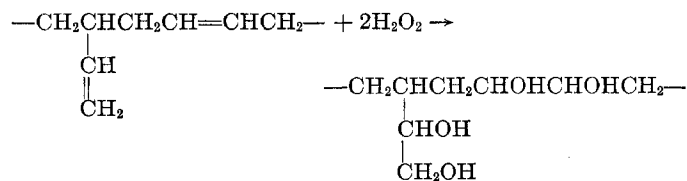


mer in carbon tetrachloride at room temperatures. Hydrogen chloride is evolved during the reaction, but no difficulty from gelation is observed. Chlorinated products of 34 to 56 weight % chlorine have been studied. The chlorinated products are light yellow, brittle solids that soften at about 200° F. They are soluble in ketones, aromatic hydrocarbons, esters, and chlorinated solvents; insoluble in water, alcohols, and aliphatic acids. The solubility in organic solvents increases as the chlorine content of the polymer increases. The products resemble chlorinated rubber in many respects; however, they are of lower molecular weight and yield solutions of somewhat lower viscosity than that of chlorinated rubbers usually employed in paints.

Hydroxylation. A solution of liquid polybutadiene reacts with hydrogen peroxide in the presence of organic acids to yield hydroxylated liquid polybutadiene of variable hydroxyl content.



Products having 21.5% oxygen have been made, but it has never been possible to approach complete reaction of the contained double bonds.

The hydroxylated products can be separated into fractions on the basis of their solubility in acetone and *n*-pentane. As hydroxylation proceeds, the acetone-soluble fraction increases at the expense of the pentane-soluble material. Products of more than about 20% oxygen content are completely soluble in acetone. The pentane-soluble material is a liquid much like the parent compound, but the more highly hydroxylated acetone-soluble fraction may vary from a viscous liquid to a rosinlike solid.

Reaction with Maleic Anhydride. A mixture of liquid polybutadiene and maleic anhydride reacts vigorously at 270° F. to yield a solid gel, insoluble in water, caustic, and organic solvents. The reaction is catalyzed by peroxides, and it may involve co-

polymerization and cross linking as well as Diels-Alder addition of the maleic anhydride.

The reaction may be moderated and controlled by the use of a solvent such as xylene. On heating a mixture of 10.1 grams liquid polybutadiene, 3.63 grams maleic anhydride, and 0.40 gram benzoyl peroxide in 40 grams xylene, a vigorous reaction began causing the xylene to reflux. Insoluble polybutadiene-maleic anhydride copolymer soon separated from the solution. After 2 hours, about half the maleic anhydride had reacted.

The highly cross-linked copolymer may be of interest for use in ion exchange resins. It reacts with sodium hydroxide solution, but the resulting sodium salt is not soluble in water.

Acknowledgment

The authors gratefully acknowledge the contribution of W. B. Reynolds, who made many helpful suggestions in this work, and of their numerous associates who collaborated in the experimental program. They include J. F. Svetlik and H. E. Railsback who conducted rubber compounding studies; C. E. Wheelock who studied casting techniques; J. C. Hillyer, E. G. Marhofer, L. O. Edmonds, and J. A. Delap who investigated vegetable oil upgrading and protective coatings; and V. L. Thornton, A. O. Frenzel, and J. A. Favre who performed the infrared and ultraviolet absorption studies.

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New Epoxide Resins By . . .

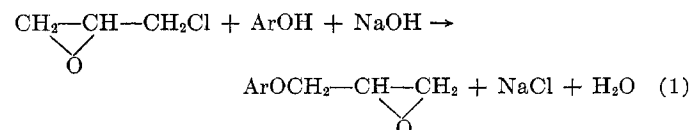
Reaction of Epichlorohydrin with Sulfonamides

MERRILL COHEN

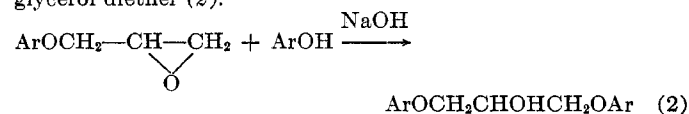
Thomson Laboratory, General Electric Co., West Lynn 3, Mass.

THE reaction of bisphenols with epichlorohydrin to produce epoxide resins is of considerable commercial importance.

