

maintained at about 0° during and after addition of the sulfuric acid in order to avoid formation of the vinylidene compound at the hydroxyl group. Inasmuch as the reaction would be expected to be slower at this lower temperature, the reaction time was extended to 5 days.

The vinylation of pinonic acid was accomplished by the Reppe procedure using pinonic acid in toluene with zinc pinonate as a catalyst. The yield of crude product, b.p. 115–150°, 1 mm., 393 g., was 80%. Fractionation of the crude product gave colorless vinyl pinonate (Table II), 50% yield, and 30% yield of a slight amber colored material. The second material was not completely characterized. However, it absorbed two equivalents of hydrogen and had an empirical formula, $C_{14}H_{20}O_3$. Polymers from bulk polymerization with benzoyl peroxide had the appearance of polystyrene foam and were insoluble in common solvents indicating crosslinking had taken place. Obviously two acetylene molecules had reacted with one molecule of pinonic acid. Vinylation of 3-(1-methyl-1-hydroxyethyl)heptanedioic acid γ -lactone by the same procedure was unsuccessful.

Characterization of cis-dl-vinyl pinolate. A 10-g. sample of freshly distilled vinyl pinolate was reduced over 5% palladium on carbon. Alcohol (50 ml., 95%) was used as the solvent and catalyst concentration was about 1%. After the reduction was completed, the solution was filtered and evaporated. Vapor phase chromatography showed the residue to contain ethyl pinolate with minor peaks corresponding to impurities in the vinyl pinolate. Five grams of the material was hydrolyzed by heating on the steam bath for about 4 hr. with excess 6*N* sodium hydroxide. The hydrolysis mixture was extracted with ether to remove the ethanol and the extracted solution was acidified. The acidified solution was extracted with three 15-ml. portions of ether; the ether solution was dried over sodium sulfate, filtered, and evaporated to yield 4.03 g., 91% of crystalline pinolic acid, m.p. 94.8–96.4. Mixed melting point with an

equal quantity of 103–104° pinolic acid was 99–102.5°. Allyl and propyl esters also allowed good recovery of pinolic acid on hydrolysis and chromatographed samples showed even less impurities than the ethyl ester.

cis-dl-Ethyl pinonate. *cis-dl*-Pinonic acid (736 g., 4 moles) was placed in a flask with 95% ethanol (1 l., 17 moles), chloroform (1 l.), and *p*-toluenesulfonic acid (20 g.). The mixture was refluxed through a 2 × 20 cm. protruded metal packed column and the water which separated was removed through a liquid decanter. After separation of water ceased, the mixture was cooled, and treated with water until no further phase separation was noted. The chloroform layer was washed with sodium bicarbonate solution until the wash remained basic to *pH* paper and then dried over sodium sulfate. Evaporation and distillation of the residue yielded water-white ethyl pinonate.

The allyl and propyl esters of pinolic acid were prepared by this method. The ethyl ester, however, (probably because of long heating periods necessary to remove the water) is difficult to obtain in pure form if catalyst concentrations as high as this are used. Azeotropic removal of water from a mixture of pinolic acid ethanol and benzene in the absence of added catalyst has produced the purest *cis-dl*-ethyl pinolate although the yield was only about 50%.

Slow dehydration of the pinolic acid esters will take place if heating is continued beyond the time required to evolve one mole of water.

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Synthesis of Some Special Types of Glycidic Esters

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Glycidic esters have been found to undergo an ester exchange reaction with a wide variety of alcohols without concomitant destruction of the epoxide function. This exchange reaction was used for the preparation of certain unsaturated glycidic esters and diepoxides which are not readily obtained by other routes. Di-, tri-, and tetraepoxides containing the glycidic ester grouping have also been prepared by epoxidation of the corresponding unsaturated esters with anhydrous peracetic acid. The relative merits of these methods for the synthesis of glycidic esters are discussed.

