo-octadecanoic acids is shown in Fig. 1. This diagram represents a simple eutectic system with solid-solution formation and limited miscibility in the solid state. The points on the liquidus curve represent experimentally determined temperatures. The approximate solidus is represented by the broken lines. The eutectic lies at or close to the 1:1 ratio of the two components.

The phase diagram for the system of 9-hydroxyand 10-hydroxyoctadecanoic acids, Fig. 2, is strikingly different from that of the oxo acids. A maximum occurs at the 1:1 ratio of the two components which is at a temperature higher than the melting point of either component. This maximum is the result of compound formation between the two hydroxy acids (actually between two racemic modifications). In this system eutectics occur between the 1:1 compound and each of the pure components; also solid solutions are formed with limited miscibility in the solid state.

With this knowledge of the two binary systems which have been described, it is now possible to comment on previous work involving 9- and 10-oxoand 9- and 10-hydroxyoctadecanoic acids. In Table I are listed melting-point values reported in the literature together with values obtained in the present work for the pure compounds and for the 9- + 10-oxo eutectic and the 9- + 10-hydroxy compound. With due allowance for differences in experimental techniques, and the fact that most of these temperature readings are uncorrected, it is still obvious that the melting point of the substance which several authors describe as 10-oxooctadecanoic acid (71-76°) does not agree with that of the synthetic material (82-83°) It also seems probable from the phase diagram that the lowermelting material is the 1:1 eutectic mixture (m.p. 73.2°) and that this mixture has resulted, directly or indirectly, from a completely random reaction of the eighteen-carbon fatty-acid chain at the 9- and 10-positions. With 10-hydroxyoctadecanoic acid the interpretation of the data in the literature is somewhat less clear-cut, as there is not so great a difference between the melting point of the synthetic material (79-82°) and that the 1:1 compound (82.6°). However, it is significant that in general the melting points of the products described as the 10-hydroxy acid, which are obtained from eighteen-carbon acids by one of the several pro-

<sup>(14)</sup> Temperatures are uncorrected.

<sup>(15)</sup> G. M. Robinson, J. Chem. Soc., 125, 228 (1924).

cedures described earlier, are higher than that of the synthetic material. This fact is in agreement with the possibility that these procedures have actually led to the 1:1 compound formed between 9- and 10-hydroxyoctadecanoic acids. This compound is indistinguishable from the pure 10isomer on the basis of melting point alone, and none of the earlier investigators reported a mixedmelting point determination with the synthetic 10hydroxy acid.

It is now possible to discount almost completely all evidence for a directive effect presented in earlier work. Baruch's<sup>3</sup> claims to have found only those products of the Beckmann rearrangement which coincide with those expected from 10-oxooctadecanoic acid are not confirmed by the results of Robinson and Robinson.<sup>4</sup> These authors definitely obtain a mixture of the 9- and 10-isomers (m.p.  $70.9^{\circ}$ ) and conclude that more of the latter is formed. However, it is difficult to defend their quantitative results based on thermal analysis. Fatty acids derived from natural sources, unless rigorous purification procedures are followed, always contain minor amounts of impurities which will carry over to derivatives and exert a significant effect upon the melting points. This argument is substantiated by the work of Myddleton and coworkers<sup>5</sup> whose purified "10-ketostearic acid" (from stearolic) melted at 76°. In each instance, the actual product is, we believe, the eutectic mixture of the 9- and 10-positional isomers.

As part of their studies of mixtures of hydroxyoctadecanoic acids, Tomecko and Adams<sup>6</sup> determined melting and solidification points of two mixtures of the synthetic 9- and 10-isomers. Two points are not sufficient to give even an indication of the nature of the phase diagram, but these authors did correctly conclude that the melting points of such compounds are not reliable criteria of purity. However, they incorrectly concluded that the major product of the sulfation of oleic acid or olive oil is 10-hydroxyoctadecanoic acid since in most cases the melting point lies in the 80-85° range. It is obvious from the complete liquidus curve that the 1:1 compound will also fit this melting range, and we believe that it is the actual product of the reaction.

The oxo-octadecanoic acid melting at 71° obtained by Ross, et al.<sup>7</sup> and Mack and Bickford<sup>8</sup> through hydrogenation of 9,10-epoxyoctadecanoic acid (or ester) followed by oxidation of the hydroxy acid is without question the 1:1 eutectic mixture of the 9and 10-isomers. The fact that Ross was able to isolate sebacic acid after Beckmann rearrangement of the oxime does not preclude the presence also of **aze**laic acid. These two dibasic acids form a eutectic system<sup>32</sup> from which, starting with a 1:1 **mixture**, it is theoretically possible to separate only **the** 10-carbon acid by fractional crystallization.<sup>33</sup>

The oxo-octadecanoic acid of Jungermann and





Fig. 2. The system 9-hydroxyoctadecanoic acid—10-hydroxyoctadecanoic acid

Spoerri<sup>9</sup> melting at  $72^{\circ}$ , which was produced from one of their chlorohydrin fractions, is also probably the eutectic mixture. This invalidates the conclusion that the two possible chlorohydrins are produced in a 3:1 ratio. Without knowledge of the binary system of the two chlorohydrins, it is not possible to predict whether either can be separated by the crystallization process, and no conclusions regarding the ratio of products should be drawn. There is no reason to believe that the hydrochlorination of 9,10-epoxyoctadecanoic acid is not a random process.