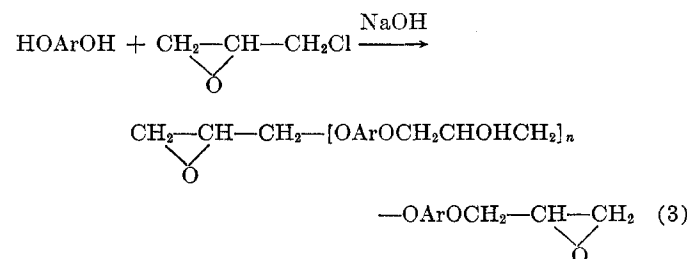
The reaction of phenols with epichlorohydrin in alkaline solution yields phenyl glycidyl ethers as primary reaction products (2, 7, 15).



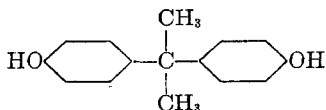
The glycidyl ether may react with excess phenol to give a glycerol diether (2).



Substitution of a dihydric phenol for the monohydric phenol in Reaction 1 yields the diglycidyl ether as one of the primary reaction products (26, 27). However, unless the reaction conditions are very carefully controlled, the reaction usually proceeds further to give polymeric epoxide-containing condensation products.



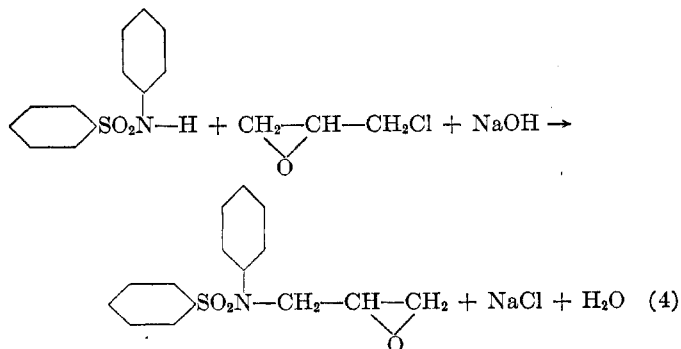
Reaction 3 is the basis for the production of most epoxide resins (4). The dihydric phenol used in the production of these resins is bisphenol A (4,4'-isopropylidenediphenol).



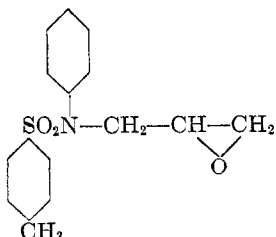
As the value of *n* in Formula 3 increases, the physical state of the resin changes from viscous liquids to brittle thermoplastic solids. The commercial utility of the epoxide resins lies in their ability to be polymerized to cross-linked structures by the action of a variety of catalysts, including acids, bases, or anhydrides (4-6). They are now finding widespread use as coating, casting, and laminating resins, and as adhesives.

In the present work, the reaction of epichlorohydrin with certain primary, secondary, and dissecondary sulfonamides has been investigated for the purpose of preparing new types of epoxide resins based on sulfonamides instead of phenols. Like the phenols, the monofunctional secondary sulfonamides (RSO₂NHR) possess one acidic hydrogen atom and would be expected to react with epichlorohydrin to form monoepoxides. Like the bisphenols, primary sulfonamides (RSO₂NH₂) or dissecondary sulfonamides [(RSO₂NH—R'—NHO₂SR), (RNHO₂S—R'—SO₂NHR)] possess two acidic hydrogen atoms and would be expected to react with epichlorohydrin to give polymeric products containing terminal epoxide groups. These polymers should then react with catalysts to form useful cross-linked polymers.

Reactions of the type discussed above have been reported in the literature. Miller (16) prepared *N*-(2,3-epoxypropyl)-*N*-phenylbenzenesulfonamide by the reaction of *N*-phenylbenzenesulfonamide with epichlorohydrin in alkaline solution.



Ohle and Haeseler (19) prepared *N*-(2,3-epoxypropyl)-*N*-phenyl-*p*-toluenesulfonamide by refluxing the corresponding chlorohydrin in an alcoholic caustic solution.



The chlorohydrin had been formed by the reaction of *N*-phenyl-*p*-toluenesulfonamide with epichlorohydrin, catalyzed by a drop of pyridine. Moss (17) reported obtaining condensation products by refluxing an alkaline solution of glycerol dichlorohydrin with *p*-toluenesulfonamide. This reaction may have proceeded through the formation of epichlorohydrin as an intermediate. While the present work was in progress, three patents were issued (16, 21, 22) describing the reactions of epichlorohydrin with various sulfonamides.

