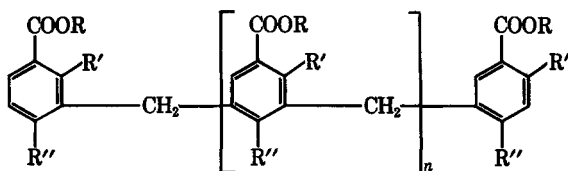


Epoxy Resins from Substituted Benzoic Acids-Formaldehyde Resins*

YOSHIO TANAKA and HIROSHI KAKIUCHI, *Department of Applied Chemistry, Faculty of Engineering, Yokohama National University, Yokohama, Japan*

Synopsis

Some polybasic acid derivatives were obtained from substituted benzoic acids such as *p*- and *o*-toluic acids, and *p*-formaldehyde in concentrated sulfuric acid by a method similar to that of Naokawa et al. The structure of these resinous substituted benzoic acid-formaldehyde materials was determined by a paper chromatography and infrared spectrum analysis, and found to be



where $n = 0-2$; $R = H, R'$, and $R'' = H$ or CH_3 , respectively. New glycidyl-ester-type epoxy resins were prepared from these substituted benzoic acid-formaldehyde resins and epichlorohydrin in the presence of sodium hydroxide, using dioxane as a solvent. These resins were considered to have the general structure shown above, where $n = 0-2$, $R = \text{CH}_2\text{CHCH}_2\text{O}$, and R' and $R'' = H$ or CH_3 , respectively.

INTRODUCTION

The reactions of formaldehyde with benzoic acid and its esters have been studied by Schöpff¹ and Weil² who obtained methylene-3,3'-dibenzoic acid or diphenylmethane-*m*-dicarboxylic acid. Welch and Smith³ obtained no dimer of *p*-toluic acid by the reaction with formaldehyde in the presence of sulfuric acid using an alcohol as a solvent. Polyoxymethylene is found to react with benzoic acid and its esters in concentrated sulfuric acid, and becomes a brownish-black resin,⁴ which can react with ethylene glycol or glycerol in the presence of *p*-toluenesulfonic acid to form a polyester resin in the gelation state.

As part of a study of the preparation and properties of epoxy derivatives of aromatic acids, it was desired to prepare the glycidyl esters of several

* Presented at 14th Annual Meeting of Gosei Jushi Kogyo Kyokai on Thermosetting of Resins, Osaka, Sept. 1964.

aromatic mono- and dicarboxylic acids. In a previous report,⁵ a series of glycidyl esters of mono- and dicarboxylic acids was obtained from epichlorohydrin and corresponding carboxylic acids or their salts, such as benzoic, phthalic, isophthalic, and terephthalic acids. This paper deals with the preparation and properties of epoxy resins from epichlorohydrin and substituted benzoic acid-formaldehyde resins, since no such reaction has been reported in detail.

EXPERIMENTAL

Reagents

Reagent-grade benzoic, *p*- and *o*-toluic acids were recrystallized from water and dried under reduced pressure at 25°C. Reagent-grade paraformaldehyde was dried under reduced pressure at 25°C. for several days. Reagent-grade sodium hydroxide and concentrated sulfuric acid were used without further purification. Reagent-grade dioxane was used with purification similar to the method of Kraus and his co-workers.⁶

General Procedure for Substituted Benzoic Acids-Formaldehyde Resins

A mixture of a substituted benzoic acid, paraformaldehyde, and concentrated sulfuric acid was heated to the desired reaction temperature for the convenient time (Table I) in a 300- or 500-ml. 3-necked flask fitted

TABLE IA
Preparative Conditions for Benzoic Acid-Formaldehyde Resins

No.	Paraformaldehyde, g.	R-C ₆ H ₄ COOH ^a		Amount of conc. sulfuric acid, cc.	Temp., °C.	Time, hr.
		R	Amount, g.			
1	3	H	18	70	50	6
2	3	H	18	60	80	6
3	1	<i>p</i> -CH ₃	7	40	50	6
4	2	<i>p</i> -CH ₃	14	60	50	2
5	1	<i>p</i> -CH ₃	7	40	80	6
6	5	<i>o</i> -CH ₃	30	100	50	6
7	1	<i>p</i> -CH ₃	7	40 ^b	120	6
8	1	<i>p</i> -CH ₃	7	40 ^c	100	6

^a Molecular weight, acid number and melting point are:⁹

^b 100% H₃PO₄ was used in place of H₂SO₄.

^c 60% HClO₄ was used in place of H₂SO₄.

TABLE IB
Preparative Conditions for Benzoic Acid-Formaldehyde Resins

R	Mol. wt.	Acid number	M. p., °C.
H	122.12	459	122
<i>p</i> -CH ₃	136.14	412	179-181
<i>o</i> -CH ₃	136.14	412	107-108

with a reflux condenser, mechanical stirrer, and thermometer, and surrounded by a water bath.

