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The Effects of Fluorine Substitution on the Properties and Reaction Rates of Glycidyl Ethers

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Organic Chemistry Branch
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13. ABSTRACT

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A series of related fluorine-containing diglycidyl ethers has been synthesized and obtained as high-purity compounds. The physical characteristics of these ethers are given. It is shown that fluorinated diols can be used as reactants with the diglycidyl ethers to produce fluorinated polyols, and some overall concentration-vs-time plots for these reactions are shown

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ABSTRACT

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PROBLEM STATUS

This is an interim report; work is continuing.

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THE EFFECTS OF FLUORINE SUBSTITUTION ON THE PROPERTIES AND REACTION RATES OF GLYCIDYL ETHERS

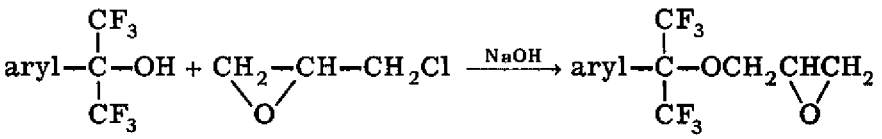
INTRODUCTION

In a previous report (1), we have introduced the problem of including large amounts of fluorine in epoxy resins. The most generally useful epoxies are glycidyl ethers, all of which contain two or more molecular units of the type $-OCH_2\underset{\underset{O}{\diagdown\!\diagup}}{CH-CH_2}$.

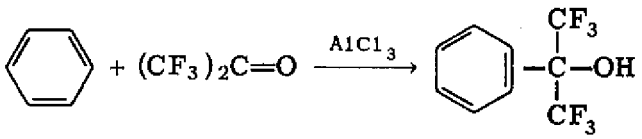
In this work, we have synthesized a number of mono- and diglycidyl ethers which contain various amounts of fluorine and have determined the effects of this substitution on physical properties and reaction rates. The eventual goal is the synthesis of useful epoxy resins and derivatives which contain large quantities of fluorine.

MONOGLYCIDYL ETHERS

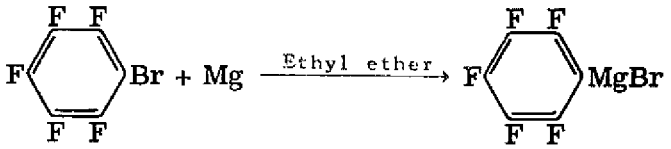
A new type of glycidyl ether can be readily formed from aryl 2-hydroxyhexafluoropropyl compounds and epichlorohydrin in the same type of reaction normally used to prepare glycidyl ethers from phenols (2):

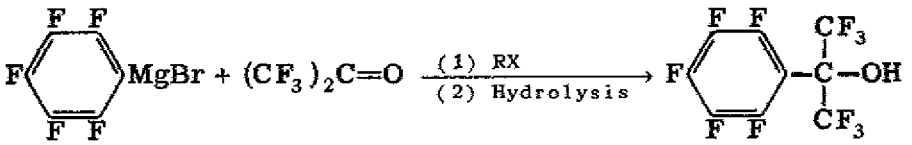


This is an effective means of including fluorine in glycidyl ethers, because the intermediates are readily available and the hexafluoropropyl group contains a high percentage of fluorine. A number of monosubstituted intermediates of this type, and a few disubstitute ones, have been prepared by the direct condensation of aromatic hydrocarbons and hexafluoroacetone using aluminum chloride as a catalyst (3):



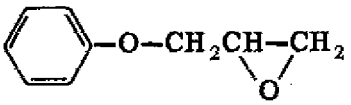
If the aromatic compound is substituted with a perfluoroalkyl group, this method of synthesis of the hydroxy compound is not effective because of undesirable side reactions (4). An alternative synthesis via Grignard reagents (5) is satisfactory for obtaining more heavily substituted intermediates, as illustrated by





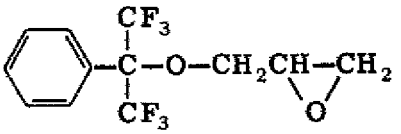
A few fluorine-substituted phenols are commercially available which react in the normal fashion with epichlorohydrin. Thus, two series of fluorine-substituted glycidyl ethers have been prepared — one series contains the hexafluoroisopropyl group (type 2) and the other consists of substituted phenyl glycidyl ethers (type 1). To simplify the subsequent tables and discussion, these monoglycidyl ethers are identified by structural formulas and numbers in Table 1.

Table 1
Structural Formulas of Fluorine-Substituted Monoglycidyl Ethers

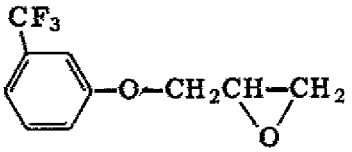


(Reference Compound)

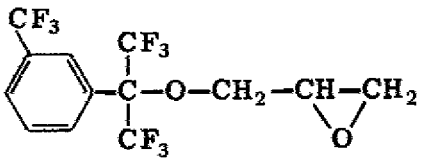
1a



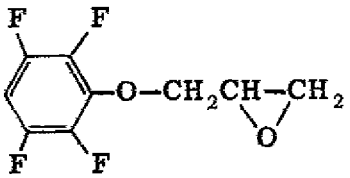
2a



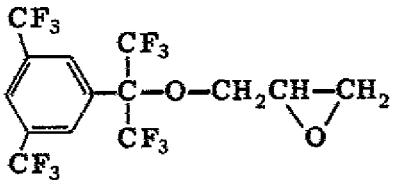
1b



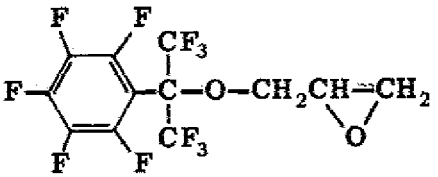
2b



1c



2c



2d

Intermediates for Monoglycidyl Ethers

Phenyl glycidyl ether and the intermediates for the type 1 glycidyl ethers were obtained from commercial sources. 2-Phenyl-2-hydroxyhexafluoropropane was prepared according to the published method (2). Other members of the type 2 intermediates were prepared as follows:

2-(3-Trifluoromethylphenyl)hexafluoro-2-propanol — 3-Bromobenzotrifluoride, 41 g (0.18 mole), magnesium turnings, 4.5 g (0.19 mole), precleaned with dilute hydrochloric acid and dried, and 100 ml of anhydrous ether were placed into a 100-ml, four-necked resin kettle equipped with a magnetic stirrer, gas inlet tube, and a dry ice-acetone reflux condenser protected from the atmosphere by a drying tube. Prior to reactant addition, the kettle was heated with a heat lamp and purged with dry nitrogen. When the flask contents were gently heated, the reaction started and proceeded smoothly for 0.5 hr to yield a dark brown solution. Hexafluoroacetone, 22 ml (0.19 mole), was condensed into a trap from a cylinder and then allowed to distill over into the resin kettle above the liquid surface at such a rate to maintain gentle reflux at the dry-ice condenser. The addition required 1.5 hr during which the Grignard solution was stirred vigorously. Excess 2N hydrochloric acid was used to decompose the magnesium salt after the reactant solution had stirred overnight. Additional ether was added, and the ethereal solution was separated, washed twice with water, once with saturated sodium chloride solution, and dried over anhydrous sodium sulfate. The solvent was evaporated under reduced pressure, and the residue was fractionated through a 6-in., vacuum-jacketed Vigreux column. The fraction boiling at 89°C/44 mm Hg was collected as a clear, colorless liquid, 36 g (63% overall yield based on starting bromide). The product was alkali-soluble, and the nmr spectrum in carbon tetrachloride displayed signals at δ 8.02 (s, 1, Ar-H), 7.70 (m, 3, Ar-H), and 3.40 (s, 1, O-H). The infrared spectrum had a sharp hydroxyl peak at 3600 cm^{-1} and a broad one between 3500 and 3200 cm^{-1}.