Reactions of epichlorohydrin with sulfonamides were investigated

Starting Materials. *N,N'*-HEXAMETHYLENEBISMETHANESULFONAMIDE. Hexamethylenediamine (90 grams, 0.65 mole), 83.5% by weight as determined by titration with 0.1*N* hydrochloric acid, was added dropwise to a stirred solution of methanesulfonyl chloride (74 grams, 0.65 mole) in 500 ml. of benzene at 10° to 20° C. During the addition, a solid precipitated from solution. The mixture was then refluxed 10 minutes, cooled, and filtered. The solids were dried in air, and stirred with 150 ml. of warm water to remove amine hydrochloride. The remaining solid was recrystallized from water. Melting point was 128-129° C. Yield of pure material was 33 grams. Analysis. Calculated for C₈H₂₀O₄N₂S₂: carbon, 35.3; hydrogen, 7.4; nitrogen, 10.3. Found: carbon, 35.2; hydrogen, 7.1; nitrogen, 10.1. This material could not be the isomer *N,N'*-di(methylsulfonyl)hexamethylenediamine, (CH₃SO₂)₂N(CH₂)₆NH₂, as an aqueous solution of the sulfonamide was neutral to litmus.

N,N'-ETHYLENEBISMETHANESULFONAMIDE was synthesized in like manner from 74 grams methanesulfonyl chloride and 39 grams of ethylenediamine. The solids (after treatment with warm water) were recrystallized from 95% ethyl alcohol. Melting point was 109-110° C. Yield of pure material was 12 grams. The lower yield is due to the greater solubility of the sulfonamide in water. Analysis. Calculated for C₄H₁₂O₄S₂N₂: carbon, 22.2; hydrogen, 5.6; nitrogen, 13.0. Found: carbon, 22.4; hydrogen, 5.7; nitrogen, 13.1.

N,N'-ETHYLENEBIS-*p*-TOLUENESULFONAMIDE was synthesized in like manner in 77% yield after one recrystallization—i.e., by a one-to-one mole ratio of *p*-toluenesulfonyl chloride to the diamine in benzene. Melting point was 159-161° C.; literature value 162.6° C. (1). The sulfonamide was recrystallized from 95% ethyl alcohol.

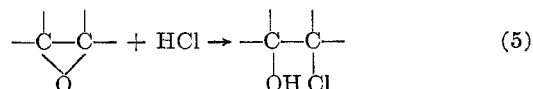
N,N-DIMETHYL DIPHENYL ETHER-4,4'-DISULFONAMIDE was prepared by the reaction of methyl amine with diphenyl ether-4,4'-disulfonyl chloride (23) in benzene (13). Melting point was 157.5° C. Analysis. Calculated for C₁₄H₁₆O₃S₂N₂: carbon, 47.2; hydrogen, 4.5; nitrogen, 7.9. Found: carbon, 47.8; hydrogen, 4.6; nitrogen, 7.8.

METHANESULFONAMIDE was prepared by the method of Field and Grunwald (9).

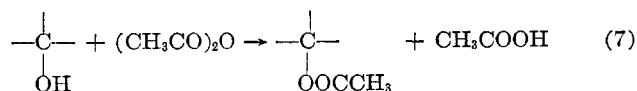
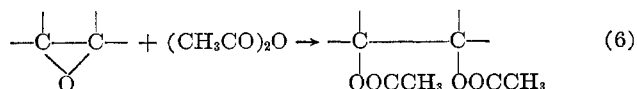
N-BUTYLBENZENESULFONAMIDE was obtained from the Monsanto Chemical Co. All the other materials were commercially available from Distillation Products Industries Co.

Analytical Methods. The epoxide content of the reaction products of epichlorohydrin with various sulfonamides was determined in the following way (10).

One gram of epoxide compound and 20 ml. of a solution of 16 ml. of concentrated hydrochloric acid diluted to 1 liter with pyridine were refluxed for 20 minutes. The resulting solution was cooled and titrated to the phenolphthalein end point with 0.1*N* alkali. In some cases the solutions darkened during the analysis, and a pH meter was used to determine the end point. Acetone was sometimes added during the titration to prevent the formation of turbid solutions due to precipitation of the resin. The amount of hydrochloric acid consumed by the epoxide could be found by running a blank titration of the reagent. The epoxide content was calculated on the basis of one equivalent of hydrochloric acid consumed per equivalent of epoxide.



The hydroxyl content was determined by the acetylation method of Ogg, Porter, and Willits (18, 20). As epoxide groups (24, 25) would also be expected to react with the pyridine-acetic anhydride reagent, the true hydroxyl content of compounds containing both epoxide and hydroxyl groups was estimated by subtracting twice the epoxide content from the observed hydroxyl content.



Experimental Procedures. REACTION OF EPICHLOROHYDRIN WITH PRIMARY SULFONAMIDES. The epichlorohydrin was added to a stirred solution of the sulfonamide (25 to 100 grams) in 10% alkali at 40° C. The total amount of alkali was in 10% molar excess of the epichlorohydrin.

