123

Epoxidation of Unsaturated Fatty Materials with Peracetic Acid in Glacial Acetic Acid Solution

By Thomas W. Findley, Daniel Swern and John T. Scanlan

The oxidation of unsaturated fatty materials with peracetic acid in acetic acid solution has been studied by numerous investigators.[2,3,4,5,6] The oxidation products were usually mixtures of hydroxy-acetoxy compounds, which on saponification gave good yields of glycols. In two instances, however, epoxy compounds were isolated. Smit[4] reported the conversion of linoleic acid to diepoxystearic acid, but the yields were not given. King,[6] in a study of the oxidation of oleic and elaidic acids with hydrogen peroxide in acetic acid (peracetic acid was the oxidizing agent), was unable to obtain the high-melting 9,10-epoxystearic acid, m. p. 59.5°, from oleic acid and obtained only 25–30% yields of the low-melting 9,10-epoxystearic acid, m. p. 55.5°, from elaidic acid. However, by using peracetic acid in an inert solvent, such as chloroform or ether, other investigators[7a,b] have obtained good yields of epoxy compounds from cyclohexene and other cyclic olefins. It may be assumed, therefore, that peracetic acid functions as an oxidizing agent in exactly the same way as perbenzoic acid to yield epoxy compounds, but that in acetic acid solution the epoxy ring is opened and mixtures of hydroxy-acetoxy compounds are obtained. This would appear to be a serious drawback to the preparation of epoxy compounds from olefins by peracetic acid oxidation, since peracetic acid is most conveniently prepared and used in acetic acid.

In studying the rate of ring opening of the high-melting 9,10-epoxystearic acid by acetic acid, we have found that at 25° ring opening occurs to the extent of about 1% per hour, whereas at 65 to 100°, the ring is opened quantitatively in one to four hours King[6] has demonstrated that the high-melting 9,10-epoxystearic acid, when dissolved in acetic acid for one week at room temperature, was almost completely converted to hydroxy-acetoxystearic acids, whereas under somewhat similar conditions, the low-melting 9,10-epoxystearic acid, from elaidic acid, was much more stable, only about 50% being converted to hydroxy-acetoxystearic acids. It is not surprising, therefore, that epoxy compounds were usually not isolated by previous workers who investigated peracetic acid oxidations of olefins in acetic acid solution, since in most cases the reactions were conducted for long periods of time or at elevated temperatures. Either of these conditions would cause the ring to open.

By following the course of the oxidative reaction of peracetic acid with a wide variety of unsaturated fatty materials in glacial acetic acid, it was observed that the reaction was usually complete within two to four hours at room temperature when 1.1–1.2 moles of peracetic acid per mole of double bond were used, 85–95% of the theoretical quantity of peracetic acid being consumed. Upon dilution of the reaction mixtures with water, the products were readily isolated in good yield by filtration or by separation of the oil obtained. The products consisted mainly of epoxy compounds and contained small amounts of unreacted double bond and hydroxy-acetoxy compounds. This reaction is quite general and, when properly controlled, affords a simple and convenient method for the preparation of large quantities of epoxy compounds. It is not necessary to use the peracetic acid in an inert solvent.

The epoxidation reaction was successfully applied to oleic acid, elaidic acid, methyl oleate, methyl 10,11-hendecenoate (methyl undecylenate), methyl ricinoleate, oleyl alcohol, glyceryl trioleate, lard oil, neatsfoot oil, castor oil, olive oil, peanut oil, rapeseed oil, cottonseed oil, corn oil,

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

(2) Boëseken and Belinfante, *Rec. trav. chim.*, **45**, 914 (1926); Boëseken, Smit and Gaster, *Proc. Acad. Sci. Amsterdam*, **32**, 377 (1929).

(3) Hilditch, *J. Chem. Soc.*, 1828 (1926); Hilditch and Lea, *ibid.*, 1576 (1928).

(4) Smit, *Rec. trav. chim.*, **49**, 675, 686, 691 (1930).

(5) Scanlan and Swern, This Journal, **62**, 2305, 2309 (1940).

(6) King, *J. Chem. Soc.*, 37 (1943).

