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Glycidyl Esters of Aromatic Acids*

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Summary

The reaction of substituted benzoic acids, dicarboxylic acids such as phthalic, terephthalic, and isophthalic acids, and the sodium or potassium salts of these acids with equimolar or excess epichlorohydrin in the presence of benzyltrimethylammonium chloride has been studied using various solvents such as toluene, dioxane, monochlorobenzene, and tetrachloroethylene. Use of the free carboxylic acids gave only fair to low yields of glycidyl esters, while sodium or potassium salts of the carboxylic acids gave excellent yields of materials of high oxirane content. The epoxidation of chlorohydrin esters of these acids by the dehydrochlorination was also studied using various dehydrochlorinating reagents such as NaOH, KOH, Na_2CO_3, and $NaAlO_2$ in such solvents as water, dichloromethane, dioxane, and monochlorobenzene at various temperatures. Reaction time, reaction temperature, and water content were found to influence the yield of glycidyl esters. It is suggested that the reaction path involves nucleophilic attack upon the terminal position of the epoxide or epichlorohydrin. The resulting alkoxide then reacts further to give either a glycidyl ester or a chlorine-containing by-product, the predominant course depending upon reaction conditions.

Glycidyl esters of carboxylic acids have been obtained by various methods, the greater part of which was described in patent literatures and is somewhat obscure. These methods contain the reaction of glycidol with acid chlorides, the epoxidation of allyl esters of carboxylic acids by organic peracids, and the reaction of epichlohydrin with carboxylic acids or their salts.

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Epoxidation of ethylenic compounds with organic peracids has been extensively reviewed by Swern (*1*), Ishii (*2*), Suhara (*3*) and Nishimura (*4*) and is beyond the scope of the present study. The direct esterification of glycidol with acid chlorides in the presence of base has been reported by Zetsche and Aeschlimann (*5*), Rider (*6*), Kester and his associates (*7*), and others (*8*), who have obtained glycidyl esters of aliphatic acids and benzoic acid, using sodium or potassium hydroxide and tertiary amines as an acceptor of hydrogen chloride. This method gives the desired product in high yield but requires uncommon or expensive reagents.

The more common starting materials for the preparation of glycidyl esters have been the carboxylic acid or its salt and epichlorohydrin. The reaction of monocarboxylic acids with epichlorohydrin (*9*), especially in the presence of catalysts of the Friedel-Crafts type (*10,11*) or of basic organic nitrogen compounds (*12,13*), results in the formation of α-carboxylic esters of γ-chloropropylene glycol which are then dehydrohalogenated in the presence of strong base to give the desired glycidyl esters. Mueller (*14*) reported that the glycidyl ester was obtained directly when epichlorohydrin was in large excess and a quaternary ammonium halide was used as catalyst.

Kester et al. (*7,15*) obtained good conversions to glycidyl esters of mono- but not of long-chain fatty acids with epichlorohydrin, taking elaborate precautions to exclude all traces of moisture. Addition of a quaternary ammonium halide was reported to increase the rate of this reaction (*16*) also, but even small amounts of water decreased yields of oxirane-containing products (*17*), while in a partly aqueous medium the formation of glycidyl esters occurred either in very low yield (*18*) or not at all (*19*).

Recently, however, Maerker et al. (*20*) studied the reaction of stearic acid, azelaic acid, and the solution salts of both acids with excess epichlorohydrin in the presence of a quaternary ammonium halide and found that use of the free carboxylic acids gave fair to lower yields of glycidyl esters, and that sodium salts of the carboxylic acids gave excellent yields of materials of high oxirane content in a nonaqueous, but anhydrous, system.

Glycidyl esters of aromatic mono- and dicarboxylic acids have been obtained by similar methods using excess epichlorohydrin (*12*) and free carboxylic acids (*21*) or their salts (*21–24*) in the presence of a quaternary ammonium halide under any or no pressure

(*24*). Almost all these methods, however, gave good yields of the desired materials of mono- but not of dicarboxylic acids with epichlorohydrin in a nonaqueous system. Addition of small amounts of water, amounts of which vary according to the type of salt added, is found to increase the rate of this reaction and to increase yields of oxirane-containing products in a nonaqueous, but anhydrous, system (*20,24*). These findings appeared in the patent literature but were not described in detail.

As an initial step in the preparation of glycidyl esters of various mono- and dicarboxylic acids, especially of aromatic carboxylic acids, a better understanding of the reaction of epichlorohydrin with these carboxylic acids and their salts was needed. Benzoic acid and phthalic, terephthalic, and isophthalic acids were chosen as representatives of the two classes of acids, and their reaction with epichlorohydrin was investigated under various conditions. The influence of reaction temperature, time, solvents, and water content was of particular interest.

EXPERIMENTAL

Reagents

Reagent-grade benzoic, *p*- and *o*-toluic acids, phthalic, terephthalic, and isophthalic acids were recrystallized from water. The resulting moist solid was placed in toluene, water was removed as toluene azeotrope, and the toluene solution was cooled and filtered. Drying in the vacuum oven gave refined acids. Sodium or potassium salts of these acids were obtained by an analogous method to that of Kester et al. (*7*).