In the reactions of epichlorohydrin with *p*-toluenesulfonamide (Table I), the temperature was usually kept below 70° C. until the initial exothermic reaction had ceased. The resulting mixture was then stirred at 100° C. for 0.5 to 1 hour. During this time the initial oily product solidified to an opaque resinous material. The mixture was cooled, the alkali decanted, and fresh water added. Unless otherwise noted (Table I), the mixture was heated to 100° C. and stirred for 15 minutes. This procedure was repeated until the washings were alkali-free. The condensation products were dried at 125° to 150° C.

In the reaction of epichlorohydrin with methanesulfonamide, the temperature was kept below 60° C. initially; and then the reaction mixture was refluxed for 1 hour.

REACTION OF EPICHLOROHYDRIN WITH SECONDARY SULFONAMIDES. Unless otherwise noted (Table II), the epichlorohydrin was added in one portion to a stirred solution of the sulfonamide and 3 to 10% aqueous sodium hydroxide at 40° to 50° C. After the initial exothermic reaction had subsided, the resulting mixture was heated for the designated period of time.

The products then were extracted with ether, and the ether solution was washed with dilute alkali and then with distilled water until the washings were alkali-free. The ether solution was dried over sodium sulfate and the ether was removed at reduced pressure.

REACTION OF EPICHLOROHYDRIN WITH DISECONDARY SULFONAMIDES. The sulfonamides were dissolved in 5 to 10% aqueous sodium hydroxide at 35° to 40° C. The total amount of alkali was in 10% molar excess of the epichlorohydrin. During the initial exothermic reaction, the temperature was not allowed to rise above 60° C. Unless otherwise noted (Table III), the resulting mixture was stirred for 1 hour at 50° to 60° C.

The mixture was cooled, the aqueous phase was decanted, and the resin was stirred with water at 60° C. until the washings were alkali-free. The products were dried at 125° to 150° C.

POLYMERIZATION OF REACTION PRODUCTS. Piperidine and phthalic anhydride were used to catalyze the polymerization of the epoxide-containing resins derived from the reaction of epichlorohydrin with primary and dissecondary sulfonamides. The catalysts were mixed or melted into the resins on a hot plate at moderate temperatures. The piperidine-catalyzed mixtures were cured overnight at 100° C., whereas the anhydride-catalyzed mixtures were cured overnight at 125° C. A final cure of a few hours at 150° C. was then employed. The amount of piperidine used to catalyze the resin was 6 parts per 100 parts of resin. The amount of phthalic anhydride used was slightly less (90 to 95%) than the amount calculated as 1 mole of anhydride per equivalent epoxide groups.

New types of epoxide resins were prepared

Primary Sulfonamides. The reaction of epichlorohydrin with *p*-toluenesulfonamide ($\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NH}_2$), benzenesulfonamide ($\text{C}_6\text{H}_5\text{SO}_2\text{NH}_2$), and methanesulfonamide ($\text{CH}_3\text{SO}_2\text{NH}_2$) was investigated. Table I gives a summary of the data obtained from the reaction of epichlorohydrin with *p*-toluenesulfonamide under various reaction conditions. The solid products were clear, brittle thermoplastic solids which melted around 100° C. The weight of condensation product isolated approximated that of the starting sulfonamide in 25- to 100-gram lots.

The reactions of *p*-toluenesulfonamide with a nominal excess of epichlorohydrin at elevated temperatures (100° C.) gave condensation products of little or no epoxide content. Condensation products of appreciable epoxide content could be prepared only by employing a large excess of epichlorohydrin or by carrying out the reaction of the sulfonamide with a nominal excess of epichlorohydrin at moderate temperatures. A *p*-toluenesulfonamide-epichlorohydrin condensation product of appreciable epoxide content was prepared at low temperatures (see run 5, Table I). The material was then refluxed in 10% alkali, washed, and dried. The resulting material had no epoxide content.

The reaction products of epichlorohydrin with *p*-toluenesulfonamide that did have an appreciable epoxide content could not be gelled by amine or anhydride catalysts. They hardened somewhat but remained thermoplastic. This is in contrast to the behavior of epoxide resins prepared by the reaction of epichlorohydrin with bisphenols, which can be gelled by these catalysts.

Table I. Reaction of Epichlorohydrin with *p*-Toluenesulfonamide

Run	Mole Ratio, Epichlorohydrin to Sulfonamide	Epoxide Content of Product, Meq./Gram	Reaction Conditions
1	1.0	0.0	Reaction mixture stirred at 100° C. for 0.5 to 1 hour after cessation of initial exothermic reaction. Solid product
2	2.6	0.0	
3	4.0	0.3	
4	6.0	1.6	Reaction mixture stirred at 45° C. 1 hour after cessation of initial exothermic reaction. Condensation product washed at 45° C. Final product was very viscous gum
5	2.6	2.5	

The hydroxyl content of the resins from runs 1 and 2, Table I, was 4.6 ± 0.5 meq. per gram.