A previous paper in this series described the preparation of saturated alcohol esters of α,β -epoxy acids by treatment of the esters of α,β -unsaturated acids with peracetic acid.¹ The present paper deals with the synthesis of some special types of glycidic esters, many of which are new, by methods which include 1) an exchange reaction of epoxy esters with alcohols, 2) an extension of the previously described peracetic acid epoxidation,¹ and 3) a combination of methods 1) and 2). Structural considerations govern the choice of method for the synthesis of a given glycidic ester. Other methods for the preparation of glycidic

esters include the Darzens method² and the treatment of esters of α,β -unsaturated acids with peroxytrifluoroacetic acid.³

Esters of α,β -epoxy acids may be exchanged with alcohols under mild conditions without destruction of the oxirane rings. This appears to be a general reaction which works with saturated and unsaturated alcohols and glycols (Table I). Success with the ester exchange reaction depends on carrying it out under mild conditions (60° or below) in the presence of alcoholates of the alkali and alkaline

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TABLE I
GLYCIDIC ESTER SYNTHESSES BY ESTER INTERCHANGE

Starting Ester	Moles	Alcohol	Moles	Catalyst	Product Ester	B.P., (mm.)	n_D^{20}	Yield, %
Methyl 2,3-epoxybutyrate ^a	1.0	Allyl alcohol	10.0	Na	Allyl 2,3-epoxybutyrate	96-97 (25)	1.4362	37
Methyl 2,3-epoxybutyrate ^a	2.79	Allyl alcohol	16.7	NaOCH ₃	Allyl 2,3-epoxybutyrate	96-98 (25)	1.4362	58
Ethyl 2,3-epoxybutyrate ^b	1.0	Allyl alcohol	10.0	Mg(OCH ₃) ₂	Allyl 2,3-epoxybutyrate ^c	97 (25)	1.4363	68
Ethyl 2,3-epoxybutyrate ^b	1.0	6-Methyl-3-cyclohexenemethanol	3.0	NaOCH ₃	6-Methyl-3-cyclohexenemethyl 2,3-epoxybutyrate ^d	117 (2.5)	1.4718	53
Ethyl 2,3-epoxybutyrate ^b	1.0	4-Pentenol	1.92	NaOCH ₃	4-Pentenyl 2,3-epoxybutyrate ^e	96 (5)	1.4405	33
Ethyl 2,3-epoxy-2-ethylhexanoate ^f	2.0	Allyl alcohol	16.0	NaOCH ₃	Allyl 2,3-epoxy-2-ethylhexanoate ^g	70 (1)	1.4402	80
Ethyl 2,3-epoxy-2-ethylhexanoate ^f	1.0	6-Methyl-3-cyclohexenemethanol	3.0	NaOCH ₃	6-Methyl-3-cyclohexenemethyl 2,3-epoxy-2-ethylhexanoate ^h	144 (2.5)	1.4680	44
Ethyl 2,3-epoxybutyrate ^b	1.0	Cyclohexanol	3.0	NaOCH ₃	Cyclohexyl 2,3-epoxybutyrate ⁱ	96 (3)	1.4575	41
Ethyl 2,3-epoxybutyrate ^b	20	Ethylene glycol	3.74	NaOC ₂ H ₅	Ethylene glycol bis(2,3-epoxy- butyrate) ^j	165 (4)	1.4535-42	45

