single compound by TLC. Analysis by MS and ^{1}H NMR revealed that the product was a mixture of monodeuterated and dideuterated reserpine, where complete deuteration at C-3 had occurred since the expected C-3H signal at δ 4.50 ppm had disappeared. The site of the second deuterium could not be identified with certainty, but presumably partial deuterium exchange occurred in the α-position of the carbomethoxy group at C-16.

Autoxidation of [3-^{2}H]Reserpine. Deuterated reserpine was placed in chloroform and allowed to autoxidize following the procedure established above. After completion, the residue was separated by HPLC to afford dioxyreserpine which had retained the deuterium at the same positions as in the starting reserpine.

This was indicated by data from MS where the compound features a molecular ion at m/z 641, indicating retention of a deuterium atom, and from ^{1}H NMR where the absence of a signal at 4.60 ppm, corresponding to C-3H in 6, confirmed the position of attachment of the deuterium atom.

Notes

Exploring the Chemistry of the 2-Arylhexafluoro-2-propanol Group: Synthesis and Reactions of a New Highly Fluorinated Monomer Intermediate and Its Derivatives

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Since the early 1960s, various reports of monomers and polymers containing the 2,2-diaryl-1,1,1,3,3,3-hexafluoropropyl group have appeared.[1] The impetus for this activity has been the often improved solubility, thermal stability, chemical inertness, mechanical properties, and electrical properties exhibited by these polymers. In an effort to produce colorless, transparent, and heat-stable coatings for aerospace applications, we have synthesized diol monomer intermediate 3 (Scheme I), which contains three 1,1,1,3,3,3-hexafluoroisopropyl groups. We now report the synthesis of diol 3, the chemistry of it and some of its derivatives, and the successful synthesis of two high molecular weight polymers which have the diol 3 incorporated into the backbone.

Diol 3 was prepared in two steps from 2,2-bis(4'-tolyl)-hexafluoropropane (1) (courtesy of Hoechst Celanese Co.) by treatment of the Grignard reagent derived from the intermediate dibromide 2 with hexafluoroacetone (HFA) as shown in Scheme I.

The initially attempted direct hydroxyalkylation of 1 under Friedel–Crafts conditions gave only low conversions to the diol.

Diol 3 was successfully reacted under a variety of conditions to afford several derivatives as shown in Scheme II.

These transformations included oxidation to form bisphthalide 4, chlorination,[2] Williamson ether syntheses with benzyl bromides under phase transfer conditions,[3] ester-

Scheme I

Scheme II
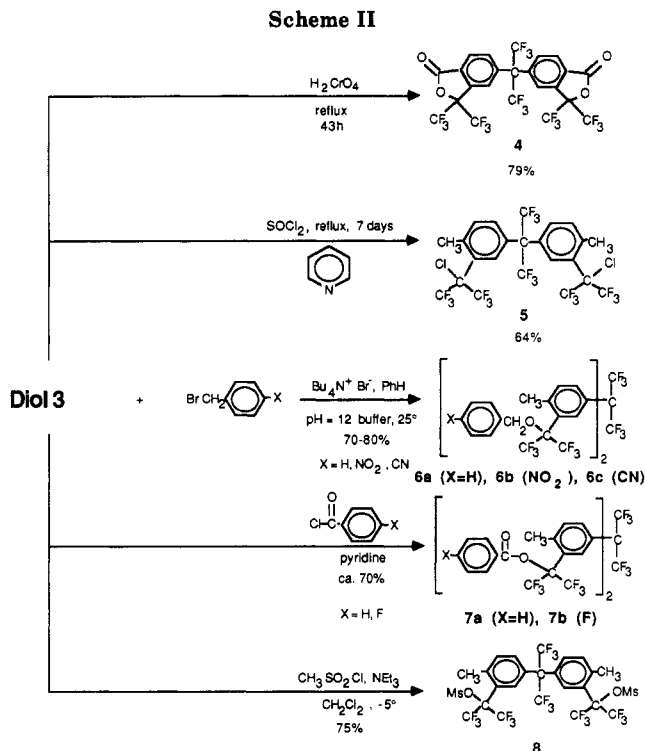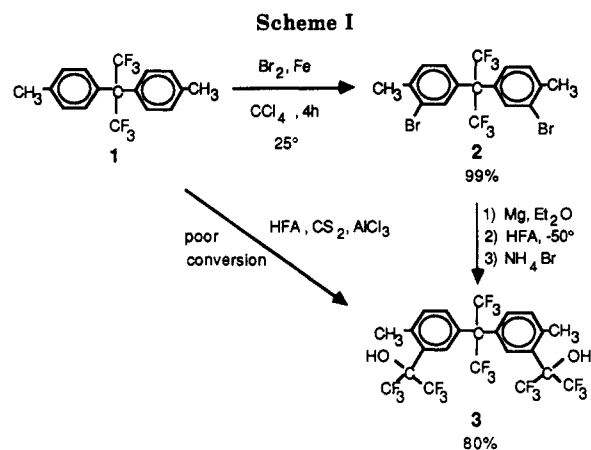
(1) For a recent review of polymers derived from hexafluoroacetone, see: Cassidy, P. E.; Aminabhavi, T. M.; Farley, J. M. *J. Macromol. Sci.: Rev. Macromol. Chem. Phys.* **1989**, *C29*, 365–429.