A portion of resin 1, Table I (melting point 90° to 100° C.) was dissolved in benzene and partially precipitated with heptane. Two fractions were collected: a small fraction of melting point 160° to 170° C. and a major fraction of melting point 95° to 100° C. The latter fraction was analyzed for carbon, hydrogen, and nitrogen. Found: carbon 52.6; hydrogen 5.6; nitrogen, 6.5. The molecular weights of resin 1 and the main fraction ranged from 1200 to 1700 as determined by freezing point depression in benzene to 680 to 750 as determined by boiling point elevation in acetone. The analytical data fit the empirical

formula $(\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NCH}_2\text{CHOHCH}_2-)_n$. Hydroxyl equivalent: 4.4 meq. per gram. Elemental analysis: carbon, 52.9; hydrogen, 5.8; nitrogen, 6.2. Formula weight: 227.

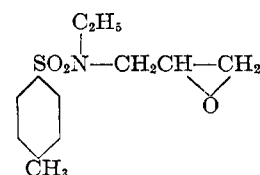
The reaction of methanesulfonamide with a 1.5*M* excess of epichlorohydrin in 10% alkali yielded no water-insoluble products. Benzenesulfonamide reacted with epichlorohydrin to give water-insoluble products similar to those of toluenesulfonamide and epichlorohydrin.

Simons (22) discloses some reaction products of epichlorohydrin with *p*-toluenesulfonamide.

Secondary Sulfonamides. Table II gives a summary of the data obtained from the reaction of epichlorohydrin with two sulfonamides, *N*-ethyl-*p*-toluenesulfonamide ($\text{CH}_3\text{C}_6\text{H}_4\text{SO}_2\text{NHC}_2\text{H}_5$) and *N*-butylbenzenesulfonamide ($\text{C}_6\text{H}_5\text{SO}_2\text{NHC}_4\text{H}_9$).

The results show that the reaction of *N*-alkyl aromatic sulfonamides with excess epichlorohydrin in alkaline solution yields products of appreciable epoxide content, while the reaction of epichlorohydrin with excess sulfonamide gives products of little or no epoxide content.

The reaction product of run 4, Table II, was distilled to give a liquid boiling at 205° C. (4 mm.). This material had an epoxide content of 3.54 meq. per gram and a sulfur content of 12.4%. The analysis agrees with that expected for *N*-(2,3-epoxypropyl)-*N*-ethyl-*p*-toluenesulfonamide,



which has an epoxide content of 3.91 meq. per gram and a sulfur content of 12.5%.

Table II. Reaction of Epichlorohydrin with Secondary Aromatic Sulfonamides

Run	Sulfonamide	Wt., G.	Mole Ratio		Epoxide Content of Product, Meq./G.	Product Isolated, G.	Estimated Hydroxyl Content of Product, Meq./G.	Reaction Conditions
			Epichlorohydrin to sulfonamide	Alkali to epichlorohydrin				
1	<i>N</i> -Ethyl- <i>p</i> -toluenesulfonamide	38	0.5	2.0	0.0	35	2.5	Epichlorohydrin added dropwise to the sulfonamide solution at 70° C. for 1 hour. Alkali concentration 10%
2	<i>N</i> -Butylbenzenesulfonamide	21	1.3	1.4	0.27	17	2.0	Reaction mixture refluxed 1 hour after initial exothermic reaction. Alkali concentration 10%
3	<i>N</i> -Butylbenzenesulfonamide	..	1.3	1.1	0.78	..	1.8	Reaction mixture refluxed 1 hour after initial exothermic reaction. Alkali concentration 3%
4	<i>N</i> -Ethyl- <i>p</i> -toluenesulfonamide	30	2.0	1.1	2.20	37	0.8	Reaction mixture kept at 80-90° C. for 1 hour after initial exothermic reaction. Alkali concentration 10%

sulfonamide(II), catalyzed by either piperidine or phthalic anhydride, were more flexible than the cured resins based on *N,N'*-dimethyl diphenyl ether-4,4'-disulfonamide(III), which tended to be somewhat brittle. Like bisphenol A-based epoxide resins, these materials softened at elevated temperatures (100° to 150° C.) but regained their initial hardness when cooled to room temperature.