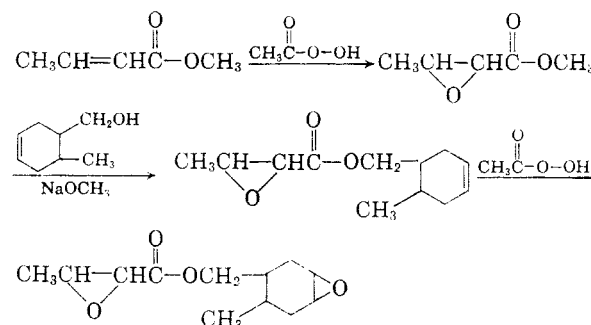
^a B.p. 81-85° at 49 mm., n_D^{20} 1.4150, d_4^{25} 1.075. Analyzed 99% pure by saponification. Identified by comparison of infrared spectrum with that of ethyl 2,3-epoxybutyrate. ¹ Prepared in 61% yield by method of ref. 1 from 3 moles of methyl crotonate and 3.9 moles of peracetic acid at 85-90° for 6 hr. ² See ref. 1. ^c *Anal.*: 100% pure by saponification; 98% pure by epoxide determination by the pyridine hydrochloride method. Infrared absorption spectrum consistent with that expected. Ref. 4 reports b.p. 100-101° at 26 mm. ^d *Anal.*: 99% pure by saponification; 78% pure by epoxide determination. Infrared absorption spectrum consistent with that expected. Ref. 4 reports b.p. 100-101° at 26 mm. ^e *Anal.*: Found C, 68.64, 68.74; H, 8.79, 8.75. Infrared absorption spectrum consistent with that expected with no evidence of other groups or impurities present. ^f *Anal.*: 99% pure by saponification; 69% pure by epoxide determination by pyridine hydrochloride method. Calcd. for C₁₁H₁₈O₃: C, 63.51; H, 8.29. Found: C, 63.63; H, 8.24. Infrared spectrum consistent with that expected. ^g See ref. 1. ^h *Anal.*: 99.6% pure by saponification; 100.2% pure by epoxide determination by addition of HBr. Calcd. for C₁₁H₁₈O₃: C, 66.6; H, 9.08. Found: C, 66.76; H, 9.12. This experiment by Dr. D. L. MacPeck. ⁱ *Anal.*: 100.9% pure by saponification; 51% pure by epoxide determination by pyridine hydrochloride method. Calcd. for C₁₆H₂₆O₃: C, 72.2; H, 9.84. Found: C, 72.79; H, 9.99. ^j *Anal.*: 98% pure by saponification. ^k *Anal.*: 99.8% pure by saponification. Calcd. for C₁₀H₁₆O₆: C, 52.17; H, 6.13. Found: C, 52.31; H, 6.44. A 15% yield of the monocarbonate, hydroxyethyl 2,3-epoxybutyrate, was also obtained.

earth metals. Such catalysts actively promote ester exchange without causing extensive side reactions of the epoxide ring. In contrast, titanium tetrabutylate and aluminum isopropylate are not useful catalysts, as they do not appear to catalyze the exchange reaction except at higher temperatures where the epoxide rings are destroyed. Acidic catalysts, such as mineral acids, boron trifluoride, and aluminum chloride, attack the epoxide ring excessively even under mild conditions.

Many of the unsaturated alcohol esters of glycidic acids are useful epoxy vinyl monomers.^{4,5} We have found the ester exchange method to be a fine and unambiguous synthetic route to these unsaturated esters of glycidic acids (Table I). A saturated alcohol ester of an α,β -unsaturated acid is first epoxidized,¹ and the epoxy ester is then exchanged with an unsaturated alcohol. This procedure avoids several difficulties which are usually encountered in epoxidizing an unsaturated alcohol ester of an α,β -unsaturated acid. For instance, mixtures of monoepoxides or mixtures of monoepoxide and diepoxide may be produced when the epoxidation is not sufficiently selective.⁵ In other cases, where the double bond in the alcohol portion is more easily epoxidized than the double bond in the acid portion of the ester, the double bond in the alcohol portion of the ester is selectively epoxidized. For example, allyl crotonate, when treated with approximately an equimolar amount of peracetic acid, yields glycidyl crotonate instead of allyl 2,3-epoxybutyrate.⁵ Although the selective epoxidation of allyl 2-ethyl-2-hexenoate to the corresponding glycidic ester (e.g., allyl 2,3-epoxy-2-ethylhexanoate) has been reported,⁵ this synthesis is not general, being confined to those esters (usually allyl or vinyl) in which the double bond in the alcohol portion is relatively electron-poor and in which the α,β -double bond in the acid portion is substituted with electron-donating groups.⁶