The reaction mixture was then poured into 250 or 300 ml. of water. The resinous material was dissolved in methyl ethyl ketone, and the mixture was shaken with an aqueous solution of sodium carbonate, washed with water, and dried over sodium sulfate. This solution was concentrated to a small volume, and poured into a large amount of dioxane. The insoluble brownish-black material (fraction II) was collected and washed with dioxane. The methyl ethyl ketone-dioxane solution separated from fraction II and the dioxane washing of fraction II were combined, and these solvents were distilled off under reduced pressure. The residue was a brown solid (fraction I). Reaction conditions and the results are shown in Tables I and II, respectively.

TABLE II
Preparative Result and Properties of BF^a

No.	Fraction I					Fraction II	
	Yield, g.	Mol. wt. ^b	Acid No. ^c	M.p., °C.	Appearance	Yield	M.p., °C.
1	8.2	240	430	240-265	Brown ^d	5.0 ^e	320
2	3.4	251	418	245-280	Brown	11.3	350
3	3.1	271	388	281-304	Brown ^e	2.3 ^a	350
4	6.0	270	391	295-300	Brown	4.3	320
5	1.9	262	390	310-312	Brown	5.0	350
6	29.2	218	327	100-138	Brownish ^f Black	Trace	—
7	None	—	—	—	—	—	—
8	None	—	—	—	—	—	—

^a Reaction conditions are the same as shown in Table I.

^b Theoretical values of (R-C₆H₃COOH)₂CH₂ are: R = H, 256; R = CH₃, 284.

^c Theoretical values of (R-C₆H₃COOH)₂CH₂ are: R = H, 438; R = CH₃, 395.

^d Calculated for C₁₅H₁₂O₄: C, 70.4%; H, 4.69%. Found: C, 70.03%; H, 4.56%.

^e Calculated for C₁₇H₁₆O₄: C, 71.9%; H, 5.16%. Found: C, 68.61%; H, 5.82%.

^f Calculated for C₁₇H₁₆O₄: C, 71.9%; H, 5.16%. Found: C, 66.96%; H, 5.89%.

^b Calculated for C₁₇H₁₆O₄: C, 71.9%; H, 5.16%. Found: C, 70.23%; H, 4.90%.

General Procedure for Glycidyl Esters

Two methods of epoxidation were estimated for the preparation of glycidyl esters of substituted benzoic acid-formaldehyde resins.

(a) **Reaction of Epichlorohydrin and an Acid in the Presence of Benzyltrimethylammonium Chloride.** The following detailed procedure illustrates the general method used to prepare crude chlorohydrin ester or glycidyl ester of an acid. Variations in this procedure, such as changes in reaction time, reaction temperature, and water content, are listed in Table IV together with the results obtained.

A mixture of epichlorohydrin and a substituted benzoic acid-formaldehyde resin (BF) 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 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. The distillation with toluene was repeated. The final residue was crude glycidyl ester. The hydrobromic-acetic acid method of Durbetaki⁷ was used in all oxirane determinations.

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

(b) 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 BF in epichlorohydrin at reflux 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 phase was again washed with water. Unchanged epichlorohydrin was removed from the organic phase by distillation under nitrogen and at reduced pressure, finally with toluene, as described above in Sec. (a). The final residue was crude glycidyl ester. Variations in the above procedure included changes in reaction time, reaction temperature, and water content and are listed in Table IV together with the results obtained.

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 resins was determined by a cryoscopic method using dioxane. The infrared absorption spectra in the region of 650–4000 cm.^{-1} were measured for the resins by a Hitachi Model EPI-2 infrared spectrophotometer equipped with a NaCl prism. The qualitative analysis for sulfur was carried out by Shriner, Fuson, and Curtin's method.⁹

The benzoic acid-formaldehyde resin was also analyzed by a paper chromatography under the following condition:

Paper: Tohyo Roshi No. 50 for paper chromatography.

Solvent: *n*-butanol/1.5*N* aq. NH_4OH solution/ $(\text{NH}_4)_2\text{CO}_3$ buffer solution (pH 9), (40/11/19-v/v/v); or *n*-butanol/ethanol (4:1)/sodium hydrogen carbonate aq. solution: at 25°C.

Reagent: phenol red alc. solution; or crystal violet aq. solution.