N,N'-Ethylenebismethanesulfonamide (CH₃SO₂NH(CH₂)₂NHO₂SCH₃) gave no water-insoluble products upon reaction with a 2.5*M* excess of epichlorohydrin in alkaline solution. Neutralization of the solution failed to give any water-insoluble products.

Furthermore, the infrared spectrum of this product revealed the absence of hydroxyl groups and starting sulfonamide and the presence of sulfone groups. The spectrum had absorption peaks at 7.96, 11.2, and 11.75 microns not present in either the spectrum of the starting sulfonamide or the spectrum of the non-epoxide-containing product from run 1, Table II. The epoxide group is known to absorb in the region of 8 microns (8).

Disecundary Sulfonamides. Table III gives a summary of the data obtained from the reaction of epichlorohydrin with three disecundary sulfonamides.

- (I) *N,N'*-Ethylenebis-*p*-toluenesulfonamide CH₃C₆H₄SO₂NH(CH₂)₂NHO₂SC₆H₄CH₃
- (II) *N,N'*-Hexamethylenebismethanesulfonamide CH₃SO₂NH(CH₂)₆NHO₂SCH₃
- (III) *N,N'*-Dimethyldiphenylether-4,4'-disulfonamide CH₃NHO₂SC₆H₄OC₆H₄SO₂NHCH₃

N,N'-Ethylenebis-*p*-toluenesulfonamide (I) reacted with a very large excess of epichlorohydrin to form a high melting solid with a very low epoxide content.

The molecular weight of one of these condensation products (run 1, Table III) was 457 ± 13, as determined by boiling point elevation in ethyl acetate, and 415 ± 35, as determined by boiling point elevation in acetone. A sample (4.2 grams) was recrystallized from benzene. The resulting material (1.7 grams) had a molecular weight of 430 as determined by boiling point elevation in ethyl acetate.

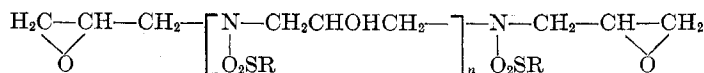
On the other hand, *N,N'*-dimethyl diphenyl ether-4,4'-disulfonamide (III) reacted with a smaller excess of epichlorohydrin to form solid products of appreciable epoxide content, and *N,N'*-hexamethylenebismethanesulfonamide (II) reacted with epichlorohydrin to form fluid products of appreciable epoxide content. The epoxide containing products from these two sulfonamides gelled to cross-linked polymers when catalyzed with piperidine or phthalic anhydride at 100° to 125° C.

The melting points of the resins from *N,N'*-dimethyl diphenyl ether-4,4'-disulfonamide (III) were in the range of 40° to 60° C. The final weight of resin isolated approximated that of the starting material in 25- and 100-gram lots. Lowering the temperature of the reaction decreased the extent of condensation of the product and raised the epoxide content (per gram) of the resin.

The cured resins based on *N,N'*-hexamethylenebismethane-

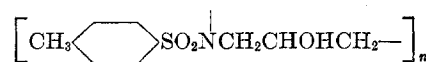
Epoxide-containing products may condense to products of little epoxide content

Primary Sulfonamides. Primary sulfonamides which are difunctional by virtue of two acidic hydrogen atoms attached to the nitrogen atom of the sulfonamide group would be expected to form epoxide-containing polymers of the type

