A Modified Peracid Process for Making . . .

Epoxy Compounds from Unsaturated Fatty Acid Esters

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EPOXY or oxirane compounds have attracted considerable interest and assumed commercial importance in recent years. Included among these have been the epoxy fatty acids and their esters. The preparation of epoxy compounds by the reaction of an unsaturated substance with an organic peracid was first demonstrated by Prileschajew (*5*) in 1909 utilizing perbenzoic acid. Other peracids that have since been employed include monoperphthalic acid, percamphoric acid, and peracetic acid. Swern and associates (*1*, *7*, *8*) studied the reaction of olefins and unsaturated fatty acids and esters with aliphatic peracids. They have described efficient procedures for the preparation of the corresponding glycol and epoxy derivatives, utilizing performic acid and peracetic acid, respectively. Their peracetic acid was an anhydrous product prepared from acetic anhydride and hydrogen peroxide. More recently, peracetic acid solutions (*2*), based on the reaction of a concentrated hydrogen peroxide and glacial acetic acid in the presence of an acid catalyst, have come into wide use. These solutions are equilibrium mixtures of hydrogen peroxide, acetic acid, water, and peracetic acid—i.e.,

$$H_2O_2 + HOAC \underset{}{\overset{H^+}{\rightleftharpoons}} HOOAC + H_2O$$

They have been applied to the epoxidation of a wide variety of olefinic compounds.

Generally, epoxidation reactions with a peracid are carried out in the absence of strong mineral acids. In using the preformed peracetic acid described, it is therefore necessary to buffer the solution, prior to use, by addition of sodium acetate or dilute alkali. Under these conditions of use, little further formation of peracetic acid from the hydrogen peroxide occurs during the epoxidation reaction, and essentially only the peracetic acid fraction of the equilibrium mixture is constructively consumed. This results in reduced epoxidation reaction efficiencies when calculated on the basis of the total active oxygen content (hydrogen peroxide plus peracetic acid) of the oxidant.

By contrast, hydroxylation reactions with a peracid have been conducted utilizing an in situ technique (*7*), whereby hydrogen peroxide is added to an aliphatic acid solution of olefinic material in the presence of a mineral acid catalyst. (When using formic acid the catalyst may be omitted.) Peracetic acid formation and reaction with the double bond occur simultaneously leading to the eventual consumption of a stoichiometric amount of hydrogen peroxide.

Despite the recognized advantages of an in situ process, comparatively little progress has been made in adapting it to an epoxidation with a peracid. In the main, this stems from the extreme difficulty of setting up reaction conditions favorable to the required peracid formation which, in turn, would not destroy the desired epoxy product. The very same conditions that favor peracid formation—high molar ratio of aliphatic acid to hydrogen peroxide, high temperature, high acidity, and long reaction times—are known to be deleterious to the survival of an epoxy compound. To date, the only published method for an in situ epoxidation of unsaturated fatty chemicals is described in the patent literature (*4*); it employs formic acid and hydrogen peroxide.

A successful procedure for the in situ epoxidation of unsaturated fatty acid esters has been developed in these laboratories employing acetic acid and hydrogen peroxide. Hydrogen peroxide is added to an acetic acid solution of the unsaturated fatty acid ester, in the presence of sulfuric acid, at 60° to 70° C. Optimum yields of epoxy compound were formed with a molar ratio of 0.5 acetic acid to 1 of ethylenic unsaturation in the presence of an inert solvent—e.g., benzene; 2% sulfuric acid on the weight of acetic acid–hydrogen peroxide mixture was employed as a catalyst. Reaction time varied from 8 to 14 hours. Shorter reaction times (5 to 6 hours) were obtained with use of excess hydrogen peroxide. Products with low iodine numbers, of particular importance for many end uses of these products, could readily be obtained. Yields varied from approximately 70 to 85% epoxy ester (Table I).

High molar ratios of acetic acid to hydrogen peroxide caused excessive ring opening with resulting low yields of the desired epoxy ester (Table II). Reaction rates at low temperatures were slow. Inert solvents, such as benzene, were beneficial in depressing the ring opening of the epoxy compound.

