propargyl alcohol, bp 112° (1 mm), was prepared by borohydride reduction of phenylpropargyl aldehyde.[19] 3,5-Dinitrobenzyl alcohol was obtained by reduction of 3,5-dinitrobenzoic acid with diborane in tetrahydrofuran. The crude product was chromatographed on silica gel (chloroform–methanol, 95:5) and recrystallized from chloroform, mp 78–81°.

Anal. Calcd for $C_7H_6N_2O_5$: C, 42.42; H, 3.05; N, 14.14. Found: C, 42.60; H, 3.25; N, 14.19.

Esters.—All esters of 3-phenylpropionic acid were prepared by a modification of the trifluoroacetic anhydride method previously described.[8c] A mixture of trifluoroacetic anhydride (210 g, 1 mol) and 3-phenylpropionic acid (150 g, 1 mol) was stored at 40° for 2 hr. Following removal of trifluoroacetic acid under reduced pressure, a residual oil (220 g) was obtained, consisting mainly of the mixed anhydride. Although the latter could be purified by distillation [bp 67° (0.3 mm)], the crude material was used for further work. To 12.5 g of the mixed anhydride, at 0°, was added 0.05 mol of alcohol, and the mixture stored at ambient temperature overnight. The reaction mixture was poured into 3% sodium bicarbonate and the ester separated by filtration or ether extraction. The esters were purified by distillation under reduced pressure or recrystallization (Table III). Yields varied from 60 to 90%. In the case of *tert*-butyl alcohol, the components were mixed at −20° and stored at 0° for 2 days.

Infrared Spectra.—Spectra were measured on solutions of esters in carbon tetrachloride (0.012–0.025 *M*) using a Perkin-Elmer Model 521 spectrophotometer, whose monochromator and source compartments were flushed continuously with dry nitrogen. The carbonyl region was scanned slowly (15 sec/cm^{-1}) and spectra were recorded in duplicate, at a chart speed of 5 cm^{-1}/cm. Intervals were marked with frequency counter-synchronized pips, whose positions were calibrated against standard water vapor lines, recorded under the same conditions. The transmittance minima given in Tables I and II are the averages of six readings (on duplicate runs) and have been corrected by calibration against water vapor. In general, readings agreed to better than ±0.2 cm^{-1}.

(19) H. H. Guest, *J. Amer. Chem. Soc.*, **47**, 860 (1925).

Acknowledgment.—We are indebted to Dr. S. Milstien for assistance in computer calculation, to Dr. I. Levin for assistance in recording of spectra, and to Dr. H. A. Saroff for valuable discussion.

Substituent Effects in the Reaction Rates of 2-Arylhexafluoroisopropyl Glycidyl Ethers with Dibutylamine

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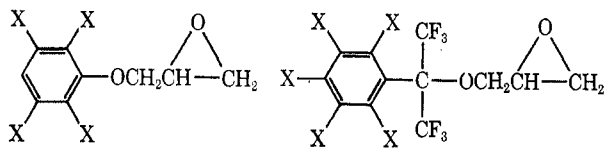
Received July 2, 1970

The effects of ring fluorine substituents upon the reactivity of compounds of structure $ArC(CF_3)_2OCH_2\overline{CHCH_2}O$ (**2**) with dibutylamine in alcohol have been studied. It was found that *o*-fluorine atoms exert a pronounced activating influence upon the rate of epoxide ring opening, whereas *m*- and *p*-fluorines exert a deactivating influence. These effects are not generally additive, however, in compounds containing several ring fluorine atoms. In addition, an *o*-bromine atom was found to accelerate the amine–epoxide reaction, while *o*-methyl groups had an opposite effect. Second-order rate constants are presented for each of the reactions studied, and a mechanism consistent with the observed substituent effects is proposed.

In a recent study[1] we observed that tetrafluorophenyl glycidyl ether[2] (**1b**) reacts more slowly with dibutylamine in alcohol than does phenyl glycidyl ether (**1a**), whereas the glycidyl ether of 2-pentafluorophenylhexafluoropropanol-2 (**2b**) under identical conditions reacts nearly twice as fast as does its non-ring-fluorinated analog **2a**. Furthermore, it was found that meta CF_3 groups deactivate both parent compounds by comparable amounts.



