tion of soybean oil esters show good agreement between mono- and dibasic acids (5). Most of the ethylenic bonds (85%) in the cis (sample 11a) fraction were at carbon 9, whereas the trans (sample 11b) fraction had high unsaturation at carbons 10 and 11. Similarly, partial hydrogenation of methyl linoleate and separation of the products gave pure cis (sample 12a) and pure trans (sample 12b) fractions. When cleaved, each gave mono- and dibasic acids in like amounts. The plot of both sets of data for sample 12b in Figure 1 shows about equal amt of ethylenic bonds at carbons 10 and 11. Treatment of methyl linolenate in the same manner also gave pure cis (sample 13a) and pure trans monoenates (sample 13b) which on cleavage analysis showed maximum unsaturation (Table IV) at carbon 12. Mono- and dibasic data were in fair agreement. The distributional pattern was somewhat abnormal, manifesting a break or distortion at carbon 10 or 11.

Iron carbonyl (6,7) has also been investigated as a catalyst in homogeneous partial hydrogenation of polyunsaturated esters, and we have included the application of our procedure to several fractions. Table IV contains the results of cleavage of three fractions from methyl linoleate; a mixture of cis and of trans monoenate (sample 14a), a pure cis fraction (sample 14b) isolated from a monoenate mixture, and a pure trans fraction (sample 14c) from a monoenate mixture. The mixture had generally good agreement of the mono- and diacids, with carbon 10 showing the greatest amt of ethylenic bonds. Similar results for the cis (sample 14b) and for the trans fractions (sample 14c) show the greatest unsaturation at carbons 11 and 10, respectively.

The application of our procedure to the analysis of conjugated dienoates formed during partial hydrogenation of methyl linoleate is illustrated by sample 15. The conjugated dienoate (sample 15d) and a complex of this dienoate with iron carbonyl (sample 15b) were isolated after hydrogenation, and the form of their ethylenic bond distribution is practically the same. Figure 1 depicts the dibasic and monobasic results for sample 15a. The iron carbonyl-dienoate complex, as separated by CCD, was decomposed chemically (sample 15c) and after cleavage the same ethylenic bond distribution was obtained. All three fractions were principally 9,11- and 10,12-conjugated

dienoates, and the amt of monobasic and dibasic acids were highly comparable.

Precision of Data. We have determined the precision of our procedure by statistical treatment of all dibasic percentages greater than 1.5% with the corresponding monobasic values.

For those sample obtained after heterogeneous hydrogenation the standard deviation was ±1.97%. The 95% confidence limits for either mono- or dibasic acids were ±3.92%; for the mean of the mono- and dibasics, ±2.77%.

For those samples obtained after homogeneous hydrogenation the standard deviation was ±1.86%. The 95% confidence limits for either mono- and dibasic acids were ±3.67%; for the mean of the mono- and dibasics, ±2.60%.

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Rearrangement of Epoxy Fatty Esters to Keto Fatty Esters

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Abstract

The rearrangement of fatty epoxyesters to ketoesters was studied. The isomerization is carried out in nonaqueous media and is catalyzed by acids. Esters containing one epoxy group per fatty acid chain are isomerized to the corresponding ketones in 70–90% yields using boron fluoride etherate catalyst in boiling dioxane. Conversion to ketonic products is measured either by chromatographic separation followed by IR analysis or by oximation. Principal byproducts are hydroxy derivatives. Fatty esters containing more than one epoxy group/fatty acid chain give low ketone yields.

Introduction

RECENT INVESTIGATIONS at this laboratory involving the acid catalyzed hydration of epoxides of fatty acids and esters indicated that a considerable amt of ketonic material could be obtained as byproduct. This result was not totally unexpected, for the rearrangement of epoxides to ketones with the aid of catalyst and/or heat has been well documented (1). However, information concerning the isomerization of epoxides of fatty materials was noticeably absent, and an investigation in this field seemed worthwhile; since ketoacids and esters had been previously prepared only by multi-stepped processes (2).

The optimum conditions for rearrangement of epoxides to ketones were determined using methyl 9,10-

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epoxystearate as a model compound. Other epoxy compounds were then subjected to the rearrangement procedure. The extent of conversion of monoepoxides into monoketones was estimated by separation of the crude product into fractions by column chromatography, and IR analysis of the fractions. This method could not be applied to the estimation of ketones obtained from polyepoxide compounds, since byproducts containing both hydroxy and ketone functions in the same molecule were not separable from polyhydroxy compounds. For such materials, then, an analytical method for the determination of ketones by oximation (3,4) was adapted for application to the small samples available.