Boron trifluoride, nitric acid, *p*-toluenesulfonic acid, ethanesulfonic acid, and a strong acid cationic exchange resin (sulfonic type) are catalysts for peracid formation (*3*). The cationic exchange resin and ethanesulfonic acid gave approximately equivalent results when substituted for sulfuric acid in the in situ epoxidation reaction. The other catalysts gave low yields of epoxy product.

TABLE I. ANALYTICAL DATA FOR EPOXY FATTY ACID ESTERS

Epoxy Ester[a]	Oxirane Oxygen, %	Yield Epoxy Ester, %	Iodine No.	Reacted, %
Methyl epoxy stearate	3.9	72	5	95
Propyl epoxy stearate	3.8	79	7	91
Butyl epoxy stearate	3.7	82	2	97
Butyl epoxy ester of cottonseed fatty acids	3.1	77	3	96
Epoxy cottonseed oil[b]	4.7	82	12	87
Butyl epoxy ester of soybean fatty acids	3.6	72	8	91
Epoxy soybean oil[b]	5.8	74	9	93
Epoxy soybean oil[c]	6.0	77	3	98

[a] Except where noted otherwise, 10% excess hydrogen peroxide was employed for the epoxidation reaction.
[b] 4% excess hydrogen peroxide used.
[c] 20% excess hydrogen peroxide used.

TABLE II. EFFECT OF VARIOUS MOLAR RATIOS OF ACETIC ACID TO UNSATURATED ESTER ON EPOXY ESTER YIELD

(Butyl oleate dissolved in benzene was epoxidized with H_2O_2 and acetic acid, in the presence of a 2% sulfuric acid catalyst, at 55–65° C.)

Molar Ratio Acetic Acid–Unsaturated Ester[a]	Reaction Time, Hr.	Oxirane Oxygen, %	Yield Epoxy Ester, %	Iodine No.	Reacted, %
15:1	3	0.0	0.0	4	95
1.7:1	8	0.2	4.4	8	89
0.5:1	13	3.6	80.0	5	93

[a] Moles of unsaturated ester refer to moles of ethylenic unsaturation present in the ester.

TABLE III. INFLUENCE OF TEMPERATURE ON REACTION EFFICIENCY

(Butyl oleate dissolved in benzene was epoxidized with H_2O_2 and acetic acid in the presence of a 2% sulfuric acid catalyst)

Temp. Range, ° C.	Oxirane Oxygen, %	Yield Epoxy Ester, %	Iodine No.	Reacted, %
25–30[a]	2.3	51	33	55
35–40[b]	2.7	60	26	65
60–65[b]	3.6	80	5	93

[a] Reaction time, 24 hours.
[b] Reaction time, 12 to 13 hours.

TABLE IV. EFFECT OF KNOWN PERACID FORMATION CATALYSTS ON EPOXY ESTER YIELD

(Butyl oleate dissolved in benzene was epoxidized with H_2O_2 and acetic acid in the presence of a 1% catalyst at 60° to 65° C.)

Catalyst	Oxirane Oxygen, %	Yield Epoxy Ester, %	Iodine No.	Reacted, %
H_2SO_4	3.6	79	6	92
HNO_3	...	...	...	53
BF_3. $(C_2H_5)_2O$	1.6	37	10	86
p-Toluenesulfonic acid	...	...	...	57
Ethanesulfonic acid[a]	3.5	78	6	92
Ion exchange resin[a] (Amberlite IR-120)	3.8	84	4	94

[a] 4% catalyst used. (Equivalent performance was obtained with strong cation exchange resins—e.g., Dowex 50X and Permutit Q.)

TABLE V. INFLUENCE OF SOLVENT ON EPOXY ESTER YIELDS

(Butyl oleate was epoxidized with H_2O_2 and acetic acid in the presence of a 2% sulfuric acid catalyst)

Solvent[a]	Oxirane Oxygen, %	Yield Epoxy Ester, %	Iodine No.	Reacted, %
Benzene	3.6	80	5	93
Hexane	3.6	80	5	93
No solvent	3.4	76	9	89

[a] Solvent, 20% on weight of unsaturated ester.

EXPERIMENTAL

Spencer Kellogg and Sons supplied the alkali-refined superior grade soybean oil (Iodine No. 135). The cottonseed oil (Iodine No. 97) was the Puritan grade of Procter and Gamble. Methyl oleate (Iodine No. 90) and propyl oleate (Iodine No. 80) were obtained from Emery Industries.