1a, X = H
b, X = F

2a, X = H
b, X = F

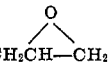
Since both F and CF_3 substituents deactivate the epoxide ring of **1a**, and meta CF_3 groups also deactivate **2a**, the activation of compound **2b** over **2a** seemed quite unusual. In order to determine the factors responsible for this behavior, it was desirable to study the rates of reaction of amines with compounds similar to **2b**. We therefore undertook an investigation of the amine reactivity of molecules of structure **2** containing various patterns of fluorine substitution on the aromatic ring. In addition, two compounds containing ring substituents other than fluorine were synthesized and studied.

Results and Discussion

Synthesis of the Glycidyl Ethers.—Table I presents structures and physical properties of the compounds, all of which are new to the literature, used for kinetic studies. Syntheses were achieved *via* the addition of Grignard or aryllithium reagents to hexafluoroacetone, followed by reaction of the tertiary alcohols with epichlorohydrin and base (*e.g.*, Scheme I). Table I lists nmr data for the compounds.

Several aspects of the synthetic work appear to be noteworthy. The reaction of 1,2,4,5-tetrafluorobenzene with stoichiometric amounts of butyllithium and hexafluoroacetone in tetrahydrofuran produced a 1:1 mixture of mono- and disubstituted products, rather than favoring monoaddition as expected.[3] However, by using diethyl ether as the solvent the ratio of mono- to disubstitution could be increased to 100:1 (Scheme II). This pronounced solvent shift is presumably due to the weaker solvating ability of the diethyl ether for the dilithio derivative.[3,4]

(1) S. A. Reines, J. R. Griffith, and J. G. O'Rear, *J. Org. Chem.*, **35**, 2772 (1970).

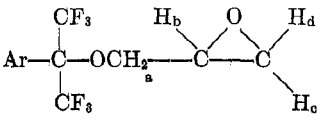
(2) The term "glycidyl" is used to denote the structure 

(3) R. J. Harper, E. J. Soloski, and C. Tamborski, *J. Org. Chem.*, **29**, 2385 (1964).

(4) R. J. Harper and C. Tamborski, *Chem. Ind. (London)*, 1824 (1962).

TABLE I

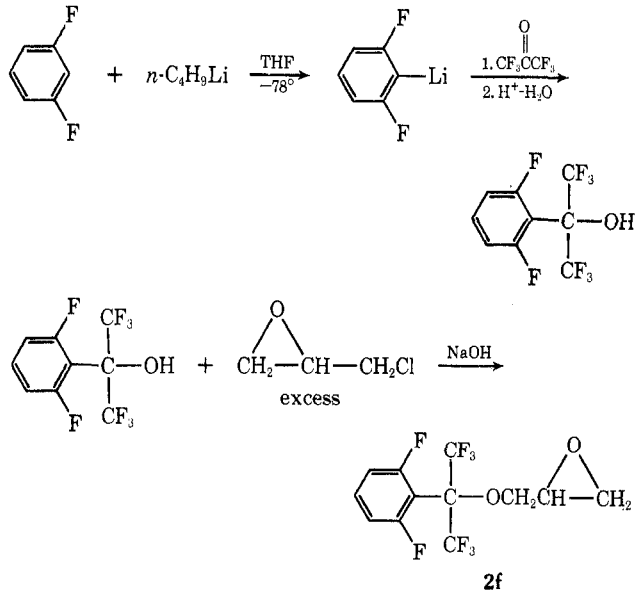
STRUCTURES AND PROPERTIES OF COMPOUNDS 2c–j