2-[3,5-di(trifluoromethyl)phenyl]hexafluoro-2-propanol — This compound was prepared via the Grignard reaction in essentially the same manner as the preceding intermediate, except that a mixture of ether and tetrahydrofuran was required as solvent. Magnesium could not easily be induced to react with 3,5-di(trifluoromethyl)bromobenzene in dry ether alone. A 60-g (0.205 mole) sample of the bromide gave an overall yield of 54.6 g (70%) of the desired product. Bp 85° to 90°C/40 mm Hg; nmr signals: δ 8.20 (s, 2, Ar-H), 8.03 (s, 1, Ar-H), and 3.79 (s, 1, O-H). The infrared spectrum contained a sharp hydroxyl peak at 3610 cm^{-1}.

2-(pentafluorophenyl)hexafluoro-2-propanol — This perfluorinated alcohol was synthesized via the readily producible Grignard reagent of pentafluorophenyl bromide in dry ether. In this case, the reaction between the Grignard reagent and hexafluoroacetone appeared to be unusually sluggish, and it was necessary to heat the ethereal solution nearly to boiling to achieve a moderately rapid reaction. From 50 g (0.20 mole) of bromide 45 g (64% overall yield) of the alcohol was obtained, bp 167° to 170°C/760 mm Hg. The infrared spectrum had a sharp hydroxyl bond at 3620 cm^{-1}.

Preparations of Monoglycidyl Ethers

All of the monoglycidyl ethers were prepared in essentially the same manner. The following procedure for the preparation of the glycidyl ether of 2-(3-trifluoromethylphenyl)hexafluoro-2-propanol is typical.

In a 2-liter, three-necked, round-bottom flask equipped with a reflux condenser, a dropping funnel, and a stirrer 195 g (0.65 mole) of 2-(3-trifluoromethylphenyl)hexafluoro-2-propanol, 500 g epichlorohydrin (5.4 mole), 600 ml acetone, and 70 ml water were

placed. A 20% aqueous solution of sodium hydroxide containing 28.0 g (0.70 mole) of the alkali was placed in the dropping funnel. The flask contents were stirred and heated to reflux. One-sixth of the sodium hydroxide solution was added slowly, and reflux was continued 15 minutes before another one-sixth portion was introduced. This was repeated until five-sixths of the alkali had been added, and after the fifth reflux period, the aqueous layer was drawn off and discarded. Then, reflux was resumed and the remaining alkali solution was added. After 15 minutes, the aqueous layer was again withdrawn. Most of the acetone and epichlorohydrin were distilled at atmospheric pressure, and the remaining solution was decanted from a residual precipitate of sodium chloride. The solution was then diluted with 300 ml of ether. This ethereal solution was washed once with water and twice with saturated aqueous sodium chloride. After it was dried over anhydrous sodium sulfate, the solution was filtered, and the ether removed on a rotary evaporator. The resulting product solution was vacuum distilled through a 6-in. Vigreux column and the fraction boiling at 120°C/13 mm Hg was collected, which amounted to 180 g (78%) of 2-(3-trifluoromethylphenyl)hexafluoro-2-propyl glycidyl ether. This fraction was redistilled through a Nester Faust spinning band column to yield 151 g of analytically pure product (Table 2).

Physical Properties of Monoglycidyl Ethers

Table 3 gives some of the physical properties of phenyl glycidyl ether and fluorine-substituted glycidyl ethers. All of these data were determined on analytically pure samples of the ethers which had been fractionally distilled on a Nester Faust Auto Annular Teflon Spinning Band Still at 10.0 mm Hg pressure.

At this pressure, the boiling points were nearly independent of fluorine content and fell within the range of 104° ± 7°C, although the molecular weights varied from 150 to 436. This independence of boiling point and molecular weight reflects a decreasing molecular affinity with increasing fluorine content of the ethers, which is also notable in the gas chromatographic and surface tension data. The trend of retention times on columns with liquid phases of silicone or polyether was toward shorter retentions as fluorine content increased. The trend of surface tension was downward as fluorine content increased, although the viscosities increased, generally. The densities clearly reflect the added mass of fluorine atoms as they increase in proportion to the amount of fluorine present. Refractive indices show the opposite trend and decrease with increasing fluorine content.

Reaction Rates with Dibutylamine

The reaction between a secondary amine and an unsymmetrical epoxide compound may proceed via two different pathways, depending on which of the epoxide-ring carbons is attacked:

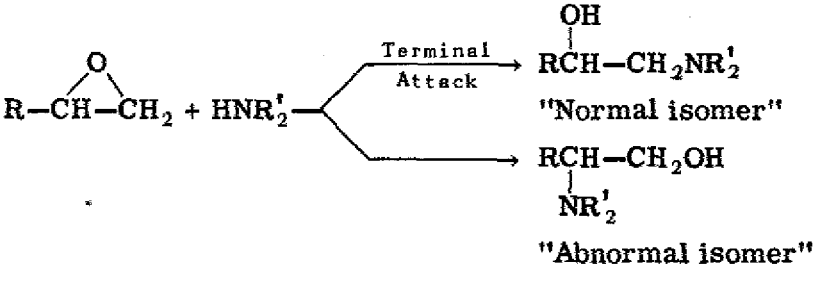


Table 2
Analytical Data for Fluorine-Substituted Monoglycidyl Ethers

Compound	Formula	Carbon (%)		Hydrogen (%)		Fluorine (%)		Epoxy Equivalent Weight*	
		Calc	Found	Calc	Found	Calc	Found	Calc	Found
1b	$C_{10}H_9F_3O_2$	55.05	55.03	4.16	4.16	26.13	26.16	218.2	221.1
1c	$C_9H_6F_4O_2$	48.66	48.87	2.72	2.83	34.21	34.44	222.1	224.1
2a	$C_{12}H_{10}F_6O_2$	48.01	48.07	3.36	3.44	37.97	38.09	300.2	301.4
2b	$C_{13}H_9F_9O_2$	42.40	42.21	2.46	2.54	46.44	46.40	368.2	369.1
2c	$C_{14}H_8F_{12}O_2$	38.55	38.56	1.85	1.94	52.27	–	436.2	434.6
2d	$C_{12}H_5F_{11}O_2$	36.94	36.97	1.29	1.28	53.57	53.67	390.2	–†

NMR Spectra

Hydrogen‡ $(R-O-CH_{2_a}-\underset{b}{CH}(\overset{O}{\triangle})-CH_{2_c})$					F19§		
$H_{Aromatic}$	H_a¶	H_b	H_c¶	$Ar-C(CF_3)_2-OR$	$Ar-CF_3$	Ar—F
1b 7.10 (4)	4.16 3.89	3.18	2.76 2.60	–	63.3 (s)	–
1c 6.79 (1)	4.41 4.09	3.26	2.77 2.59	–	–	152.6 (2,m) (ortho to oxygen) 169.3 (2,m) (meta to oxygen)
2a 7.56 (2) 7.46 (3)	3.82 3.57	3.15	2.75 2.60	71.6 (doublet of quartets)	–	–
2b 7.92 (1) 7.68 (3)	3.91 3.57	3.20	2.78 2.63	71.6 (doublet of quartets)♦	63.8♦	–
2c 8.16 (2) 8.03 (1)	3.99 3.53	3.25	2.84 2.67	71.4 (doublet of quartets)	64.0	–
2d –	3.63	3.18	2.78 2.51	72.7♦ (triplet)	–	145.9♦ (2,broad) (ortho to $-C(CF_3)_2-$) 160.9♦ (1,m) (para) 172.2♦ (2,m) (meta)

*Determined with 1N pyridine hydrochloride in pyridine.
†Pyridine hydrochloride method not applicable due to color formation.
‡Ppm downfield from tetramethylsilane in CCl_4 solution.
§Ppm upfield from CCl_3F reference.
¶Listing of dual signals for H_a or H_c indicates chemical nonequivalence of the geminal protons.
♦In CCl_4.