Although no claims for a directive influence in the formoxylation of oleic acid were made by Knight, Koos, and Swern,<sup>31</sup> these authors produced hydroxyoctadecanoic acid which, after repeated crystallization, melted at 81.5–82.5° and which showed no depression when mixed with an "authentic sample" of 10-hydroxyoctadecanoic acid. The reference sample was prepared by hydrogenation of

#### COCHRANE AND HARWOOD

	Literature Values	Present Work
9-Oxo	83, <sup>4,21</sup> 81.5, <sup>8</sup> 81.7-81.9, <sup>19</sup> 80, <sup>9</sup> 81 <sup>12</sup>	82.6
10-Oxo	76, <sup>3,5</sup> 74, <sup>22</sup> 82 (cor), <sup>4</sup> 82–82.8, <sup>33</sup> 71, <sup>8</sup> 83, <sup>24</sup> 82.4–82.6, <sup>19</sup> 72, <sup>3,9</sup> 81–82 <sup>12</sup>	<i>83.2</i>
9- + 10-Oxo eutectic		73. <i>2</i>
9-Hydroxy	74-75,675.4-75.9,1970-7213	77.1
10-Hydroxy	$84-86,^{s_5}$ $81-81.5,^{s_6}$ $83-84,^{s_7}$ $84.5,^{s_3}$ $81-82,^{e}$ $85,^{s_9}$ $82.5,^{s_0}$ $79.2-79.5,^{s_9}$ $81.5-82.5,^{s_1}$ $80,^{9}$	
	78-7912	<i>80.3</i>
9- + 10-Hydroxy		
1:1 compound		82.6

TABLE ]	I
---------	---

MELTING POINTS OF OXO- AND HYDROXYOCTADECANOIC ACIDS<sup>d</sup>

<sup>a</sup> Those in italics are for synthetic preparations.

9,10-epoxyoctadecanoic acid. Both materials are, we believe, the 1:1 compound formed by the 9-and 10-isomers.

On the basis of what has been presented, we conclude that there is no basis in the work of others

(21) O. Behrend, Ber., 29, 806 (1896).

(22) A. A. Shukoff and P. V. Schestakoff, J. prakt. Chem., 67, 414 (1903).

(23) C. R. Fordyce and J. R. Johnson, J. Am. Chem. Soc., 55, 3368 (1933).

(24) D. E. Ames, R. E. Bowman, and R. G. Mason, J. Chem. Soc., 174 (1950).

(25) M. C. Saytzeff and A. Saytzeff, J. prakt. Chem., [2], 35, 384 (1887).

(26) A. C. Geitel, J. prakt. Chem., [2], 37, 82 (1888).

(27) A. Arnaud and S. Posternak, Compt. rend., 150, 1527 (1910).

(28) G. M. Robinson and R. Robinson, J. Chem. Soc., 127, 175 (1925).

(29) L. G. Radcliffe and W. Gibson, J. Soc. Dyers Colourists, 39, 4 (1923).

(30) G. V. Pigulevskii and Z. Y. Ruboshko, J. Gen. Chem. (U.S.S.R.), 9, 829 (1939); Chem. Abstr., 34, 378 (1940). which we have discussed for the belief that eighteencarbon fatty acids which contain unsaturation or an epoxy group at the 9–10 position reaction in other than a random manner at these two positions.

CHICAGO, ILL.

(31) H. B. Knight, R. E. Koos, and D. Swern, J. Am. Chem. Soc., 75, 6212 (1953).

(32) D. F. Houston and W. A. van Sandt, Ind. Eng. Chem., Anal. Ed., 18, 538 (1946).

(33) A private communication from Dr. David B. Howton, University of California Medical Center, Los Angeles, California, reports the unequivocal confirmation of the conclusion that a 1:1 mixture of 9- and 10-hydroxyoctadecanoic acids results from the catalytic hydrogenation of cis-9,10epoxyoctadecanoic acid. This was accomplished through the following sequence of reactions: epoxy  $\rightarrow$  hydroxy  $\rightarrow$  ox  $\rightarrow$ oximino, followed by Beckmann rearrangement of the oximes, hydrolysis of the amides and esterification of the mixture of mono- and dibasic acids. Gas-liquid chromatography of the mixture of esters yielded equimolar amounts of azelaic and sebacic and of capric and pelargonic esters.