acid (95.5%) to oleic acid.[5] The sulfated product was hydrolyzed with alcoholic potassium hydroxide, reacidified with dilute sulfuric acid, and converted to methyl esters. The yield was 86.2%. These esters were distilled under reduced pressure through a twelve-inch Vigreux column. The methyl monohydroxystearate fraction (yield, 34.9% of theoretical), which distilled at 170°, and a pressure of 0.22 mm., solidified to a white crystalline material having the following properties: melting point, 29–31°; iodine value, 2.3; acid value, 2.6; saponification value, 179.4 (theoretical, 178.4); hydroxyl, 4.88% (theoretical, 5.41%).

Oxidation.—The methyl monohydroxystearate (70 g.) was oxidized by the method described by Hall and Reid[6] using 280 cc. of concentrated nitric acid and 0.07 g. of ammonium vanadate (*meta*). Subsequent steam distillation yielded two main fractions, a volatile portion containing most of the monobasic acids and a non-volatile portion containing the dibasic acids and the longer-chain monobasic acids. Each of these fractions was further divided into water-soluble and water-insoluble portions.

All of these fractions were examined and evidence was found for the presence of considerable quantities of short chain monobasic and dibasic acids, but these could conceivably have been formed by oxidative degradation. Consequently only the results obtained by the detailed examination of the non-volatile, water-insoluble portion are presented.

Non-volatile, Water-insoluble Portion.—The solid acids were filtered from the cold solution and washed, yielding 34.5 g. of air-dried solid. This was converted to the methyl esters, and distilled at 1.5–2 mm. Six fractions were taken. Data regarding the recovery of the fractions and their analyses are shown in Table I. Comparison of saponification equivalents with molecular weights obtained by the cryoscopic method indicates that the composition of the higher boiling fractions was quite different from that of the lower boiling fractions. For example, fraction I was essentially monobasic, whereas fractions V and VI were composed almost completely of dibasic material. Since fraction I consisted almost exclusively of monobasic esters derived from acids having an average chain length of nearly 10 carbon atoms, it seems reasonable to assume that fractions III and IV contained appreciable amounts of monobasic acids having a chain length above 10 carbon atoms.

The data indicate that fractions V and VI consisted almost exclusively of dibasic acids having a chain length of about 14 to 16 carbon atoms. This was confirmed by the isolation of the dimethyl ester of 1,14-tetradecanedicarboxylic acid from fraction VI. After two crystallizations from petroleum ether, 4.9 g. of this fraction yielded 1.8 g. of a white crystalline solid, m. p. 49.5–50.3°. The dimethyl ester of 1,14-tetradecanedicarboxylic acid is reported to melt at 51.6°.[7] *Anal.* Calcd. for $C_{18}H_{34}O_4$: C, 68.74; H, 10.89; mol. wt., 314.4. Found: C, 69.06; H, 10.81; saponification equivalent, 157.2, corresponding to a mol. wt. of 314.4.

The close agreement of the saponification equivalent and cryoscopic molecular weight of fraction I indicates that this material is the corresponding methyl ester of a C_{10} monocarboxylic acid. The refractive index, n^{20}_{D} 1.4268, of this fraction plotted on a curve for the normal methyl esters of the acetic acid series gives a value in close agreement with the number of carbon atoms determined by saponification equivalent and cryoscopic molecular weight.

The intermediate fractions, II, III and IV are evidently mixtures of methyl esters of mono- and dicarboxylic acids, corresponding to monocarboxylic acids of 10 carbon atoms or higher and dicarboxylic acids of 13 carbon atoms or lower. The distillation temperature and the values for saponification equivalents and cryoscopic molecular weights of these fractions support this statement. Attempts to separate the fractions further by crystallization were not successful.

Summary

Hydroxy acids resulting from the sulfation and subsequent hydrolysis of oleic acid were oxidized with nitric acid. Esters of dibasic acids having more than 10 carbon atoms were found by fractionation of the methyl esters of the steam-non-volatile, water-insoluble portion. The dimethyl ester of 1,14-tetradecanedicarboxylic acid was isolated and identified. Esters of monobasic acids longer than decanoic appeared to be present. The sulfation of oleic acid leads not only to 9- and 10-hydroxystearic acids but also to other isomeric hydroxy acids.

