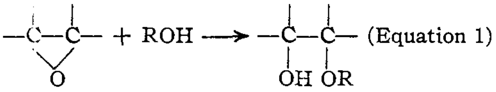
[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Chemistry of Epoxy Compounds. V.[2] Preparation of Some Hydroxy-ethers from 9,10-Epoxystearic Acid and 9,10-Epoxyoctadecanol

BY DANIEL SWERN, GERALDINE N. BILLEN AND JOHN T. SCANLAN

The reaction of oxirane compounds with compounds containing a hydroxyl group offers a convenient way of preparing many types of hydroxy-ethers (Equation 1).



$$\underset{\diagdown\,O\,\diagup}{-\overset{|}{C}-\overset{|}{C}-} + ROH \longrightarrow -\underset{OH}{\overset{|}{\underset{|}{C}}}-\underset{OR}{\overset{|}{\underset{|}{C}}}- \quad \text{(Equation 1)}$$

Acidic or alkaline materials are usually employed to catalyze this reaction, although for the more reactive oxirane compounds, a catalyst is not necessary. The reaction is generally applicable, and numerous hydroxy-ethers which contain a variety of functional groups can be readily prepared. Most of the published work has described the reaction of short-chain oxirane compounds with saturated aliphatic alcohols, and little information is available on the reaction of long-chain oxirane compounds with hydroxyl compounds. In this paper, the preparation of some hydroxy-ethers by the reaction of 9,10-epoxystearic acid and 9,10-epoxyoctadecanol with methyl, ethyl, *n*-propyl, *n*-butyl, *iso*-butyl, *n*-octadecyl, allyl, and β-chloroallyl alcohol and phenol, respectively, is reported. (Mixtures of products are obtained, since it is equally probable that the oxirane ring is opened between the oxygen atom and C_9 or C_{10}.)

The reaction of 9,10-epoxystearic acid (prepared from oleic acid by hypochlorination followed by dehydrohalogenation) with a large excess of ethyl, *n*-propyl and *n*-butyl alcohol, respectively, in the presence of catalytic quantities of sulfuric acid, has been reported by Nicolet and Poulter.[3] The reaction products which they obtained were saponified with aqueous alkali, and the three compounds isolated were mixtures of the 9- and 10-monoalkyl ethers of 9,10-dihydroxystearic acid. Yields were not reported. The oxirane ring of 9,10-epoxystearic acid can best be opened by heating the acid with a large molar excess of the alcohol and catalytic quantities of sulfuric acid, and under these conditions the carboxyl group is quantitatively esterified. By omitting the saponification step we obtained the hydroxy-ethers shown in Table I, in which the alkyl radicals in the ester and ether groups are identical. These products were isolated by vacuum distillation of the reaction products. We also treated 9,10-epoxystearic acid with *n*-octadecyl alcohol, phenol and β-chloroallyl alcohol under the conditions described above in an attempt to prepare *n*-octadecyl 9,10(10,9)-octadecoxyhydroxystearate, 9,10(10,9)-phenoxyhydroxystearic acid, and β-chloroallyl-9,10(10,9)-chloroalloxyhydroxystearate, respectively, but we were unable to purify the products completely. The analytical data which we obtained indicated, however, that in the main the reaction had proceeded in the expected manner.

We were unable to find any literature references to the reaction of 9,10-epoxyoctadecanol with hydroxyl compounds. We prepared the compounds shown in Table II in 25 to 65% yields, by heating 9,10-epoxyoctadecanol with a large molar excess of the appropriate alcohol in the presence of sulfuric acid as catalyst, and subsequently distilling the reaction products. We were unable to isolate pure 9,10(10,9)-*n*-octadecoxyhydroxyoctadecanol, 9,10(10,9)-phenoxyhydroxyoctadecanol and 9,10(10,9)-β-chloroalloxyhydroxyoctadecanol, although as mentioned earlier, the reactions proceeded in the expected manner.

The purified hydroxy-ethers are colorless, odorless, high-boiling liquids, soluble in all the common organic solvents and insoluble in water. They do not solidify when stored at 0° for long periods of time. Yields and characteristics of the products are shown in Tables I and II. Their high boiling points, insolubility in water, and stability suggest their possible use as plasticizers.

