material and 1,9-decadiene. The basic fraction was worked up in the manner previously described and distilled at 138–139° (50 mm.) (literature[11] b.p. 118–120° (17 mm.)). The resultant colorless liquid (6.5 g.) showed an infrared absorption spectrum identical with that of I and formed a picrate derivative, m.p. 54°, and a methiodide derivative, m.p.

150°, both indistinguishable by mixed melting point determinations from the corresponding derivatives of I.

The residue from distillation (1.1 g.) showed no double bond absorption in the infrared region and was presumably decamethylene bis-(dimethylamine).

ITHACA, N. Y.

Synthesis of Glycidic Esters by Epoxidation of α,β-Unsaturated Esters with Peracetic Acid

BY DONALD L. MACPEEK, PAUL S. STARCHER AND BENJAMIN PHILLIPS

An efficient, single step synthesis of glycidic esters via the epoxidation of α,β-unsaturated esters with peracetic acid is described. The method is characterized by the ease of following the reaction and by the general applicability of the procedure. In this way, novel types of glycidic esters were prepared.

The first synthesis of a glycidic ester was reported in 1892 by Erlenmeyer,[1] who prepared ethyl 2,3-epoxy-3-phenylpropionate by the condensation of benzaldehyde and ethyl chloroacetate in the presence of sodium. Darzens[2] expanded the scope of this general method of synthesis which now bears his name. This route and its more recent modifications have been reviewed by Newman and Magerlein.[3]

Several investigators have studied the action of perbenzoic acid on α,β-unsaturated acids and esters. Braun,[4] in 1930, succeeded in epoxidizing crotonic acid by the use of perbenzoic acid in chloroform solution, but the yield of epoxy acid was low, and the reaction conditions—three months at room temperature—were clearly indicative of the slow reaction rate. Other early work has been reviewed by Swern,[5] who concluded that the reaction of an organic peracid with an olefin is slowed down considerably or completely suppressed by the presence of a carboxyl or carboalkoxy group in close proximity to the double bond. More recent studies by Dry and Warren[6] and Plisov and Bykovets,[7] confirmed these conclusions.

In 1955, Emmons and Pagano[8] reported the successful preparation of glycidic esters from acrylic, methacrylic and crotonic esters by an epoxidation procedure employing peroxytrifluoroacetic acid in a system buffered with disodium hydrogen phosphate. The success of this technique was ascribed to the great difference in acidity between peroxytrifluoroacetic acid and the coproduct trifluoroacetic acid. This made it possible, by proper buffering, to neutralize the trifluoroacetic acid as rapidly as it was formed without making the reaction mixture so basic as to affect the stability of the peracid.

The suitability of any peracid solution as an

epoxidation reagent depends, among other things, on its purity. Traces of ions of heavy metals, for example, can catalyze peracid decomposition, and if such ions are present and improperly sequestered, a severe limitation on reaction temperature is imposed. Other impurities, including mineral acids, salts, water and excessive concentrations of carboxylic acids, can destroy the epoxide products by participating in or catalyzing the opening of the oxirane rings. It therefore appeared desirable to study the feasibility of making glycidic esters through the use of peracetic acid solutions containing a minimum of these objectionable impurities and without the use of a buffering agent. Such solutions were obtained for the present study by the acetaldehyde-oxidation method.[9] Using peracetic acid solutions in either ethyl acetate or acetone it was found possible to prepare glycidic esters from α,β-unsaturated esters in good yield and under convenient operating conditions. This general reaction may be represented by the equation
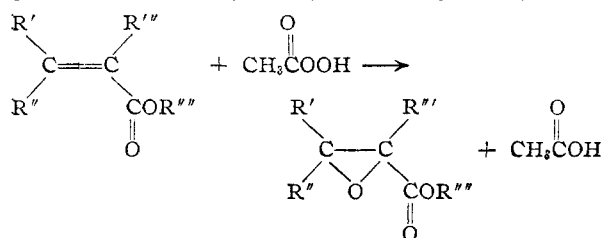
wherein the groups R', R'', R''' and R'''' represent a wide variety of alkyl, aryl and oxygen-containing substituents normally unreactive to peracids.