(7) (a) Arbusow and Michailow, *J prakt. Chem.*, **127**, 1, 92 (1930). (b) Boëseken and Schneider, *ibid.*, **131**, 285 (1931).

soybean oil, tobacco-seed oil, menhaden oil, linseed oil and perilla oil.

The peracetic acid solution was prepared in 60–80% yield by treating 26–30% hydrogen peroxide with acetic anhydride, without a catalyst.[4] This method is convenient for the laboratory preparation of peracetic acid. Other methods described in recent patents[8,9] may be more adaptable to industrial application.

The purity of the epoxy compounds was determined by the method of Nicolet and Poulter,[10] which is based on the quantitative addition of hydrogen chloride to the oxirane ring $\left(\begin{array}{c}-CH-CH-\\ \diagdown O \diagup\end{array}\right)$ by means of a solution of anhydrous hydrogen chloride in ether. With carefully purified epoxy compounds, prepared by perbenzoic acid oxidation, this method was found to give results within 1% of the theoretical value. Nicolet and Poulter have shown that 9,10-dihydroxystearic acid and 10-ketostearic acid do not interfere. We have found that the reagent does not react with either the double bond or the primary alcohol group of oleyl alcohol nor with the aliphatic, cyclic ether groups in dioxane and tetrahydrofurfuryl alcohol. This specificity of reaction was especially valuable when pure epoxy compounds were not isolated, as in the epoxidation of triglycerides, and it was important to know what percentage of the iodine-number reduction was due to the formation of oxirane derivatives.

The decrease in ratio of oxirane ring formation to total oxidation (measured by iodine-number reduction) observed with triglycerides of increasing iodine number (Table I) is undoubtedly due to the presence of the more highly unsaturated constituents. An explanation of this phenomenon would be of considerable interest and further work is being done with this as the objective.

Experimental

Preparation of Peracetic Acid Solution.[11]—A well-stirred mixture consisting of 4500 g. of acetic anhydride (97.5%) and 1000 g. of hydrogen peroxide (26–30%) was maintained at 40° with external cooling. Samples were withdrawn at intervals, and the peracetic acid content of the solution was determined by Smit's method[4] for the determination of peracetc acid in the presenec of hydrogen peroxide and diacetyl peroxide. After the mixture reacted about four hours at 40° and stood overnight at room temperature, the concentration of peracetic acid reached a maximum (about 1 *M*, 60–80% yield). This solution is quite stable and may be stored for several weeks at 5° without appreciable reduction in the peracetic acid content.

The peracetic acid also may be prepared by Smit's method, in which a sulfuric acid catalyst is used.[4] This reaction, however, may be extremely vigorous and exothermic, owing to the rapid rate of hydrolysis of acetic anhydride in the presence of sulfuric acid. In this preparation, we prefer to add the acetic anhydride–sulfuric acid solution dropwise to the well-stirred hydrogen peroxide solution at 40°, instead of at 0 to 10° as recommended by Smit, and to maintain the temperature at 40° by means of a cooling bath as well as by adjustment of the rate of addition of the acetic anhydride–sulfuric acid solution. The peracetic acid prepared in this way has the advantage over the peracetic acid prepared in the absence of a catalyst in that the acetyl peroxide concentration is often exceedingly low. Before this peracetic acid solution can be used for epoxidation, however, it must be treated with a slight excess of sodium acetate in acetic acid solution to neutralize the sulfuric acid present. Sulfuric acid catalyzes the opening of the oxirane ring by acetic acid.

Epoxidation of Oleic Acid.—To 2000 ml. of a well-stirred solution of peracetic acid (2.04 moles) at 20°, 500 g., (1.7 moles) of 95% oleic acid[12] (iodine number, 86.0) was added slowly. The temperature was maintained below 25° by external cooling. After three hours, about 96% of the calculated quantity of peracetic acid had been consumed. The reaction mixture was poured into several liters of cold water and allowed to stand until the granular solid had risen to the surface. The lower aqueous acetic acid layer was siphoned off, and the solid was washed twice with cold water and filtered. After being air-dried, the crude 9,10-epoxystearic acid (m. p. 52.5–55.0°) weighed 521 g.; composition, 90% epoxystearic acid, 3.5% unreacted double bond, and 6.5% hydroxy-acetoxy compounds and saturated acids originally present. Crystallization from Skellysolve B (3 ml./g.) at 5–10° yielded 410 g. (82% yield) of slightly impure 9,10-epoxystearic acid; m. p. 55.5–56.5°. Calcd. for epoxy oxygen: 5.36; found, 5.10. The correct melting point of 59–59.5°[6] was obtained after three additional crystallizations from Skellysolve B, acetone and methanol, respectively.