Allyl 9,10(10,9)-alloxyhydroxystearate (Table I) was co-polymerized in various proportions (from 1 to 40% by weight of total monomers) with vinyl acetate, according to the procedure of Guile and Huston.[4] Over the entire percentage range, insoluble, infusible products were obtained which ranged in physical appearance from hard, glass-like resins to soft, rubbery gels, thereby indicating that cross-linking probably had occurred and that both allyl groups must have reacted. That the fatty derivative was probably completely chemically bound was demonstrated by the fact that no oil was extruded when the co-polymers were squeezed in thin layers between sheets of absorbent paper.

In the reactions of 9,10-epoxystearic acid with hydroxyl compounds, small quantities of by-products, tentatively identified as esters of 9,10-dihydroxystearic acid,[5] were formed, and in the re-

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[2] For previous papers, see THIS JOURNAL, **66**, 1925 (1944); **67**, 412, 1786 (1945); **68**, 1504 (1946).

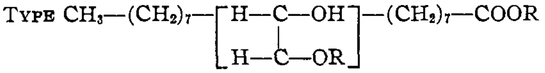
[3] Nicolet and Poulter, *ibid.*, **52**, 1186 (1930). These workers gave 53.8° as the melting point of the 9,10-epoxystearic acid which they employed. It has been shown by Ellis, *Biochem. J.*, **30**, 753 (1936), and confirmed in our laboratory, that the correct melting point of 9,10-epoxystearic acid prepared from oleic acid by hypochlorination followed by dehydrohalogenation is 59.5°.

[4] Guile and Huston, "A Revised Laboratory Manual of Synthetic Plastics and Resinous Materials," Michigan State College, 1944, p. 99.

[5] Swern and Jordan, THIS JOURNAL, **67**, 902 (1945); Swern, Jordan and Knight, *ibid.*, **68**, 1673 (1946).

TABLE I

9,10(10,9)-HYDROXY-ALKOXY ESTERS OF THE TYPE



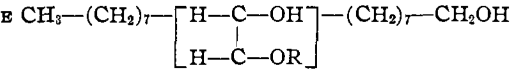
$$CH_3—(CH_2)_7—\left[\begin{array}{c} H—C—OH \\ | \\ H—C—OR \end{array}\right]—(CH_2)_7—COOR$$

R	Formula	Yield, %[a]	Boiling range °C.	Boiling range Mm.	Saponification equivalent Calcd.	Saponification equivalent Found	Hydroxyl, % Calcd.	Hydroxyl, % Found	Carbon, %[b] Calcd.	Carbon, %[b] Found	Hydrogen, %[b] Calcd.	Hydrogen, %[b] Found	n^{30}_D	d^{30}_4	Molecular refraction Calcd.	Molecular refraction Found
Methyl	$C_{20}H_{40}O_4$	85	186–189	0.7–1.1	344.5	344.7	4.94	4.95	69.7	69.9	11.7	11.8	1.4500	0.9306	99.4	99.5
Ethyl	$C_{22}H_{44}O_4$	50	160-190	.02–0.2	372.6	368.2	4.56	4.57	71.0	70.7	11.9	12.0	1.4479	.9154	108.6	108.9
n-Propyl	$C_{24}H_{48}O_4$	45	180–184	.02–0.04	400.7	399.5	4.25	4.20	72.0	72.1	12.1	12.0	1.4490	.9099	117.9	118.1
n-Butyl	$C_{26}H_{52}O_4$	45	185–190	.01	428.7	425.2	3.97	3.95	72.9	72.6	12.2	12.2	1.4498	.9051	127.1	127.1
iso-Butyl	$C_{26}H_{52}O_4$	40	172–180	.02–0.04	428.7	427.2	3.97	3.76	72.9	73.2	12.2	12.4	1.4471	.8989	127.1	127.5
Allyl[c]	$C_{24}H_{44}O_4$	60	196–202	.35–0.5	396.6	387.5	4.59	4.71	72.7	72.2	11.2	11.2	1.4589	.9266	116.9	117.1

[a] Purified products, after at least two distillations. [b] Analyses by Mary J. Welsh of this Laboratory. [c] Iodine number: calcd., 128.0; found, 126.0.