(2) Knunyants, I. L.; Ching-Yun, N. P.; Gambaryan, N. P.; Roklin, E. M. *Zh. Uses. Khim. Obshchestra im D. I. Mendeleeva* **1960**, *5*, 114; *Chem. Abstr.* **1960**, *54*, 20962. The bromide is also known, see: Polishchuk, V. R.; Bubnov, N. N.; German, L. S.; Lur'e, E. P.; Solodovnikov, S. P.; Tamanskii, B. L. *Izv. Akad. Nauk. SSSR, Ser. Khim.* **1979**, *3*, 659; *Chem. Abstr.* **1979**, *91*, 4737x.

ification, and mesylation. In contrast, the diol 3 failed to react under Friedel–Crafts conditions with anisole [(a)-

Scheme III

Scheme IV
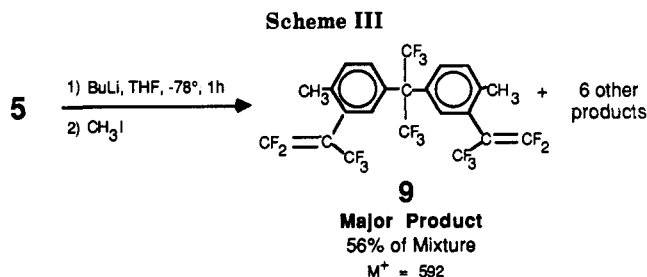
AlCl$_3$; (b) CS$_2$, AlCl$_3$; (c) CH$_3$NO$_2$, AlCl$_3$] or phenol [TsOH, PhBr, reflux], to participate in Ullman ether syntheses[3] with 4-nitrofluorobenzene or 2,4-dinitrofluorobenzene under phase-transfer conditions, or to form carbamates with phenylisothiocyanate or α-naphthyl isocyanate under a variety of conditions [(1) PhNCS, (a) KH, THF; (b) neat, Δ; (2) α-naphthyl isocyanate, (a) neat, Δ; (b) Li, THF; (c) KH, THF; (d) DBTDL in THF; (e) DBU in THF].[4]

Bisphthalide 4 proved completely inert to conditions which usually cleave esters and lactones. Indeed, even treatment of bisphthalide 4 with ArLi reagents afforded stable bis hemiketals. The chemistry of the bisphthalide is discussed in greater detail below. Dichloride 5 (Scheme II) failed to undergo nucleophilic substitution with phenoxide or thiophenoxide under phase-transfer conditions. It was recovered unreacted from Friedel–Crafts conditions. Attempts to oxidize 5 to the corresponding diacid with chromic acid or by KMnO$_4$ under phase-transfer conditions[5] resulted in destruction of starting material and no reaction, respectively. Not surprisingly, treatment of dichloride 5 with *n*-BuLi at -78 °C followed by addition of CH$_3$I afforded primarily a diolefin according to GC/MS analysis (M$^+$ = 592, Scheme III).