Commercial epichlorohydrin was redistilled at atmospheric pressure through a 30-cm Vigreux column, and the fraction boiling at 115–116°C was collected for use. The crystalline solid of commercial benzyltrimethylammonium chloride(BTA) was used after drying at 100°C. Reagent-grade sodium or potassium hydroxide was used without further purification.

Toluene, xylene, dioxane, acetone, ether, monochlorobenzene, tetrachloroethylene, and N,N-dimethylformamide were all reagent grade and used with purifications similar to those of Riddick and Toops (*25*), Kraus and Fuoss (*26*), and McAlpine and Smyth (*27*), respectively.

TABLE 1

Reaction Condition for Epichlorohydrin(E) and Benzoic Acids[a]

No.	R—C_6H_4COOH		E,[b] moles	BTA,[c] g	Solvent	Amount of solvent, cc	Time, hr	Temp., °C
	R	mole						
1	H	0.1	0.8	0.5	—	—	0.5	110-120
2	H	0.1	0.8	1.5	—	—	2.0	110-120
3	H	0.33	0.37	4.0	Xylene	150	2.0	110-120
4	*p*-CH_3	0.15	0.15	4.0	Xylene	150	1.0	110-120
5	*o*-CH_3	0.15	0.15	4.0	Xylene	150	1.0	110-120
6	Na—H*	0.28	0.27	2.0	Toluene	250	2.0	100-110
7	Na—H*	0.28	0.27	2.0	Toluene	250	5.0	100-110
8	Na—H*	0.6	0.5	4.0	Xylene	250	2.0	110-120
9	Na—H*	0.21	2.7	2.5	—	—	1.0	100-110
10	Na—H*	0.35	2.6	3.0	—	—	0.5	100-110
11	K—H**	0.28	2.7	3.0	—	—	1.0	100-110
12	K—H**	0.21	0.27	2.0	Toluene	250	2.0	100-110
13	*p*-OH	0.6	1.3	24.0[d]	Water	150	4.5[e]	50-60

[a] Detailed procedure is described in the text. * and ** are the sodium and potassium salts of benzoic acid.

[b] Epichlorohydrin.

[c] Benzyltrimethylammonium chloride.

[d] Sodium hydroxide was used as catalyst.

[e] Epichlorohydrin was added dropwise for 30 min.

General Procedure for Glycidyl Esters

The following detailed procedure illustrates the general method used to prepare crude chlorohydrin ester or glycidyl ester of an acid. Two methods of epoxidation were estimated for preparation of glycidyl esters of substituted benzoic acids, phthalic, terephthalic, and isophthalic acids. Variations in these procedures, such as change in reaction time, temperature, and water content, are listed in Tables 1 and 2.

Reaction of Epichlorohydrin and an Acid in the Presence of Benzyltrimethylammonium Chloride. A mixture of epichlorohydrin and an acid was heated to 100°C with or without a solvent, and solid benzyltrimethylammonium chloride was added in one batch. The mixture was heated at reflux for the desired time, cooled to 40°C, and washed twice with water. The wash waters were discarded, and unchanged epichlorohydrin with or without solvents was removed from the organic phase by distillation under nitrogen and at reduced pressure until the temperature of the residue reached 50°C at 10 mm. Toluene was added to the residue, and the remaining epichlorohydrin was removed as the toluene azeotrope by distillation until the temperature of the residue again reached 50°C at 10 mm. Distillation with toluene was repeated. The final residue was crude glycidyl ester.

TABLE 2

Reaction Condition for Epichlorohydrin(E) and Dibasic Acids[a]

No.	Phthalic acid[b]			E, moles	BTA, g	Solvent	Amount of solvent, cc	Time, hr	Temp., °C
			mole						
1	K	*o*-	0.20	0.40	5.0	Dioxane	200	2.0	ca. 100
2	K	*o*-	0.20	0.40	5.0	Dioxane	200	5.0	ca. 100
3	K	*o*-	0.20	0.40	5.0	Dioxane	200	10.0	ca. 100
4	K	*o*-	0.20	0.40	5.0	Dioxane	200	10.0	80–90
5	K	*o*-	0.20	0.40	5.0	N,N-dimethylformamide	200	5.0	120–130
6	K	*o*-	0.20	0.40	5.0	Xylene	200	2.0	110–120
7	K	*o*-	0.20	0.40	5.0	Cyclohezane	200	5.0	120–130
8	K	*o*-	0.20	0.40	5.0	Cyclohexanone	200	5.0	120–130
9	K	*o*-	0.20	4.0	5.0	—	—	5.0	ca. 110
10	K	*o*-	0.13	0.50	5.0	Tetrachloroethylene	200	3.0	ca. 120
11	K	*o*-	0.13	0.50	5.0	Monochlorobenzene	200	3.0	ca. 125
12	Na	*o*-	0.13	0.50	5.0	Monochlorobenzene	200	3.0	ca. 125
13	Na	*o*-	0.13	0.50	5.0	Monochlorobenzene	200	10.0	95–105
14	Na	*o*-	0.13	0.50	5.0	Monochlorobenzene	200	10.0	80–90
15	K	*m*-	0.13	0.25	5.0	Monochlorobenzene	200	3.0	ca. 125
16	K	*m*-	0.13	0.25	5.0	Monochlorobenzene	200	5.0	ca. 100
17	K	*m*-	0.13	0.25	5.0	Tetrachloroethylene	200	3.0	ca. 120
18	H	*p*-	0.14	2.5	6.0	—	—	1.0	ca. 115
19	H	*p*-	0.14	2.5	6.0	—	—	3.0	ca. 115
20	H	*p*-	0.14	2.5	6.0	—	—	5.0	ca. 115
21	K	*p*-	0.15	2.5	5.0	—	—	5.0	ca. 115
22	K	*p*-	0.2	4.0	7.0	—	—	5.0	ca. 115

