

benzophenones), treated with decolorizing carbon, and cooled to induce crystallization.

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RECEIVED for review December 2, 1965. Accepted February 21, 1966.

Synthesis of Aromatic Glycidyl Esters

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An improved procedure for the preparation of aromatic glycidyl esters uses simultaneous addition of triethylamine and acid chloride to glycidol at 0° to 5° C. Several new di-, tri-, and tetraglycidyl esters are described. *m*-Chloroperbenzoic acid can be used for the peroxidation of diallyl esters to diglycidyl esters.

GLYCIDYL ESTERS of aromatic acids appear to have been relatively unexplored, compared to those of the aliphatic acids (4), except for descriptions in some patents (1, 2, 3, 5, 7, 8, 9, 11, 12, 13). The patents have described the preparation of these materials rather crudely, except for one case where carbon and hydrogen analyses have been reported for crystalline diglycidyl terephthalate (2, 8). The object of this investigation was to synthesize pure glycidyl esters of aromatic acids, in order to explore their use for adhesives.

Diglycidyl phthalate and diglycidyl terephthalate are described in detail in a procedure (2, 8) which recommends addition of the acid chloride to a mixture of glycidol in the presence of triethylamine at 0° to 5° C. in benzene or toluene solution. This procedure suffers from the disadvantage that glycidol itself polymerizes exothermically in the presence of basic materials and, thus, contaminates the products, which are subsequently isolated in low yields. The products are easily polymerized by the application of heat in the presence of basic catalysts such as triethylamine. Some investigators (2, 8) have neglected this fact and give procedures wherein the products are heated to 160° at 10-mm. pressure in vessels which originally contained basic catalysts. Therefore, to prepare purer products with acceptable analyses, a modified procedure was developed which utilized low temperatures and separate addition of triethylamine. Many of the crystalline products obtained in this investigation have been reported by earlier investigators as resins. The melting points and analyses for the glycidyl esters prepared by this method appear in Table I. The general procedure is illustrated below, utilizing the preparation of diglycidyl isophthalate, as an example. The properties of diglycidyl hexahydroterephthalate are shown for comparison, although this is not an aromatic system.

An additional method that is useful for the preparation of glycidyl esters is the reaction of the allyl esters of aromatic acids with *m*-chloroperbenzoic acid. Although peracetic acid (1) has been reported to peroxidize diallyl esters, the epoxy esters decomposed in the presence of acetic acid. *m*-Chloroperbenzoic acid gave a clean product and was separated from the by-product *m*-chlorobenzoic acid by washing the organic layer with dilute sodium carbonate or sodium hydroxide. Recently other investigators (6) have also found *m*-chloroperbenzoic acid useful for preparing volatile epoxides. The procedure for preparing diglycidyl ether epoxides. The procedure for preparing diglycidyl tere-

terephthalate from diallyl terephthalate is given below.

EXPERIMENTAL

Glycidyl Esters from Glycidol and an Acid Chloride—Diglycidyl Isophthalate. A 1-liter resin kettle was fitted with a stirrer, thermometer, condenser with drying tube, and two 300-ml. dropping funnels. All the equipment was carefully dried and flushed with nitrogen for 10 minutes. Glycidol (74.1 grams, 1.0 mole) and 200 ml. of benzene were placed in the flask and cooled, with stirring, to 0° C. in an ice water-methanol bath. A solution of isophthaloyl chloride (101.5 grams, 0.5 mole) in 150 ml. of benzene was placed in one dropping funnel and a solution of triethylamine (101 grams, 1.0 mole) in 150 ml. of benzene in the second funnel. The dropwise addition of the acid chloride was begun first, then dropwise addition of the triethylamine solution. The rates were controlled so that the pot temperature did not exceed 5° C. and the acid chloride addition was slightly faster than that of the triethylamine. Complete addition required 3 hours. Stirring was continued for 3 hours longer while the pot reached room temperature. The solids (triethylamine hydrochloride) were filtered, rinsed with 50 ml. of benzene, and dried. The weight of triethylamine hydrochloride was 123 grams (theoretical weight 137.5 grams).

The filtrates were washed in a separatory funnel with 200 ml. of saturated aqueous sodium chloride, twice with 200-ml. portions of distilled water, and dried over anhydrous calcium chloride. The salt was removed by gravity filtration and the benzene was stripped from the filtrate by means of a vacuum pump and a warm water (40° to 45° C.) bath. The residue, a white solid, was mixed with petroleum ether and filtered. The crude product weighed 111 grams (theoretical yield 139 grams) and melted at 48° to 53° C. The product was dissolved in 700 ml. of petroleum ether-benzene (1 to 1) solution, stirred with about 5 grams of activated charcoal, filtered, and cooled. About 25 ml. of petroleum ether was added. The recrystallized material was filtered and dried in a vacuum oven at room temperature. Final yield was 36 grams (m.p. 60–63° C.).