Di- and polyepoxides constitute an important class of compounds which have widespread use as resin intermediates⁷ and as plasticizers and stabilizers for chlorine-containing resins.⁸ However,

polyepoxides which contain one or more α,β -epoxyacyloxy groups have been very rare. The only diepoxides of which the authors are aware that contain the glycidic ester group are those obtained from the condensation of aromatic dialdehydes or diketones with α -haloesters⁹ via the Darzens method; e.g., dimethyl 3,3'-*p*-phenylenebis(2,3-epoxybutyrate). We have used the ester-exchange method to prepare diepoxides of a different type from those obtained by the Darzens route. This method lends itself readily to the preparation of diepoxides, either through an intermediate unsaturated glycidic ester or directly by an exchange reaction between a glycidic ester and a glycol. In some cases the exchange method offers the only practical route. For example, treatment of 6-methyl-3-cyclohexenemethyl crotonate with peracetic acid gave 3,4-epoxy-6-methylcyclohexanemethyl crotonate,⁵ but further treatment of the monoepoxide resulted only in destruction of most of the epoxy function and a very low yield of diepoxide (Table II). The preparation of 3,4-epoxy-6-methylcyclohexanemethyl 2,3-epoxybutyrate (and many other diepoxy esters) can be accomplished in much better yield by the following reaction sequence in which the ester exchange technique is used:



However, the direct epoxidation method with anhydrous peracetic acid is superior in those cases where there is not too great a disparity in the epoxidation rates of the two unsaturated sites and where neither of the resulting oxirane rings is extremely sensitive to acetic acid under the conditions required for epoxidation (Table II).

In the special case where all of the oxirane rings to be formed are of the glycidic ester type and where the olefinic precursors are highly resistant to epoxidation, the ester exchange method appears to be superior to direct epoxidation. Ethylene glycol bis(2,3-epoxybutyrate) was prepared in 45% yield by exchange of ethylene glycol with ethyl 2,3-epoxybutyrate, while epoxidation of ethylene glycol dicrotonate gave only a 29% yield of the same diglycidic ester (Tables I and II). In both cases the corresponding monoepoxides were also formed. However, suitably substituted α,β -un-

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TABLE II
DIEPOXIDE SYNTHESIS BY ESTER EXCHANGE

Starting ester	Moles	Peracetic Acid Solution, Moles	Reaction		Product	B.P., ° (Mm.)	n_D^{20}	Yield, %	Carbon, %		Hydrogen, %	
			Time, hrs.	Temp., °					Calcd.	Found	Calcd.	Found
Allyl crotonate ^a	1.0	3.14	8	70	2,3-Epoxypropyl 2,3-epoxybutyrate ^b	96-97(1.5)	1.4480	57	53.20	53.90	6.37	6.66
Allyl 2-ethyl-2-hexenoate ^a	2.0	5.0	9	60	2,3-Epoxypropyl 2,3-epoxy-2-ethylhexanoate ^c	114-115(2)	1.4470-1.4478	54	61.66	61.62	8.43	8.58
6-Methyl-3-cyclohexenemethyl 2,3-epoxybutyrate	0.5	0.55	1.75	40	3,4-Epoxy-6-methylcyclohexanemethyl 2,3-epoxybutyrate	142(1)	1.4734	77	63.70	63.64	7.96	7.76
3,4-Epoxy-6-methylcyclohexanemethyl crotonate ^a	1.0	1.2	6	60-80	3,4-Epoxy-6-methylcyclohexanemethyl 2,3-epoxybutyrate	142(1)	1.4734	<10	—	—	—	—
6-Methyl-3-cyclohexenemethyl 2-ethyl-2-hexenoate ^a	1.4	4.2	2.25	65	3,4-Epoxy-6-methylcyclohexanemethyl 2,3-epoxy-2-ethylhexanoate ^e	175-180(4)	1.4696-1.4708	63	68.05	67.72	9.28	9.12
Ethylene glycol dicrotonate ^f	1.0	2.5	12	75	Ethylene glycol bis(2,3-epoxybutyrate) ^g	165(4)	1.4335-1.4350	29	52.17	52.40	6.13	6.44
1,5-Pentanediol bis(2-ethyl-2-hexenoate) ^h	0.284	0.882	3	75	1,5-Pentanediol bis(2,3-epoxy-2-ethylhexanoate)	214-217(2)	1.4540-1.4550	88	65.61	65.90	9.44	9.64
1,1,1-Trimethylolpropane tris(2-ethyl-2-hexenoate) ⁱ	0.48	2.2	7	50-70	1,1,1-Trimethylolpropane tris(2,3-epoxy-2-ethylhexanoate) ^j	Colorless residue	1.4261	>80	64.91	64.51	9.09	9.09
Pentaerythritol tetrakis(2-ethyl-2-hexenoate) ^k	0.50	3.0	5	65	Pentaerythritol tetrakis(2,3-epoxy-2-ethylhexanoate) ^l	Pale yellow residue	1.4696	>80	63.76	62.47	8.68	8.28