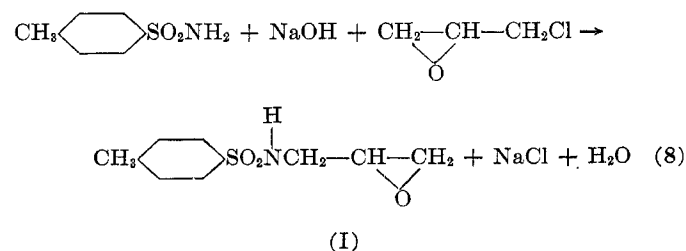


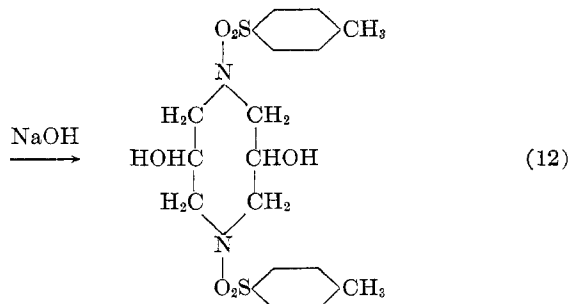
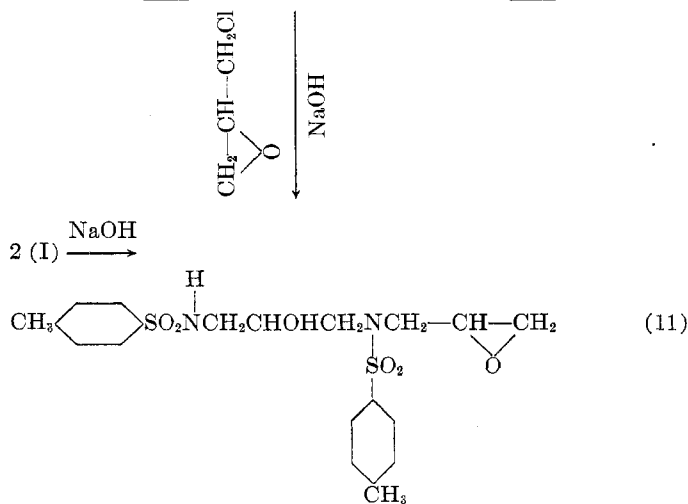
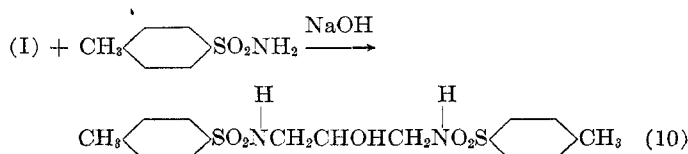
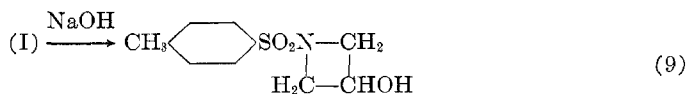
Such materials would be expected to form cross-linked polymers when catalyzed with amines or anhydrides analogous to the epoxide resins based on bisphenols.

However, the experimental results with *p*-toluenesulfonamide and a nominal excess of epichlorohydrin show that epoxide-containing products are initially formed and then condense further to reaction products of little or no epoxide content. The intermediate products of high epoxide content can be isolated by running the reaction at moderate temperatures but are not gelled by amine or anhydride catalysts. Data obtained from the analysis of the final reaction products of no epoxide content agree with the following empirical formula (see experimental results).

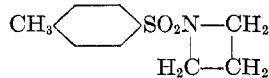


As sulfonamide epoxides apparently are fairly stable to hydrolysis under the reaction conditions employed, one possible explanation of these experimental results is based on cyclization of the initially formed epoxides to structures with no epoxide content rather than further reaction to linear diepoxide polymers. For example:

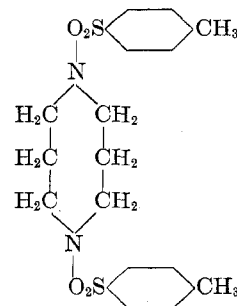




Compounds of similar structure have been reported in the literature. For example, Marckwald (14) reported the synthesis of



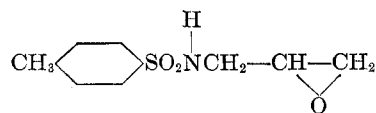
and



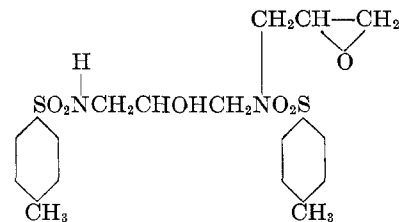
from *p*-toluenesulfonamide and 1,3-dibromopropane in the presence of alkali. The sulfonamides were then hydrolyzed or reduced to the cyclic amines (11, 12, 28).

The molecular weights of the reaction products of epichlorohydrin with *p*-toluenesulfonamide which contained no epoxide groups were higher than those expected for the cyclic structures listed above, indicating the presence of compounds of higher molecular weight. However, as the values obtained varied considerably (see experimental results), these data could not be used to establish the presence of these cyclic structures. This behavior may be due to association or other effects in the various solvents used for the molecular weight determinations.

The failure of the condensation products with appreciable epoxide content to form cross-linked structures when catalyzed may be attributed to the reaction products being a mixture of "inert" nonoxide-containing products and/or monoepoxides such as



and



etc.