RESULTS AND DISCUSSION

The acid-catalyzed condensation of a number of aromatic compounds with formaldehyde or formaldehyde derivatives is known to yield diaryl-methanes under the proper conditions. The arylmethylation reaction is known chiefly for such reactive benzene derivatives as the phenols and arylamines. A smaller number of the less reactive compounds have been studied, examples being benzene,¹⁰ toluene,^{11,12} benzyl chloride,^{11,12} diphenyl,^{11,12} iodobenzene,¹³ naphthalene,¹⁴ mesitylene,¹⁵ chlorobenzene,³ *p*-xylene,³ and benzoic acid or its ester.⁴

In these examples formaldehyde was used in a variety of forms such as formalin, paraformaldehyde, methylal, trioxymethylene, and methylene diacetate. Sulfuric acid, often with a diluent, was used as the catalyst.

The present study, shown in Tables I and II, was made to determine further applications and limitations of the reaction when used with nonphenolic and nonaminated derivatives of benzene. Samples of *p*- and *o*-toluic acid were condensed with paraformaldehyde in the presence of concentrated sulfuric acid by the same method as used for as benzoic acid. The results appear in Table II, which shows that the higher the reaction temperature the larger the amounts of fraction II and that no catalysts other than concentrated sulfuric acid gave di- and polyarylmethanes. These results agree with Naoakawa et al.⁴ who found that no condensed materials were obtained for the reaction of benzoic acid and methyl benzoate with a polyoxymethylene in the presence of 100% H_3PO_4 , 60% HClO_4 , AlCl_3 , $\text{BF}_3 \cdot \text{O}(\text{C}_2\text{H}_5)_2$, and *p*-toluenesulfonic acid.

No sulfur was found in any of the condensed materials with the method of Shriner, Fuson, and Curtin⁹ and the sulfonation reaction is unlikely to occur in these reactions. However, Welch and Smith³ have found that a reaction other than esterification occurs only at high concentrations of sulfuric acid for the reaction of *p*-toluic acid with paraformaldehyde and results chiefly in sulfonation.

Fraction I of benzoic and *p*-toluic acid-formaldehyde resins (Nos. 1 and 3 in Table II) were dissolved into acetone or dioxane, and analyzed by paper chromatography using mixed solvents of *n*-butanol/ethanol/1.5*N* aq. NH_4OH solution- $(\text{NH}_4)_2\text{CO}_3$ buffer (pH 9) and *n*-butanol/ethanol (4:1) saturated with 1% sodium hydrogen carbonate aq. solution as solvents for development at 25°C.

Spraying a mixed solvent of phenol-red alcoholic solution and phosphate salt buffer (pH 7.2) solution, or crystal violet aq. solution on the paper

TABLE III
R_f Values of Benzoic and *p*-Toluic Acids-Formaldehyde Resins^a

Derivative	Method I Free acid	Method II Potassium salt	Method III Free acid
Solvent	<i>n</i> -Butanol/ethanol → 1.5 <i>N</i> aq. NH ₄ OH → (pH 9), aq. (NH ₄) ₂ CO ₃	40/11 19	<i>n</i> -butanol, 4 Ethanol Satd. with 1% aq. NaHCO ₃ , 3
Reagent	0.1% Phenol red alc., 15/phosphate ^b buffer (pH 7.2), 30	Bromocresol purple alc.	Crystal violet aq. ^c
Acid			
Benzoic	0.59	0.17	0.66
<i>p</i> -Toluic	0.65	0.17	0.69
Isophthalic	0.21	0.15	—
BF-1	0.47	—	0.10, 0.24, 0.37
BF-3	0.38, 0.49	0.17	0.39, 0.48

^a Acetone or dioxane solution of fraction I in Table II: BF-1, No. 1; BF-3, No. 3. The method used is similar to that of ref. 17.

^b Phosphate buffer is obtained from 7 ml. of 1/15*M* aq. Na₂HPO₄ solution and 3 ml. of 1/15*M* aq. KH₂PO₄ solution. This reagent mixture gives yellow spots on a red background.

^c Whitish or redish violet spots are obtained on a violet background. cf. K. Nerai, M. Idehara, T. Kishimoto, H. Hiyama, and K. Ohshima, *Kogyo Kagaku Zasshi*, **62**, 846 (1959).

gives yellow spots on a red background or redish and whitish-violet on a violet background, respectively. The resulting *R_f* values are shown in Table III together with those of benzoic, *p*-toluic, and isophthalic acids obtained by the same procedure. In addition to the above analysis, unsuccessful attempts were made to separate these acids and the *p*-toluic acid-formaldehyde resin (No. 3 in Table II) by a method using the potassium salts of these acids (method II in Table III).