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(5) Complete details of the sulfation procedure are described in a paper now in preparation on the sulfation of oleic and linoleic acids.

(6) W. P. Hall and E. E. Reid, THIS JOURNAL, 65, 1468 (1943).

(7) P. Chuit, *Helv. Chim. Acta*, 9, 264–278 (1926).

PHILADELPHIA, PA.

RECEIVED JULY 5, 1944

[CONTRIBUTION FROM THE EASTERN REGIONAL RESEARCH LABORATORY,[1] PHILADELPHIA, PENNSYLVANIA]

Epoxidation of Oleic Acid, Methyl Oleate and Oleyl Alcohol with Perbenzoic Acid

BY DANIEL SWERN, THOMAS W. FINDLEY AND JOHN T. SCANLAN

The best procedure available for the preparation of 9,10-epoxystearic acid is the reaction of oleic acid with perbenzoic acid.[1a] The perbenzoic acid is usually prepared from benzoyl peroxide, which is not only expensive but inconvenient to use for the preparation of large quantities of perbenzoic acid in the laboratory. Search of the literature revealed a more promising method, namely, the preparation of perbenzoic acid by air or oxygen oxidation of benzaldehyde. Jorissen and his co-workers[2] prepared perbenzoic acid on a small scale in 63% yield by the air or oxygen oxidation of benzaldehyde. Raymond,[3] in a study of the effect of various unsaturated compounds on the inhibition of oxidation of benzaldehyde, demonstrated that pure oleic acid dissolved in a large excess of benzaldehyde could be oxidized by oxygen in the presence of ultraviolet light to form 9,10-epoxystearic acid in good yield. Perbenzoic acid was undoubtedly the oxidizing agent although it was not actually isolated.

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(1) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, United States Department of Agriculture. Article not copyrighted.

(1a) Bauer and Bähr *J. prakt. Chem.*, 122, 201 (1929).

(2) Jorissen and van der Beek, *Rec. trav. chim.*, 45, 245 (1926); 46, 42 (1927); van der Beek, *ibid.*, 47, 286 (1928).

(3) Raymond, *J. chim. phys.*, 28, 480 (1931).

The present investigation was undertaken for the purpose of developing a feasible large-scale laboratory procedure for the preparation of epoxy compounds from oleic acid, methyl oleate and oleyl alcohol by improvements of Raymond's technique. A set of conditions was determined for the oxidation of oleic acid in which air could be employed instead of oxygen and in which the molar ratio of benzaldehyde to oleic acid was reduced to 10:1. Since our oxidation was conducted in acetone solution, the mixture was homogeneous throughout (no precipitation of benzoic acid) and the 9,10-epoxystearic acid could be readily isolated by cooling the reaction mixture.

Since lower ratios of benzaldehyde to oleic acid were unsatisfactory by the modified Raymond procedure, perbenzoic acid was prepared essentially by Jorissen and van der Beek's method, modified to permit large-scale preparation of perbenzoic acid. In this way, only three moles of benzaldehyde was required for each mole of unsaturated compound oxidized to epoxy compound. Of the total benzaldehyde employed, 25–30% was readily recovered unchanged; 35–40% was recovered as benzoic acid.

No reference to the preparation of 9,10-epoxyoctadecanol could be found in the literature. This compound, prepared from oleyl alcohol, was a white, odorless solid, m. p. 54–54.5°, which crystallized from acetone in lustrous plates. It readily formed a chlorohydrin, m. p. 61–62°, by reaction with hydrogen chloride in dry ether. 9,10-Dihydroxyoctadecanol was prepared from this epoxy alcohol by heating it in glacial acetic acid at 100° for two hours and saponifying the acetoxyhydroxy compound obtained. Over-all yields of 9,10-dihydroxyoctadecanol were about 90% on the basis of the epoxy compound and about 80% on the basis of the oleyl alcohol.