Experimental Procedures and Data

Materials

Methyl 9,10-Epoxystearate. This compound was prepared by epoxidation of methyl oleate (5). Oxirane oxygen: 5.04%; theory: 5.12%.

Catechol bis-9,10-Epoxystearate. Material prepared by Port and Komanowsky (6) was used. Oxirane oxygen: 4.69; theory: 4.77%.

Ethylene Glycol bis-9,10-Epoxystearate. Material prepared by Gelb et al. (7) was used. Oxirane oxygen: 4.99%; theory: 5.15%.

Methyl 9,10,12,13-Diepoxystearate. This compound was prepared according to the procedure of Findley et al. (5), except that chloroform was used as the solvent. Oxirane oxygen: 9.62%; theory: 10.2%.

Glycidyl Stearate. Material prepared during previous research (8) was used. Oxirane oxygen: 4.50%; theory: 4.69%.

Epoxol 7–4 (Reference to commercial products does not imply endorsement by the United States Department of Agriculture over similar products not mentioned.). An epoxidized triglyceride obtained from Swift & Co. Oxirane oxygen: 7.11%.

Boron Fluoride Ethyl Ether (Purified). The Eastman Kodak product was used as received.

1,4-Dioxane. Eastman Kodak practical grade material was purified according to the method of Hess and Frahm (9).

Benzene. ACS grade was dried over Drierite and filtered.

Aluminum Chloride (Anhydrous). Fisher reagent grade was used as received.

Silica Gel. Davisson No. 923 dried at 100C for two hr and then equilibrated with 4% by wt of water.

Fluoboric Acid (18N). Prepared by concn of Baker Fluoboric Acid (48–50%) (10).

Methods of Analysis for Ketones

Chromatographic Procedure. The chromatographic column was prepared from a slurry of 30 g silica gel/g of sample in petroleum ether using a ⅝ in. column. The sample was placed on the column using 7 ml of chloroform/g of sample. Elution was started with benzene, continued with benzene-ether mixtures and ended with ether. Solvents were evaporated on a steam bath under nitrogen. The residues were identified from their infrared spectra.

Volumetric Procedure. An analytical procedure for the determination of ketones by oximation in the presence of a long-chain fatty amine was adapted from the procedures of Metcalfe and Schmitz (3), and Fritz et al. (4) for application to small samples.

The sample, containing approx 0.08 mmole of ketonic oxygen, is weighed into a 50-ml glass stoppered Erlenmeyer flask. Five ml of the amine solution (0.05M Armeen 18D in isopropanol) is added to the

flask followed by 5 ml of 0.1M hydroxylamine hydrochloride solution (35% methanol, 65% isopropanol). Two blanks are also prepared. The flasks are tightly stoppered and heated at 80C for one hr. The solutions are cooled to room temp, and then titrated potentiometrically with 0.05N hydrochloric acid in methyl cellosolve. The percentage of ketonic material is calculated using the following formula:

$$\% \text{ ketone} = \frac{(B - S) \times N \times E}{S.W. \times 10}$$

where

B = ml HCl consumed by the blank
S = ml HCl consumed by the sample
N = normality of the HCl
E = mol wt of the ketone divided by the number of ketonic carbonyl groups
S.W. = sample wt

Isomerization Procedures

Rearrangement of Methyl 9,10-Epoxystearate with Aluminum Chloride. In a 500-ml round-bottom flask, fitted with addition funnel, stirrer, thermometer and condenser with drying tube, was placed a solution of 6.29 g (0.047 mole) anhydrous aluminum chloride in 175 ml dioxane. To the solution at 90C was added rapidly 5.0 g (0.0157 mole) of methyl 9,10-epoxystearate dissolved in 75 ml dioxane. The reaction mixture was refluxed for three hr, was then cooled to room temp and was poured into 125 ml of benzene. The solution was washed successively with 100 ml of slightly acidic water and with five 50-ml portions of water, and was dried over Drierite. The solvent was evaporated on the steam bath under nitrogen, giving 4.79 g of amber colored product.

One g of crude product was chromatographed on silica gel using the procedure described above. IR analysis of the fraction residues indicated the following composition for the crude product: methyl 10(9)-ketostearate (77%), methyl 9,10-dihydroxystearate (5%), and an unidentified material containing hydroxyl functions (15%). The methyl 9,10-dihydroxystearate was identified by comparison of its IR spectrum with that of an authentic sample. The ketone fraction was recrystallized from acetone, mp 44–44.5C, literature values (11), methyl 10-ketostearate 46–47C, methyl 9-ketostearate 47–48C. The IR spectrum had strong bands at 1745 and 1710 cm⁻¹.