Separations of aromatic acids were described by Evans et al.¹⁷ in their study of phenols, by Bray et al.¹⁸ for organic acids in the rabbit, also by

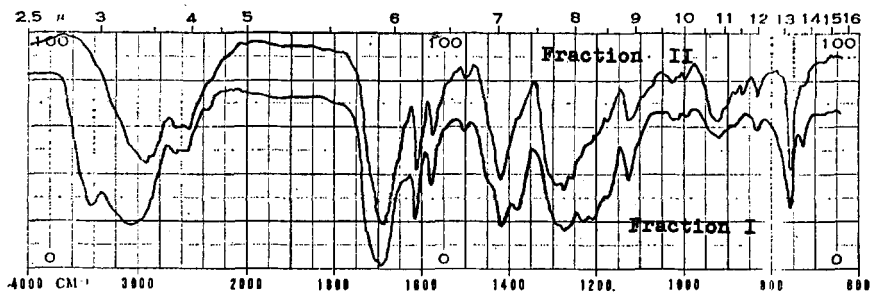


Fig. 1. Infrared spectra of *p*-toluic acid-formaldehyde resin (No. 3 in Table II).

Lederer,¹⁹ and Fewster and Hall.²⁰ In general the non-ionized acids travel too fast and a solvent containing NH_3 , collidine, or pyridine is used to ionize the acids. Fewster and Hall²⁰ aimed at buffering the paper with an ammonia-ammonium carbonate buffer, however, the resulting R_f values are essentially the same as with butanol-ammonia.¹⁹

Figures 1 and 2 show the typical infrared spectra of *p*-toluic and *o*-toluic acid-formaldehyde resins (Nos. 3 and 6 in Table II), respectively. The bands arising from the stretching modes of the OH group, and of C=O group are found at 2500–3600, and 1700 cm^{-1} , respectively, in both spectra.

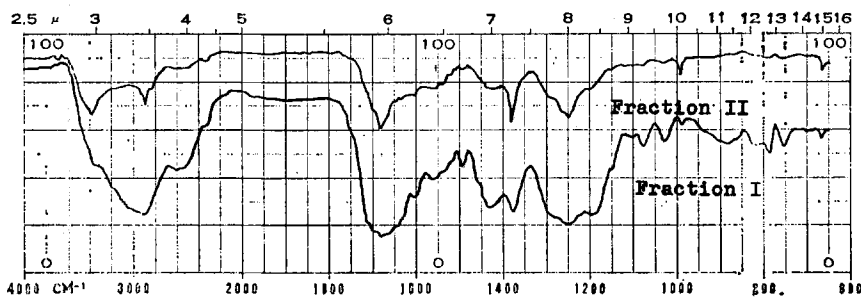
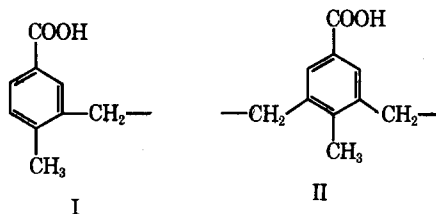
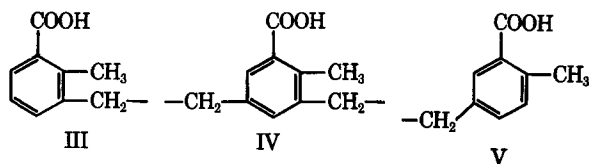


Fig. 2. Infrared spectra of *o*-toluic acid-formaldehyde resin (No. 6 in Table II).

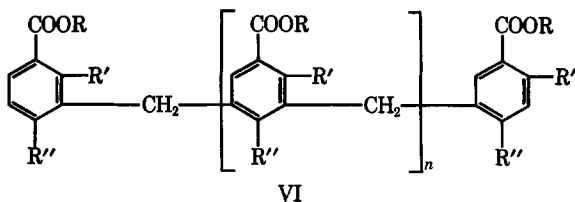
The bands at 1420 and 1300 cm^{-1} can be assigned to the coupling of the in-plane deformation of OH with the stretching mode of C=O group, and the band which can be assigned to the out-of-plane deformation mode of OH group is found at 920 cm^{-1} . These suggest the existence of COOH groups in these resins, BF.^{4,21} The bands which can be assigned to the out-of-plane hydrogen deformations of 1,2,4-trisubstituted (I) and of 1,2,3,4,5-tetrasubstituted (II) benzenes are found at 830 and 920 cm^{-1} , and 905 cm^{-1} , respectively, in the spectra of both fractions of I and II of *p*-toluic acid-formaldehyde resins.



The bands in the region of 650–1100 cm^{-1} for *o*-toluic acid-formaldehyde resins can be assigned to the out-of-plane hydrogen deformation modes of various substituted benzenes: The bands at 750, 790, 940, and 1080 cm^{-1} are due to the 1,2,3-trisubstituted benzene (III); at 820 and 940 cm^{-1} due to 1,2,4-trisubstituted benzene (IV); and at 905 cm^{-1} due to 1,2,3,5-tetrasubstituted benzene (V), respectively.