Furfural was unsatisfactory as a substitute for benzaldehyde.

Experimental

Starting Materials.—Oleic acid, methyl oleate and oleyl alcohol were prepared from commercial materials.[4] The benzaldehyde was Eastman Kodak Company purest grade and was used without further treatment. The acteone was A. C. S. analytical reagent grade.

Coöxidation of Oleic Acid and Benzaldehyde.—In a two-liter three-neck Pyrex flask equipped with a thermometer, a reflux condenser cooled with solid carbon dioxide, and two fritted-glass discs, 426 g. (4.0 moles) of benzaldehyde and 120.3 g. of oleic acid of 95% purity (0.4 mole) were dissolved in 730 ml. of acetone. A constant stream of dry air was passed through the solution by means of the fritted-glass discs while it was exposed to radiation from two 125-watt mercury-vapor lamps. The reaction temperature was maintained between 25 and 35° by directing a strong current of air on the reaction vessel. The reaction was stopped after eight hours when it was found that the rate of peroxide formation had increased considerably, indicating that little, if any, peroxide was being consumed in the oxidation. The solution was cooled to −50° and filtered on a pre-cooled, jacketed Buchner funnel. The product was washed once with cold acetone. The crude 9,10-epoxystearic acid (purity, 92%), a white powder with a benzaldehyde-like odor, weighed 106 g. Crystallization from acetone at −20° (10 ml. acetone/gram) yielded 84 g. of 9,10-epoxystearic acid (70% yield), m. p. 53.5–56°. This product was actually the high-melting isomer (m. p. 59.5°), but when prepared by this method it always contained sufficient impurities to depress its melting point below that of the low-melting isomer (m. p. 55.5°). Its identity was established by alkaline hydrolysis in 75% yield to 9,10-dihydroxystearic acid, m. p. 92–93°.

Anal. Calcd. for $C_{18}H_{34}O_3$: acid no., 188.0; epoxy oxygen, 5.36. Found: acid no., 189.0; epoxy oxygen, 5.35.

Preparation of Perbenzoic Acid from Benzaldehyde.—In a five-liter, three-neck, Pyrex flask, equipped with a thermometer and two fritted-glass discs, 518.5 g. of benzaldehyde (4.89 moles) was dissolved in 4000 ml. of acetone. The flask was immersed in an ice-bath and irradiated with three 125-watt, mercury-vapor lamps while a constant stream of dry air was passed through the solution for twenty-five hours (reaction temperature, 5–10°). The peroxide content of the solution was determined at frequent intervals; after about twenty-five hours the rate of peroxide formation decreased considerably. At the end of this period 3700 ml. of solution containing 1.9 moles of active oxygen was obtained. The yield of peroxide (calculated as perbenzoic acid) from benzaldehyde was about 40%.

Epoxidation of Oleic Acid.—75.7 grams of oleic acid of 92% purity (0.25 mole) was dissolved in 700 ml. of perbenzoic acid solution (0.36 mole of active oxygen) at 0–5°. The temperature rose fairly rapidly to about 35°. After standing for forty hours at room temperature (25°), the solution was cooled to −50° and filtered, and the precipitate was washed once with cold acetone. The crude 9,10-epoxystearic acid (purity, 89%), a white powder with a benzaldehyde-like odor, weighed 74 g. Two crystallizations of this product from acetone (10 ml. acetone/gram) at −25° yielded 47 g. of 9,10-epoxystearic acid (63% yield), m. p. 59.5–59.8°.[5]

Anal. Calcd. for $C_{18}H_{34}O_3$: acid no., 188.0; epoxy oxygen, 5.36. Found: acid no., 188.0; epoxy oxygen, 5.33.