The conventional Darzens condensation is not a completely general synthesis. For example, when formaldehyde is used as the carbonyl component of the reaction, the yields of the desired glycidic esters are low.[10] With normal alkanals the competing aldol condensation causes unsatisfactory results.[10,11] Likewise, the self-condensation of ketones[12] may adversely influence the yield of desired products, and in addition the alkylation of the

(1) E. Erlenmeyer, Jr., Ann., 271, 161 (1892).

(2) G. Darzens, Compt. rend., 139, 1214 (1904).

(3) M. S. Newman and B. J. Magerlein, "Organic Reactions," Vol. V, J. Wiley and Sons, Inc., New York, N. Y., 1949, p. 413.

(4) G. Braun, THIS JOURNAL, 52, 3185 (1930).

(5) D. Swern, Chem. Revs., 45, 1 (1949).

(6) L. J. Dry and F. L. Warren, J. S. African Chem. Inst., 6, 14 (1953).

(7) A. K. Plisov and A. I. Bykovets, J. Gen. Chem. USSR, 24, 852 (1954).

(8) W. D. Emmons and A. J. Pagano, THIS JOURNAL, 77, 89 (1955).

(9) B. Phillips, F. C. Frostick, Jr., and P. S. Starcher, ibid., 79, 5982 (1957).

(10) G. Darzens, Compt. rend., 142, 214 (1906).

(11) B. N. Rutowski and N. A. Dajew, Ber., 64, 693 (1931).

(12) H. A. Weidlich and G. H. Daniels, ibid., 72, 1596 (1939).

TABLE I

GLYCIDIC ESTERS FROM α,β-UNSATURATED ESTERS AND PERACETIC ACID

$$\begin{array}{c} R' \\ \diagdown \\ R'' \end{array} C \underset{O}{\overset{}{\diagup\!\!\diagdown}} C \begin{array}{c} R''' \\ \diagup \\ CO_2R'''' \end{array}$$

Compound	R'	R''	R'''	R''''	Yield, % Via peracetic acid	Yield, % Via best Darzens modification	Ref.
I	CH₃–	H–	H–	C₂H₅–	74.8	..[a]	11
II	H–	H–	H–	C₂H₅–	22.2[b]	..[c,d]	..
III	H–	H–	CH₃–	CH₃–	47.5	20–30[e]	10
IV	CH₃–	CH₃–	H–	C₂H₅–	84.2	66	14
V	C₂H₅–	H–	H–	C₂H₅–	57.4	20–30	10
VI	C₆H₅–	H–	H–	C₂H₅–	69.7	68	14
VII	C₆H₅–	H–	CH₃–	C₂H₅–	87.1	71	3
VIII	H–	–(CH₂)₄–		C₄H₉–	87.0	..[c]	..
IX	C₃H₇–	H–	C₂H₅–	CH₃–	72.6	..[c]	..
X	C₃H₇–	H–	C₂H₅–	C₂H₅–	79.0	..[c]	..
XI	CH₃–	H–	C₆H₅–	C₂H₅–	95.0	..[c]	..
XII	CH₃–	H–	C₂H₅OCCH₂	C₂H₅–	63.4	..[c]	..

(R''' for XII shown as $C_2H_5OCCH_2$ with a carbonyl O and an epoxide group bearing CH_3.)

[a] Darzens yield not disclosed; yield via peroxytrifluoroacetic acid, 73%.[8] [b] Based on the amount of peracetic acid actually consumed. [c] Literature shows no preparation of this ester by any modification of the Darzens condensation. [d] Yield via peroxytrifluoroacetic acid, 54%.[8] [e] Figures for the analogous ethyl ester; yield via peroxytrifluoroacetic acid, 84%.[8]

enolates of ketones by the haloester must always be considered a source of isomeric impurities. α-Arylglycidic esters do not result from condensations attempted with carbonyl compounds having α-hydrogen,[13] further limiting the scope of the Darzens method. Still another common deficiency is the difficulty of ascertaining the extent of the reaction at any given time.