These bands of *o*-toluic acid-formaldehyde resins seem to correspond to those at 755, 796, 950, and 1086 cm.^{-1} for 1,2,3-trisubstituted, at 830 and 950 cm.^{-1} for 1,2,4-trisubstituted, and at 900 cm.^{-1} for 1, 2,3,5-tetrasubstituted derivatives of salicylic acid,²² respectively. The structures of these *p*- and *o*-toluic acid-formaldehyde resins seem to be as:



where $n = 0-2$; $R = \text{H}$, R' and $R'' = \text{H}$ or CH_3 , respectively. The infrared spectra of these resins show the absence of methylol, acetal, and ether groups (Figs. 1 and 2), which is consistent with Naokawa's result for the benzoic acid-formaldehyde resin.

In refluxing epichlorohydrin containing benzyltrimethylammonium chloride (BTA), BF was consumed in a few minutes, and the main product, chlorohydrin ester, was obtained in 90% or more yield. A decrease in glycidyl ester yield, accompanied by an increase in the formation of chlorinated esters, was also observed when a sodium salt of BF was used in toluene solution (No. 2 in Table IV).

Separation of the crude reaction mixture into its major components was not achieved, 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 content and saponification number. If it is assumed that only glycidyl ester and 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 33-44% glycidyl ester and of 70-60% chlorohydrin ester. Optimum catalyst concentration was not determined, but a large catalyst effect can be considered as Mearker, Carmichael, and Port²³ pointed out.

Mueller²⁴ reported that the glycidyl ester can be obtained directly if epichlorohydrin is in large excess and if a quaternary ammonium halide is used as catalyst. 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

TABLE IV
Reaction of Epichlorohydrin (E) and Substituted Benzoic Acid-Formaldehyde Resins (R-BF)^a

No.	R-BF		E, g.	Catalyst g.	Solvent, cc.	Temp., °C.	Time, hr.	Yield, g.	Cl ^b	Acid No. ^c	Sapon. No. ^d	Oxiran-oxygen, %	Mol. wt. ^f
	R	g.											
1	H	50	150	BTA, ⁱ 5	—	110	1	76	+	0	306	2.85	390
2	H(Na) ^g	18	40	BTA, ⁱ 1	Toluene, 200	110	1	16	+	0	294	2.06	448
3	H	37	30 ^h	NaOH, 24 ^j	Water, 150	60	5	23	+	0	312	0.67	470
4	<i>p</i> -CH ₃	10	45	BTA, ⁱ 2	—	110	1	15	+	0	418	2.61	406
5	<i>o</i> -CH ₃	43	40	NaOH, 17 ^j	Water, 70	60	4	45	+	0	350	3.47	388
6	<i>o</i> -CH ₃	45	45	NaOH, 17 ^j	Water, 70	60	4	48	+	0	340	3.62	400
7	<i>p</i> -CH ₃	45	45	NaOH, 17 ^j	Water, 70	60	4	46	+	0	354	3.55	398

^a Properties of BF used here are similar to those of Nos. 1, 4, and 6 in Table II. Preparative procedure of glycidyl esters, BFE, is described in Experimental.

^b Beilstein's copper wire test.

^c Calculated values for $(\text{OCH}_2\text{CHCH}_2\text{O}_2\text{CC}_6\text{H}_4)_x\text{CH}_2$, $(\text{ClCH}_2\text{CHCH}_2\text{O}_2\text{CC}_6\text{H}_4)_x\text{CH}_2$, $(\text{ClCH}_2\text{CHCH}_2\text{O}_2\text{CC}_6\text{H}_4\text{CH}_2)_x\text{CH}_2$, and $(\text{ClCH}_2\text{CHCH}_2\text{O}_2\text{CC}_6\text{H}_4\text{CH}_2)_x\text{CH}_2$ which are named VII, VIII, IX, and X are all zero.

^d Calculated values for VII to X are 305, 509, 283, and 478, respectively.

^e Determined by the hydrogen bromide-acetic acid method of Durbetaki.⁷ Calculated values for VII and IX are 8.71 and 8.08%, respectively.

^f Determined by a cryoscopic method using dioxane. Calculated values for VII to X are 368, 441, 396, and 469, respectively.

^g Sodium salt of benzoic acid-formaldehyde resin was used.

^h Epichlorohydrin was added dropwise to the mixture of BF, NaOH (12 g.) and water at 60°C.

ⁱ Benzyltrimethylammonium chloride.

^j NaOH was added separately at initial and after epichlorohydrin was added.

