Epoxidation of Alkyl Esters of 12,13-Epoxyoleic Acids and Evaluation of the Diepoxides as Plasticizers for Poly(vinyl Chloride)

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Abstract

Methyl, propyl, butyl, isobutyl, hexyl, cyclohexyl, octyl and 2-ethylhexyl esters of 9,10:12,13-diepoxystearic acid were prepared by peracetic acid oxidation of the corresponding esters of 12,13-epoxyoleic acid. Using a 60 mole per cent excess of peracid at 30 C in chloroform as solvent, epoxidation was complete in 5 hr. A small aqueous phase was observed in the reaction mixture which decreases the amount of peracid available for reaction. This is due to the water and H_2O_2 present in the commercial peracetic acid used. Thin-layer and gas chromatographic analysis showed that the diepoxides formed as isomers. These did not react quantitatively with HBr by the Durbetaki method. Isomers of methyl and propyl diepoxy esters were separated by crystallization.

The methyl (pure and mixed isomers), isobutyl, 2-ethylhexyl and octyl (all mixed isomers) diepoxy esters were evaluated as plasticizers of poly(vinyl chloride). Delta values showed that these esters have good compatibility. Results are compared with commercial epoxidized soybean oil control. These diepoxy esters show better low temperature properties and have higher migration and volatility values than the control. They are more efficient plasticizers than the control. The liquid isomer of the methyl ester, as well as the 2-ethylhexyl ester, should be useful as primary plasticizers and in combination with other plasticizers as plasticizer stabilizers.

Introduction

THE EPOXIDATION OF unsaturated fatty acids with peracetic acid has been studied by Swern et al. (1,2). Recently it has been shown that the epoxidation of methyl 12,13-epoxyoleate yields a product consisting of two isomers of methyl 9,10:12,13-diepoxystearate (3). Since a series of esters of 12,13-epoxyoleic acid had already been prepared (4) and evaluated as plasticizers for poly(vinyl chloride) (5) at this laboratory, it was considered expedient to prepare the diepoxides of these esters to determine if two isomers were formed and to evaluate their performance as plasticizers for poly(vinyl chloride).

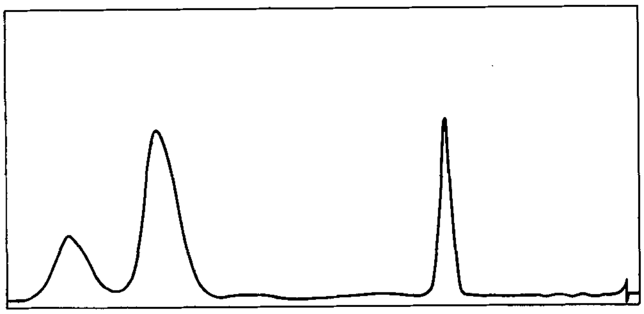

FIG. 1. GLC curve of retention time vs. recorder response. First peak, starting at right of figure, is propyl 12,13-epoxyoleate (retention time (t) = 8.7 min). Second and third peaks are the solid (t = 22.1 min) and liquid (t = 26.4 min) isomers, respectively, of propyl 9,10:12,13-diepoxystearate.

Experimental Procedures

Materials

Methyl, propyl, butyl, isobutyl, hexyl, cyclohexyl, octyl and 2-ethylhexyl esters of 12,13-epoxyoleic acid were prepared as described previously (4), and were 98% to 99.9% pure. The commercial peracetic acid in acetic acid (37–42%) used in the epoxidations was analyzed by the following modification of the method recommended by Greenspan and MacKellar (6): a 0.2 to 0.3 g sample of peracetic acid solution was diluted with 50 ml of 4N H_2SO_4. Three milliliters of a saturated KI solution was added and the resulting solution was titrated rapidly with 0.1 N $Na_2S_2O_3$ to a starch-iodide end point in order to determine the combined amount of peracetic acid and hydrogen peroxide in the sample. Hydrogen peroxide was determined by adding to a second sample of peracetic acid solution (0.4 to 0.5 g) 50 ml of cold (0 C) 2N H_2SO_4 and three drops of ferroin indicator (*o*-phenanthroline ferrous sulfate complex), placing the solution in an ice bath and titrating with 0.1 N $Ce(SO_4)_2$ solution to the disappearance of the salmon color of the indicator. The amount of peracetic acid was determined by difference. Analogous methods employing $KMNO_4$ instead of $Ce(SO_4)_2$ have been described (3,7).