We have found the epoxidation of α,β-unsaturated esters with peracetic acid in an inert solvent to be a convenient, single-step route to glycidic esters. The applicability of the method is restricted mainly by the limited availability of the more complex α,β-unsaturated esters. The reaction may be easily followed by the disappearance of peracetic acid as shown by a conventional iodimetric technique. Since the reaction mixtures from such epoxidations with peracetic acid contain no salts or high-boiling carboxylic acids, the products are obtained in high yields by straightforward distillation.

Table I lists twelve glycidic esters which we have prepared by this method and compares our yields with the best results described in the literature for the preparation of these compounds. Some of these glycidic esters are reported here for the first time. These examples also provide a comparison of the yields obtainable with variously substituted α,β-unsaturated esters. Invariably, the more highly substituted esters gave higher yields of glycidic esters, with aromatic substituents facilitating the reaction more effectively than aliphatic substituents. In some instances, with aromatic, aliphatic or a combination of both types of substituents, the yields were nearly quantitative. In addition, it was found that the peracetic acid route was comparable in efficiency to the peroxytrifluoroacetic acid method[8] except in the case of

acrylic esters, wherein the competing polymerization of the unsaturated ester lowered the yield. We have found that the molar ratio of unsaturated ester to peracetic acid is not narrowly critical. In some cases the reaction was sufficiently rapid to permit use of nearly equimolar amounts. Excess peracid was sometimes employed to effect more complete conversion of olefin to epoxide. Excess olefin, on the other hand, was used advantageously in certain cases to shorten the reaction time and to facilitate the separation of the product glycidic esters from the coproduct acetic acid during subsequent fractional distillation.

Peracetic acid epoxidation is an economically attractive method for the large-scale preparation of these interesting compounds.

Experimental

General Epoxidation Technique.—In the individual examples which follow, a standard method of epoxidation was employed. The candidate α,β-unsaturated ester was placed in a suitable vessel equipped with a stirrer, a thermometer, a reflux condenser and an addition funnel. The unsaturated ester was continuously agitated as a solution of peracetic acid in ethyl acetate or acetone was gradually added at a temperature such that a reasonable reaction rate was obtained. The temperature and time required for consumption of peracid were different for each ester.

The concentration of peracetic acid in the solvent (ethyl acetate or acetone) was determined iodimetrically.[9] The same technique was employed on the reaction mixture at intervals to determine the point at which satisfactory conversions of olefin to epoxide had been reached. Subsequent distillation provided the glycidic esters. Any unreacted peracetic acid always codistilled with acetic acid and solvent during this work-up. Nevertheless, care was taken to avoid the concentration of peracetic acid in any part of the distillation system, and when a preparation was being carried out for the first time, such a distillation was always performed behind a suitable safety shield.

Ethyl 2,3-Epoxybutyrate (I).—Ethyl crotonate (2736 g., 24.0 moles), from commercial crotonic acid by the method

(13) H. H. Morris, R. H. Young, Jr., C. Hess and T. Sottery, THIS JOURNAL, 79, 411 (1957).

(14) W. S. Johnson, J. S. Belew, L. J. Chinn and R. H. Hunt, ibid. 75, 4995 (1953).

of Michael,[15] was allowed to react with 4130 g. of a 22.2% solution of peracetic acid (12.0 moles) in ethyl acetate. After an addition and reaction period totaling 5.5 hours at 85°, a 92.7% conversion of olefin to epoxide was observed based on disappearance of peracid. Direct fractionation of the reaction mixture gave 1167 g. (74.8%) of ethyl 2,3-epoxybutyrate (I), b.p. 94–95° (50 mm.), n^{30}D 1.4150, d^{20} 1.0345; lit.[11] b.p. 172–174° (760 mm.). The excess ethyl crotonate facilitated the separation of the by-product acetic acid from the epoxide.

Anal. Calcd. for $C_6H_{10}O_3$: C, 55.37; H, 7.75; sapn. equiv., 130.1. Found: C, 55.60; H, 7.67; sapn. equiv., 127.8.