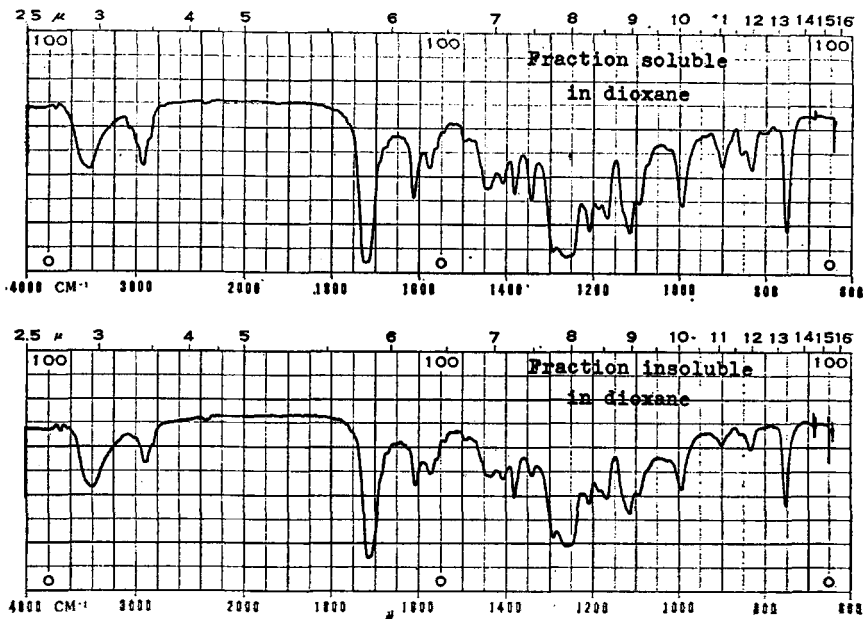


Fig. 3. Infrared spectra of epoxide from *p*-toluic acid-formaldehyde resin (No. 4 in Table V).

troublesome problem of secondary reactions of glycidyl esters with hydrogen chloride, some workers, such as Kester^{25,26} and Port,²³ used salts of carboxylic acids rather than the acids themselves as starting materials, and obtained good conversions to glycidyl esters of mono- and dicarboxylic acids.

Unsatisfactory results were obtained in this reaction of BF or its salt with large excess epichlorohydrin in the presence of BTA, which are shown in Table IV (Nos. 1 and 2). The similar result was obtained for the reaction of *p*-toluic acid-formaldehyde resin and epichlorohydrin and shown in Table IV (No. 4). The lower yields of the glycidyl esters of aromatic dicarboxylic acid, as compared to those of glycidyl benzoate⁵ and of mono- and diglycidyl esters of the long chain fatty acids,²³⁻²⁶ are probably due to the lower solubilities of these acids in epichlorohydrin, resulting in poor contact of the two reagents. Improvement of contact was achieved by dissolving BF in aq. sodium hydroxide solution before combining it with epichlorohydrin. As a result, higher oxirane-oxygen contents were observed as shown in Table IV (Nos. 5-7). Analysis of the crude product revealed that dropwise addition of epichlorohydrin causes the destruction of some of the glycidyl ester formed initially and gives rise to a oxirane-containing product not found after brief heating (No. 3 in Table IV). The use of water in this reaction is contrary to the recommendations of previous workers in this field²⁷⁻²⁹ but consistent with the findings of Maerker, Carmichael, and Port.²³

TABLE V
Epoxidation of Chlorohydrin Ester (R-E') of Substituted Benzoic Acid-Formaldehyde Resin(BF)^a

No.	R-E' ^b		Catalyst, g.	Solvent, g.	Temp., °C.	Time, hr.	Yield, g.	Cl ^c	Oxiran-oxygen, % ^d	Mol. wt. ^e	Ref.
	R	g.									
1	H	57	Na, 24	Dioxane, 400	100	8	54	+	2.32	310	j
2	H	73	Na, 24 + NaOH, 50 ^f	Dioxane, 450	100	9 ^f	10	+	3.98	290	j
3	H	54	Na, 20 + NaOH, 50*	Dioxane, 200	100	8	16	+	3.26	300	k
4	<i>p</i> -CH ₃	12	NaOH, 4	Dioxane, 100	60	13	4 ^h	+	5.06	390	j
							2 ⁱ	-	2.41	—	j
5	<i>o</i> -CH ₃	17	NaOH, 6	Dioxane, 100	60	10	5 ^h	-	5.02	407	k
							4 ⁱ	-	1.92	—	k

^a Epoxidation procedure is described in Experimental. Oxirane oxygens are 2.80, 2.01, and 2.06% for Nos. 1-3, 4, and 5, respectively. Preparation of R-E' is similar to that of BFE.

^b R from R-C₆H₄COOH, starting substituted benzoic acid.

^c Beilstein's copper wire test.