Epoxidation of Esters

The following procedure describing the epoxidation of *n*-hexyl 12,13-epoxyoleate was found satisfactory for the epoxidation of the esters. A quantity of peracetic acid solution containing 0.1018 moles of peracetic acid in which 2 g of sodium acetate trihydrate had been dissolved was added to 25 g (0.0629 moles) of *n*-hexyl 12,13-epoxyoleate in 200 ml of chloroform. The addition was carried out over a period of 2 to 5 min with vigorous stirring while the reaction temperature was maintained at 30 C. After addition was complete, the reaction mixture was stirred for 5 hr at 30 C and then terminated by the addition of cold 20% aqueous (w/v) Na_2SO_3 solution. After washing once with 250 ml of 2% aqueous (w/v) $NaHCO_3$ solution and three times with 250 ml of water, the chloroform solution was dried with anhydrous sodium sulfate and the solvent removed on a rotary evaporator.

Analytical Procedures

TLC and GLC were used to determine the amount of unreacted ester and the relative amounts of the isomers in the product. The GLC analyses were

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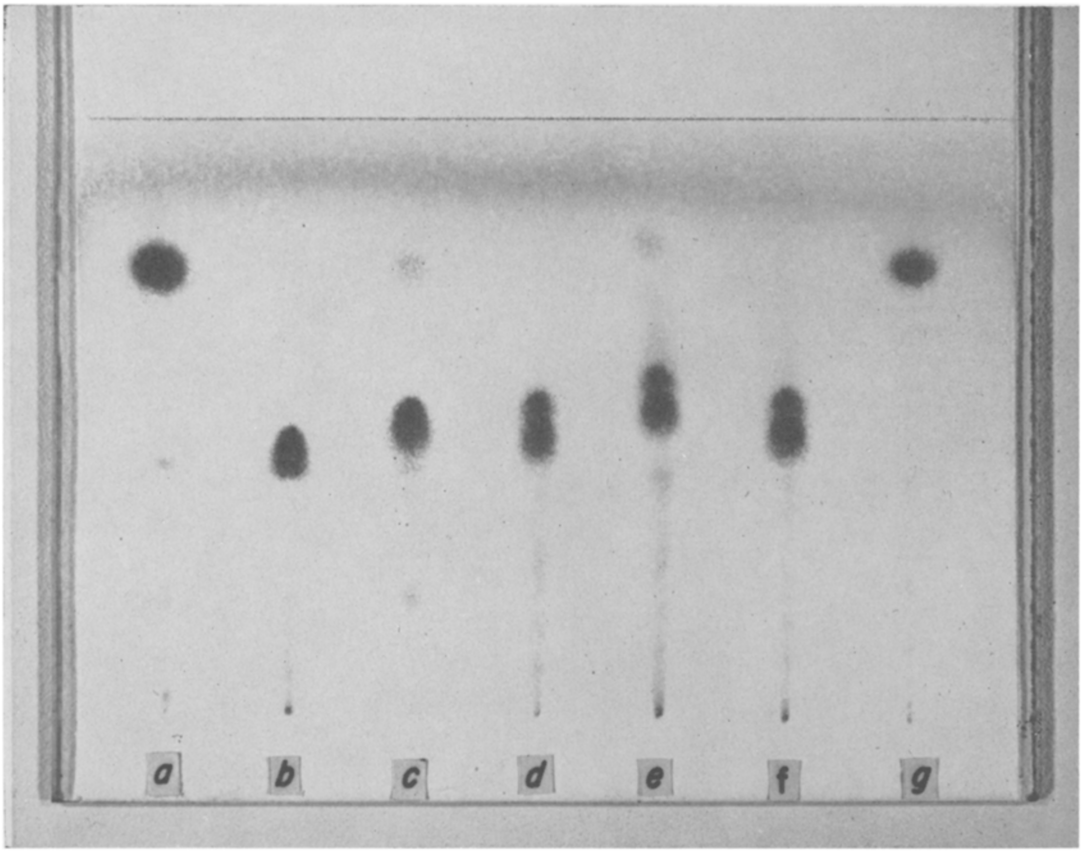