Ethyl 2,3-Epoxypropionate (II).—Ethyl acrylate (300 g., 3.0 moles), stabilized with 0.2% of hydroquinone, was placed in an amber glass reaction flask. At 75°, peracetic acid was added over a 45-minute period until 365 g. (0.97 mole of a 21.0% solution in ethyl acetate) had been added. After 5 more hours of continuous agitation and heating, analysis showed that only 40% of the available peracid had been consumed. Rapid distillation through a one-plate column removed the volatile components of the reaction mixture from the residual acrylate polymer (240 g.). Careful redistillation gave 10 g. of ethyl 2,3-epoxypropionate (II), b.p. 72–73° (26 mm.), n^{30}D 1.4150, d^{20} 1.085; lit.[8] b.p. 88–90° (60 mm.), n^{20}D 1.4180; also[16] b.p. 162–163° (760 mm.), $d^{21.6}$ 1.0933. The low yield was attributed to the rapid competing polymerization of the olefin and subsequent retention of the product in the residual polymer during distillation.

Anal. Calcd. for $C_5H_8O_3$: C, 51.72; H, 6.94; sapn. equiv., 116.1. Found: C, 51.70; H, 6.77; sapn. equiv., 114.9.

Methyl 2,3-Epoxy-2-methylpropionate (III).—Commercial methyl methacrylate (900 g., 9.0 moles) stabilized with 0.5% of hydroquinone was treated with 1836 g. of peracetic acid solution (5.05 moles of a 21% solution in ethyl acetate) over a 5.5 hour period at 75–85°. Analysis for peracid showed a conversion of 69.5% had been reached. At that point, the reaction mixture was rapidly distilled from the by-product methyl methacrylate polymer. Careful reduced pressure fractionation gave 278 g. (47.5% or 68.4% based on the peracid actually consumed) of methyl 2,3-epoxy-2-methylpropionate (III), b.p. 66° (30 mm.), n^{30}D 1.4134, d^{20} 1.0972; lit.[8] b.p. 62–65° (32 mm.), n^{20}D 1.4174.

Anal. Calcd. for $C_5H_8O_3$: C, 51.72; H, 6.94; sapn. equiv., 116.1. Found: C, 51.86; H, 6.78; sapn. equiv., 116.2.

Ethyl 2,3-Epoxy-3-methylbutyrate (IV).—Ethyl β,β-dimethylacrylate (b.p. 75–76° (50 mm.), n^{30}D 1.4317) was prepared by the esterification of β,β-dimethylacrylic acid with ethanol under the usual conditions. The starting acid was prepared by the method of Boese.[17] A weight of 733 g. (5.72 moles) of this ester was allowed to react with 1045 g. (2.86 moles of a 20.8% solution) of peracetic acid in ethyl acetate. After 3.75 hours at 83°, analysis for peracid indicated a conversion of 96.8% of the theoretical. Distillation gave 346 g. (84.2%) of ethyl 2,3-epoxy-3-methylbutyrate (IV), b.p. 100° (50 mm.), n^{30}D 1.4172, d^{20} 1.0059; lit.[14] b.p. 87–89.5° (30 mm.), n^{25}D 1.4181.

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.31; H, 8.39; sapn. equiv., 144.2. Found: C, 58.58; H, 8.26; sapn. equiv., 143.8.

Ethyl 2,3-Epoxypentanoate (V). (a) 2-Acetoxyvaleronitrile.—n-Butyraldehyde (2160 g., 30 moles) was charged to a large flask equipped with a stirrer, thermometer, reflux condenser and an addition funnel. After sufficient triethylamine had been added to provide a system pH of 7.6, 890 g. of liquid hydrogen cyanide was added over a 2-hour period at 21 to 28°. Then, excess hydrogen cyanide was removed by direct water aspiration at 125° at 120 mm. The reaction mixture was acidified with concentrated sulfuric acid to a pH of 3.0. The resulting butyraldehyde cyanohydrin was added to 3820 g. (37.4 moles) of stirred, refluxing acetic anhydride containing 0.5% of sulfuric acid. Sufficient heat was evolved to require constant cooling of the

reaction mixture over the 2-hour addition period. Then sodium acetate was added to neutralize the sulfuric acid. Distillation provided 3121 g. (74.4%) of 2-acetoxyvaleronitrile, b.p. 60° (3 mm.), n^{30}D 1.4110; lit.[18] b.p. 194° (762 mm.).