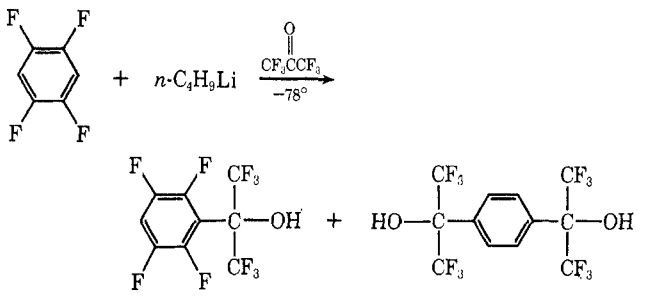
Compd[a]	Ar	Yield, %[b]	$n^{20}D$	Bp, °C (10 mm)	Nmr data[e,f] Haromatic	H_a[g]	H_b	H_c	H_d	CH_3
2c	2-FC_6H_4	50	1.4373	113	7.67 (1) 7.43 (1) 7.2–7.0 (2)	3.80 3.54	3.19	2.77	2.59	
2d	3-FC_6H_4	44	1.4355	107	7.5–7.0 (4)	3.90 3.53	3.18	2.76	2.63	
2e	4-FC_6H_4	40	1.4308	105	7.62 (2) 7.14 (2)	3.88 3.49	3.19	2.78	2.64	
2f	2,6-$F_2C_6H_3$	82	1.4292	124	7.48 (1) 7.01 (2)	3.63	3.19	2.74	2.50	
2g	3,5-$F_2C_6H_3$	53	1.4190	100	7.21 (2) 6.93 (1)	3.93 3.56	3.18	2.79	2.64	
2h	2,3,5,6-F_4C_6H	76	1.4164	119	7.33[i]	3.65	3.21	2.79	2.53	
2i	2-BrC_6H_4	40	1.4770	128[c]	7.76 (1) 7.60 (1) 7.5–7.1 (2)	3.65	3.32	2.76	2.54	
2j	2,6-$(CH_3)_2C_6H_3$	62	*d*	134	7.06 (3)	3.62 3.37	3.14	*h*	*h*	2.67 (3)[j] 2.45 (3)[k]

[a] Satisfactory analytical data have been obtained for all of the compounds listed. [b] Per cent conversion from corresponding hydroxy compounds. [c] Boiling point at 5.0 mm. [d] Solid, mp 53–54°. [e] Parts per million downfield from tetramethylsilane in CCl_4 solution. [f] Assignment of epoxide protons is based on that made for monosubstituted epoxides by P. A. Cruickshank and M. Fishman, *J. Org. Chem.*, **34**, 4060 (1969). [g] Listing of dual signal indicates chemical nonequivalence of the geminal protons. [h] Obscured by CH_3 absorption. [i] Quintet. [j] Singlet. [k] Multiplet.

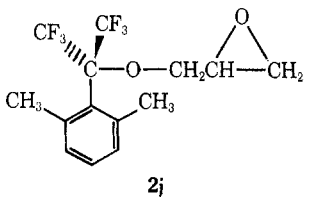
SCHEME I



SCHEME II

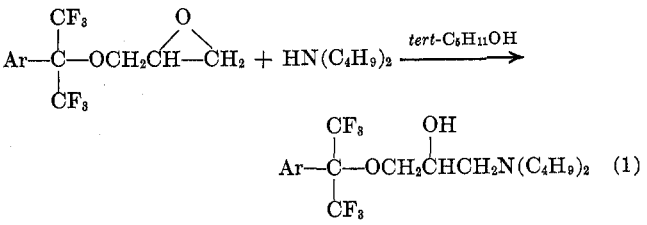


Compound **2j** is of interest because of the extreme hindrance, created by the *o*-methyl groups, to rotation



of the aromatic ring around the Ar–$C(CF_3)_2$ bond. The nmr spectrum of this compound at room temperature exhibits two distinct methyl absorptions (Table I), indicating that the ring is essentially prevented from rotating. Models indicate only one possible conformation for the molecule, that in which the CF_3 groups are perpendicular to the plane of the ring, and the ether oxygen is jammed into one of the methyl groups.

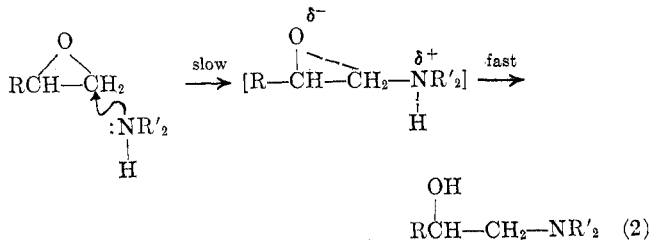
Amine–Epoxide Reaction.—The reaction of compounds of type **2** with dibutylamine in alcohol proceeds *via* nucleophilic attack at the terminal epoxide carbon atom to form a β-amino secondary alcohol. No evidence of attack by the amine at the substituted ring position has been found for this system,[1] presum-



(1)

ably because steric hindrance prohibits that mode of reaction.