Table III. Reaction of Epichlorohydrin with Dissecondary Sulfonamides

Run	Sulfonamide	G.	Mole Ratio Epichlorohydrin to Sulfonamide	Product Isolated, G.	Epoxide Content of Product, Meq./G.	Remarks
1	<i>N,N'</i> -Ethylenebis- <i>p</i> -toluenesulfonamide (I)	18	4	15	0.19	Solid product, m.p. 163-166° C. Temperature kept below 60° C. during entire reaction. Alkali concentration 6%
2	<i>N,N'</i> -Ethylenebis- <i>p</i> -toluenesulfonamide (I)	..	12	..	0.43	Solid product. Temperature kept below 60° C. during entire reaction
3	<i>N,N'</i> -Hexamethylenebismethanesulfonamide (II)	23	2.3	17	2.5	Viscous product that gelled to cross-linked polymer with piperidine or phthalic anhydride. Reaction temperature kept at 50-60° C. throughout. Alkali concentration 5%
4	<i>N,N'</i> -Hexamethylenebismethanesulfonamide (II)	18	3.3	10	3.3	Viscous product that gelled to cross-linked polymer with piperidine or phthalic anhydride. Reaction temperature kept at 50-60° C. throughout. Alkali concentration 5%
5	<i>N,N'</i> -Dimethyl diphenyl ether 4,4'-disulfonamide (III)	50	3	47	1.2	Reaction mixture refluxed for 0.5 hour after initial exothermic reaction. Solid product that gelled to a cross-linked polymer with piperidine or phthalic anhydride. Alkali concentration 10%
6	<i>N,N'</i> -Dimethyl diphenyl ether 4,4'-disulfonamide (III)	18	3	25	2.1	Solid product that gelled to cross-linked polymer with piperidine or phthalic anhydride. Reaction temperature kept below 60° C. throughout. Alkali concentration 10%
7	<i>N,N'</i> -Dimethyl diphenyl ether 4,4'-disulfonamide (III)	75	5	77	2.1	Solid product that gelled to a cross-linked polymer with piperidine or phthalic anhydride. Reaction temperature kept below 60° C. throughout. Alkali concentration 10%

from *N,N'*-dibutyldiphenyl ether-4,4'-disulfonamide and epichlorohydrin.

Summary and conclusions

Like the bisphenols, primary aromatic sulfonamides such as *p*-toluenesulfonamide react with epichlorohydrin in alkaline solution at moderate temperatures to form epoxide-containing products. However, unlike the reaction products of bisphenols with epichlorohydrin, these products cannot be gelled by amine or anhydride catalysts and will condense further to products of no epoxide content unless the reaction conditions are carefully controlled. The epoxide-containing products can also be formed by employing a very large excess of epichlorohydrin.

Like phenols, secondary aromatic sulfonamides react with epichlorohydrin in alkaline solution to form epoxide-containing products. These can react further with excess sulfonamide to form hydroxyl-containing derivatives.

Depending on their structure, certain disecundary sulfonamides react with epichlorohydrin to form one of two products—either high melting products of low epoxide content or products of appreciable epoxide content. Like the bisphenol-based resins, the latter materials can be gelled by amine or anhydride catalysts.

The tendency of the disecundary sulfonamides to form one or the other of these products can be correlated with their ease of ring formation. This cyclization hypothesis can be extended as one possible explanation of the reaction products observed with *p*-toluenesulfonamide and epichlorohydrin.

Certain sulfonamides give no water-insoluble products with epichlorohydrin in alkaline solution.

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Uncatalyzed Coal Hydrogenolysis

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HYDROGENOLYSIS of Rock Springs coal at 400° C. in the presence of tin and molybdenum and under initial hydrogen pressures of 500 to 4000 lb. per sq. inch gage has been studied, and the results have been reported (2). In that study the rate of transformation of benzene-insoluble matter of coal to benzene solubles, water, and gaseous product was used for quantitative evaluation of catalyst activity and for estimation of the extent of hydrogenolysis as a function of initial hydrogen pressure. For a better understanding of the function of the catalyst, a similar study has now been made of the uncatalyzed hydrogenolysis of Rock Springs coal.

Material used was bituminous C Rock Springs coal

Bituminous C coal from the Rock Springs bed, Superior, Wyo., was used. It was air-dried and pulverized to pass through a 200-mesh screen. Its ultimate composition was as follows:

	%
Hydrogen	4.54
Carbon	71.50
Nitrogen	1.48
Sulfur	1.20
Oxygen	11.88
Ash	5.40
Moisture	2.00

The experimental procedure and method of evaluation of the results were similar to those described previously (3, 4).

Conversion of benzene-insoluble matter of coal to benzene solubles, water, and gas is a first-order reaction

Operational conditions, product distribution, and hydrogen consumption are summarized in Table I. As in the case of catalytic hydrogenolysis of coal, asphaltene is the main product of uncatalyzed hydrogenolysis at 400° C. The time of reaction reported in Table I includes a 5-minute correction factor for the preheating and cooling periods. Figure 1 shows the logarithms of the percentage of remaining benzene insolubles as functions of contact time. Extensive experience with Rock Springs coal has

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