^a See ref. 5. ^b Sapon. equiv. found 157.5 (theory 158.2). ^c Sapon. equiv. found 215 (theory 214.2). ^d Prepared in 88% yield by esterification of 6-methyl-3-cyclohexenemethanol with 2-ethyl-2-hexenoic acid; b.p. 145-146° at 3 mm., n_D^{20} 1.4749, 99.9% pure by saponification. ^e Sapon. equiv. found 282 (theory 282.4). ^f Prepared in 52% yield by esterification of ethylene glycol with crotonic acid; b.p. 108-109° at 2 mm., n_D^{20} 1.4653, 101% pure by saponification. ^g Sapon. equiv. found 115.5 (theory 115.1). A 47% yield of the corresponding monoepoxide, ethylene glycol crotonate 2,3-epoxybutyrate, was also obtained. ^h Prepared by T. F. Carruthers in 71% yield by esterification of 1,5-pentandiol with 2-ethyl-2-hexenoic acid; b.p. 169° at 0.75 mm., n_D^{20} 1.4672, d_4^{20} 0.9565, 99% pure by saponification. ⁱ Prepared in 80% yield by esterification of 1,1,1-trimethylolpropane with 2-ethyl-2-hexenoic acid; b.p. range (one-plate column) 195-240° at 3 mm., n_D^{20} 1.4747. ^j *Anal.* Calcd. for $C_{30}H_{50}O_6$: C, 71.0; H, 9.95; sapon. equiv., 168.9. Found: C, 70.1; H, 9.84; sapon. equiv., 171. ^k The infrared spectrum of this compound gave a strong epoxide band (11.1 μ) and no absorption characteristic of residual unsaturation (6.2 μ). There was a very weak band at 2.9 μ indicating a small amount of epoxide ring opening. ^l Prepared as a residue product by esterification of pentaerythritol with an excess of 2-ethyl-2-hexenoic acid. Product stripped, washed, and dried; n_D^{20} 1.4810, 99.3% pure by saponification. ^m The infrared spectrum of this compound gave a strong epoxide band (11.0-11.1 μ) and very weak bands at 2.9 μ and 6.2 μ indicating very small amounts of epoxide ring opening and residual unsaturation.

saturated esters, such as the 2-ethyl-2-hexenoic esters of 1,5-pentanediol, trimethylolpropane, and pentaerythritol, afford the corresponding di-, tri-, and tetraglycidates in good yield by direct epoxidation with anhydrous peracetic acid (Table II).