Glycidyl Esters by Peroxidation of Diallyl Esters with *m*-Chloroperbenzoic Acid—Glycidyl Terephthalate. The reaction of diallyl terephthalate with *m*-chloroperbenzoic acid consisted of cooling to 0° to 3° C. a solution of the acid (0.4 mole) in chloroform (700 ml.) and adding the diester (0.2 mole) in small portions with gentle agitation over a period of 4 hours. The stoppered reaction flask was stored

Table I. Preparation of Polyglycidyl Esters of Polycarboxylic Acids

Product	Yield, %	Analysis				M.P., °C. ^b	Ref. to Previously Reported M.P., °C.	Characteristic Infrared Absorption Bands, Microns ^c
		Calcd.		Found				
		%C	%H	%C	%H			
Diglycidyl isophthalate	78	60.43	5.07	60.42	5.13	60-63	Viscous liquid (10)	3.40(w), 5.80(s), 6.20(w), 7.65(s), 8.20(s), 9.40(m), 11.04(m), 13.68(s), 14.05(m)
Diglycidyl terephthalate	67	60.43	5.07	60.37	5.19	94-96 ^d	108-09(2)	3.40(w), 5.80(s), 6.12(w), 7.85(s), 8.95(s), 9.08(s), 9.35(m), 11.08(m), 11.80(m), 13.27(m), 13.70(s)
Diglycidyl hexahydroterephthalate	25	59.14	7.09	58.67	6.86	88-90	...	3.40(w), 5.76(vw), 5.77(s), 7.26(w), 7.58(m), 8.05(m), 8.55(s), 8.65(s), 9.57(m), 11.00(w), 13.26(w)
Diglycidyl phthalate	94	60.43	5.07	60.04	5.39	Viscous Liquid	Viscous liquid (2)	3.40(m), 5.75(vs), 6.23(m), 6.30(m), 7.85(vs), 8.95(s), 8.40(s), 11.05(m), 13.50(m), 14.25(m)
Diglycidyl 3,5-dichloroterephthalate	53	48.44	3.45	48.66	3.68	113-14	...	3.40(vw), 5.76(vs), 7.45(s), 7.80(vs), 8.10(vs), 8.94(vs), 9.25(s), 9.33(vs), 11.15(m), 12.83(m), 13.18(m)
Diglycidyl diphenolate	85	67.80	5.08	68.04	5.10	Viscous liquid	...	3.40(vw), 5.80(vs), 6.25(m), 6.33(w), 7.77(vs), 8.00(vs), 8.30(m), 8.60(w), 8.90(s), 9.25(s), 11.03(m), 13.25(s), 14.17(m)
Triglycidyl trimesate ^e	58	57.44	4.80	57.18	4.86	58-63	...	3.40(m), 5.75(s), 6.20(w), 6.92(m), 7.43(m), 7.57(m), 8.10(s), 9.05(m), 9.34(w), 11.00(m), 13.55(s), 14.02(m), 14.56(m)
Triglycidyl trimellitate ^f	52-63	57.14	4.80	57.98	5.35	Liquid	...	3.40(m), 5.78(s), 6.12(w), 6.18(w), 7.43(m), 7.80(s), 8.10(s), 9.00(s), 9.40(m), 11.03(m), 11.75(m), 13.30(m)
Tetraglycidyl pyromellitate	30	55.23	4.64	55.18	4.81	113-23	...	3.40(vw), 5.77(vs), 6.15(vw), 8.0(vs), 8.85(s), 9.02(m), 9.25(w), 11.05(m), 12.10(m), 13.30(m), 13.42(m)

^a For crude reaction products before recrystallization. ^b Solid products recrystallized from petroleum ether-benzene. ^c Intensity of absorptions: (s) strong, (vs) very strong, (m) medium, (w) weak, and (vw) very weak. ^d After preparing this compound several times and recrystallizing from petroleum ether-benzene or benzene alone melting point was not raised to 108-09° as previously reported (2).

^e Obtained as an oil and could not be crystallized. Attempted distillations under high vacuum gave a resinous polymer. ^f Triglycidyl trimellitate was obtained as an oil in 46% yield when triethylamine was present with glycidol and trimesoyl chloride was added at 0-5°. If a procedure similar to that for *di*-glycidyl isophthalate was followed, a crystalline solid (m.p. 50°) was obtained. Three recrystallizations from petroleum ether-benzene gave a solid (m.p. 58-63°).

at 3° to 5° C. for 3 days and then brought to room temperature. The solids were removed by filtration and the filtrate was washed with a solution of Na₂CO₃ (0.2 mole) in 250 ml. of water, then several times with water, and finally dried over CaSO₄. The washings were acidified and the solids collected. The weight of the combined recovered solids was equal to the theoretical weight of *m*-chlorobenzoic acid (62.6 grams). The dried chloroform filtrate was concentrated by water suction, then residual chloroform was removed by the vacuum pump. The product was obtained as a pale yellow liquid from which solids separated. Recrystallization from petroleum ether-benzene yielded the pure diglycidyl terephthalate (28% yield). Similarly obtained were diglycidyl iso-phthalate (87% yield) and liquid glycidyl phthalate (100% yield). The infrared spectra of the above products were identical to those of the epoxy esters prepared using glycidol and the acid chlorides.

ACKNOWLEDGMENT

Carbon and hydrogen were determined by Stephen M. Nagy, Microchemical Laboratory, 78 Oliver Road, Cambridge, Mass.

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RECEIVED for review September 27, 1965. Accepted March 24, 1966. Investigation supported by Contract NAS 811518 from the National Aeronautics and Space Administration.