(b) **2-Pentenenitrile.**—2-Acetoxyvaleronitrile (1113 g., 7.88 moles) was fed continuously at a rate of 350 ml./hour (requiring 3.5 hours) to the top of a 40-inch section of 1-inch type 304 stainless steel tubing heated through an external high temperature magnesia insulation by two 15-amp. sections of Nichrome ribbon. The top third of the tube was operated as a preheater at 300°, while the bottom two-thirds of the tube was maintained at 550° by proper voltage application to the two Nichrome windings. The tube was filled with an inert, neutral silica packing of $^1/_4$ × $^1/_8$ inch dimension. Observations of tube temperature were made through a thermocouple well extending through the center of the packed section. The effluent from the bottom of the tube was collected in chilled flasks and subsequently distilled to provide on fractionation 210 g. (32%) of a mixture of *cis*- and *trans*-2-pentenenitrile, b.p. 67–74° (100 mm.), n^{30}D 1.4215–1.4245; lit.[19] *cis* isomer b.p. 127–127.2° (769 mm.), n^{20}D 1.4238; *trans* isomer b.p. 144.2–144.4° (769 mm.), n^{20}D 1.4264. No attempt was made to separate the isomers. A recovery of 479 g. (43%) of 2-acetoxyvaleronitrile was also effected on continuation of the distillation.

(c) **2-Pentenoic Acid.**—A mixture of *cis*- and *trans*-2-pentenenitrile (648 g., 8.0 moles) was stirred with 672 g. (12 moles) of potassium hydroxide dissolved in 2700 ml. of water. The temperature was maintained at 90–95° for 4 hours. At that point the reaction mixture was cooled and acidified with concentrated hydrochloric acid used in slight excess. The organic phase was extracted by means of four 1-liter portions of benzene. Combination of the extracts and subsequent distillation gave 216 g. (27%) of 2-pentenoic acid (predominantly *trans* isomer), b.p. 65–66° (2.0 mm.), n^{30}D 1.4374; lit.[20] b.p. 71° (2.0 mm.). Analysis for neutralization equivalent gave a purity of 100.5% as 2-pentenoic acid. A second preparation on the same scale gave similar results.

(d) **Ethyl 2-Pentenoate.**—The 2-pentenoic acid (507 g. or 5.07 moles) was esterified in the conventional manner employing excess absolute ethanol with toluene as an azeotroping agent. Sulfuric acid (0.2% by weight) was employed as catalyst. Distillation of the neutralized reaction mixture gave 425 g. (65.4%) of ethyl 2-pentenoate, b.p. 52–53° (15 mm.), n^{30}D 1.4201–1.4206; lit.[20] b.p. 48° (11 mm.).

Anal. Calcd. for $C_7H_{12}O_2$: sapn. equiv., 128.2. Found: sapn. equiv., 125.1.

(e) **Ethyl 2,3-Epoxypentanoate (V).**—Ethyl 2-pentenoate (457 g., 3.57 moles) was treated with 1474 g. of a 21.0% solution of peracetic acid (4.07 moles) in ethyl acetate in the usual way. After 5.5 hours at 65° a peracid consumption of 69% was observed. After a rapid preliminary flash distillation of the ethyl acetate and acetic acid fractions from the reaction mixture there was obtained 295 g. (57.4%) of ethyl 2,3-epoxypentanoate (V), b.p. 80° (15 mm.), n^{30}D 1.4176, d^{20} 1.0157.

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.31; H, 8.39; sapn. equiv., 144.2. Found: C, 58.53; H, 8.20; sapn. equiv., 144.6.