EXPERIMENTAL

General procedure for ester exchange. Sodium methoxide (2-10 mole % based on epoxy ester) was dissolved in the appropriate alcohol (2-10 moles) in a still kettle equipped with a condenser maintained at -5° . Then the ester of the α , β -epoxy acid was added and the reaction mixture refluxed under reduced pressure, the kettle temperature being kept at about 40° . During the period of reflux, the low-boiling alcohol was removed from the still head until no more was obtained. The kettle residue was then cooled to room temperature, the catalyst destroyed with an equivalent of acetic acid, and the mixture filtered, if necessary. The products were isolated by fractional distillation. In some cases metallic sodium, magnesium alcoholate, or other catalyst was substituted for the sodium methoxide. A summary of the results is found in Table I.

General procedure for epoxidation. The techniques were similar to those previously described.¹ In the preparation of di- or polyepoxides an excess of 25-30% peracetic acid solution¹⁰ in either ethyl acetate or acetone was used. The oxidations were continued until the peracetic acid consumption leveled out at its decomposition rate at the temperature employed. The volatile components were removed by feeding the reaction mixture dropwise into a kettle containing ethylbenzene under reflux at 50° under reduced pressure. The solvent, acetic acid, and excess peracetic acid were removed continuously at the still head. After removal of the excess ethylbenzene the epoxides were purified by distillation except in the cases of the trimethylolpropane and pentaerythritol esters. In these cases the epoxy esters were vacuum stripped, diluted with toluene, washed with sodium carbonate solution and water, and dried by vacuum stripping. A summary of the results is found in Table II.

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[CONTRIBUTION FROM SOUTHERN REGIONAL RESEARCH LABORATORY,¹ UNITED STATES DEPARTMENT OF AGRICULTURE]

Reaction of Epichlorohydrin with Ammonia, Aniline, and Diethanolamine

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The reaction of epichlorohydrin with ammonia, aniline, and diethanolamine in various reaction media has been investigated. The hydrochloride of *N,N,N*-tris(3-chloro-2-hydroxypropyl)amine and *N,N,N*-tris(2,3-epoxypropyl)amine have been prepared from the crude reaction product of ammonia and epichlorohydrin in a 1:3 mole ratio in methanol. Formation of 1,3-dichloro-2-propanol, when ammonia or ammonium chloride and epichlorohydrin are treated in aqueous medium, has been demonstrated. *N*-(3-Chloro-2-hydroxypropyl)aniline, *N*-(2,3-epoxypropyl)aniline, and *N,N*-bis(2,3-epoxypropyl)aniline have been isolated. *N*-(3-Chloro-2-hydroxypropyl)-*N,N*-bis(2-hydroxyethyl)amine has been prepared and it has been demonstrated that this compound slowly forms a quaternary salt, probably by cyclization.

In the synthesis of polyepoxide finishing agents for cotton, it became necessary to prepare certain *N*-substituted amine epoxides. The *N*-(3-chloro-2-hydroxypropyl)amines, obtained by addition of epichlorohydrin to an amine, were dehydrohalogenated to the respective epoxides. An interesting chlorohydroxyamine, *N,N,N*-tris(3-chloro-2-hydroxypropyl)amine (I), formed by saturating epichlorohydrin with ammonia gas at room temperature in a five-day reaction is mentioned by Fauconnier,² but no yields are given. In our experience with this reaction, one is apt to obtain an alcohol-insoluble resin, as it is difficult to know when epichlorohydrin is saturated. Other references to the action of epichlorohydrin and ammonia,³⁻¹⁰ are

concerned chiefly with aqueous ammonia, and frequently the conditions imposed could scarcely be classed as mild. The only compound definitely isolated was 1,3-diamino-2-propanol in the work by Bottoms,⁵ who carried out the reaction in the presence of strong alkali. Aqueous solutions of ammonium salts, such as ammonium chloride, have been reported to react with epichlorohydrin.^{11,12} The kinetics of the reaction were determined, but no products were isolated. The action of liquid ammonia on epichlorohydrin is not reported in the literature. Neither have the present investigators been successful in isolating and identifying the

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