Epoxidation of Methyl Oleate.—As described for oleic acid, 139.5 g. of methyl oleate of 95% purity (0.45 mole) was oxidized with 1000 ml. of perbenzoic acid solution (0.51 mole active oxygen). The solution was cooled to −60° and filtered, and the precipitate was washed once with cold acetone. The product obtained after removal of the occluded acetone was a pale yellow oil (purity, 92%) with a benzaldehyde-like odor. It weighed 125 g. Crystallization of this product from acetone (10 ml. acetone/gram) at −50° yielded 95 g. of colorless, odorless, methyl 9,10-epoxystearate (67% yield), m. p. 15–16.5°.

Anal. Calcd. for $C_{19}H_{36}O_3$: saponification no., 179.5; epoxy oxygen, 5.12. Found: sapn. no., 181.0; epoxy oxygen, 5.08.

Epoxidation of Oleyl Alcohol.—As described for oleic acid, 274 g. of oleyl alcohol of 98% purity (1 mole) was oxidized with 3140 ml. of perbenzoic acid solution (1.15 moles active oxygen). The solution was cooled to −25° and filtered, and the precipitate was washed once with cold acetone. The crude 9,10-epoxyoctadecanol (purity, 99%), a white crystalline solid, m. p. 53.8–55.5°, with a benzaldehyde-like odor, weighed 247 g. (85% yield). Crystallization of this product from acetone (5 ml./gram) at 0–5° yielded 211 g. of 9,10-epoxyoctadecanol (74% yield), m. p. 54.0–54.5°.

Anal. Calcd. for $C_{18}H_{36}O_2$: epoxy oxygen, 5.62; C, 76.0; H, 12.8. Found: epoxy oxygen, 5.65; C, 75.7; H, 12.4.

Preparation of Chlorohydroxyoctadecanol.—Five grams of 9,10-epoxyoctadecanol, m. p. 54–54.5°, was dissolved in 200 ml. of 0.17 *N* dry hydrogen chloride in anhydrous ether (100% excess of hydrogen chloride). After standing for two and one-half hours at room temperature, the ether was evaporated. The semi-solid residue in the flask (6.0 g.) was recrystallized twice from acetone (4 ml./gram) at

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(4) Swern, Knight and Findley, *Oil and Soap*, **21**, 133 (1944).

(5) Ellis, *Biochem. J.*, **30**, 753 (1936).

0–5°. Three grams of chlorohydroxyoctadecanols, m. p. 61–62°, was obtained (55% yield).

Anal. Calcd. for $C_{18}H_{37}O_2Cl$: C, 67.4; H, 11.6; Cl, 11.0; OH, 10.6. Found: C, 67.5; H, 11.8; Cl, 10.5; OH, 10.2.

Preparation of 9,10-Dihydroxyoctadecanol (1,9,10-Octadecanetriol).—Five grams of 9,10-epoxyoctadecanol, m. p. 54–54.5°, was heated for two hours at 100° with 100 ml. of glacial acetic acid. The solution was then poured into 1000 ml. of water, and the upper semi-solid layer was refluxed with 0.2 *N* alcoholic potassium hydroxide for forty-five minutes. The alkaline solution was poured into 1000 ml. of cold water, and the precipitate was filtered off and washed free of alkali. A yield of 4.7 g. of 9,10-dihydroxyoctadecanol, m. p. 84.5–86°, was obtained.

Determination of Epoxy Oxygen.—The method of Nicolet and Poulter[6] was employed, using a 0.2 *N* solution of dry hydrogen chloride in anhydrous ether and a two-hour reaction time.

Determination of Peroxides.—Wheeler's method[7] was employed.

Summary

1. A large-scale laboratory procedure for the preparation of perbenzoic acid, based upon the work of Jorissen,[2] has been developed. Benzaldehyde in acetone solution was oxidized with air in the presence of ultraviolet radiation to yield perbenzoic acid in 40–45% yield. This solution was satisfactory for the epoxidation of oleic acid, methyl oleate, and oleyl alcohol.

2. Raymond's method[3] for the coöxidation of oleic acid and benzaldehyde has been improved. The mole ratio of benzaldehyde to oleic acid has been reduced from 27:1 to 10:1, and the isolation of 9,10-epoxystearic acid has been simplified.