Table 3
Physical Data for Fluorine-Substituted Monoglycidyl Ethers

Compound	Yield* (%)	BP (°C/10.0 mm Hg)	Refractive Index n_D^{20}	Density† (g/cm³)	Surface Tension‡ (dynes/cm)	Viscosity§ (cs)	GLC Retention Time¶ (min)	
							Silicone 550 Column	UCON 50-HB 2000 Column
1a	—	103	1.5312	1.104	42.05	5.19	15.1	1.35
1b	88	110	1.4676	1.289	31.00	5.23	13.0	1.21
1c	67	99	1.4552	1.439	34.58	2.99	8.6	0.80
2a	65	104	1.4371	1.403	28.43	15.96	10.3	0.80
2b	78	108	1.4095	1.488	26.05	17.97	6.4	0.60
2c	62	97	1.3901	1.605	23.25	25.20	2.8	0.39
2d	38	111	1.4074	1.720	27.39	39.40	5.5	0.57

*Percent conversion from corresponding hydroxy compound.
†Determined at 24°C.
‡Determined at 23°C.
§Determined at 25°C.
¶Determined at one time with fixed instrument settings: 160°C column temperature and 35 psig He head pressure.

Terminal attack, leading to the formation of a secondary alcohol, is the exclusive or predominant pathway followed by nearly all nucleophiles under neutral or basic conditions (6-8). This is due primarily to the steric hindrance exerted by the R group on the more substituted ring carbon atom. The product corresponding to terminal attack is commonly labeled the "normal isomer," because of the overwhelming tendency for this mode of reaction. Previous workers (9) have shown that phenyl glycidyl ether and piperidene conform to the trend, reacting in ethanol to give greater than 99% of the normal isomer.

Our kinetic data were obtained by reacting various glycidyl ethers with dibutylamine, using t-amyl alcohol as a solvent. Because dibutylamine is even more hindered than is piperidine, a negligible yield of the abnormal isomers is expected under the reaction conditions employed. Investigation of the products of each of the glycidyl ether-dibutylamine reactions supported this prediction. Gas-liquid phase chromatographic analysis of the reaction mixtures at various column temperatures indicated only a single, sharp product peak in each case. These products were identified by their nmr spectra as the corresponding normal isomers. No evidence of formation of the abnormal isomer could be detected, using these techniques, for any of the systems. For this reason, and in light of the above discussion, we have considered terminal attack to be the exclusive reaction pathway for the kinetic studies reported. The formation of trace amounts of abnormal isomer, although not rigorously excluded, would have a negligible effect on our rate measurements.

The possibility of alcoholysis of the epoxide ring by solvent molecules has been ruled out by previous studies. It has been shown (9) that ethanol does not attack phenyl glycidyl ether in neutral solution, and even refluxing in the presence of phenoxide anion led to only 2% reaction between ethanol and phenyl glycidyl ether (8). Our work was carried out using hindered t-amyl alcohol at 60°C or less, so it is not surprising that no sign of alcoholysis was found.

Order of the Reaction — As anticipated from various studies, which show that nucleophilic attack on an epoxide ring in neutral or basic media proceeds according to second order kinetics (10,11), all of the glycidyl ethers, 1a through 1c and 2a through 2d, follow a second order rate law in their reactions with dibutylamine. Using equal initial concentrations of amine and glycidyl ether in t-amyl alcohol and plotting the reciprocal concentration of the reactants as a function of time, we obtained straight lines for each system at three different reaction temperatures (Figs. 1 and 2). This linear behavior is characteristic of second order reactions in which

$$\frac{dC_A}{dt} = -k_2 C_A C_B \ .$$

For

$$C_A = C_B \ ,$$

$$\frac{dC_A}{dt} = -k_2 C_A^2$$

and

$$\frac{1}{C_A} = -k_2 t + C_A^0 \ .$$

Concentrations were determined as a function of time by analyzing aliquots of the reaction solution in the gas chromatograph and measuring integrated peak areas as percentages of initial areas. This technique allows for the determination of the amounts of each

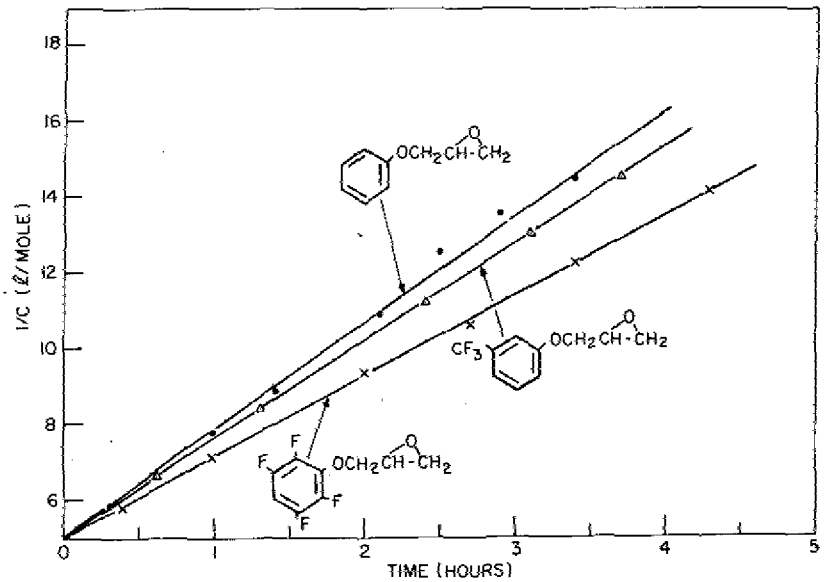


Fig. 1 - Reaction of dibutylamine with glycidyl ethers of type 1 in t-amyl alcohol (T = 60°C), using equimolar amounts of reactants. Reciprocal concentration of the glycidyl ether is plotted as a function of time.

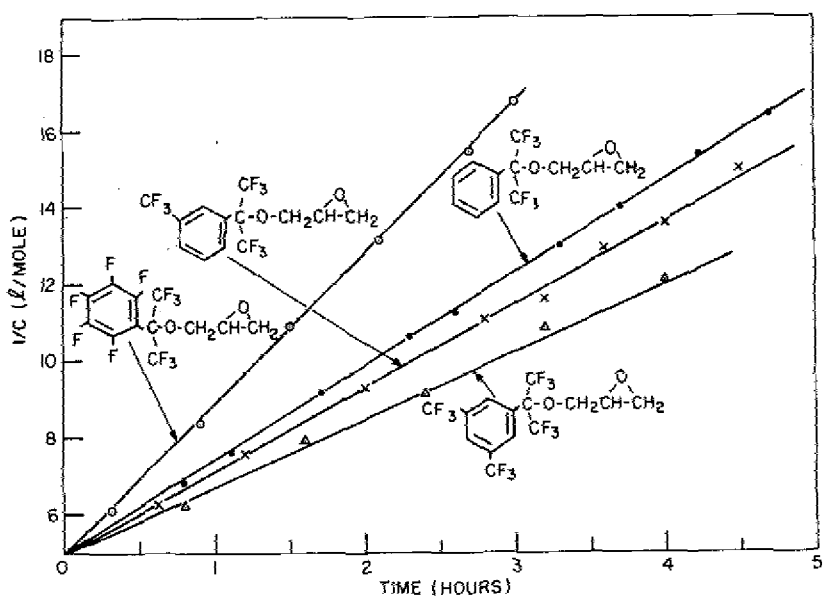


Fig. 2 - Reaction of dibutylamine with glycidyl ethers of type 2 in t-amyl alcohol (T = 60°C), using equimolar amounts of reactants. Reciprocal concentration of the glycidyl ether is plotted as a function of time.

reactant remaining at any time. However, rate measurements were based on the glycidyl ether concentrations only, which could be determined more accurately due to complete isolation of the gas chromatographic peak. It was clear from the simultaneous measurement of the amine concentration that a 1:1 reaction was taking place.