In protic solvents, formation of the C–N bond with simultaneous cleavage of the epoxide C–O bond is believed to be the slow step of amine–epoxide reactions. This rate-limiting step is then followed by rapid proton transfer to the incipient hydroxyl group.[5-7] In agreement with this SN2 mechanism, reaction 1 has been found to obey second-order kinetics when dilute (0.2 *M*) solutions of the reactants are employed.[1]



(2)

Fluorine Substituent Effects.—In order to isolate the factors responsible for the high reactivity of **2b**, rates of reaction of the mono- and disubstituted compounds **2c–g** with dibutylamine were measured. Compound **2h** was also studied, because of its direct analogy to **1b**. Disappearance of the reactants was followed by gas chromatographic analysis. Figure 1 depicts the straight-line plots obtained by graphing glycidyl ether concentration as a function of time, for the reaction of equimolar quantities of amine and epoxide. Under these conditions the slope of each line represents an individual rate constant.

$$\frac{1}{[\text{glycidyl ether}]_t} = -k_2 t + [\text{glycidyl ether}]_{t_0}$$

It is clear from Figure 1 that *m*- and *p*-fluorine atoms deactivate the epoxide ring toward nucleophilic attack by dibutylamine.[8] The magnitude of deactivation appears to be very similar for both ring positions. In addition, the effects appear to be roughly additive, since two meta F atoms decrease the rate constant of **2a** by about twice as much as does a single *m*-fluorine substituent. CF_3 groups in the meta positions exhibit identical behavior.[1]

Figure 1 shows that *o*-fluorine atoms exert an opposite, activating influence upon amine–epoxide reactivity. All compounds containing ortho F atoms were activated relative to **2a**, in spite of "deactivating" substituents on other ring positions. That the *o*-fluorine effects are not additive with those of the meta or para positions can be seen by comparing the slope of **2h** or **2b** with that of **2f**. The combination of two *o*- and two *m*-fluorines is expected to make compound **2h** considerably less reactive than **2f**, which contains only "activating" *o*-fluorines. Likewise, **2b**, which contains three "deactivating" and two "activating" fluorines, should be the least reactive of these three compounds. However, all three produced similar rate constants when treated with dibutylamine, and, in fact, **2b** reacted

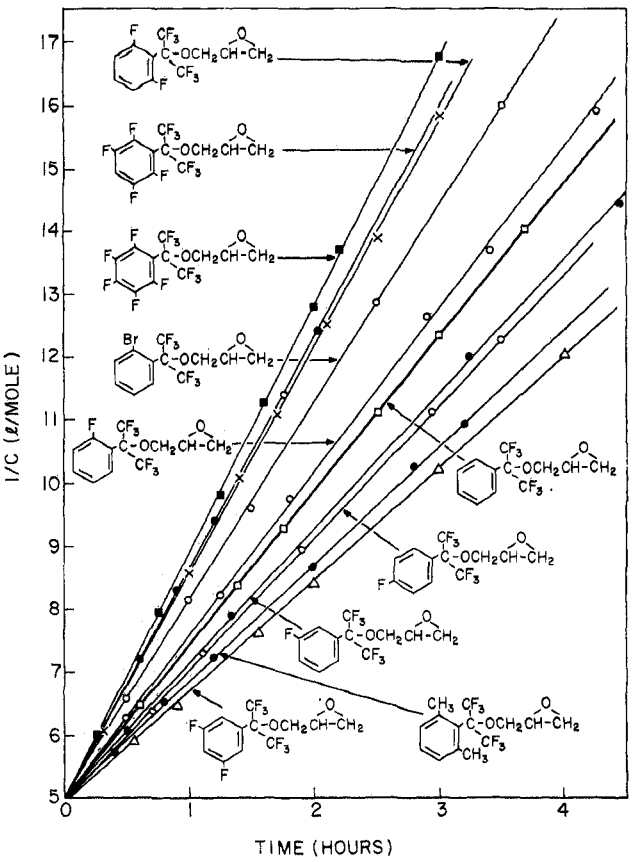


Figure 1.—Reaction of dibutylamine with various glycidyl ethers using equimolar amounts of reactants in *tert*-amyl alcohol (T = 60°). Reciprocal concentration of the glycidyl ether is plotted as a function of time.