FIG. 2. TLC of mono- and diepoxides using a solvent system of Skellysolve F-diethyl ether-acetic acid (6:40:2, v/v/v) at 15 C. a. propyl 12,13-epoxyoleate; b. solid isomer of propyl 9,10:12,13-diepoxystearate; c. liquid isomer of propyl 9,10:12,13-diepoxystearate; d. isomers of isobutyl 9,10:12,13-diepoxystearate; e. isomers of 2-ethylhexyl 9,10:12,13-diepoxystearate; f. isomers of *n*-hexyl 9,10:12,13-diepoxystearate; g. *n*-hexyl 12,13-epoxyoleate.

performed as described by Maerker et al. (3) for the isomers of methyl 9,10:12,13-diepoxystearate. A typical GLC curve is shown in Fig. 1.

TLC was performed on Silica Gel G plates (250 μ) which were activated for 2 hr at 120 C before use. Mono- and diepoxides were eluted with solvent systems of diethyl ether-Skellysolve F-acetic acid in proportions varying from 60:40:2 to 30:70:2 (v/v/v). Best separation of the isomers was obtained by maintaining the temperature at 15 C. Figure 2 shows a TLC of isomers of several of the esters by this method. Iodine numbers (Wijs) and oxirane oxygen values (8) were also determined. Results of the analyses are shown in Table I. Isomer 1, which appears as the first diepoxide peak on the GLC, is the higher melting (solid) diepoxy isomer and isomer 2 is the lower melting isomer.

Separation of Isomers

The product obtained from the epoxidation of methyl epoxyoleate was crystallized from methanol (1:10, w/v) at 5 C. A second crop of crystals was collected at −20 C. The two crops were combined and dissolved in Skellysolve F (1:8, w/v) and the solution cooled to −65 C to obtain a crystalline product (oxirane oxygen 8.47%, 99+% solid isomer by GLC). Recrystallization of this product from Skellysolve F (1:8, w/v) at 0 C yielded pure solid isomer of methyl 9,10:12,13-diepoxystearate (oxirane oxygen 8.83%, 99.9% pure by GLC). The filtrates from the original two crops of crystals were combined and concentrated and the concentrate was crystallized from methanol (1:7.5, w/v) at −20 C. After removing the solvent, the filtrate from the methanol crystallization was crystallized from Skellysolve F at −20 C. The precipitate was filtered off and the filtrate was crystallized at −35 C to yield the liquid isomer of methyl 9,10:12,13-diepoxystearate, purity: 92% by GLC, oxirane oxygen, 8.19%. This 92% pure isomer was crystallized at −25 C from Skellysolve F (1:15, w/v) to yield

TABLE I
Analysis of Mixtures of Epoxidation Products

Diepoxy ester	Oxirane oxygen %		Iodine value		Weight % (GLC)		
	Found	Theory	Found	Theory	Unreacted monoepoxide	Isomer 1	Isomer 2
Methyl	8.67	9.80	0.26	0.0	00.0	64.5	34.8
Propyl	8.03	9.02	......	0.0	1.2	65.2	33.6
Butyl	7.39	8.66	......	0.0	21.6	56.5	21.6
Isobutyl	7.45	8.66	0.29	0.0	00.6	65.1	34.3
Hexyl	6.76	8.05	0.09	0.0			
Cyclohexyl	7.26	8.90	......	0.0			
Octyl	6.43	7.52	3.09	0.0			
2-Ethylhexyl	6.38	7.52	2.64	0.0			
Control							
Commercial epoxidized soybean oil	6.60	......	2.70	....			