The dibutylamine used for kinetic studies was purified by careful distillation through a 3-ft, helix-packed column. A single fraction, bp 158° to 159°C/760 mm Hg, was used for all runs. Distillation of the t-amyl alcohol was carried out on the same column, and the central fractions, bp 101.0° to 101.5°C/760 mm Hg, were combined for use. After purification, neither the amine nor the alcohol solvent showed any traces of impurity in the gas chromatograph. All runs were made using materials from the same batch of amine, and from the same batch of solvent, to insure further against variations in the relative reaction rates due to trace impurities. The glycidyl ethers used showed no traces of impurity by glpc analysis on the columns described below.

Rate Measurements — Gas chromatographic analyses were performed using a Beckman GC-2A gas chromatograph, equipped with a 10-in. recorder and disk integrator, and containing a 2-ft-by-1/4-in. column of 30% silicone 550 on 42/60 mesh firebrick. Concentrations were obtained as a function of time by comparing the integrated area of a reactant peak at time t to the area of that peak at time t_0. Since the t_0 peak corresponded to a known initial concentration, the actual concentration at time t was found from the ratio of peak areas.

In a typical run, 2.00×10^{-4} moles of glycidyl ether and 2.00×10^{-4} moles of dibutylamine were weighed into a 10-ml volumetric flask and enough t-amyl alcohol was added to bring the total volume to exactly 10 ml. The solution was then immediately transferred to a round-bottom flask equipped with a magnetic stirrer and a self-sealing rubber septum cap. The flask was capped and placed in a constant temperature bath, which was maintained at the reaction temperature ±0.05°. The t_0 reading was then taken by piercing the septum cap with a syringe and withdrawing a 10.0-μl aliquot, which was injected directly into the gas chromatograph for analysis. Subsequent 10.0-μl samples were withdrawn at various times and analyzed in an identical manner. Variation in the height of the sharp t-amyl alcohol peak, which served as an internal standard, was generally less than 1% during a run and never more than 2.5%. All reactions were followed to at least 60% completion.

Each of the reactions was run at three different temperatures — 41.0°, 51.0°, and 60.0°C — using initial concentrations of 0.200M in t-amyl alcohol for each reactant. All of the 60° reactions were run in duplicate. Rate constants were reproducible to within 1% in most cases, and to within 3% in the least favorable case.

Product Analysis — Product investigation was done by glpc analysis of the infinite-time kinetic samples. A 6-ft-by-1/4-in. column packed with 30% UCON 50-HB 2000 on 42/60 mesh firebrick was used for analytical and preparative work.

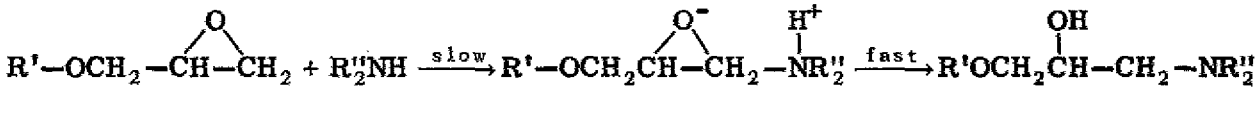
Glpc analysis of the reaction mixtures indicated a single, sharp product peak for each of the reactions. After purification by preparative glpc, these products were characterized by their nmr spectra as the normal isomers (products of terminal attack by the amine on the epoxide ring). No trace of the second (abnormal) isomer could be found in any of the systems. In each case, the ratio of the nmr integral of the N–C–H vs O–C–H protons was 2:1, corresponding to that required for the normal isomer.

Since all products are identical on the amino side of the glycidyl ether oxygen, the features of interest in their spectra are extremely similar. These features are illustrated by the following example.

Adduct of Dibutylamine and Glycidyl Ether 1c — The reaction product had a retention time of 2.5 min at 35 psig, T = 200°C, on the column described above. Its nmr spectrum showed maxima at δ 6.73 (triplet of triplets, 1, Ar—H), 4.18 (d, 2, O—CH_2), 3.83 (m, 1, CHOH), 3.60 (s, 1, O—H), 2.52 (m, 6, N—CH_2), 1.36 (m, 8, C—CH_2), and 0.93 (t, 6, CH_3).

The infrared spectrum showed absorptions at 3440 cm^{-1} (hydroxyl); 2900, 1460 (C—H); 1640, 1540, and 1490 (aromatic); 1175 (Ar—O—R); and 1100 (C—F, alcoholic C—O).

Predicted Effect of Fluorinated Substituents — Because of the second order appearance of these reactions, it seems clear that the mechanism is S_N2, with dibutylamine attacking the terminal carbon of the epoxy ring in the rate-determining step. This slow step may then be followed by rapid proton transfer, probably via the hydroxylic solvent (12):



It has been inferred (9) from this mechanism that the sharp increase in reactivity of phenyl glycidyl ether as compared to styrene oxide or 1,2-epoxy-3-phenylpropane in ethanol is due to polarization of the bonds in structure A as in B:

A B

The overall effect of polarizing the epoxy ring in this fashion is to facilitate the reaction by enhancing the approach of the nucleophilic amine (9,13). It was felt that the greater electronegativity of phenoxymethyl vs phenyl or benzyl activated the epoxide ring, thereby causing its increased reactivity. If we extend this reasoning to the introduction of fluorine into the aromatic nucleus of A, the subsequent increase in electronegativity of that part of the molecule is expected to produce an epoxide even more reactive than A itself. Tetrafluorophenoxy, for example, being more electron-withdrawing than phenoxy, should cause tetrafluorophenyl glycidyl ether (1c) to react with nucleophiles faster than does phenyl glycidyl ether (1a). This argument also pertains to compounds of type 2, in which increased fluorine substitution on the aromatic nucleus should coincide with increasing rate constants.

Observed Effect of Fluorinated Substituents — For both series of analogous compounds, the surprising finding of our kinetic studies is that increased fluorine substitution on the aromatic ring slows the rate of epoxide ring opening in all cases but one. The actual decrease in reactivity is substantial, in view of the fact that the substituents are quite distant from the site of attack.

As seen in Figs. 1 and 2, and in Table 4, rate constants tend to decrease rather than increase as fluorinated substituents are added to 1a and 2a. Only compound 2d exhibits the predicted acceleration in its reaction with dibutylamine. For all other compounds, there is a decrease in reactivity within each series which is roughly proportional to the degree of fluorine substitution. Arrhenius parameters for the reactions studied are plotted in Figs. 3 and 4 and given in Table 5. As can be seen, activation energies and entropies are quite similar in all cases.

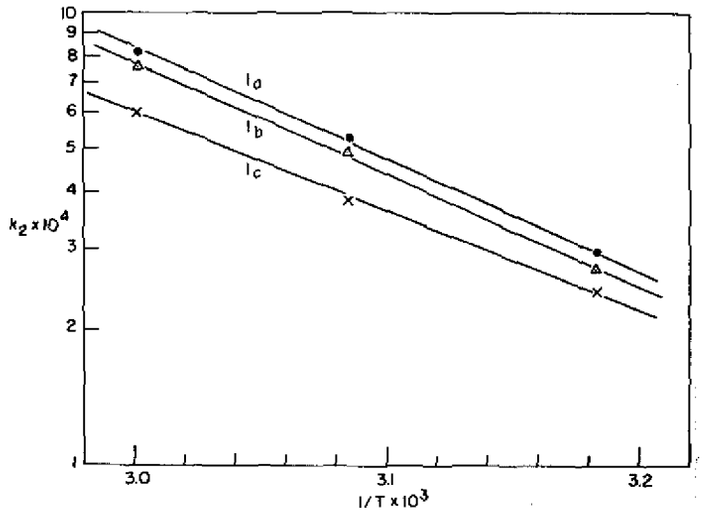


Fig. 3 - Arrhenius plots for the reaction of dibutylamine with glycidyl ethers of type 1 in t-amyl alcohol