The rearrangement catalyzed by aluminum chloride was repeated, but ether was used as solvent instead of dioxane. Methyl 9(10)-chloro-10(9)-hydroxystearate was the sole product of the reaction. It was identified by comparison of its IR spectrum with that of authentic material prepared by the action of hydrochloric acid on pure methyl 9,10-epoxystearate.

Rearrangement of Methyl 9,10-Epoxystearate with Fluoboric Acid. Five g (0.157 mole) of methyl 9,10-epoxystearate dissolved in 60 ml of dioxane was placed in a 200-ml, 3-neck round-bottom flask which was fitted with a stirrer, a thermometer, a dropping funnel and a condenser protected by a calcium chloride drying tube. The solution was stirred and its temp was raised to 50C. Fifteen ml of dioxane containing 0.14 g (0.0016 mole) 18N fluoboric acid was added to the solution over a 4-min period. The mixture was stirred at 50C for 30 min and poured into 300 ml of benzene. The benzene solution was washed with 25 ml of 5% aqueous sodium bicarbonate solution, then with five 50-ml portions of water. The benzene solution was dried over Drierite and the solvent removed on the steam bath under nitrogen, giving 4.7 g of crude product, oxirane oxygen: 0.57%.

TABLE I
Isomerization of Methyl 9,10-Epoxystearate Catalyzed by HBF₄
Variation of Product Composition with Reaction Variables

Conc of HBF₄	Time hr	Temp C	Mole ratio catalyst / epoxide	Product composition %		
				Methyl 9(10)-ketostearate	Methyl 9,10-dihydroxy-stearate	Other compounds
2.7N	0.5	15	1.5	5.3	89.0	6.2
5.7N	0.5	15	1.5	26.0	65.0	......
18.0N	0.5	15	1.5	34.0	47.0	8.0
18.0N	0.5	50	0.1	41.0	26.0	23.0
18.0N	2.0	50	0.1	53.0	12.0	24.0
18.0N	2.0	50	1.0	52.0	23.0	20.0

Chromatography of the crude product followed by IR analysis of the eluted fractions indicated that the crude product was composed of methyl 10(9)-keto-stearate (41%), methyl 9,10-dihydroxystearate (26%), and an unidentified compound containing hydroxyl functions (23%).

The procedure described above was repeated with variations in time, temp or catalyst-substrate ratio (See Table I).

Rearrangement of Methyl 9,10-Epoxystearate with Boron Fluoride-Etherate. The following example is typical of the procedure adopted for the isomerization of epoxides to ketone derivatives. Boron fluoride-etherate (2.82 g; 0.0188 mole) dissolved in 80 ml of dioxane was placed in a 200-ml, 3-neck round-bottom flask, fitted with stirrer, thermometer, addition funnel and condenser protected with a drying tube filled with Drierite. The dioxane solution was heated to reflux, and 2.0 g (0.0063 mole) of methyl 9,10-epoxystearate dissolved in 20 ml of dioxane was added quickly. The reaction mixture was refluxed for three hr, cooled rapidly to room temp and poured into 80 ml of benzene in a separatory funnel. The benzene solution was washed with ten 30-ml portions of water to remove catalyst and dioxane, dried over Drierite, and evaporated on the steam bath under nitrogen, leaving 2.0 g of an oily product, which crystallized slowly upon standing.

Chromatography of the crude product on silica gel followed by IR analysis of the eluted fractions indicated a composition of 90% methyl 10(9)-ketostearate and 4% methyl 9,10-dihydroxystearate. The ketone content of the crude product as determined by the oximation method was 91% calculated as methyl keto-stearate.

Rearrangement of Catechol bis-9,10-Epoxystearate with Boron Fluoride-Etherate. Two g (0.00297 mole) of catechol bis-9,10-epoxystearate in 80 ml of dioxane was treated as above with 1.27 g (0.00892 mole) of boron fluoride-etherate, giving 2.03 g of product. Chromatography of the crude product on silica gel followed by IR analysis of the eluted fractions indicated the following composition: catechol bis-10(9)-ketostearate (58%), mixture of catechol bis-9,10-dihydroxystearate and catechol 9,10-dihydroxy-10′(9′)-ketodistearate

TABLE II
Isomerization of Methyl 9,10-Epoxystearate
Catalyzed by Lewis Acids [a]

Catalyst	Time hr	Temp C	Mole ratio catalyst/ epoxide	Product composition %		
				Methyl 9(10)-keto-stearate	Methyl 9,10-dihydroxy-stearate	Other compounds
Aluminum chloride	3	35 [b]	3	0 [c]	..	....
	3	100	3	77	5	15
Boron fluoride etherate	3	100	3	90	4	....
	3	98	3	89	4	7

[a] Solvent: 1,4-dioxane.
[b] Solvent: ether.
[c] Principal product: methyl 9(10)chloro-10(9) hydroxystearate.