Epoxidation of Elaidic Acid.—To the semi-solid mixture of 93.1 g. (0.32 mole) of elaidic acid[13] (iodine number, 87.6; m. p. 44–46°) and 100 ml. of glacial acetic acid at 20°, 380 ml. of peracetic acid solution (0.385 mole) was added. After three hours at 20–25°, about 90% of the calculated quantity of peracetic acid had been consumed. The product was isolated as described under epoxidation of oleic acid. After being air-dried, the crude 9,10-epoxystearic acid (m. p. 53.5–55.5°) weighed 96 g. Composition: 95% epoxystearic acid, 3% unreacted double bond, and 2% hydroxy-acetoxy compounds and saturated acids originally present. Two crystallizations from acetone (3.3 ml./g.) at 0–5° yielded 68 g. (71% yield) of pure 9,10-epoxystearic acid, m. p. 55.0–55.5° [lit., 55.5°[6]]. Calcd. for epoxy oxygen, 5.36; found, 5.35.

Epoxidation of Methyl Oleate.—Ten grams (0.0333 mole) of methyl oleate[12] (iodine number, 84.5) was oxidized for three hours at 20–25° with 32 ml. of peracetic acid solution (0.0366 mole). The solution was poured into cold water and the oil obtained was dissolved in ether. The ether solution was washed acid-free, dried over anhydrous calcium sulfate, and filtered. Evaporation of the ether yielded 9.7 g. of crude methyl 9,10-epoxystearate, a colorless liquid. Composition: 89% methyl epoxystearate, 7% unreacted double bond, and 4% hydroxy-acetoxy compounds and saturated esters originally present. Crystallization from acetone (4 ml./g.) at −20° yielded 4.7 g. (45% yield) of fairly pure methyl 9,10-epoxystearate, m. p. 15–16.5° [lit., 18°[10]]. Calcd. for epoxy oxygen, 5.12; found, 4.93.

Epoxidation of Methyl 10,11-Hendecenoate (Methyl Undecylenate).—Methyl 10,11-hendecenoate was prepared by fractional distillation of the Eastman Kodak Co. Practical grade. It was a colorless oil, b. p. 112–114° (7 mm.); iodine number, 123.3. Fifty grams of methyl 10,11-hendecenoate (0.243 mole of double bond) was oxidized for twenty-four hours at 20–25° with 351 ml. of peracetic acid solution (0.365 mole), at which time 93% of the calculated quantity of peracetic acid had been consumed. The solution was poured into cold water and the oil obtained was washed acid-free, dried over anhydrous calcium sulfate, and filtered. The crude methyl 10,11-

(8) U. S. Patent 2,314,385 (1943).

(9) German Patent 730,116 (1942).

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

(11) All preparations of peracetic acid should be conducted behind a safety shield since the reaction proceeds occasionally with uncontrollable violence.

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

(13) Bertram, *Chem. Weekblad*, **33**, 3 (1936).

epoxyhendecanoate was a pale-yellow oil which weighed 47 g. Composition: 70% methyl epoxyhendecanoate, 6% unreacted double bond, and 24% hydroxy-acetoxy compounds and saturated esters originally present. Fractional distillation through a short Vigreux column yielded 22 g. of fairly pure methyl 10,11-epoxyhendecanoate, a colorless oil, boiling range 87–93° (0.02 mm.).

Anal.	Epoxy oxygen, %	Saponification equivalent
Calcd.	7.48	214.2
Found	7.28	212.0

Epoxidation of Methyl Ricinoleate.—Ten grams (0.0332 mole) of methyl ricinoleate[14] (iodine number, 81.7) was oxidized for three hours at 20–25° with 31 ml. of peracetic acid solution (0.0365 mole), and the product was isolated as described under epoxidation of methyl oleate. Evaporation of the ether yielded 8.7 g. of crude methyl 9,10-epoxy-12-hydroxystearate, a colorless liquid.