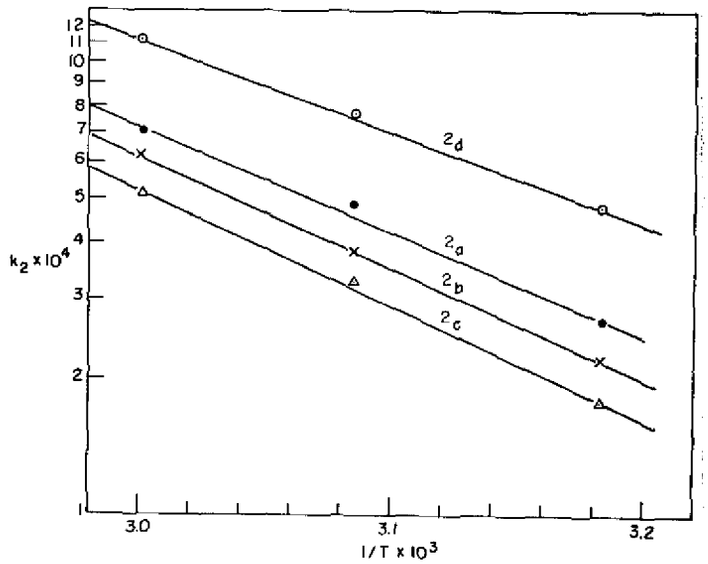


Fig. 4 - Arrhenius plots for the reaction of dibutylamine with glycidyl ethers of type 2 in t-amyl alcohol

Table 4
Measured Rate Constants

Compound	10^4 k_2* (T = 41°C)	10^4 k_2 (T = 51°C)	10^4 k_2 (T = 60°C)
1a	2.96	5.28	8.15
1b	2.72	4.87	7.59
1c	2.41	3.83	6.00
2a	2.68	4.88	7.03
2b	2.24	3.81	6.17
2c	1.78	3.27	5.12
2d	4.78	7.71	11.14

*k_2 is given in l/mole-sec.

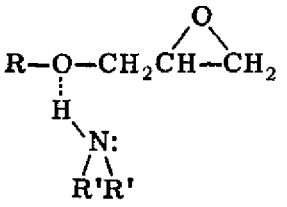
Table 5
Arrhenius Parameters

Compound	Entropy of Activation (kcal/mole)	$\log_{10}$ A	ΔS^{+*} (eu)
1a	11.0 ± 1	4.2 ± 0.5	-42 ± 3
1b	11.2 ± 1	4.3 ± 0.5	-41 ± 3
1c	10.4 ± 1	3.6 ± 0.5	-44 ± 3
2a	10.5 ± 1	3.7 ± 0.5	-44 ± 3
2b	10.9 ± 0.6	3.9 ± 0.3	-43 ± 2
2c	11.4 ± 1	4.2 ± 0.5	-42 ± 3
2d	9.3 ± 1	3.2 ± 0.5	-46 ± 3

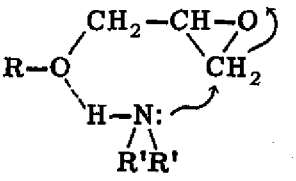
*Activation parameter, calculated at 300°K according to J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," New York:Wiley, p. 71, 1963.

Mechanistic Considerations — The steric situation in the vicinity of the epoxide ring is identical for each of the compounds of type 1, as it is for those of type 2. Therefore, differences in reactivity within either of the two groups of compounds must be attributed to electronic effects caused by substituents on the aromatic ring, or to steric considerations involving the glycidyl ether oxygen, rather than the epoxide ring itself.

The unexpected behavior of fluorine-substituted compounds led us to consider an alternative to the simple inductive explanation for the highly reactive nature of glycidyl ethers in the S_N2 reactions discussed. The assumption of activation of the epoxide ring via a simple inductive effect is inconsistent with the observed deactivating influence of fluorinated substituents in compounds 1a through 1c and 2a through 2c. Therefore, it appears that at least part of the activation caused by the glycidyl ether oxygen may be due to its ability to hydrogen bond with the attacking amine as in compound C. This possibility has recently been suggested (14).



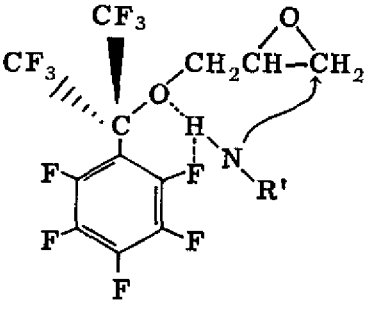
C



D

Association of this type between the amino hydrogen and the ether oxygen would enhance the approach of the amine and place it in a favorable position for attacking the epoxide ring. In the six-membered ring intermediate D which results from terminal attack, the ether oxygen might also stabilize the transition state by delocalizing the positive charge on the nitrogen during formation of the C–N bond. This mechanism is consistent with the absence of the abnormal isomer, which would require a five rather than six-membered ring intermediate for its formation. Fluorine or fluorocarbon substituents on the R group of D are expected to decrease the electron density around the glycidyl ether oxygen and consequently reduce its ability to associate with the amino hydrogen. Formation of a complex such as D should therefore be less favored. If this effect outweighs the activation of the epoxide ring due to polarization (as in A), it would account for the decreasing rate constants corresponding to increasing fluorine content in compounds 1a through 1c and 2a through 2c.

Compound 2d, our most heavily fluorinated epoxide, is anomalous to the trend of deactivation by fluorine substitution and, in fact, is the most reactive of all the glycidyl ethers studied. Only this compound, of the seven tested, reacts faster than phenyl glydidyl ether. It seems unlikely that the inductive effect of the fluorine in this case should suddenly activate the epoxide ring, since the trend established in all other cases is toward deactivation. A study of the molecular model of compound 2d suggests one possible explanation for its anomalous behavior. Due to the steric hindrance of the two ortho fluorine atoms, the gem-trifluoromethyl groups in this molecule appear to be somewhat constrained perpendicular to the aromatic ring. The preferred orientation appears to be that shown, in which the glycidyl ether oxygen is found to be very close to one of the ortho fluorine atoms.



E

It appears that a complex such as D could be formed through association of the amino hydrogen not only with the glycidyl ether oxygen but also with the ortho fluorine atoms as in E. Of the compounds studied, then, 2d seems to be unique for two reasons: (a) the rotation of the gem-trifluoromethyl groups may be hindered by adjacent fluorine substituents and (b) fluorine atoms (on the benzene ring) are positioned such that association with the amino hydrogen might lead to a favorable geometry for attack on the epoxide

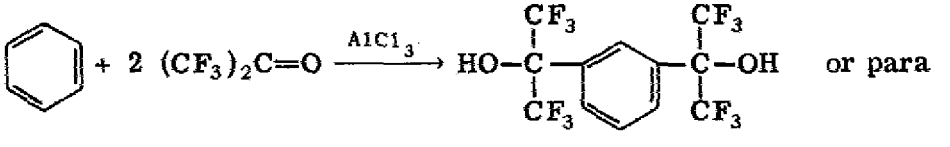
ring. One or both of these factors may be responsible for the anomalous behavior of this compound. The synthesis of compounds closely related to 2d is in progress to determine the basic requirements for enhanced reactivity in fluorosubstituted glycidyl ethers.