[a] Detailed procedure is described in the text.

[b] H, Na, and K are free acids and their sodium and potassium salts, respectively. *o*-, *m*-, and *p*- are phthalic, isophthalic, and terephthalic acids, respectively.

A mixture of a dehydrochlorinating reagent, such as sodium or potassium hydroxide, and the chlorohydrin ester obtained from epichlorohydrin and an acid by a method similar to that described above was heated to the desired temperature for the convenient time in a solvent such as dioxane or N,N-dimethylformamide. The reaction mixture was filtered and the filtrate was dried over sodium sulfate. The solvent was distilled off under reduced pressure and the resinous material was collected, dissolved into a solvent, and this solution was filtered. The distillation of the solvent from this solution resulted in a residue or an oxirane-containing material.

Reaction of Epichlorohydrin and a Sodium or Potassium Salt of an Acid in the Presence of Benzyltrimethylammonium Chloride. To a vigorously agitated suspension of sodium or potassium salts of acids in epichlorohydrin with or without refluxing was added crystalline benzyltrimethylammonium chloride, and agitation and heating at reflux were continued for the desired time. The suspension was then cooled to 50°C, water was added, and the resulting mixture was shaken vigorously. A small amount of solid was removed by filtration, the two layers of the filtrate were separated, and the epichlorohydrin with or without a solvent was again washed with water. Unchanged epichlorohydrin was removed from the organic phase by distillation under nitrogen and at reduced pressure, and finally with toluene, as described above. The final residue was crude glycidyl ester.

The hydrobromic–acetic acid method of Durbetaki (28) was used in all oxirane determinations. The experimental saponification numbers reported in this paper were obtained by saponifying the sample in refluxing alcoholic potassium hydroxide for 5 hr, a period sufficient to achieve quantitative hydrolysis of chlorine atoms. The reported values, therefore, reflect the alkali consumption due to hydrolysis of ester groups as well as that due to hydrolysis of chlorine atoms. The molecular weight of products was determined by a cryoscopic method using dioxane. The infrared absorption spectra in the region 650–4000 cm^{-1} were measured for the product by a Hitachi Model EPI-2 infrared spectrophotometer equipped with a NaCl prism.

RESULTS AND DISCUSSION

In the reaction with epichlorohydrin containing benzyltrimethylammonium chloride(BTA) using xylene as solvent, a sub-

TABLE 3

Results of Equimolar Reaction of Epichlorohydrin and Substituted Benzoic Acids Under Conditions of Table 1 (Nos. 3, 4, and 5)

Fraction	b.p., °C	Yield, %[a]	C, %	H, %	Mol. wt.[b]	d_{25}	Sapn. value[c]	Oxirane oxygen[d]	n^{25}_{D}	Acid value[e]
Benzoic acid (No. 3)										
1	47–50[f]	3.9	29.1[g]	5.00[g]	—	—	—	—	—	—
2	126–130[f]	77.7	55.9[h]	5.14[h]	211	1.261	530	0.23	1.536	0.24
3	146–155[f]	11.6	56.3	5.57	234	—	527	0.08	1.544	0.20
4	Residue	6.8	54.2	6.12	—	—	—	—	—	—
p-Methylbenzoic acid (No. 4)										
1	−140[i]	5.0	—	—	—	—	—	—	—	—
2	156–158[i]	77.9	57.4[j]	5.76[j]	216	1.221	490	0.15	1.537	0.24
3	Residue	17.1	63.1	6.08	260	—	438	—	—	—
o-Methylbenzoic acid (No. 5)										
1	−130[i]	7.8	—	—	—	—	—	—	—	—
2	145–147[i]	75.0	57.8[j]	5.90[j]	218	1.201	491	0.20	1.535	0.21
3	Residue	17.2	64.8	5.98	246	—	404	—	—	—

[a] Ratio in product. Total yield of Nos. 3, 4, and 5 were 103, 30, and 29 g, respectively.

[b] Determined by a cryoscopic method using benzene. Calculated values for I and II are 214.5 and 228.5, respectively, shown in Table 5.

[c] Calculated values for I and II are 524 and 492, and discussed in the text (Experimental).

[d] Calculated values for I and II are both 0; determined by the method of Durbetaki (28).