slightly faster than the others. The presence of fluorine in both ortho positions seems to cancel the effect of *m*- or *p*-fluorines and defines the molecule's reactivity somewhat independently of these more distant substituents.

A comparison of the reactivity of **2c** to that of **2f** reveals the pronounced change associated with the addition of a second *o*-fluorine atom to the singly substituted compound **2c**. A single *o*-fluorine produces only slight activation relative to the unsubstituted parent compound **2a**. This slight effect is magnified by a factor of 8 however, when the remaining *o*-hydrogen is replaced by fluorine.

Rate constants illustrating these phenomena are presented in Table II. The activation energy of the reac-

TABLE II

RATE CONSTANTS FOR THE REACTION OF COMPOUNDS OF TYPE 2 WITH DIBUTYLAMINE IN *tert*-AMYL ALCOHOL

Compd	$10^4 k_2$[a] (T = 51°)	$10^4 k_2$ (T = 60°)
2a	4.88	7.03
2b	7.71	11.14
2c	5.24	7.43
2d		6.0
2e		5.98
2f	7.13	10.27
2g	3.36	5.12
2h	6.99	10.25
2i		9.03
2j	3.44	5.32

[a] k_2 in l. mol^{-1} sec^{-1}.

(5) N. B. Chapman, N. S. Isaacs, and R. E. Parker, *J. Chem. Soc.*, 1925 (1959).

(6) L. Schecter, J. Wynstra, and R. P. Kurkjy, *Ind. Eng. Chem.*, **48**, 94 (1956).

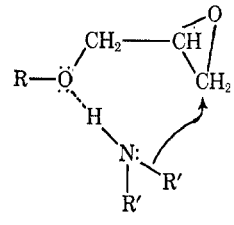
(7) N. S. Isaacs and R. E. Parker, *J. Chem. Soc.*, 3497 (1959).

(8) The rate curves for compounds **2a,b**, taken from ref 1, have been redrawn in this paper for the purpose of comparison.

tion of dibutylamine with compounds of type 2 in *tert*-amyl alcohol is about 10–11 kcal/mol, and the entropy of activation[9] is about −43 eu.[1]

Effects of Other Ortho Substituents.—In order to determine the influence of some ortho substituents other than fluorine, compounds 2i and 2j were synthesized. As can be seen from Table II, these two compounds differ widely in their reactivity with dibutylamine. An *o*-bromine atom exerts an activating influence, whereas *o*-methyl groups cause significant deactivation relative to unsubstituted 2a.

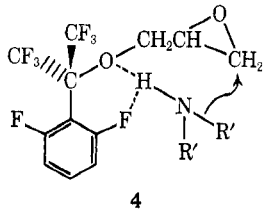
Mechanistic Interpretation.—We have shown[1] that the mechanism of glycidyl ether–amine reactions in alcohol appears to involve a hydrogen-bonded intermediate such as 3. In the case of compounds of type



3

1 (R = Ar), electron-withdrawing groups on the aromatic ring deactivate the epoxide ring toward attack by the amine. This deactivation presumably results from decreased electron density around the ether oxygen[10] and consequent reduction of its ability to associate with the amino hydrogen atom. The deactivation of compounds of type 2 (R = $ArC(CF_3)_2$–) by electron-withdrawing substituents in meta or para positions is believed to occur for this same reason.