TABLE II

9,10(10,9)-HYDROXY-ETHERS OF THE TYPE



$$CH_3—(CH_2)_7—\left[\begin{array}{c} H—C—OH \\ | \\ H—C—OR \end{array}\right]—(CH_2)_7—CH_2OH$$

R	Formula	Yield, %[a]	Boiling range °C.	Boiling range Mm.	Hydroxyl, % Calcd.	Hydroxyl, % Found	Carbon, %[b] Calcd.	Carbon, %[b] Found	Hydrogen, %[b] Calcd.	Hydrogen, %[b] Found	n^{30}_D	d^{30}_4	Molecular refraction Calcd.	Molecular refraction Found
Methyl	$C_{19}H_{40}O_3$	65	158–161	0.007–0.008	10.7	10.8	72.1	71.5	12.7	12.6	1.4584	0.9151	94.6	94.5
Ethyl	$C_{20}H_{42}O_3$	60	179–185	.005–0.01	10.3	9.82	72.7	73.0	12.8	12.5	1.4565	.9078	99.3	99.7
n-Propyl	$C_{21}H_{44}O_3$	30	156–168	.005–0.01	9.87	9.32	73.2	73.1	12.9	12.7	1.4559	.9040	103.9	103.6
n-Butyl	$C_{22}H_{46}O_3$	50	170–175	.007	9.49	9.42	73.7	73.5	12.9	13.1	1.4562	.9002	108.5	108.3
iso-Butyl	$C_{22}H_{46}O_3$	25	163–170	.007–0.02	9.49	9.29	73.7	73.8	12.9	13.0	1.4550	.8980	108.5	108.3
Allyl[c]	$C_{21}H_{42}O_3$	40	171–188	.02–0.03	9.93	9.83	73.6	73.4	12.4	12.3	1.4627	.9166	103.4	102.9

[a] Purified products, after at least two distillations. [b] Analyses by Mary J. Welsh of this Laboratory. [c] Iodine number: calcd. 74.1; found, 73.3.

actions of 9,10-epoxyoctadecanol, the by-product was 9,10-dihydroxyoctadecanol. These side-reaction products were separated from the hydroxy-ethers by crystallization from acetone.

Experimental

Starting Materials.—9,10-Epoxystearic acid, m. p. 59.5°, and 9,10-epoxyoctadecanol, m. p. 54°, were prepared by epoxidation of pure oleic acid and oleyl alcohol, respectively.[3] The short-chain aliphatic alcohols were the purest commercial grades, and they were distilled through an efficient fractionating column (40 to 50 theoretical plates) before use. The *n*-octadecyl alcohol, m. p. 57–58°, was the Eastman Kodak purest grade. The phenol was the U. S. P. grade.

Preparation of Hydroxy-ethers from 9,10-Epoxystearic Acid.—A typical reaction procedure suitable for the short-chain alcohols is given: 9,10-Epoxystearic acid (29.9 g., 0.1 mole) was dissolved in the freshly distilled anhydrous alcohol (4 ml. per gram), with gentle heating. The solution was cooled below 30°, and 0.3 g. of 95% sulfuric acid was added dropwise while the reaction mixture was shaken by hand. A temperature rise of several degrees was always observed during the addition of the catalyst. The solution was heated on the steam-bath for two hours, and a quantity of sodium bicarbonate equivalent to the sulfuric acid was then added. The reaction mixture was fractionally distilled, first at atmospheric pressure to recover unreacted alcohol and then under high vacuum to isolate the hydroxy-ether. A short Vigreux column was employed during the vacuum distillation, which was carried out as rapidly as possible, otherwise some dehydration of the product occurred. The hydroxy-ether was dissolved in acetone (2 to 3 ml. per gram), and the solution was cooled to −20° to precipitate the ester of 9,10-dihydroxystearic acid, which was always obtained as a by-product. This was separated by filtration and rejected. The acetone was evaporated from the filtrate, and the residual oil consisted of almost pure hydroxy-ether without further treatment (yield 60 to 95%). This residue was rapidly redistilled, and fractions having the same refractive index were combined for analysis. The results are summarized in Table I.