[e] Calculated values for I and II are both 0; shown in Table 5.

[f] At 0.5 mm Hg pressure.

[g] Calculated values for $(CH_2Cl)_2CHOH$: C, 27.9; H, 4.65.

[h] Calculated values for I: C, 55.9; H, 5.13.

[i] At 1.5 mm Hg pressure.

[j] Calculated values for II: C, 57.8; H, 5.69.

stituted benzoic acid was consumed in a few minutes, and the main product, chlorohydrin ester, was obtained in 90% or more yield (Table 3). A small amount of 1,3-dichloropropanol-2, which seems to appear in the addition reaction of hydrogen chloride eliminated in epoxidation to epichlorohydrin, was obtained in the reaction of benzoic acid (note g in Table 3). An increase in glycidyl ester yield, accompanied by an decrease in the formation of chlorohydrin esters, was also observed when an equimolar sodium or potassium salt of benzoic acid was used in toluene or xylene solution (Nos. 6–8 and 12 in Table 4).

Separation of the crude reaction mixture into its major components was not achieved in any cases but No. 1, 3–5, and 11 in Table 4, but a procedure was devised for estimating the relative amounts of the two types of esters, glycidyl and chlorohydrin, in the crude product, which was analyzed for oxirane oxygen content and saponification number. If it is assumed that only glycidyl ester and

TABLE 4

Results of Reaction of Epichlorohydrin with Benzoic Acids Under Condition of Table 1 (Nos. 1, 2, and 6–13)

					Concentration	
No.	Yield, %	Oxirane oxygen,[a] %	Saponification value[b]	Mol. wt.[c]	Epoxide,[d] %	Chlorohydrin,[e] %
1[j]	76.7[f]	3.11	423	217	34.6	60.0
2	75.4[f]	3.92	397	214	43.6	49.6
6	68.4[g]	6.74	360	215	74.9	23.5
7	51.7[g]	7.48	338	220	83.3	14.5
8	62.9[g]	5.70	375	221	63.4	33.6
9	134[g]	4.11	416	234	45.6	52.0
10	141[g]	3.69	431	230	41.0	57.7
11[k]	126[g]	4.30	411	227	47.8	49.9
12	55.4[g]	7.31	348	211	81.2	17.7
13	98.4[h]	6.74[i]	238[i]	435[i]	93.6[i]	0.2[i]

[a] Determined by the method of Durbetaki (28). Calculated values for III and IV ($n = 1$) are 9.00 and 7.22%, as shown in Table 5.

[b] Calculated values for I, III, IV, and V ($n = 1$) are 524, 315, 253, and 434, respectively, shown in Table 5.

[c] Determined by a cryoscopic method using benzene. Calculated values for I, III, IV, and V are 214.5, 178, 444, and 517, respectively.

[d] Based on oxirane determination by the method of Durbetaki (28).

[e] Obtained from Eq. (2), where B_e and B_c are 315 and 524 for Nos. 1, 2, 6–12; 253 and 434 for No. 13(i).

[f] As I or $C_6H_5CO_2CH(CH_2Cl)CH_2OH$ (I′).

[g] As III.

[h] As IV ($n = 1$).

[i] Calculated values for IV and V: Oxirane oxygen, 7.22 and 0%; saponification value, 253 and 434; molecular weight, 444 and 517; epoxide % is based on oxirane oxygen %.

[j] Fraction, boiling point, yield (ratio in product), oxirane oxygen %, n_D^{30} are 1, 41–48/4, 24.4, 0.12, 1.4756; 2, 90–120/2, 11.1, 1.40, 1.5148; 3, 121–130/2, 16.3, 5.81, 1.5230; 4, 135–150/2, 40.7, 3.64, 1.5267; 5, residue, 7.5, 2.28, -.

[k] Fraction, boiling point, yield (ratio in product, %), oxirane oxygen % are 1, –110/2, 9.3, -; 2, 110–120/2, 16.3, 3.5; 3, 120–140/2, 37.3, 5.85; 4, 140–145/2, 20.9, 2.95; 5, residue, 16.2, 0.72. Redistillation of fractions 2 and 3 resulted in two fractions, boiling point, yield and oxirane oxygen of which are 125–130/2, 82.4, 7.90; 130–135/2, 17.5, 7.42.

chlorohydrin ester were present in significant amounts, an estimation can be made from the analytical data of the amounts of each type of ester. Thus the crude product seems to be composed of 34–83% glycidyl ester and 14–60% chlorohydrin ester, amounts of which were calculated as

$$\text{epoxide }\% = 100 \times \text{oxirane oxygen }\%/A \tag{1}$$

where A is the calculated value of oxirane oxygen %, which is shown in Table 5, and

$$\text{chlorohydrin }\% = \frac{\text{saponification value} - B_e \times \text{epoxide }\%}{B_c} \times 100 \tag{2}$$

Here B_e and B_c are the calculated values of saponification numbers for an epoxide and a corresponding chlorohydrin, respectively, shown in Table 5.