(13%), and an unidentified compound (24%). The oximation method for ketone content failed with this material. A sample of the diketone was purified by repeated recrystallizations fro methanol mp 66.1–67C.

Anal. Calc'd for C₄₂H₇₀O₆: C, 75.18; H, 10.52; found: C, 75.39; H, 10.44.

Rearrangement of Ethylene Glycol bis-9,10-Epoxy-stearate with Boron Fluoride-Etherate. Ethylene glycol bis-9,10-epoxystearate (1.5 g, 0.00241 mole) was caused to react with 1.05 g (0.0072 mole) of boron fluoride-etherate in 85 ml of boiling dioxane, yielding 1.5 g of crude product. Chromatography of the crude product on silica gel followed by IR analysis of the fraction residues indicated that the product was composed of ethylene glycol bis-9(10)-ketostearate (75%), and ethylene glycol-bis-9,10-dihydroxy stearate and ethylene glycol 9,10-dihydroxy-10′(9′)-ketodistearate (21%). Application of the oximation method described above indicated that the crude product had a ketone content equivalent to 81% ethylene glycol bis-9(10)-ketostearate.

A sample of the diketone was purified by recrystallization, first from Skellysolve B and then repeatedly from methanol, mp 81.5–82.5C.

Anal. Calc'd for C₃₈H₇₀O₆: C, 73.26; H, 11.33. found: C, 73.10; H, 11.33.

Rearrangement of Epoxol 7–4 with Boron Fluoride-Etherate. Twenty g of Epoxol 7–4 (0.088 mole) were treated with 75 g (0.264 mole) of boron fluoride-etherate in 800 ml of dioxane, giving 19.9 g of a brown oil which slowly deposited crystals upon standing. Analysis of the crude product by the oximation method indicated that 27% of the epoxide groups had been converted into ketone groups.

Rearrangement of Methyl 9,10,12,13-Diepoxystearate with Boron Fluoride-Etherate. Two g (0.00613 mole) of methyl 9,10,12,13-diepoxystearate were treated with 5.26 g (0.0184 mole) of boron fluoride-etherate in 100 ml of boiling dioxane to obtain 2.0 g of dark brown oil which partially solidified upon standing at room temp, oxirane oxygen: trace. Chromatography of the crude product on silica gel followed by IR analysis of the eluted fractions indicated the following product composition: compounds containing ketones (27%), polyhydroxy compounds (15%) and unidentified compounds (50%).

Rearrangement of Glycidyl Stearate with Boron Fluoride-Etherate. Two g (0.00588 mole) of glycidyl stearate were treated with 2.5 g (0.0176 mole) of boron fluoride-etherate in 105 ml of refluxing dioxane, giving 1.56 g of product, oxirane oxygen: none. Chromatography of the crude product on silica gel followed by IR analysis of the eluted fractions indicated that the bulk of the product (70%) was a mixture of 1,2- and 1,3-distearin with no apparent rearrangement of epoxide to ketone or aldehyde.

Results and Discussion

The treatment of fatty epoxides with acids usually leads to the complete disappearance of epoxide functions and to the formation of ketones, dihydroxy derivatives and other products. The extent to which the desired reaction, isomerization to ketone, is attained depends largely upon the catalyst, the reaction conditions and the amt of water present. Comparison of reaction conditions most favorable to the hydration of methyl 9,10-epoxystearate (12) with those reported in the present work to give high conversions to the keto-stearate would indicate that isomerization proceeds at a slower rate than hydration under similar conditions. Achievement of high yields of isomerization

product would therefore be aided by the exclusion, or at least minimization of water in the reaction mixture and by elevation of the reaction temp. That these expectations are realized can be seen from the data of Table I. Treatment of methyl 9,10-epoxystearate with equal amt of fluoboric acid in varying concn at 15C demonstrates a direct relationship between the amt of methyl ketostearate formed and the concn of the acid catalyst. Using the most concd solution of fluoboric acid (18N) and increasing the reaction temp and time further increases the extent of isomerization, but a limiting concn of ca. 50% methyl ketostearate is not exceeded. The reason for this practical limit appears to be two-fold. With decreasing amt of water present in the reaction mixture and at elevated temp, a new side reaction, catalyzed by strong acid, possibly a dimerization, becomes prominent and competes with increasing success with the desired isomerization. Failure to suppress formation of methyl dihydroxystearte may be attributable to the fact that 18N fluoboric acid is in reality a mixture of many acids and water obtained by concentrating the commercially available 48–50% acid. The latter undoubtedly consists of a mixture of fluoboric acid, partially hydrated fluoboric acids, fluosilicic acid, hydrogen fluoride and water, and the 48% HBF_4 label simply reflects a titer expressed as HBF_4. Concn of the commercial acid results in the so-called 18N acid which obviously cannot be what it claims to be since 100% HBF_4 (d = 1.51) would be 17.2N.