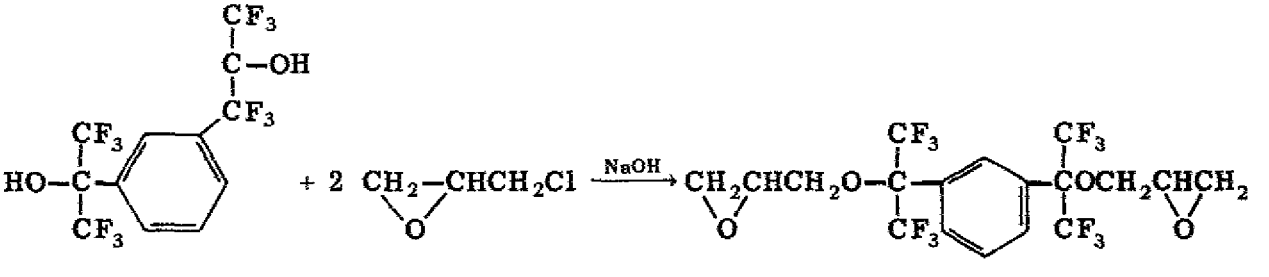
DIGLYCIDYL ETHERS

Whereas the monoglycidyl ethers can be studied kinetically with convenience, diglycidyl ethers must be synthesized to assess the practical effects of fluorine on technically important epoxy resins. To produce difunctional glycidyl ethers of the type studied in this report (i.e., those without fluorosubstituents on the glycidyl group), a molecular weight of 146 units for the two glycidyl groups is appended to available fluorinated dihydroxy intermediates. Thus, the fluorine content of a diglycidyl ether product will be relatively low unless the intermediate is large and contains a high percentage of the halogen.

Large, aromatic-structured intermediates may result in glycidyl ethers which are too high melting to be conveniently used as liquid resins. Such considerations also apply with regard to the suitability of any given intermediate structure in its effects on adhesive quality and the mechanical strength of polymeric products resulting from "cure" of the resin. Actually, the number of fluorinated dihydroxy compounds reported in the chemical literature is so limited at present that there is little opportunity to select an optimum structure from the standpoint of desirable epoxy resin properties. A few fluorodiglycidyl ethers have been reported. Two were derived from 2,2,3,3,4,4-hexafluoropentane-1,5-diol and 2,2-bis(4-hydroxyphenyl)hexafluoropropane (15). We have reported the compound derived from 4,4'-dihydroxyoctafluorobiphenyl (1). We have purified thoroughly the latter two, which contain aromatic structure, to determine the properties of the diglycidyl ethers with little, if any, dimer and trimer contaminants. Also, we needed high-purity diglycidyl ethers for the synthesis of linear fluoropolyols. These will be discussed later in the report.

The meta and para diols derived from the condensation of benzene and hexafluoroacetone in the presence of aluminum chloride (3) have also been used to synthesize diglycidyl ethers (14):



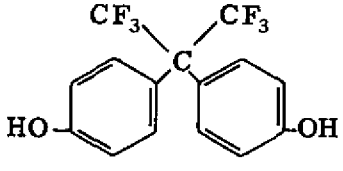
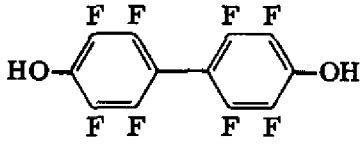
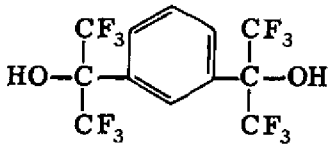
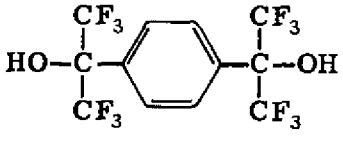


We have also synthesized these two diglycidyl ethers and obtained them as analytically pure compounds.

Diol Intermediates

2,2-Bis(4-hydroxyphenyl)hexafluoropropane is a white, powdery compound, which is commercially available. 4,4'-Dihydroxyoctafluorobiphenyl is a high-melting crystalline material. 1,3-Bis(2-hydroxyhexafluoro-2-propyl)benzene is a liquid, and the corresponding 1,4 compound is a crystalline solid. Although the latter two hydroxy compounds are formally tertiary alcohols, the reaction behavior is quite similar to that of phenols. They dissolve readily in dilute alkaline solution and separate as a second phase when the solution is acidified. They are incapable of undergoing the usual tertiary alcohol dehydration reactions since there are no hydrogen atoms β to the hydroxyl group. The diol intermediates are listed in Table 6.

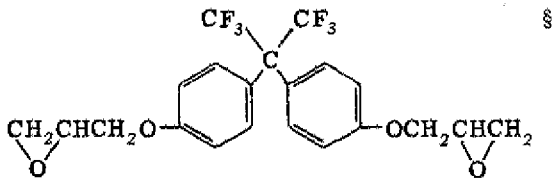
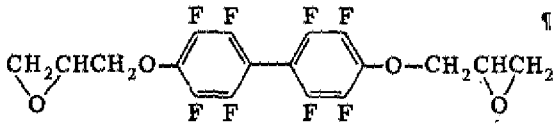
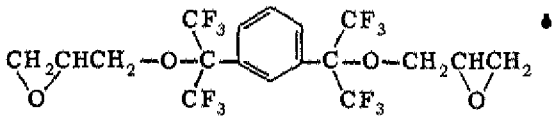
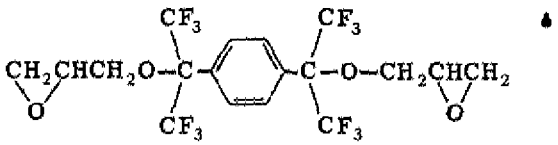
Table 6
Fluorine-Substituted Diols

Formula	MP or BP/mm Hg (%)	Reference
$HOCH_2(CF_2)_3CH_2OH$	77.5-78.5	–
	101-102	–
	210-213	1
	99/20.0	3
	91-94	3

Preparations of Diglycidyl Ethers

The diglycidyl ethers were prepared in the same manner as the monoglycidyl ethers (2), except that recrystallization rather than fractional distillation was used for purification (Table 7). The following procedure for the diglycidyl ether of 4,4'-dihydroxyoctafluorobiphenyl is typical and varies slightly in detail from the method given previously (1).

Table 7
Analytical and Physical Data for Fluorosubstituted Diglycidyl Ethers

Structure	MP* (°C)	Yield† (%)	Formula	Epoxy Equivalent Weight		Carbon‡ (%)		Hydrogen (%)		Fluorine (%)		Major Infrared Bands (cm^{-1})
				Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	
 §	71-73	83	$C_{21}H_{18}F_6O_4$	224	240	56.26	56.00	4.05	4.25	25.42	25.14	—
 ¶	75-78	52	$C_{18}H_{10}F_8O_4$	221	232	48.88	48.86	2.28	2.23	34.37	34.66	1650, 1495 1250, 1100 905, 720
 ♠	73-74	46	$C_{18}H_{14}F_{12}O_4$	261	269	41.39	41.16	2.70	2.56	43.65	43.93	1500, 1220 1275, 1175 1030, 910 730
 ♠	117-120	28	$C_{18}H_{14}F_{12}O_4$	261	274	41.39	41.35	2.70	2.69	43.65	43.42	1520, 1200 1270, 1105 1005, 940 910, 830 720

*Mp of analytical sample.
†Yield after one crystallization from methanol.
‡Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratory.
§Previously reported in Ref. 15.
¶Previously reported in Ref. 1.
♠Previously reported in Ref. 14 but not as analytically pure compounds.

4,4'-Dihydroxyoctafluorobiphenyl (81 g, 0.25 mole) and epichlorohydrin (227 g, 2.5 mole) were placed into a suitable flask along with acetone (229 g) and water (33 g). The resulting solution was stirred and heated to reflux while a 20% aqueous sodium hydroxide solution was added in six equal increments at 15-minute intervals. The aqueous layer which separated was removed after the fifth and sixth reflux periods. The organic layer was flash evaporated to remove volatiles (finally at 100°C/2 mm Hg). The residue was dissolved in hot methanol (210 g). Crystals were deposited as the solution was cooled to -60°C, and these were collected by vacuum filtration. (Note: In one experiment the methanolic solution was allowed to stand at room temperature for 24 hours before cooling, and 80% of the possible product was lost due to polymerization.) The yield of crude diglycidyl ether was 56 g (52%); mp 65° to 71°C. Four recrystallizations from methanol at -20°C gave 43 g (40%) of the analytical product reported in Table 7.