Ethyl 2,3-Epoxy-3-phenylpropionate (VI).—Ethyl cinnamate (352 g., 2.0 moles) was treated in the usual way with 914 g. of a 20.8% solution of peracetic acid (2.5 moles) in ethyl acetate. The peracid was fed to the reaction vessel over a 1-hour period at 80°. After 7 hours, analysis of the reaction mixture indicated that sufficient peracid had been consumed to convert all of the olefin to epoxide. The reaction mixture was stored overnight at ice temperature and rapidly freed of ethyl acetate, acetic acid and unspent peracetic acid by rapid reduced-pressure distillation. Continued fractionation gave 268 g. (69.7%) of ethyl 2,3-epoxy-3-phenylpropionate (VI), b.p. 104° (0.3 mm.), n^{30}D 1.5095, d^{20} 1.1023; lit.[14] b.p. 168–172° (28 mm.), n^{25}D 1.5126.

(15) A. Michael, *Ber.*, **33**, 3766 (1900).

(16) P. Melikow and N. Zelinsky, *ibid.*, **21**, 2052 (1888).

(17) A. B. Boese, U. S. Patent 2,382,464 (Aug. 14, 1945).

(18) L. Henry, *Bull. Acad. roy. Belg.*, [3] **36**, 241 (1898); *Chem. Zentr.*, **70**, I, 194 (1899).

(19) A. Castille and J. Gueurden, *Ann. soc. sci. Bruxelles, Ser. B*, **47**, 1, 56 (1927); *Chem. Zentr.*, **98**, II, 802 (1927).

(20) K. von Auwers, *Ann.*, **432**, 63 (1923).

Anal. Calcd. for $C_{11}H_{12}O_3$: C, 68.73; H, 6.29; sapn. equiv., 192. Found: C, 68.77; H, 6.35; sapn. equiv., 193.5.

Ethyl 2,3-Epoxy-2-methyl-3-phenylpropionate (VII).—Ethyl α-methylcinnamate was prepared in 70% yield by the esterification of α-methylcinnamic acid[21] under essentially the same conditions described for the esterification of 2-pentenoic acid. Careful fractionation gave pure ester distilling at 124° (5 mm.), n^{30}D 1.5441; lit.[22,23] b.p. 142–143° (12 mm.), $n^{20.6}$D 1.5475. Treatment of 285 g. (1.5 moles) of the above ester with 815 g. of a 21.0% solution of peracetic acid (2.25 moles) in ethyl acetate over a 6-hour period at 80° (at which time, analysis indicated the reaction was 97% complete) gave, after rapid removal of the lower boiling components of the reaction mixture, 269 g. (87.1%) of ethyl 2,3-epoxy-2-methyl-3-phenylpropionate (VII), b.p. 121° (4 mm.), n^{30}D 1.5052, d^{20} 1.0865; lit.[10] b.p. 153–154° (18 mm.).

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84; sapn. equiv. 206.2. Found: C, 70.19; H, 6.70; sapn. equiv., 205.2.

Butyl 7-Oxabicyclo[4.1.0]heptane-1-carboxylate (VIII). (a) **1-Cyclohexenecarbonitrile.**—Cyclohexanone (1568 g., 16 moles) containing 10 ml. of triethylamine was allowed to react with 476 g. (17.6 moles) of hydrogen cyanide in exactly the same fashion used for the synthesis of 2-acetoxyvaleronitrile described previously. Of the crude cyclohexanone cyanohydrin so produced, 1825 g. (14.6 moles) was fed over 1 hour into refluxing acetic anhydride (1860 g. or 18.3 moles) containing 0.5% sulfuric acid. After neutralization of the sulfuric acid catalyst with a slight excess of sodium acetate, the reaction mixture was distilled to provide 1907 g. of 1-acetoxycyclohexanecarbonitrile, b.p. 87–88° (1 mm.). The crude product, which gradually turned solid, was dissolved in half its weight of benzene and pyrolyzed in the same tube and under the same conditions of rate and temperature which were used for the preparation of 2-pentenenitrile. Distillation of the pyrolysis product gave 1071 g. (89.5%) of 1-cyclohexenecarbonitrile, b.p. 72° (9 mm.), n^{30}D 1.4769; lit.[24] b.p. 81° (12 mm.).