According to this theory, compounds of type 2 which contain *o*-fluorine atoms should also be deactivated. Since these compounds instead show increased reactivity with dibutylamine, it would appear that *o*-fluorines exert a special influence. We believe that the influence results from an intermediate such as 4, in



4

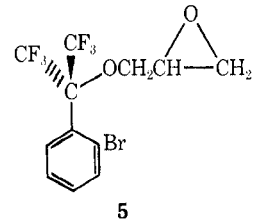
which *o*-fluorine atoms contribute to the hydrogen bond formed with the amino hydrogen.[11] Models indicate that in compounds containing two ortho F atoms the *gem*-CF_3 groups are somewhat constrained in the conformation shown. This constraint forces the glycidyl ether oxygen to lie very close to an ortho F atom, which should then allow a hydrogen bonded complex such as 4 to form. This effect appears to outweigh the expected deactivation resulting from electron-withdrawing substituents and produces an activated epoxide ring.

In compound 2c, which contains only one ortho F atom, the rotation of the benzylic carbon atom appears to be hindered only slightly. The glycidyl ether oxygen atom is not held in position near the *o*-fluorine, and therefore a complex such as 4 should be relatively unimportant. In accordance with this reasoning, compound 2c shows only slight activation relative to the parent compound 2a.

The *o*-fluorine atoms in compound 1b are not in close proximity to the glycidyl ether oxygen, as they are in similarly ring-substituted compounds of type 2. The deactivating inductive effect of the ring fluorines upon the glycidyl ether oxygen appears to be the determining factor in the reactivity of 1b with dibutylamine. No special activating influence seems to operate in compounds of this structure.

As further evidence for the existence of an intermediate of type 3 or 4, the diminished reactivity of compound 2j may be cited. In this molecule the glycidyl ether oxygen is buried beneath one of the *o*-methyl groups and the *gem*-CF_3 groups, and should be barely accessible for hydrogen bonding to the amine. Decreased reactivity is therefore predicted for this compound and is also observed.

The predicted reactivity of compound 2i, which contains an *o*-bromine atom, is somewhat ambiguous. The bromine substituent provides considerable steric hindrance to rotation around the Ar–$C(CF_3)_2$ bond, and one of the two preferred conformations (5) places it against



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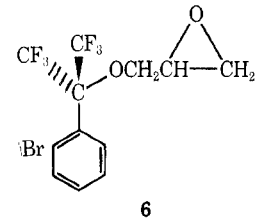

6

the ether oxygen atom. It is not clear, however, whether the bromine atom would participate in hydrogen bonding with an amino hydrogen.[12,13] In any case, the reaction rate of 2i is considerably greater than that of 2a, or even 2c, which contains a single *o*-fluorine atom. This observation leads us to believe that the bromine atom may, in fact, participate in a complex such as 4, when the molecule is in conformation 5.

Experimental Section

Nuclear magnetic resonance spectra were obtained at 24° as 10–20% solutions in CCl_4 on a Varian HA-100 spectrometer, using tetramethylsilane as an internal standard. Infrared spectra were run as smears of the neat liquids between salt plates on a Perkin-Elmer Model 457 grating spectrophotometer. All glycidyl ethers were fractionated on a Nester-Faust auto annular teflon spinning-band still at reduced pressure, prior to use in kinetic experiments. Analytical samples of the glycidyl ethers were used for all kinetic runs. Elemental analyses were performed at the Schwarzkopf Laboratories, Woodside, N. Y.

Materials.—Purification of the dibutylamine and *tert*-amyl alcohol used for kinetic studies has been described previously.[1] Starting materials including *m*-difluorobenzene, 1,2,3,4-tetrafluorobenzene, 2-bromo-*m*-xylene, and *o*-, *m*-, and *p*-fluoro-

(9) Calculated at 300°K according to J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," Wiley, New York, N. Y., 1963, p 71.

(10) It can be seen that the ring substituents are "insulated" from the ether oxygen by the $-C(CF_3)_2-$ group. However, studies of ring-substituted phenylacetic acid show that substituent effects are transmitted with nearly 50% efficiency through an "insulating" carbon atom.

(11) This intermediate was tentatively suggested by us in ref 1, to account for the high reactivity of compound 2b.

(12) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience, New York, N. Y., 1967, p 215.

(13) P. A. Cruickshank and M. Fishman, *J. Org. Chem.*, **34**, 4060 (1969).

bromobenzene were obtained from the Aldrich Chemical Co. and used as received.