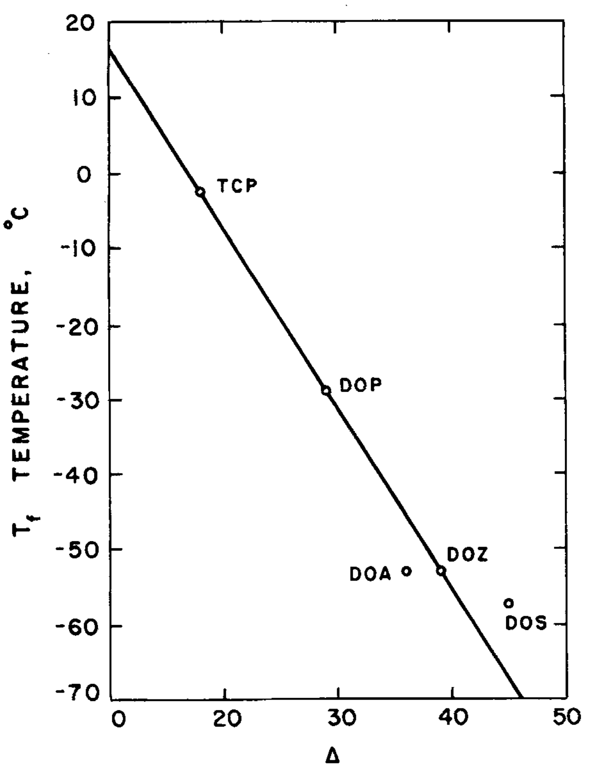

FIG. 3. Torsional stiffness T_f temperature versus compatibility number Δ.

liquid isomer of methyl 9,10:12,13-diepoxystearate, purity: 94.5% by GLC, oxirane oxygen 8.28%.

Epoxidation of propyl 12,13-epoxyoleate yielded a mixture containing two isomers of propyl 9,10:12,13-diepoxystearate and some unreacted propyl epoxyoleate. By a series of low temperature crystallizations solid diepoxy isomer with an oxirane oxygen value of 8.10% and a purity of 99% by GLC was obtained. An oil was recovered from the filtrates of this product which had the following GLC analysis: 48% propyl 12,13-epoxyoleate, 1% solid diepoxy isomer and 50% liquid diepoxy isomer. Elution of this mixture on an Absorbosil column with mixtures of diethyl ether-Skellysolve F ranging from 1% to 33% ether by volume yielded a liquid diepoxy isomer that was 93% pure by GLC.

Plasticizer Evaluation

A three component formulation of resin, plasticizer and stabilizer was used. The formulation was Geon 101, PVC poly(vinyl chloride) resin 65% by weight of the total mix, plasticizer 34%, and Mark M 1%, a barium-cadmium complex stabilizer. No attempt was made to determine the stabilizer system necessary to obtain maximum heat and light stability. The formulations were milled at 160 C for 7 min. Samples were molded from the milled sheets at 160 C in the manner previously reported (9). The molded samples were stored and conditioned at 23 C and 50% relative humidity.

It has become common practice to measure the stiffness in torsion as a function of temperature. This method was introduced by Clash and Berg (10) who empirically selected an apparent modulus of elasticity of 135,000 psi as the borderline between a rigid and nonrigid material. This is a value called the flex temperature T_f. The temperature at which the stiffness of 10,000 psi is observed is called T_4 and is significant because of its equivalence to the temperature of maximum slope. The difference between the T_f and T_4 values Δ is a measure of the compatibility of the plasticizer (11). The compatibility number Δ is a value which constantly increases with decreasing T_f temperature. Figure 3 shows a plot of T_f versus Δ values for TCP (tricresyl phosphate), DOP (di-2-ethylhexyl phthalate), DOZ (di-2-ethylhexyl azelate). The straight line plot defines the limits of compatibility at the T_f temperatures along the plot. A plasticizer with a compatibility number plotted above (to the right of) the line will be less compatible than the standards and, conversely, a plasticizer plotted below (to the left of) the line will be more compatible than these standards.

Determination of tensile strength, 100% modulus, per cent elongation, volatility and migration, were obtained by previously reported methods (12). Volatility values were obtained with silicic acid at 23 C.