The use of potassium salt rather than sodium salt results in a decrease in yield but in an increase in oxirane oxygen content. Indeed, yield of No. 12 (55.4%) is smaller than that of No. 6 (68.4%), but the oxirane oxygen content of No. 12 (7.31) is higher than No. 6 (6.74). Epoxide content decreases with the increase of temperature (No. 6, 6.74, and No. 8, 5.70) and increases with increasing reaction time (No. 6, 6.74, and No. 7, 7.48) as shown in Table 4. The total yield decreases with the increase of temperature (No. 6, 68.4, and No. 8, 62.9) and with increasing reaction time (No. 6, 68.4,

TABLE 5

Calculated Values of Oxirane Oxygen Content, Saponification Value, and Molecular Weight for Various Esters

No.	Ester structure[b]	Oxirane oxygen, %	Saponification value[a]	Mol. wt.
I	$C_6H_5CO_2CH_2CHOHCH_2Cl$	0.00	524	214.5
II	$CH_3C_6H_4CO_2CH_2CHOHCH_2Cl$	0.00	492	228.5
III	$C_6H_5CO_2CH_2\overline{CHCH_2O}$	9.00	315	178
IV[c]	$\overline{OCH_2CH}CH_2OC_6H_4(CO_2CH_2CHOHCH_2OC_6H_4)_nCO_2CH_2\overline{CHCH_2O}$	7.22	253	444
V[c]	$ClCH_2CHOHCH_2OC_6H_4(CO_2CH_2CHOHCH_2OC_6H_4)_nCO_2CH_2CHOHCH_2Cl$	0.00	434	517
VI	$CH_3C_6H_4CO_2CH_2\overline{CHCH_2O}$	8.34	292	194
VII	$C_6H_4(CO_2CH_2\overline{CHCH_2O})_2$	11.5	403	278
VIII	$C_6H_4(CO_2CH_2CHOHCH_2Cl)_2$	0.00	640	351
IX	$ClCH_2CHOHCH_2O_2CC_6H_4CO_2CH_2\overline{CHCH_2O}$	5.09	535	314.5
X[c]	$\overline{OCH_2CH}CH_2OC_6H_4(CO_2CH_2CHOHCH_2OC_6H_4)_nCO_2CH_2CHOHCH_2Cl$	3.34	350	480.5

[a] This value reflects the alkali consumption due to hydrolysis of ester groups as well as that due to hydrolysis of chlorine atoms; see the text.

[b] This is a representative formula. Other isomers, such as $C_6H_5CO_2CH(CH_2OH)CH_2Cl$ (I′), are also considered; however, their values of oxirane content, saponification value, and molecular weight are not different from those of one of their isomers such as I.

[c] Where $n = 1$.

and No. 7, 51.7). Optimum catalyst concentration was not determined, but a large catalyst effect can be considered, as Mearker et al. (*20*) pointed out.

It has been reported that the glycidyl ester can be obtained directly if epichlorohydrin is in large excess and if a quaternary ammonium halide is used as a catalyst (*12*). The hydrogen chloride eliminated in the reaction is largely absorbed by the excess epichlorohydrin, but at least some of the hydrogen chloride is likely to react with the glycidyl ester present to give the α-carboxylic ester of β- or γ-chloropropylene glycol. To avoid the troublesome problem of secondary reactions of glycidyl esters with hydrogen chloride, some workers such as Kester et al. (*7,15*), and Maerker et al. (*20*) used salts of carboxylic acids, rather than the acids themselves, as starting materials, and obtained good conversions to glycidyl esters of mono- and di-fatty acids.

Unsatisfactory results were obtained in this reaction of benzoic acid with large excess epichlorohydrin (Nos. 1 and 2 in Table 4). The similar poorer results (Nos. 9–11) were obtained for the reaction of sodium or potassium salt of benzoic acid with large excess epichlorohydrin in the presence of BTA, compared with the higher epoxide contents (Nos. 6–8 and 12) of the product for the reaction of this salt with equimolar epichlorohydrin using toluene as solvent. With large excess epichlorohydrin, epoxide content increases with increasing reaction time (No. 1, 3.11, and No. 2, 3.92 for free acid; No. 10, 3.69, and No. 9, 4.11 for sodium salt). The use of potassium salt rather than sodium salt results in a decrease in yield but an increase in oxirane oxygen content. Indeed, the yield of No. 11 (126%) is smaller than that (134%) of No. 9, but the oxirane oxygen content of No. 11 (4.30) is higher than that (4.11) of No. 9 when there is a large excess of epichlorohydrin. The lower oxirane oxygen contents of Nos. 9–11, compared with the higher ones (Nos. 6, 7, and 12), seem to be due to the shorter reaction time of 0.5 or 1 hr than that of Nos. 6 or 7 or 12 (2, 5, and 2 hr, respectively). Optimum catalyst concentration was not determined.