All of these diglycidyl ethers are crystalline solids which in the pure state are excessively high melting for use in the normal manner of liquid epoxy resins. The purified diglycidyl ether of 1,3-bis(2-hydroxyhexafluoro-2-propyl)benzene crystallizes from methanol as beautifully shaped rhomboid crystals, which can be grown to large sizes (Fig. 5).

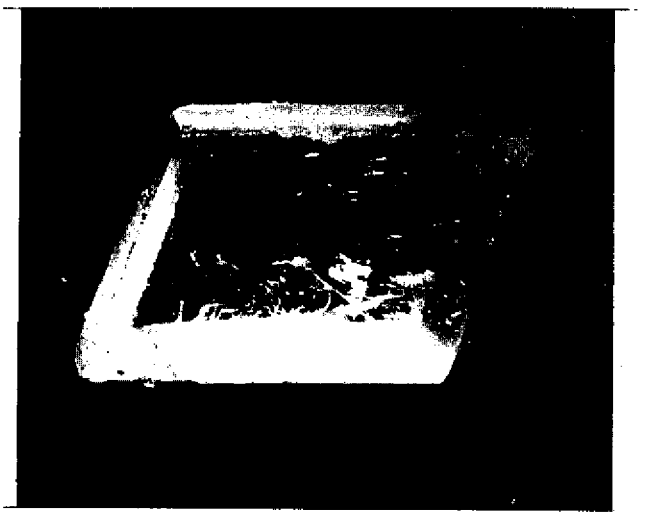


Fig. 5 - Single crystal of purified diglycidyl ether of 1,3-bis(2-hydroxyhexafluoro-2-propyl)benzene (5-mm maximum length)

"Cure" Reactions of Fluorodiglycidyl Ethers

When a diglycidyl ether reacts with a second di- or polyfunctional molecule to form a three-dimensional polymeric network (a process which if often in evidence by a liquid ⟶ gel ⟶ solid transformation), the second reactant is commonly called a "curing agent." The most widely used curing agents for liquid epoxies are polyamines, such as diethylene triamine. However, aliphatic amines are not practical for use with the pure fluorine-bearing glycidyl ethers because the melt temperatures are so high that violent exothermic reactions (which apparently involve C–F bond fission) often occur when the components are blended in the liquid state. Also, any type of curing agent which does not bear a high percentage of fluorine in its molecular composition dilutes the fluorine content of the entire system. For this reason, most of the commonly used amines and anhydride curing agents are not desirable for the fluorine-containing materials.

The most promising reactants for fluorodiglycidyl ethers presently known are fluorinated diols. Most of our work to date has been with 2,2,3,3,4,4-hexafluoropentane-1,5-diol, a commercial compound which is readily purified. This type of material has the advantages that fluorine contents can be maintained at high levels and that controllable reactions occur. Diols are not normally used as epoxy curing agents because reactions are sluggish at temperatures below 100°C (16). However, those with fluorine atoms on the carbon atom β to the hydroxyl groups are relatively acidic (17), and in the presence of a tertiary amine promoter, they will react fairly rapidly with an epoxy of the glycidyl ether type at moderate temperatures. The reaction probably involves an anionic intermediate, which attacks the epoxy ring:

(1) $-CF_2CH_2OH + :NR_3 \longrightarrow -CF_2CH_2O^{\ominus}HNR_3^{\oplus}$

(2) $-\underset{\diagdown O \diagup}{CH-CH_2} + {}^{\ominus}OCH_2CF_2- \longrightarrow -\underset{\underset{O^{\ominus}}{|}}{CH}-CH_2OCH_2CF_2-$

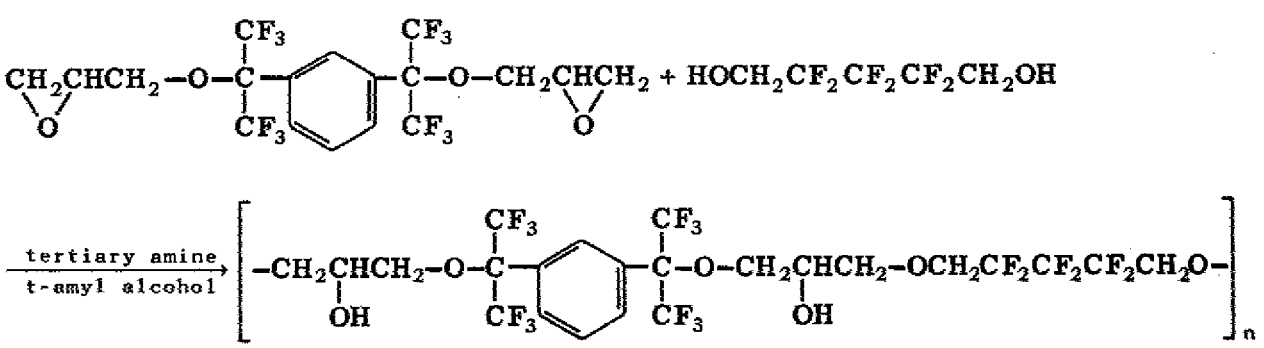
(3) $-\underset{\underset{O^{\ominus}}{|}}{CH}-CH_2OCH_2CF_2- + HOCH_2CF_2- \longrightarrow -\underset{\underset{OH}{|}}{CH}-CH_2OCH_2CF_2- + {}^{\ominus}OCH_2CF_2-$

There is some experimental evidence for the proton exchange between the secondary anion generated in step 2 and the fluoroalcohol, as shown in step 3, in addition to the argument that the more basic ion should take the proton. This evidence, presented below, is that polymerization between equivalent amounts of fluorodiol and diglycidyl ether leads to soluble products rather than to gels. If the secondary anion should exist for an appreciable time, such polymers should crosslink and become insoluble.

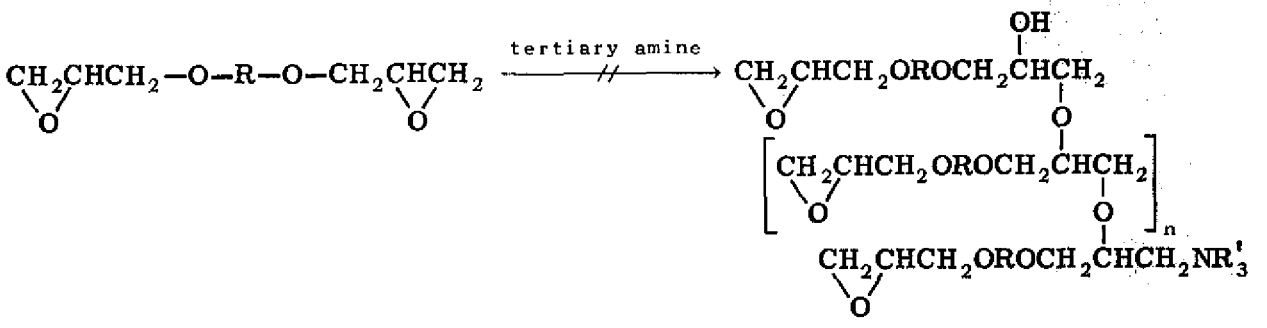
Although these reactions can be carried out neat at melt temperatures, it is desirable to use a solvent to obtain linear polyols in solution. t-Amyl alcohol was chosen because it provides a good reaction medium in which all reactants and products are soluble and does not enter into the reaction itself.