2-(2,6-Difluorophenyl)hexafluoro-2-propanol.—To a predried 500-ml flask equipped with N_2 atmosphere, Dry Ice condenser, and mechanical stirrer were added 250 ml of dry THF and 56 ml (0.15 mol) of 22% C_6H_5Li in hexane. The solution was cooled to −78°, and 17 g (0.15 mol) of *m*-difluorobenzene in 30 ml of THF was added over a period of 10 min.[14] The clear solution was stirred at −78° for 2 hr, after which time 30 g (0.18 mol) of hexafluoroacetone was distilled from a Dry Ice trap into the flask. After 2 hr more the solution was allowed to warm to room temperature. Most of the THF was then distilled from the flask before hydrolysis of the lithium complex in order to avoid formation of a THF–product azeotrope. HCl (2 *N*, 200 ml) was then added to the residue, followed by 150 ml of ether. The two-phased mixture was transferred to a separatory funnel, and the ethereal layer was separated, washed twice with H_2O and twice with saturated aqueous NaCl, and dried over Na_2SO_4. Clear, colorless material (22 g, 82%), bp 98–100° (41 mm), was collected after distillation through a 6-in. Vigreux column. The infrared spectrum of this product showed a sharp OH absorption at 3620 cm^{-1}, strong C–F bands at 1300–1100 cm^{-1}, and characteristic aromatic bands at 1630, 1580, and 1470 cm^{-1}. Its nmr spectrum displayed signals centered at 7.45 (m, 1, Ar H), 6.98 (m, 2, Ar H), and 4.78 (s, broad, 1, OH).

2-(3,5-Difluorophenyl)hexafluoro-2-propanol.—2,4-Difluoroaniline was converted to 3,5-difluorobromobenzene by published procedure.[15] The Grignard reagent was prepared from 40 g (0.2 mol) of this product in 200 ml of Et_2O, using a few drops of MeI to initiate the reaction. Hexafluoroacetone was introduced at room temperature, followed by gentle heating for 1 hr. The magnesium complex was then hydrolyzed with 2 *N* HCl, and work-up was carried out as described above. Distillation of the ethereal solution yielded an azeotrope, bp 160° (760 mm), composed of Et_2O and about 30 g (52% yield) of the desired product. The nmr spectrum of a pure product sample (collected by glc) displayed signals at δ 7.27 (d, 2, Ar H), 6.93 (triplet of triplets, 1, Ar H), and 4.26 (s, 1, OH), and the infrared spectrum revealed a characteristic hydroxyl band at 3600 cm^{-1}.

2-(2,3,5,6-Tetrafluorophenyl)hexafluoro-2-propanol.—To 15 g (0.1 mol) of 1,2,4,5-tetrafluorobenzene at −78°, under a nitrogen atmosphere, were added 250 ml of anhydrous Et_2O and 27.7 g (0.1 mol) of 23.1% butyllithium in hexane. The solution was stirred for 2 hr and then 16.6 g (0.1 mol) of hexafluoroacetone was added. After warming to room temperature, the stirred solution was treated with 200 ml of 2 *N* HCl. The usual work-up, followed by distillation on a 6-in. Vigreux column, led to 23 g (73%) of the desired prouct: bp 90–91° (40 mm); nmr δ 7.21 (quintet, 1, Ar H) and 4.13 (s, 1, OH); ir 3620 cm^{-1} (OH).

Use of THF as the solvent in this reaction produced 1,4-di(2-hydroxyhexafluoro-2-propyl)tetrafluorobenzene in about 30% yield, along with a 30% yield of the above-named product. The disubstituted compound had mp 99–101° and was characterized by its mass spectrum, which showed a parent ion at *m/e* 482 (calcd 482) and a consistent fragmentation pattern. Its nmr spectrum had a single, broad absorption at δ 4.17, and an ir spectrum of the solid on NaCl plates displayed a very sharp OH stretch at 3590 cm^{-1}.