Preparation of Hydroxy-Ethers from 9,10-Epoxyoctadecanol.—These were prepared and isolated as described under the preparation of hydroxy-ethers from 9,10-epoxystearic acid. The results are summarized in Table II.

Benzoyl Peroxide-Catalyzed Co-polymerization of Allyl 9,10(10,9)-Alloxyhydroxystearate with Vinyl Acetate.—This was conducted as recommended by Guile and Huston,[4] a maximum content of allyl 9,10(10,9)-alloxyhydroxystearate of 40% by weight of the total monomers and 0.5% by weight of benzoyl peroxide being used. Solubility tests on the co-polymers were conducted in acetone at the boiling point and in acetic acid and amyl acetate at 100°. When thin layers of the co-polymers were squeezed between sheets of absorbent paper, no extrusion of oil was observed.

Summary

Twelve hydroxy-ethers have been prepared from 9,10-epoxystearic acid and 9,10-epoxyoctadecanol by reaction with methyl, ethyl, *n*-propyl, *n*-butyl, isobutyl and allyl alcohol, respectively. The high boiling points of the products, their insolubility in water and their stability suggest their possible use as plasticizers.

The benzoyl peroxide-catalyzed co-polymerization of allyl 9,10(10,9)-alloxyhydroxystearate (prepared from 9,10-epoxystearic acid and allyl alcohol) with vinyl acetate has been studied. Over the entire percentage range investigated (allyl 9,10(10,9)-alloxyhydroxystearate content from 1 to 40% by weight of total monomers), insoluble and infusible co-polymers which ranged from hard, glass-like resins to rubbery gels were obtained, thereby indicating that cross-linking probably occurred and that both allyl groups take part in the co-polymerization reaction.

The reaction of 9,10-epoxystearic acid and 9,10-epoxyoctadecanol with *n*-octadecyl alcohol,

phenol and β-chloroallyl alcohol was also investigated. Although pure hydroxy-ethers were not obtained, analytical data indicated that the reaction proceeded mainly in the expected manner.

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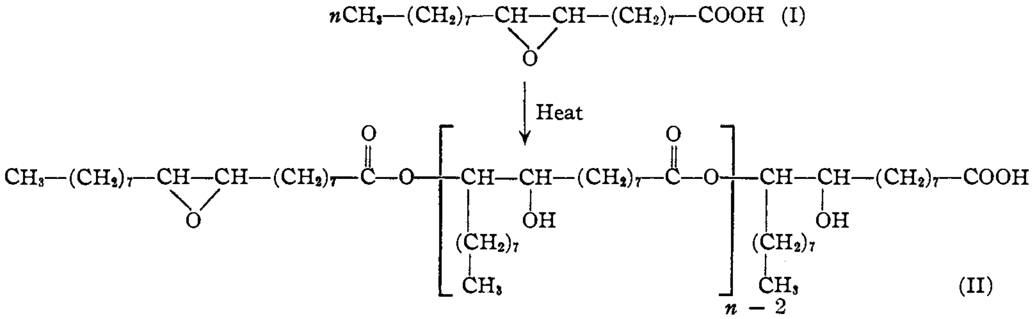
[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY[1]]

Chemistry of Epoxy Compounds. VI.[2] Thermal Polymerization of the Isomeric 9,10-Epoxystearic Acids[1a]

BY DANIEL SWERN, GERALDINE N. BILLEN AND C. ROLAND EDDY

The isomeric 9,10-epoxystearic acids[3,4] (I), m. p. 59.5° and 55.5°, contain two very reactive functional groups, and theoretically they should yield linear polyesters of structure II on thermal polymerization at relatively low temperatures. (Mixtures of isomers would be obtained, since it is equally probable that the oxirane ring would be opened between the oxygen atom and C_9 or C_{10}).