Anal.	Iodine number	Epoxy oxygen, %
Calcd.	0	4.87
Found	7.6	4.15

Composition: 85% methyl epoxyhydroxystearate, 9% unreacted double bond, and 6% hydroxy-acetoxy compounds. It was not further purified.

Epoxidation of Oleyl Alcohol.—Ten grams (0.036 mole) of oleyl alcohol[12] (iodine number, 92.6), was oxidized for three hours at 20–25° with 35 ml. of peracetic acid solution (0.0401 mole). The product was isolated as described under epoxidation of oleic acid. The white, granular precipitate of crude 9,10-epoxyoctadecanol (m. p. 50–53.5°) weighed 10.5 g. Composition: 88% epoxyoctadecanol, 7% unreacted double bond, and 5% hydroxy-acetoxy compounds and saturated alcohols originally present. Crystallization from acetone (4 ml./g.) at 5° yielded 8.4 g. (80% yield) of fairly pure 9,10-epoxyoctadecanol, m. p. 52.5–54° [lit., 54°[15]]. Calcd. for epoxy oxygen, 5.62; found, 5.45.

Epoxidized Oils.—Thirteen oils and glyceryl trioleate were epoxidized. Since the procedure employed was the same for all the materials, the experimental details are given for lard oil only. The products from triolein and olive oil were white, semi-solids; the others were viscous, yellow oils.

Epoxidation of Lard Oil.—Ten grams of lard oil (iodine number, 63.8) was mixed with 29 ml. of 1.04 *M* peracetic acid solution (20% excess) and maintained at 20° for about four hours with occasional stirring. The solution was poured into cold water and the oil which separated was dissolved in ether. The ether solution was washed acid-free, dried over anhydrous calcium sulfate, and filtered. Evaporation of the ether yielded 9.6 g. of viscous yellow oil. Iodine number, 11.5. Epoxy (oxirane) oxygen, 2.87%.

A summary of the results obtained with the various oils is shown in Table I.

TABLE I

SUMMARY OF RESULTS OBTAINED IN THE EPOXIDATION OF TRIGLYCERIDES WITH PERACETIC ACID IN ACETIC ACID SOLUTION

Starting Materials				Final Products		
		Peracetic acid solution				
Oil	Iodine number	Vol. per 10 g. of oil, ml.	Concn. moles/kg.	Iodine number	% Yield of oxirane derivatives[a]	Ratio of oxirane ring formation to total oxidation
Triolein	83.7	32	1.14	6.8	86	0.93
Lard oil	63.8	29	1.04	11.5	74	.90
Neatsfoot	75.5	34.3	1.04	11.8	77	.91
Olive	85.2	38.8	1.04	10.5	81	.92
Peanut	99.8	45.3	1.04	13.8	75	.87
Cottonseed	114.5	52	1.04	18.4	71	.84
Corn	125.4	57	1.04	18.9	71	.83
Soybean	129.4	59	1.04	14.3	67	.74
Tobacco seed	142.6	115	0.753	4.0	73	.75
Menhaden	180.4	118	0.90	16.1	57	.62
Linseed	182.5	83	1.04	26.0	66	.77
Perilla	207.1	94	1.04	28.4	64	.73
Castor	84.3	32	1.14	8.4	73	.80
Rapeseed	101.6	42.6	1.04	13.8	71	.82

[a] $\% \text{ Yield} = \dfrac{\% \text{ Epoxy (Oxirane) Oxygen Found}}{\% \text{ Epoxy (Oxirane) Oxygen Calcd.}} \times 100$

Determination of Epoxy (Oxirane) Oxygen.—The method of Nicolet and Poulter[10] was employed, using a 0.2 *N* solution of dry hydrogen chloride in anhydrous ether and a two-hour reaction time.

Summary

1. A procedure has been described for the preparation of epoxy compounds in good yields from a wide variety of unsaturated fatty materials by oxidation under mild temperature conditions for short periods of time with peracetic acid in glacial acetic acid solution.

2. Epoxidized oils, a new class of chemical reaction products from triglycerides, have been prepared and isolated for the first time.

(14) Kass and Radlove, THIS JOURNAL, **64**, 2253 (1942).

(15) Swern, Findley and Scanlan, *ibid.*, **66**, 1925 (1944).