2-(2,6-Dimethylphenyl)hexafluoro-2-propanol.—Into a three-neck flask equipped with magnetic stirrer, Dry Ice condenser, and N_2 atmosphere were placed 400 ml of anhydrous Et_2O and 30 g (0.16 mol) of 2-bromo-*m*-xylene. An excess of *n*-C_4H_9Li in hexane was added slowly, causing a white suspension to form. The reaction mixture was heated to reflux and held there for 2 hr, after which time glc analysis revealed little remaining starting material. Excess hexafluoroacetone was added, causing the suspension to disappear. The clear solution was hydrolyzed with 2 *N* HCl, and after work-up and distillation 16 g (36%) of product, bp 130° (40 mm), was obtained: nmr δ 7.04 (m, 3, ArH), 3.25 (s, 1, OH), 2.62 (s, 3, CH_3), and 2.47 (m, 3, CH_3); ir 3600 (OH), 2750 (aliphatic CH), 1590, and 1460 cm^{-1} (aromatic).

2-Fluorophenylhexafluoro-2-propanol.—The ortho, meta, and para isomers were made from the Grignard reagent of the corresponding bromofluorobenzene and hexafluoroacetone, using ether as a solvent. These materials were not isolated as pure compounds but were reacted without extensive purification to form the corresponding glycidyl ethers. The Grignard reagent of *o*-bromofluorobenzene was produced in the presence of hexafluoroacetone and gave rise to the desired product in 30% yield.

2-Bromophenylhexafluoro-2-propanol.—In addition to producing the expected 2-fluorophenylhexafluoro-2-propanol, the Grignard reaction of *o*-bromofluorobenzene with hexafluoroacetone led to the formation of 2-bromophenylhexafluoropropanol-2 in variable yield.[16] It was necessary to add the hexafluoroacetone to the ethereal solution of starting material as soon as reaction with magnesium had begun, to minimize the formation of benzyne products.

o-Bromofluorobenzene (25 g) treated with Mg and hexafluoroacetone as described above, produced about 10 g of white solid. This material formed nearly colorless crystals, mp 37–40°, when recrystallized carefully from hexane. Its ir spectrum showed a strong band at 3500 cm^{-1} (OH), bands at 1595, 1570, and 1480 (aromatic), 1060, 1030, 760 cm^{-1} (ortho-substituted aromatic), and broad absorption around 1200 cm^{-1} (CF). Mass spectral analysis indicated the presence of bromine (parent peak at *m/e* 322 and P + 2 = 98% P) and showed strong peaks at 253, 255 (loss of CF_3) and 184, 186 (loss of $2CF_3$). The nmr contained signals centered at δ 7.66 (m, 2, Ar H), 7.28 (m, 2, Ar H), and 5.20 (s, 1, OH).

Preparation of the Glycidyl Ethers.—These compounds were synthesized and purified according to published procedure[1] from the intermediate alcohols described above. Table I presents the physical properties of the glycidyl ethers.

Rate Measurements.—The kinetic procedure employed has been described previously.[1] Rate constants have been shown to be reproducible to within 1% in a typical case and to within 3% in the least favorable case.

Registry No.—**2a,** 25056-11-5; **2b,** 25080-58-4; **2c,** 28180-36-1; **2d,** 28180-37-2; **2e,** 28180-38-3; **2f,** 28180-39-4; **2g,** 28292-00-4; **2h,** 28180-40-7; **2i,** 28180-41-8; **2j,** 28180-42-9; dibutylamine, 111-92-2; 2-(2,6-difluorophenyl)hexafluoro-2-propanol, 28180-43-0; 2-(3,5-difluorophenyl)hexafluoro-2-propanol, 28180-44-1; 2-(2,3,5,6-tetrafluorophenyl)hexafluoro-2-propanol, 13732-54-2; 1,4-di(2-hydroxyhexafluoro-2-propyl)tetrafluorobenzene, 13732-55-3; 2-(2,6-dimethylphenyl)hexafluoro-2-propanol, 28180-47-4; 2-bromophenylhexafluoro-2-propanol, 28180-48-5.

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(16) An analogous product has been reported in very low yield in the original study of the Grignard reaction of *o*-bromofluorobenzene: G. Wittig and L. Pohmer, *Ber.*, **89**, 1334 (1956).