Use of anhydrous benzyltrimethylammonium fluoborate as catalyst led to complete recovery of unreacted starting material.

Aluminum chloride and boron fluoride, two Lewis acids, were tested as isomerization catalysts. The results are summarized in Table II. Treatment of methyl epoxystearate dissolved in dioxane with aluminum chloride at 100C yielded a product mixture composed of 77% methyl 9(10)-ketostearate and 20% of products containing hydroxyl functions. At 35C aluminum chloride yielded no ketostearate. The product isolated instead in high yield was methyl 9(10)-chloro-10(9)-hydroxystearate, probably formed by the addition of hydrogen chloride to the epoxide when the catalyst was hydrolyzed during the work-up of the reaction mixture.

Best conversions to the ketostearate (90%) were achieved by use of boron fluoride-etherate in dioxane at 100C. Conversions were reproducible within one or two per cent.

In compounds which contain more than one epoxide function/molecule isomerization yields are more difficult to estimate, and yields of compounds which have been ketonized completely decrease. Since each oxirane function of a polyepoxide may isomerize or hydrate or react in some other way independently of the other oxirane functions, products result which contain a mixture of functions in the same molecule. Furthermore, if two or more oxirane functions are located in suitable proximity in the same molecule, they may interact and thus give rise to product types not normally encountered among the reaction products from monoepoxides.

Since the degree of isomerization to ketone could not be followed by measuring the disappearance of the epoxide function, other means of determining the ketone content had to be employed. IR analysis of the crude product mixture could indicate the presence of ketonic product but allowed only a rough estimation of the relative proportions of the compounds present.

TABLE III
Isomerization of Epoxides to Ketones in 1,4-Dioxane at 100C
Catalyst: $BF_3 \cdot (C_2H_5)_2O$

Epoxide	Yield of ketone (%)	
	Estimated by chromatography and IR	By oximation method
Methyl 9,10-epoxystearate	90	91
Catechol bis-9,10-epoxystearate	70	a
Ethylene glycol bis-9,10-epoxystearate	80	81
Epoxol 7–4	b	26
Methyl 9,10,12,13-diepoxystearate	25	b
Glycidyl stearate	0	b

a Catechol diketone gave erroneous results.
b Analysis not attempted.

Column chromatography, employing silica gel, coupled with IR analysis of the eluted fractions, was of limited use for the analysis of the product mixtures resulting from the isomerization of polyepoxides. The compounds containing ketone functions only were separable from the compounds containing hydroxy functions only or hydroxy and ketone functions, but the latter two types could not be separated from each other.

A more general method for the determination of the ketone content was adapted from previously reported procedures (3,4) and made applicable to small samples. The procedure is conducted in nonaqueous medium and consists in the oximation of the ketone group by hydroxylamine hydrochloride in the presence of a long-chain fatty amine, followed by potentiometric titration of the excess base with HCl. The hydroxylamine hydrochloride and fatty amine solutions are stable, the HCl solution deteriorates slowly and must be standardized daily against trishydroxymethylaminomethane. The equivalence point potential (−200 mV) is about the same for each of the various compounds tested, and the titration curve exhibits a fairly sharp break at the equivalence point.

Results of the analysis of various compounds by chromatography and by oximation are compared in Table III. Those compounds having one epoxy group/fatty acid chain give relatively high conversions (70–90%) to the corresponding keto derivatives. On the other hand, polyepoxides having, on the average, more than one oxirane function on each fatty acid chain seem to be subject to interaction of the epoxide functions and give rather low conversions to ketones. Glycidyl esters, e.g. glycidyl stearate, prefer, apparently, to undergo acid-catalyzed rearrangement (13) to diglycerides.

In Table III, the excellent agreement between the two methods of analysis is rather unexpected since the yields obtained by chromatographic analysis represent rather rough estimates of the ketone content of fraction residues as judged from IR data. The oximation method, has a precision of ca. ±1-2%.

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