$$n\mathrm{CH_3{-}(CH_2)_7{-}\underbrace{CH{-}CH}_{O}{-}(CH_2)_7{-}COOH}\quad\mathrm{(I)}$$

$$\mathrm{CH_3{-}(CH_2)_7{-}\underbrace{CH{-}CH}_{O}{-}(CH_2)_7{-}\overset{O}{\overset{\|}{C}}{-}O{-}\left[\underset{\underset{CH_3}{|}}{\underset{(CH_2)_7}{\underset{|}{CH}}}{-}\underset{OH}{\underset{|}{CH}}{-}(CH_2)_7{-}\overset{O}{\overset{\|}{C}}{-}O\right]_{n-2}{-}\underset{\underset{CH_3}{|}}{\underset{(CH_2)_7}{\underset{|}{CH}}}{-}\underset{OH}{\underset{|}{CH}}{-}(CH_2)_7{-}COOH}\quad\mathrm{(II)}$$

Since no product of reaction would be eliminated in their formation and since the molecular formula of the recurring unit would be identical with that of the monomer, they would resemble addition polymers, but on hydrolysis they would yield a monomer whose molecular formula is not identical with that of the recurring unit, and in this respect they would resemble condensation polymers.[5] This interesting point, coupled with the fact that convenient methods for the laboratory preparation of the isomeric 9,10-epoxystearic acids in a high degree of purity were available,[3,4] prompted us to study the quantitative thermal polymerization of these compounds.

A limited amount of work on the thermal polymerization of the 9,10-epoxystearic acids has been published,[6] but the starting materials were apparently impure and, in general, higher temperatures than necessary were employed, thereby encouraging side reactions.

Experimental

Starting Materials.—The isomeric 9,10-epoxystearic acids, m. p. 59.5° and 55.5°, were prepared from pure oleic and elaidic acids, respectively, by epoxidation with peracetic or perbenzoic acids.[3,4] *Anal.* Calcd. for $C_{18}H_{34}O_3$: neutralization equivalent, 298.5; oxirane oxygen,[6,7] 5.36. Found: neutralization equivalent, 297.5–299.5; oxirane oxygen, 5.32–5.37.

Polymerization Procedures.—Approximately 5-g. portions of the 9,10-epoxystearic acids were weighed into a series of test-tubes. The tubes were flushed with nitrogen, tightly stoppered and immersed in a constant temperature oil-bath which maintained the desired temperature to ±0.2°. Fifteen minutes was allowed for the establishment of temperature equilibrium before polymerization times were counted. At selected time intervals, a tube was removed from the oil-bath and rapidly cooled to room temperature. The required analytical information was usually obtained within twenty-four hours.

Analytical Procedures.—Acid numbers were determined by means of 0.1 *N* aqueous sodium hydroxide on 0.15–0.30 g. of sample dissolved in neutralized 95% ethanol, phenolphthalein being employed as indicator. Oxirane oxygen was determined by the modified method of Nicolet and Poulter.[6,7] Carbonyl oxygen analyses were conducted by the method described by Leithe,[8] except that a *p*H meter was employed to determine the end-point.

Discussion

The course of the polymerization of 9,10-epoxystearic acid, m. p. 59.5°, at 65°, 75° and 85° is shown in Tables I, II and III, and that of its isomer, m. p. 55.5°, at 75°, 100° and 120° is shown in Tables IV, V and VI. The rate of disappearance of the oxirane and carboxyl groups is plotted in

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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.

[1a] This paper was presented at the meeting-in-miniature of the Philadelphia section of the American Chemical Society held in Philadelphia, Pa., Jan. 22, 1948.

[2] For the previous paper in this series, see THIS JOURNAL, **70**, 1226 (1948).

[3] Swern, Findley and Scanlan, *ibid.*, **66**, 1925 (1944).

[4] Findley, Swern and Scanlan, *ibid.*, **67**, 412 (1945).

[5] Carothers, *ibid.*, **51**, 2548 (1929).

[6] Nicolet and Poulter *ibid.*, **52**, 1186 (1930).

[7] Swern, Findley, Billen and Scanlan, *Anal. Chem.*, **19**, 414 (1947).

[8] Leithe, *Fette u. Seifen*, **45**, 615 (1938).