^d Calculated values for VII and X are 8.71 and 8.08%, respectively, by method of Durbetaki.⁷

^e Calculated values for VII to X are 368, 441, 396, and 469, respectively. Determined by a cryoscopic method using dioxane.

^f Reaction for 8 hr. with NaOH 50 g. after dehydrochlorination for 1 hr. with Na 24 g.

^g Mixture of Na 20 g. and NaOH 50 g. was added at initial stage.

^h Fraction soluble to dioxane at room temperature.

ⁱ Fractionation soluble to *N,N*-dimethylformamide but insoluble to dioxane at room temperature.

^j Brown or brownish-black resinous materials.

^k Brown or brownish-black solids.

It is conceivable that other methods can be found to improve contact and shorten reaction time. Two obvious methods are the use of a higher reaction temperature under pressure and the employment of a noninterfering mutual solvent for sodium salts of BF and epichlorohydrin. These, however, were not tried in the present study but discussed in a previous paper.⁵

The effect of reaction temperature in the absence of water was tested, and the results are shown in Table V together with those of dehydrochlorination efficiency of metallic sodium on this reaction. Lowering of the reaction temperature from 100 to 60°C. with longer reaction times increased the production of glycidyl ester or the oxirane-oxygen contents of

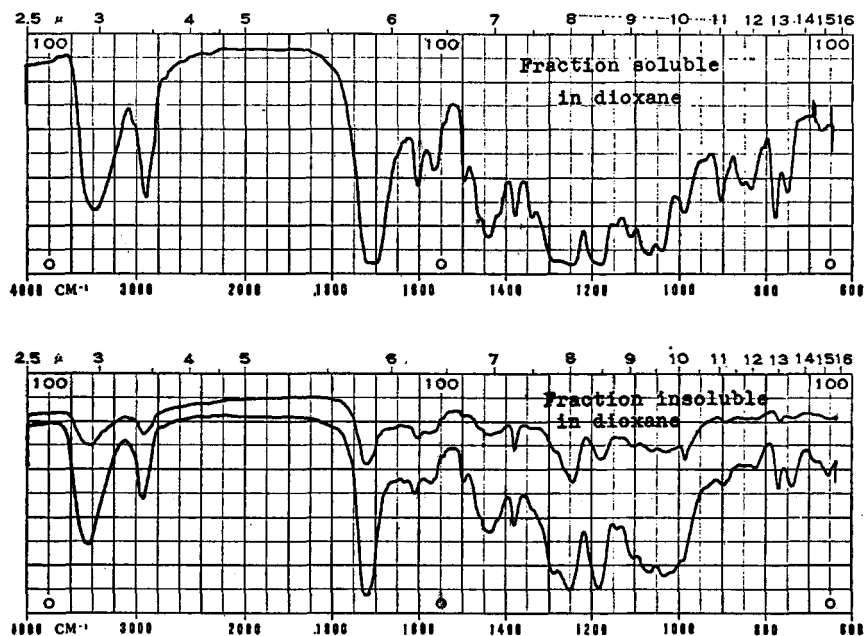


Fig. 4. Infrared spectra of epoxide from *o*-toluic acid-formaldehyde resin (No. 5 in Table V).

the product (Table V). The higher yields of glycidyl esters were obtained with NaOH rather than with metallic sodium. Hydrolysis of chlorine atoms of chlorohydrin esters seems to occur under the same conditions as those Nos. 4 and 5 in Table V.

Figures 3 and 4 show the infrared spectra of the dioxane-soluble and insoluble fractions (Nos. 4 and 5 in Table V) obtained from epichlorohydrin and *p*- and *o*-toluic acid-formaldehyde resins, BFE, respectively. The bands which can be assigned to the symmetrical and asymmetrical stretching modes of the epoxy group²¹ are found at 840 and 950 cm^{-1} , respectively, in all spectra of these epoxides.

The authors are grateful to Dr. W. Fukuda for his discussion on this study, and wish to acknowledge the assistance of K. Yamagishi in carrying out many of the experiments.