Fluoropolyol Ethers

The major reaction in t-amyl alcohol solution between a pure fluorodiglycidyl ether and a pure fluorodiol (employed in the exact stoichiometric amounts and catalyzed by dimethylbenzylamine) is apparently a simple linear coupling. For example, in the reaction



the chain is a polyether with pendant hydroxyl groups and the repeating unit shown. The terminal groups not shown are epoxy and hydroxyl, which should be capable of indefinite reaction to give high-molecular-weight polymers. Since gelation has not been observed, the normal reaction of diglycidyl ethers catalyzed by tertiary amines (18) must not occur to any appreciable extent:



Also, if the tertiary amine should simply polymerize the glycidyl ether in this fashion, the fluorodiol should remain unreacted and be present in a constant amount. That the diol does in fact react has been ascertained by the use of gas chromatography to follow its disappearance. Simultaneously, the epoxide equivalent weight of the entire reaction solution has been determined by the pyridine hydrochloride method. In this manner the progress of the polymerization reactions was monitored as shown in Figs. 6 and 7.

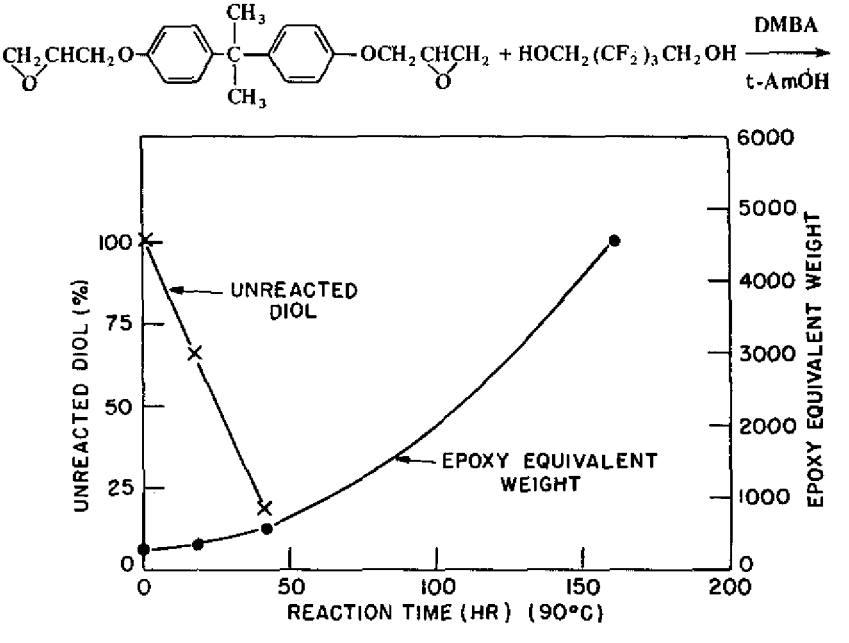
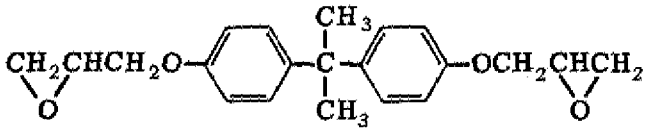
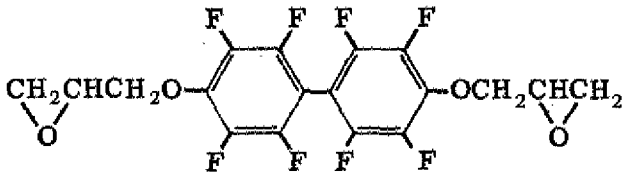
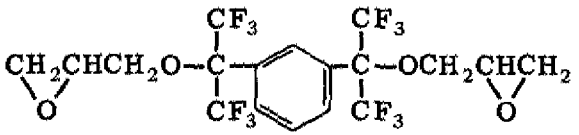
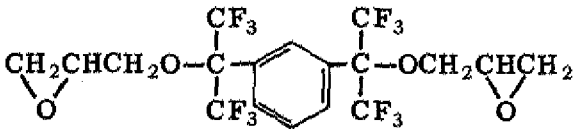
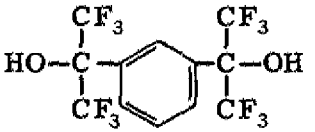
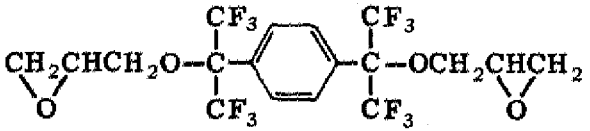


Fig. 6 - Reaction rate of the diglycidyl ether of bisphenol-A with hexafluoropentane diol

Table 8
Diglycidyl Ether — Diol* Reaction Data

Diglycidyl Ether	Diol	Unreacted Diol After 10 hr at 90°C (%)	Epoxy Equivalent Weight† at 140 hr	Calculated No. of Repeating Copolymer Units, n
	$HOCH_2(CF_2)_3CH_2OH$	79	3700	5.70
 (I)	$HOCH_2(CF_2)_3CH_2OH$	56	3545	4.43
 (II)	$HOCH_2(CF_2)_3CH_2OH$	58	5100	5.94
 (II)		80	‡	—
 (III)	$HOCH_2(CF_2)_3CH_2OH$	24	6180	8.39

*1:1 Molar ratios; tertiary amyl alcohol solvent; dimethylbenzylamine catalyst.
†Corrected to a basis of neat diglycidyl ether, diol, and intermediate products.
‡Indeterminate by pyridine hydrochloride method.

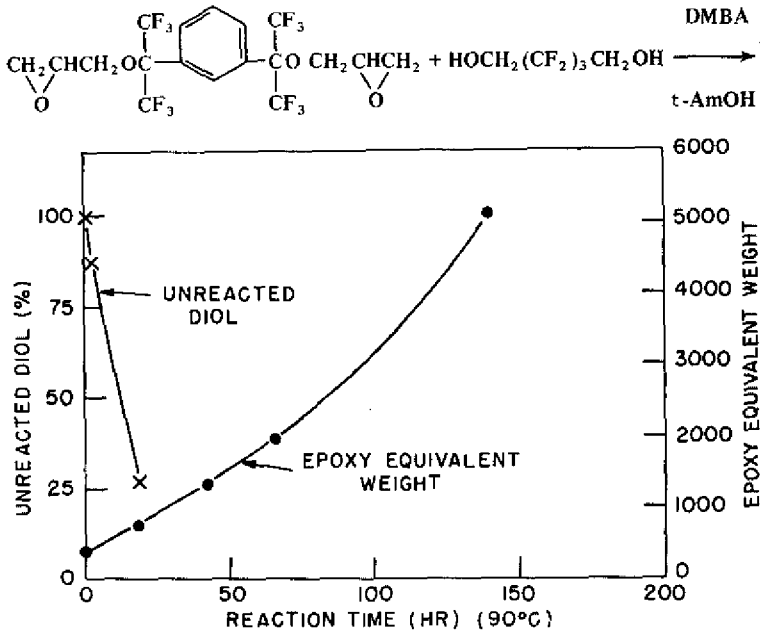


Fig. 7 - Reaction rate of a fluorodiglycidyl ether with hexafluoropentane diol

So far, we have been unable to establish suitable experimental conditions to study the kinetics of the glycidyl ether-fluoroalcohol reaction with the precision of the glycidyl ether-secondary amine reaction. The complexities of the reaction between difunctional reactants are such that we have made little attempt to analyze the polymerization mathematically. However, in Table 8 a rough comparison of the relative reactivities of the various diglycidyl ethers is given.

CONCLUSIONS

All aspects of the work reported here are being continued. We believe that the analytical tools and techniques are developed sufficiently that a fruitful study of the kinetics and mechanisms of epoxy reactions is in order. Syntheses of even more highly fluorinated diglycidyl ethers are in progress. A start has been made on syntheses of compounds containing fluorine on the glycidyl portion.

The polyols bearing fluorine are of obvious potential utility as prepolymers for polyurethanes or as coatings and adhesives without further reaction. The surface chemistry of such materials should also be interesting, with particular regard to the wetting behavior of solvent solutions of the fluoropolymers for solid surfaces and to the manner in which dry films of these polymers are wetted by liquids. As work along these lines progresses, we anticipate that some new materials of practical importance will emerge.

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