Epoxidation reactions of chlorohydrin ester of substituted benzoic acids were studied under various conditions which are shown in Table 6 together with the results obtained. Glycidyl esters were obtained in 48% or lower yields in all cases. The effect of reaction temperature in the presence and absence of water added was tested (Table 6). Water increased the oxirane oxygen contents of prod-

TABLE 6

Epoxidation of Chlorohydrin Esters of Substituted Benzoic Acids[a]

$R{-}C_6H_4CO_2H$[a]										
No.	R	Base	Amount of base, g	Temp., °C	Time, hr	Solvent	Amount of solvent, cc	Yield,[b] %	Oxirane oxygen,[c] %	Sapn. value[d]
3	H	$NaAlO_2$	6.0	100	1	Dioxane	150	66.0[e]	2.59	395
3	H	$NaAlO_2$	6.0	100	3	Dioxane	150	64.8[f]	2.70	400
4	p-CH_3	NaOH	5.0	60	1	Water	250	52.4	4.10	344
4	p-CH_3	NaOH	5.0	60	3	Water	250	6.9	3.86	367
4	p-CH_3	$NaAlO_2$	6.0	100	1	Dioxane	150	67.1	2.87	386
4	p-CH_3	$NaAlO_2$	6.0	100	3	Dioxane	150	65.8	2.96	387
4	p-CH_3	$NaAlO_2$	6.0	100	5	Dioxane	150	60.5	3.46	400
5	o-CH_3	$NaAlO_2$	6.0	100	1	Dioxane	150	67.3	2.61	379
5	o-CH_3	NaOH	5.0	60	1	Water	250	32.6	3.89	329
3	H	NaOH	5.0	60	1	Benzene	200	68.0	2.37	403

[a] Chlorohydrin esters were those (Nos. 3, 4, and 5) in Table 3, and 5 g of them was used in all cases. Numbers in this table are the same as those in Table 3.

[b] Ratio in product.

[c] Calculated values for III and VI are 9.00 and 8.34, respectively, shown in Table 5.

[d] Calculated values for I, II, III, and VI are 524, 492, 315, and 292, respectively.

[e] $n_D^{30} = 1.5263$.

[f] $n_D^{30} = 1.5246$.

ucts but decreased their yields. Lowering the reaction temperature increased the oxirane oxygen content but decreased the yield of products. The data indicate that glycidyl ester formation is favored by low reaction temperatures and the presence of water. No significant difference was observed in catalytic efficiency between NaOH and $NaAlO_2$ in nonaqueous solvents such as benzene and dioxane.

To determine the effect of prolonged heating upon the reaction mixture, the experiments of three sets, the first and second; third and fourth; fifth to seventh, in Table 6 were carried out. Analysis of the product revealed that prolonged heating causes the conversion of consumed chlorohydrin esters to glycidyl esters and/or the destruction of some of the glycidyl esters formed initially and gives rise to glycol-containing or no-chlorine-containing by-products not found after brief heating, especially in the presence of NaOH and in water solution.

Glycidyl ester ether such as IV was obtained in 98% or higher yield with higher oxirane oxygen content of 94% of theoretical by a method similar to that of Hoppe (29).

In the equimolar reaction with epichlorohydrin containing BTA using a variety of solvents as dioxane and xylene, a potassium or sodium salt of aromatic dicarboxylic acid was consumed, and low

TABLE 7

Results of Reaction of Epichlorohydrin with Dicarboxylic Acids Under Conditions of Table 2[a]

	Fraction I[b]				Fraction II			
No.	Yield, g	Oxirane oxygen,[c] %	Sapn. value[d]	Mol. wt.[e]	Yield, g	Oxirane oxygen,[c] %	Sapn. value[d]	Mol. wt.[e]
1[f]	29.6	1.85	624	366	—	—	—	—
2[f]	34.5	4.40	605	315	—	—	—	—
3	32.0	3.41	615	290	14.5[h]	3.02	650	—
4	18.3	2.52	631	320	5.8[h]	1.80	627	—
5[f]	—	—	—	—	52.6[h]	0.76	656	372
6[f]	—	—	—	—	39.4[h]	1.46	648	400
7[f]	33.4	1.96	621	352	—	—	—	—
8[f]	34.0	1.92	630	354	—	—	—	—
9[f]	28.4	1.23	629	381	—	—	—	—
10	23.2	0.31	648	302	2.7[i]	0.50	653	—
11	20.1	1.71	618	300	17.0[j]	2.60	618	—
12	25.4	2.01	612	298	7.6[j]	0.89	643	—
13	28.7	3.56	605	298	10.0[j]	4.25	648	—
14	16.5	2.54	625	308	6.6[h]	1.81	636	—
15	16.7	0.96	658	378	5.9[j]	4.12	614	—
16	27.5	1.86	628	304	3.7[j]	0.92	—	—
17	21.0	0.52	612	298	3.7[i]	0.49	652	—
18[f]	55.0	2.76	637	333	—	—	—	—
19[f]	59.8	2.75	635	316	—	—	—	—
20[f]	74.6	2.65	642	293	—	—	—	—
21[f]	36.3	1.74	649	351	—	—	—	—
22[f]	27.6	1.12	639	355	—	—	—	—

[a] Numbers in this table are the same as those in Table 2.

[b] Soluble in dioxane.