(b) **1-Cyclohexenecarboxylic Acid.**—The conversion of 1-cyclohexenecarbonitrile was performed according to the procedure of Boorman and Linstead.[25] A 76% over-all yield of 1-cyclohexenecarboxylic acid was obtained. The product distilled sharply at 104–105° (3 mm.), m.p. 37°; lit.[25] b.p. 107° (3 mm.), m.p. 38°.

(c) **Butyl 1-Cyclohexenecarboxylate.**—1-Cyclohexenecarboxylic acid (300 g., 2.38 moles) was refluxed for 4.5 hours with 880 g. (11.9 moles) of 1-butanol containing 6 g. of sulfuric acid. After neutralization of the sulfuric acid, careful fractionation gave 345 g. (79.6%) of butyl 1-cyclohexenecarboxylate, b.p. 91° (3 mm.), n^{30}D 1.4647.

Anal. Calcd. for $C_{11}H_{18}O_2$: sapn. equiv., 182.2. Found: sapn. equiv., 181.7.

(d) **Butyl 7-Oxabicyclo[4.1.0]heptane-1-carboxylate (VIII).**—In the usual manner, 367 g. (2.01 moles) of butyl 1-cyclohexenecarboxylate were allowed to react with 902 g. of a 21% solution (2.5 moles) of peracetic acid in ethyl acetate over 5.5 hours at 65°. At the end of this period, analyses indicated a conversion of 93.2% based on the olefin charged. Careful fractionation, after rapid removal of the solvent and acetic acid fractions, gave 336 g. (87.0%) of butyl 7-oxabicyclo[4.1.0]heptane-1-carboxylate (VIII), b.p. 94° (1.2 mm.), n^{30}D 1.4553, d^{20} 1.0353.

Anal. Calcd. for $C_{11}H_{18}O_3$: C, 66.64; H, 9.15. Found: C, 67.04; H, 9.02.

Methyl 2,3-Epoxy-2-ethylhexanoate (IX). (a) Methyl 2-Ethyl-2-hexenoate.—2-Ethyl-2-hexenoic acid[26,27] (427 g., 3.0 moles) was refluxed with 2968 g. (87.4 moles) of anhydrous methanol containing 8.5 g. of sulfuric acid as catalyst

in order to obtain methyl 2-ethyl-2-hexenoate. After 40 hours, the reaction mixture was neutralized with sodium acetate. Then the resulting solution was freed of methanol by rapid distillation. The residual higher boiling material was washed four times with 5% aqueous sodium bicarbonate and dried over anhydrous sodium sulfate. After filtration, distillation gave 407 g. (87%) of methyl 2-ethyl-2-hexenoate, b.p. 72° (10 mm.), n^{30}D 1.4405.

Anal. Calcd. for $C_9H_{16}O_2$: sapn. equiv., 156.2. Found: sapn. equiv., 156.2.

(b) **Methyl 2,3-Epoxy-2-ethylhexanoate (IX).**—In the general manner previously described, methyl 2-ethyl-2-hexenoate (368 g., 2.36 moles) was allowed to react with 1120 g. of a 24.0% solution of peracetic acid (3.54 moles) in acetone. A reaction period of 11 hours at 50° provided a conversion of 97% of the available olefin to epoxide, based on analysis for peracid. Azeotropic removal of the lower-boiling components of the reaction mixture with ethylbenzene, followed by fractional distillation, gave 295 g. (72.6%) of methyl 2,3-epoxy-2-ethylhexanoate (IX), b.p. 80° (5 mm.), n^{30}D 1.4289, d^{20} 0.9857.

Anal. Calcd. for $C_9H_{16}O_3$: C, 62.76; H, 9.36. Found: C, 62.88; H, 9.19.

Ethyl 2,3-Epoxy-2-ethylhexanoate (X). (a) Ethyl 2-Ethyl-2-hexenoate.—The esterification of 2-ethyl-2-hexenoic acid with ethanol was conducted in the normal manner employing benzene for removal of water as the ternary azeotrope. The reaction mixtures were worked up in the same manner as was methyl 2-ethyl-2-hexenoate. Yields of 82.5% of the ethyl ester, b.p. 72–74° (5 mm.), n^{30}D 1.4382, were obtained.