References

1. M. Schöpf, *Ber.*, **27**, 2321 (1894).
2. H. Weil, *Ber.*, **27**, 3315 (1894).
3. C. M. Welch and H. A. Smith, *J. Am. Chem. Soc.*, **73**, 4391 (1951).
4. J. Naokawa, K. Ishii, and H. Kakiuchi, *Kogyo Kagaku Zasshi*, **66**, 135 (1963).
5. H. Kakiuchi and Y. Tanaka, presented at the 13th Annual Meeting of Gosei Jushi Kogyo Kyokai on Thermosetting Resins, Tokyo, Oct. 1963.
6. (a) C. A. Kraus and R. M. Fuoss, *J. Am. Chem. Soc.*, **55**, 21 (1933); (b) C. A. Kraus and R. A. Vingee, *ibid.*, **56**, 511 (1934).
7. A. J. Durbetaki, *Anal. Chem.*, **28**, 2000 (1956).
8. *Merck Index*, Merck & Co., Inc., Rahway, N.J., 1960, 7th Ed.
9. R. L. Shriner, R. C. Fuson, and D. Y. Curtin, *The Systematic Identification of Organic Compounds*, Wiley, New York, 1956, 4th Ed., Chap. 5.
10. A. Baeyer, *Ber.*, **6**, 222 (1873).
11. J. Weiler, *Ber.*, **7**, 1181 (1874).
12. T. Reichstein and K. Oppenauer, *Helv. Chim. Acta.*, **16**, 1373 (1933).
13. A. M. Nastukov and V. V. Shelyagin, *J. Prakt. Chem.*, **119**, 303 (1928).
14. J. Grabowski, *Ber.*, **7**, 1605 (1874).
15. A. Baeyer, *Ber.*, **5**, 1098 (1872).
16. M. Shibata, *Peipah Kuromatogurafujo no Jissai (Paper Chromatography in Practice)*, Kyoritsu, Tokyo, 1957.
17. R. A. Evans, W. H. Parr, and W. C. Evans, *Nature*, **164**, 674 (1949).
18. (a) H. G. Bray, W. V. Thorpe, and K. White, *Biochem. J.*, **46**, 271 (1950); (b) H. G. Bray, W. V. Thorpe, and P. B. Wood, *ibid.*, **48**, 394 (1951).
19. M. Lederer, *Nature*, **165**, 529 (1950).
20. M. E. Fewster and D. H. Hall, *Nature*, **168**, 78 (1951).
21. (a) T. Shimanouchi, *Sekigaisen Kyushu Supekutoru Kaiseikiho (Analysis of Infrared Spectra)*, Nankodo, Tokyo, 1960; (b) K. Nakanishi, *Sekigaisen Kyushu Supekutoru (Infrared Absorption Spectra)*, Nankodo, Tokyo, 1962.
22. Y. Moriguchi and M. Miura, *Nippon Kagaku Zasshi*, **84**, 600 (1963).
23. G. Maerker, J. F. Carmichael, and W. S. Port, *J. Org. Chem.*, **26**, 2681 (1961).
24. A. C. Mueller, U.S. Pat., 2,772,296 (Nov. 27, 1956).
25. E. B. Kester, C. J. Gaiser, and M. E. Lazar, *J. Org. Chem.*, **8**, 550 (1943).
26. E. B. Kester and H. M. Preusser, U. S. Pat. 2,448,602 (Sept. 7, 1948).
27. R. Kohler and H. Pietsch, Ger. Pat., 944,995 (June 28, 1956); Brit. Pat., 766,771 (Jan. 23, 1957).
28. G. L. Dorough, U. S. Pat., 2,524,432 (Oct. 3, 1950).
29. R. J. Chamberlain, U. S. Pat. 2,893,875 (July 7, 1959).

Résumé

Certains dérivés d'acide polybasique ont été obtenus au départ d'acides benzoïques substitués tels que les acides *p*- et *o*-toluïques, et le *p*-formaldéhyde dans l'acide sulfurique concentré par des méthodes semblables à celles de Naokawa et coll. La structure du matériau résineux d'acide benzoïque substitué-formaldéhyde a été déterminée par chromatographie sur papier et par analyse spectrométrique infrarouge. (Voir la structure dans le texte anglais). Des résines nouvelles de type époxy ester glycidylique ont été préparé au départ de ces résines formaldéhyde-acides benzoïques substitué et d'épichlorhydrine en présence de soude caustique utilisant le dioxane comme solvant. La structure générale était celle de I, où $n = 0$ à 2, $R = CH_2CHCH_2O$, et R' et $R'' = H$ ou CH_3 , respectivement.

Zusammenfassung

Einige Derivate mehrbasischer Säuren werden aus substituierten Benzoesäuren, wie *p*- und *o*-Toluylsäure und *p*-Formaldehyd in konzentrierter Schwefelsäure nach einer Methode ähnlich der von Naokawa et al. erhalten. Die Struktur dieser Harze aus substituierten Benzoesäuren und Formaldehyd wurde durch Papierchromatographie und Infrarotanalyse bestimmt; bzgl. Struktur vgl. englische Zusammenfassung. Aus den angeführten Harzen und Epichlorhydrin wurden in Gegenwart von Natriumhydroxyd mit Dioxan als Lösungsmittel neue Epoxyharze vom Glycidylestertyp dargestellt; bzgl. ihrer Struktur siehe englische Zusammenfassung.

Received December 29, 1966

Prod. No. 1561