[c] Calculated value for $C_6H_4(CO_2CH_2\overline{CHCH_2O})_2$ (VII) is 11.5

[d] Calculated values for VII and VIII are 403 and 640, respectively.

[e] Calculated values for VII and VIII are 278 and 351, respectively.

[f] Not fractionated.

[h] Soluble in N,N-dimethylformamide.

[i] Soluble in tetrachloroethylene.

[j] Soluble in monochlorobenzene.

oxirane-containing product, a great part of which seems to be chlorohydrin ester isomers, was obtained in 90% or higher yield (Tables 2 and 7). Separation of the crude reaction mixture into its major components was not achieved in all cases, but a procedure was devised for estimating the relative amounts of the two types of esters, as described in the case of monocarboxylic acids, in the crude product from the saponification number and oxirane oxygen content [see Eqs. (1) and (2)].

No significant difference was observed in oxirane oxygen contents between sodium and potassium salts of dicarboxylic acids (No. 12, 2.01, and No. 7, 1.96, or No. 8, 1.92), *o*, and *p*-phthalic acids (No. 9, 1.23, and No. 21, 1.74, or No. 22, 1.12), and among solvents other than dioxane, N,N-dimethylformamide and tetrachloroethylene (No. 6, 1.46, No. 7, 1.96, No. 8, 1.92, and No. 11, 1.71), respectively. The more available solvent in nonaqueous system was dioxane, while N,N-dimethylformamide and tetrachloroethylene were most unsuccessful solvents for this reaction under these conditions (No. 5, 0.76, No. 10, 0.31, and No. 17, 0.52).

Unsatisfactory results were obtained in the reaction of these dicarboxylic acids with a large excess of epichlorohydrin (Nos. 18–20), and the similar poorer yields of oxirane-containing products were also observed (Nos. 9, 21, and 22) for the reaction of sodium or potassium salt of these acids with a large excess of epichlorohydrin in the presence of BTA, compared with the higher epoxide contents (Nos. 2, 3, and 13) of the product obtained from the reaction of this salt with equimolar epichlorohydrin using various solvents. These facts disagree with the findings of Kester et al. (*7,15*) and Maerker et al. (*20*), who used salts of carboxylic acids, rather than the acids, as starting materials, and obtained good conversions to glycidyl esters of mono- and di-fatty acids.

The low reactivity of sodium or potassium salt of these acids seems to be ascribed to low solubility in epichlorohydrin and such solvents as xylene, cyclohexane, and cyclohexanone, resulting in poor contact of the two reagents. Improvements of contact were achieved by dissolving or suspending these salts in polar solvents such as dioxane, monochlorobenzene, and dichloroethylene before combining them with epichlorohydrin.

The need for improved contact between epichlorohydrin and these salts of acids to shorten reaction time, coupled with the relatively low yield losses experienced in similar experiments by Maerker et al. (*20*), prompted the use of a partly aqueous system in this case. The use of water, however, was not tried in the present work.

Lowering the reaction temperature less than 100°C decreases

TABLE 8

Epoxidation of Chlorohydrin Esters of Dicarboxylic Acids[a]

$C_6H_4(CO_2H)_2$[a]	Base	Amount of base, g	Solvent	Amount of solvent, cc	Temp., °C	Time, hr	Yield, g	Oxirane oxygen,[b] %	Sapn. value[c]
1 *o*-	NaOH	20	ClC_6H_5	200	130	15	18.4	2.41	576
2 *o*-	Na_2CO_3	20	ClC_6H_5	200	130	15	18.2	2.37	575
3[d] *o*-	NaOH	20	CH_2Cl_2	200	40	24	4.4	7.24	501
4[d] *o*-	Na_2CO_3	20	CH_2Cl_2	200	40	24	4.8	2.32	580
5 *o*-	NaOH Na_2SO_4	20 45	Dioxane	200	65	25	7.4	8.50	401
6[d] *m*-	NaOH	20	CH_2Cl_2	200	40	24	4.0	7.23	500
7 *m*-	NaOH	20	Dioxane	200	65	25	6.9	7.30	486
8 *p*-	NaOH	20	Dioxane	200	65	25	7.1	7.41	490
9[d] *p*-	NaOH	20	CH_2Cl_2	200	40	24	4.6	7.16	479
10 *p*-	NaOH[e]	20	Water[e] Benzene	150 100	10	2	11.2	5.92	—
11 *p*-	NaOH[e]	6	Water[e] Benzene	200 100	80	20	7.9	4.23	—
12 *p*-	NaOH[e]	15	Acetone Water	100 50[e]	−5	2	4.3	7.36	—
13 *p*-	NaOH[e]	10	Water[e] Ether	50 250	0	1	8.8	4.82	—

[a] Chlorohydrin esters of *o*-, *m*-, and *p*-phthalic acids were obtained by the method shown in Table 2 (Nos. 1, 16, and 21, respectively), and 20 g of them were used in all cases. Their oxirane oxygens were 1.86, 1.79, and 1.80, respectively.

[b] Calculated values for VII, VIII, and IX are 11.5, 0.0, and 5.09, respectively, as shown in Table 5.