Butyl oleate (Iodine No. 74) was prepared by the esterification of butyl alcohol with a distilled oleic acid (Emery 210) in the presence of 1% sulfuric acid, water washed, alkali refined, and vacuum distilled. The butyl ester of cottonseed fatty acids (Iodine No. 67) was similarly prepared from butyl alcohol and distilled cottonseed fatty acids from W. C. Hardesty Co. (Iodine No. 90). The butyl ester of soybean fatty acids (Iodine No. 88) was prepared by the esterification of soybean fatty acids (from W. C. Hardesty Co.) with butyl alcohol. Both esters were distilled. The hydrogen peroxide was the 50% commercial product of the Buffalo Electro-Chemical Co.

Oxirane oxygen was determined by the modified method of Swern and associates (*9*). The Hanus method (*6*) was employed for iodine number determinations.

EPOXIDATION OF BUTYL OLEATE. The in situ epoxidation of butyl oleate is typical for monohydric alcohol esters of unsaturated fatty acids:

One hundred grams of butyl oleate (Iodine No. 74, equivalent to 0.29 mole of ethylenic unsaturation) was weighed into a three-necked flask equipped with a reflux condenser, thermometer, and mechanical stirrer. Twenty grams of benzene and 9.2 grams of glacial acetic acid (0.153 mole) were added to the butyl oleate, and the mixture was warmed to 50° C. 1.24 grams of 50% sulfuric acid was added, and then 21.78 grams of 50% hydrogen peroxide (0.32 mole) was slowly added over a 2-hour period. The temperature was then raised to 60° C. and controlled between 60° and 65° C. until the reaction was complete as determined by periodic titrations of reaction mixture for unreacted hydrogen peroxide. Approximately 5 to 10% remained unreacted at the end of 12 to 14 hours. The reaction mixture was poured into a separatory funnel and the aqueous layer drawn off. The oil layer was washed with successive portions of warm water (40° to 45° C.) until acetic acid free. The benzene and traces of water were removed in a vacuum stripping column at 60° to 70° C. and 5 to 10 mm.

The resultant product showed the following analysis:

Oxirane oxygen, %	
Theoretical	4.5
Analysis	3.7
Iodine No.	2

EPOXIDATION OF SOYBEAN OIL. The in situ epoxidation of soybean oil is representative of the procedure used for triglycerides:

Two hundred grams of soybean oil (Iodine No. 135, equivalent to 1.06 moles of ethylenic unsaturation), 40.0 grams of benzene, 33.0 grams of glacial acetic acid (0.55 mole), and 4.28 grams of 50% sulfuric acid were mixed in a three-necked flask equipped with a reflux condenser, thermometer, and mechanical stirrer; 74.88 grams of 50% hydrogen peroxide (1.1 moles) was then slowly added over a 2-hour period at 50° C. The reaction mixture was warmed to 60° C. and maintained at that temperature for 12 to 14 hours. The oil layer was washed and stripped of benzene and water as already outlined.

The resultant product showed the following analysis:

Oxirane oxygen, %	
Theoretical	7.8
Analysis	5.8
Iodine No.	9

When following the same procedure, by employing 1.27 moles of 50% hydrogen peroxide, the reaction was completed in 6 hours and gave a product as follows:

Oxirane oxygen, %	6.0
Iodine No.	3

EFFECT OF REACTION VARIABLES ON EPOXY ESTER YIELDS

The influence of molar ratio of acetic acid to ethylenic unsaturation of the ester, temperature, catalyst, and solvent were studied using the in situ epoxidation of butyl oleate as a model. The procedure, except for the variables noted, was the same as detailed above.

Molar ratios of acetic acid to ethylenic unsaturation in the fatty acid ester were varied from 0.5:1.0 to 15:1. Results are shown in Table II.

The influence of temperature on reaction efficiency was studied at 25° to 30°, 30° to 35°, and 50° to 65° C., with the results that are recorded in Table III.

Boron trifluoride–ether complex, nitric acid, *p*-toluenesulfonic acid, ethanesulfonic acid, and a strong acid cationic exchange resin (Amberlite IR-120) were evaluated as substitutes for the standard sulfuric acid catalyst with results as indicated in Table IV.

The influence of solvent on epoxy ester yield was studied utilizing benzene and *n*-hexane with the results noted in Table V.

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