Anal. Calcd. for $C_{10}H_{18}O_2$: sapn. equiv., 170.2. Found: sapn. equiv., 170.

(b) **Ethyl 2,3-Epoxy-2-ethylhexanoate (X).**—Ethyl 2-ethyl-2-hexenoate (232 g., 1.36 moles) was allowed to react with 544 g. of a 23.8% solution of peracetic acid (1.70 moles) in acetone. After 9 hours at 60°, analysis for peracid indicated a conversion of 88%. The reaction mixture was distilled in exactly the same manner as the previous example to give 200 g. (79%) of ethyl 2,3-epoxy-2-ethylhexanoate (X), b.p. 86° (5 mm.), n^{30}D 1.4279, d^{20} 0.9638.

Anal. Calcd. for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.66; H, 9.62.

Ethyl 2,3-Epoxy-2-phenylbutyrate (XI).—α-Phenylcrotonic acid was prepared in 25% yield by the method of Oglialoro[28] and converted by conventional methods into ethyl α-phenylcrotonate, b.p. 111° (5 mm.), n^{30}D 1.5166; lit.[29] b.p. 128–131° (15 mm.). This ester (27 g., 0.142 mole) was allowed to react with 163 g. (0.592 mole) of a 27.5% solution of peracetic acid in ethyl acetate. After 5 hours at 50°, analysis indicated that the theoretical amount of peracid had been consumed. Distillation of the reaction mixture through a small packed column gave 28 g. (95%) of ethyl 2,3-epoxy-2-phenylbutyrate (XI), b.p. 110–111° (3 mm.), n^{30}D 1.4993.

Anal. Calcd. for $C_{12}H_{14}O_3$: C, 69.88; H, 6.84; sapn. equiv., 206.2. Found: C, 69.68; H, 6.66; sapn. equiv., 206.0.

Ethyl 3-Methyl-4-carboethoxy-4,5-epoxyhexanoate (XII).—Diethyl α-ethylidene-β-methylglutarate[30] (912 g., 4.0 moles) was charged to a flask and allowed to react with peracetic acid (1828 g., 6.0 moles, of a 25% solution in ethyl acetate) at 70°. After 4 hours, analysis indicated that 65.8% of the available olefin had been converted to epoxide. An additional 6 hours of heating at 70° was sufficient to cause complete epoxidation of the available olefin. The low-boiling components of the reaction mixture were removed by azeotropic distillation with ethylbenzene. Then, reduced pressure fractionation gave 619 g. (63.4%) of ethyl 3-methyl-4-carboethoxy-4,5-epoxyhexanoate, b.p. 100° (0.2 mm.), n^{30}D 1.4370, d^{20} 1.0355.

Anal. Calcd. for $C_{12}H_{20}O_5$: C, 59.00; H, 8.25. Found: C, 59.19; H, 8.15.

SOUTH CHARLESTON, W. VA.

(21) L. Edeleano, *Ber.*, **20**, 617 (1887).

(22) H. Rupe, *Ann.*, **395**, 143 (1913).

(23) K. von Auwers and F. Eisenlohr, *J. prakt. Chem.*, [2] **84**, 85 (1911).

(24) L. Ruzicka and W. Brugger, *Helv. Chim. Acta*, **9**, 399 (1926).

(25) E. J. Boorman and R. P. Linstead, *J. Chem. Soc.*, 261 (1935).

(26) J. Lichtenberger and M. Naftali, *Bull. soc. chim.*, [5] **4**, 325 (1937).

(27) B. Duval, A. Elce and K. H. W. Tuerck, U. S. Patent 2,465,012 (Mar. 22, 1949).

(28) A. Oglialoro, *Gazz. chim. ital.*, **15**, 514 (1885).

(29) O. Dimroth and H. Feuchter, *Ber.*, **36**, 2253 (1903).

(30) H. von Pechmann, *ibid.*, **33**, 3331 (1900).