[c] Calculated values for VII, VIII, and IX are 403, 640, and 535.

[d] Corresponding dibasic acids were recovered from reaction mixtures.

[e] NaOH aqueous solution was added dropwise.

both the rate of salt consumption and the conversion of consumed salt to glycidyl ester. Analysis data of the crude product, as shown in Table 7, revealed that prolonged heating causes the destruction of some of the glycidyl ester formed initially. This effect of reaction time was found to be different between two cases using the free acids and their salts as starting materials.

Epoxidation reactions of chlorohydrin ester, containing some glycidyl ester, of dicarboxylic acids were also studied under various conditions, which are shown in Table 8 together with the results obtained. In some cases such as No. 5, high oxirane-containing products were obtained but their yields were low, probably due to the hydrolysis of both types of esters, glycidyl and chlorohydrin esters.

Four procedures, Nos. 10–13, differing only slightly in detail, were used to combine the aqueous sodium hydroxide with chlorohydrin ester. Highest results were obtained by slow addition of the aqueous solution of sodium hydroxide to cold chlorohydrin ester solution in acetone (at −5°C). Procedures of Nos. 10, 12, and 13 are similar to each other but differ in the solvents used. The procedure for No. 11 is composed of slow addition of an aqueous solution of sodium hydroxide to chlorohydrin ester solution and of removal of the water continuously as the benzene azeotrope. The rate of water removal was somewhat slower than the rate of addition, and the temperature of the reaction mixture decreased slowly as the water content of the mixture increased. In modifications of this procedure, the water added slowly as aqueous sodium hydroxide solution was kept in the reaction mixture at total reflux (Nos. 10, 12, and 13). Water increased the oxirane oxygen content of product but decreased its yield significantly. The data indicate that glycidyl ester formation is favored by lower reaction temperatures and the presence of polar solvents such as water, acetone, dichloroethylene, and dioxane, with removal of the water continuously as a solvent azeotrope. The use of various dehydrochlorination reagents was not tried in the present work.

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Zusammenfassung

Die Reaktion zwischen substituierter Benzoesäuren, Dicarbonsäuren, wie Phtalsäure, Terephtalsäure und Isophtalsäure, und den Natrium- oder Kaliumsalzen dieser Säuren mit äquimolaren Mengen oder Uberschuss an Epichlorhydrin wurde in Gegenwart von Benzyltrimethylammoniumchlorid in den Lösungmitteln Toluol, Dioxan, Monochlorbenzol und Tetrachloräthylen untersucht. Die freien Carbonsäuren geben nur mässige oder geringe Ausbeuten an Glyzidester, während die Natrium-oder Kaliumsalze der Carbonsäuren eine ausgezeichnete Ausbeute an Material ergab, das einen hohen Oxirangehalt hatte. Die Epoxidierung der Chlorhydrinester dieser Säuren durch Dehydrochlorierung wurde ebenfalls untersucht, wobei verschiedene Dehydrochlorierungsmittel, wie z.B. NaOH, KOH, Na_2CO_3, und $NaAlO_2$ in Lösungsmitteln wie Wasser, Dichlormethan, Dioxan und Monochlorbenzol bei verschiedenen Temperaturen verwendet wurden. Die Reaktionszeit, die Reaktionstemperatur und der Wassergehalt beeinflussen die Ausbeute an Glyzidester. Es wird angenommen, dass die Reaktion über einen nukleophilen Angriff auf die endständigen Epoxide und Epichlorhydrine vor sich geht. Die daraus sich ergebenden Alkoxide reagieren dann weiter, um je nach den Reaktionsbedingungen entweder einen Glyzidester oder ein chlorhaltiges Neben produkt zu bilden.

Résumé

L'étude de la réaction des acides benzoiques substitués, des acides dicarboxyliques tels que l'acide phthalique, terephthalique et l'isophthalique, des sels de sodium et de potassium des ces acides avec l'épichlorhydrine en quantité équimolaire ou en excès et en presence du chlorure de benzyltrimethylammonium, dans des solvants divers, tels que le toluène, le dioxanne, le monochlorobenzène, et le tetrachloroéthylène. Les acides carboxyliques libres donnent des rendements mediocres ou bas en esters glycidyl, tandis que leurs sels de sodium ou de potassium donnent des rendements excellents en materiaux contenant beaucoup d'oxirane. On a aussi etudié l'époxydation des ester de chlorhydrine de ces acides par la deshydrohalogénation avec l'emploi des divers agents deshydrohalogénants tels que NaOH, KOH, Na_2CO_3, et $NaAlO_2$ dans l'eau, le dichloroéthane le dioxanne et le monochlorobenzène comme solvants, à des temperatures variées. On a trouvé que la duree de la réaction, la température de la réaction et la teneur en eau influencent le rendement en esters glycidyliques. On suggère que le cours de la reaction comporte une attaque nucléophile sur la position terminale de l'époxyde ou de la chlorhydrine. L'alcoxide resultant réagit alors plus loin pour donner soit un ester glycidyl soit un produit sécondaire contenant du chlore, le cours prédominant dependant des conditions réactionelles.

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