Discussion

Using the procedure described above for the epoxidation of *n*-hexyl 12,13-epoxyoleate the reaction was complete in 5 hr. After addition of peracetic acid was completed, a small aqueous phase separated from the reaction mixture. The aqueous phase was found to contain about 8% of the total peracetic acid added, thus decreasing the amount of peracetic acid available for reaction. Consequently, a 40 mole per cent excess of peracid resulted in incomplete epoxidation after 5 hr, and the amount of peracetic acid added was increased to a 60 mole per cent excess to insure a sufficient concentration of peracid for the reaction to be complete in 5 hr. The partitioning of peracetic acid mentioned above has been explored in a kinetic study of the epoxidation of methyl 12,13-diepoxyoleate (13). It can be seen from Table I that in the cases where a 40 mole per cent excess of peracid was used, i.e., for the epoxidation of the butyl, cyclohexyl, octyl and 2-ethylhexyl monoepoxy esters, the reaction was not complete after 5 hr. Methyl and propyl monoepoxy esters were reacted with a 40 mole per cent excess of peracid for 6.5 hr, and isobutyl and hexyl monoepoxy esters were reacted with a 60 mole per cent excess for 5 hr.

The existence of two isomers of each of the diepoxy esters was confirmed by TLC. TLC also indicated that in all cases more of the higher melting isomer was formed in the reaction. This was confirmed by GLC for the isomers of the four diepoxy esters which were chromatographed. Chromatographic behavior of the esters was influenced by the chain length of the attached alcohol groups. The longer the alcohol group, the longer the GLC retention time, and the shorter the TLC elution time. Hexyl, cyclohexyl, octyl and 2-ethylhexyl diepoxy esters were found to have peak widths too large and retention times too long for quantitative GLC analysis.

GLC analysis indicated the presence of unknown substances in some of the reaction products. These unknown compounds are probably products of the attack by the acetic acid in the reaction mixture on the oxirane rings of the mono- or diepoxides or both.

Oxirane oxygen values of the diepoxides were consistently lower than theoretical values. There is evidence that one of the isomers does not react quantitatively with HBr (3,14). Maerker suggests that this is due to the tendency for the diepoxides to undergo acid-catalyzed rearrangement (3).

TABLE II

Mechanical Properties of Molded PVC Sheets

Ester	Torsional stiffness		Compatibility	Tensile strength	Elongation	100% Modulus	Migration wt loss	Volatility wt loss
	Temp. T_f	C T_4	Δ	psi	%	psi	%	%
Methyl diepoxide mixed 1 and 2 isomers	—37	—15	22	2425	310	625	13.8	3.1
Methyl diepoxide solid isomer	—35	—11	24	2425	250	700	11.6	3.0
Methyl diepoxide liquid isomer	—37	—19	18	2200	330	590	11.4	2.5
Isobutyl diepoxide mixed	—35	—14	21	2725	310	790	9.8	1.1
2-Ethylhexyl diepoxide, mixed	—36	—10	26	2600	220	1150	8.5	0.7
Octyl diepoxide mixed	—40	— 6	34	2890	320	1255	9.0	1.0
Control								
Commercial epoxidized soybean oil	—19	6	25	2750	360	1320	1.4	0.4

All the materials investigated as plasticizers were found to be compatible at the 34% level during processing. No exudation was observed after molding and conditioning the samples overnight. A dry white surface exudate was noted after two days on the solid isomer of the methyl diepoxide plasticized sample and after eight months on the specimen containing the mixed methyl isomers. The octyl-containing specimen showed a dry exudate after three months. The liquid isomer of the methyl ester and the 2-ethylhexyl ester have shown no signs of exudation after more than two years.

The physical properties of the molded PVC sheets are tabulated in Table II. Also included is a commercial epoxidized soybean oil control.

These materials show better low temperature properties than the control and are more efficient plasticizers. Delta values show that all materials are compatible. The migration and volatility values are higher than the control values. However, higher values are to be expected in conjunction with the lower torsional stiffness values.

No heat or light stability tests were made. However, procedures employed to make the test samples indicate good heat stability. The samples which have been exposed to light in the laboratory for more than two years show no apparent visual changes in physical properties.

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