3. 9,10-Epoxyoctadecánol, m. p., 54–54.5°, and a mixture of 9,10- and 10,9-chlorhydroxyoctadecanols, m. p 61–62°, were prepared for the first time.

PHILADELPHIA, PA. RECEIVED AUGUST 31, 1944

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(6) Nicolet and Poulter, THIS JOURNAL, **52**, 1186 (1930).

(7) Wheeler, *Oil and Soap*, **9**, 89 (1932).

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF WINTHROP CHEMICAL CO., INC.]

Catalytic Hydrogenation of Pyridinyl and Quinolinyl Esters of Sulfonic Acids

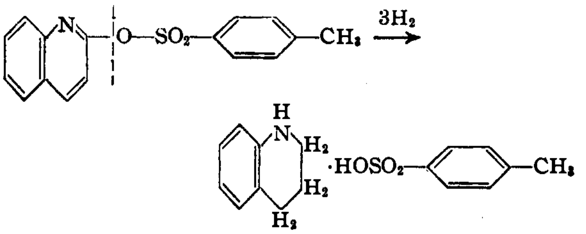
BY CHESTER J. CAVALLITO AND THEODORE H. HASKELL

The authors have recently[1] described the catalytic hydrogenation of pyridinols, quinolinols and their esters with aromatic carboxylic acids. The aromatic sulfonic acid esters have now been prepared and it has been found that some types behave differently on hydrogenation than the analogous carboxylic acid esters.

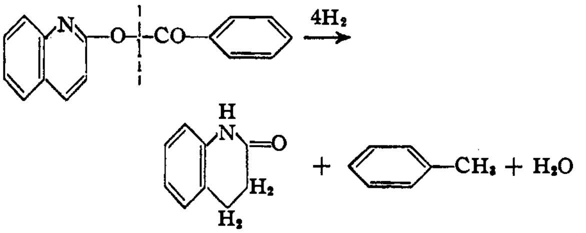
Hydrogenation was carried out in a dioxane solution at 55° with a palladium catalyst as described in the previous publication. The pyridinol and quinolinol esters of *p*-toluenesulfonic acid served as type compounds in this investigation.

Catalytic hydrogenation of the 5-, 6-, 7- and 8-(*p*-toluenesulfonoxy)-quinolines yielded primarily the corresponding 1,2,3,4-tetrahydro derivatives. It will be recalled that the 5-, 6- and 7-benzoxyquinolines behave in a similar manner. Whereas 8-benzoxyquinoline after hydrogenation undergoes rearrangement to N-benzoyl-1,2,3,4-tetrahydro-8-quinolinol, 8-(*p*-toluenesulfonoxy)-1,2,3,4-tetrahydroquinoline was stable and did not undergo rearrangement. This is similar to the behavior of the *ortho* aminophenyl esters.[2]

Hydrogenation of the 2- and 3-(*p*-toluenesulfonoxy)-quinolines yielded the same end-product, a water-soluble crystalline compound which was identified as the 1,2,3,4-tetrahydroquinoline salt of *p*-toluenesulfonic acid. Three molar equivalents of hydrogen were absorbed during the hydrogenation.



This behavior is considerably different from that of 2-benzoxyquinoline which underwent cleavage at a different point[1]



or that of 3-benzoxyquinoline which yielded the corresponding 1,2,3,4-tetrahydro derivative.

The 4-(*p*-toluenesulfonoxy)-quinoline was too unstable to allow isolation in sufficiently pure form for hydrogenation.

With the observation that hydrogenolysis and hydrogenation reactions could proceed to yield the water soluble tetrahydroquinoline salt of *p*-toluenesulfonic acid, closer examination of the reduction products from the 5-, 6-, 7- and 8-esters showed the presence of small amounts of the water soluble salt along with the tetrahydro-

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(1) Cavallito and Haskell, THIS JOURNAL, **66**, 1166 (1944).

(2) Raiford and Shelton, *ibid.*, **65**, 2048 (1943).