Benzyl ether formation via PTC with diol 3 was effective except when X = OMe (Scheme II), where benzyl alcohol formation predominated. The dinitro diether 6b was subjected to a variety of reducing reagents [(1) FeCl$_2$·4H$_2$O, NaBH$_4$, EtOH; (2) H$_2$, PtO$_2$, EtOH; (3) Fe$_3$(CO)$_{12}$, PTC][6] in hopes of preparing the corresponding dianiline; unfortunately, cleavage of the benzyl ether moiety to afford diol 3 was consistently observed.
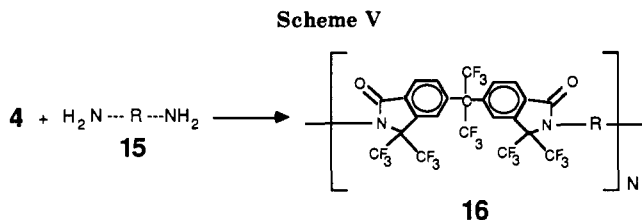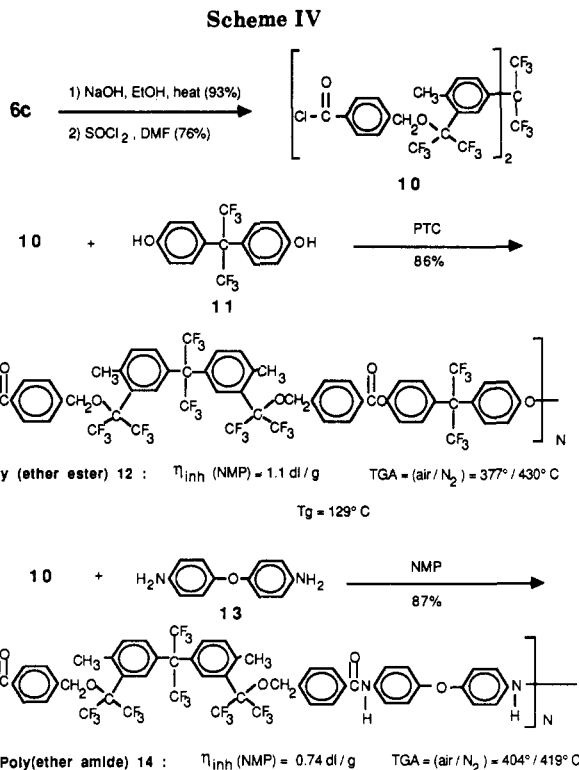
The dibenzonitrile diether 6c (Scheme II) was hydrolyzed with NaOH to afford the corresponding diacid in 93% yield. The diacid was converted into the corresponding diacid chloride 10 (Scheme IV), a monomer which proved useful for preparing high molecular weight polyesters and polyamides, in 76% yield (Scheme IV). Bis-4-fluorobenzoate 7b (Scheme II) was only saponified upon attempting an Ullman ether synthesis with phenoxide generated by K$_2$CO$_3$ in DMAC or with PTC. Dimesylate 8 was cleaved back to the diol 3 by simply heating in ethanol. A similar result was obtained in a Friedel–Crafts reaction attempt upon heating dimesylate 8 in toluene in the presence of H$_2$SO$_4$ for 17 h. Diol 3 was again produced when dimesylate 8 was reacted under mildly alkaline phase-transfer conditions in the presence of phenol.

Poly (ether ester) 12 : η$_{inh}$ (NMP) = 1.1 dl / g   TGA = (air / N$_2$) = 377° / 430° C

Tg = 129° C

Poly(ether amide) 14 : η$_{inh}$ (NMP) = 0.74 dl / g   TGA = (air / N$_2$) = 404° / 419° C

Scheme V

An attempt to form a polyether from diol 3 and α,α'-dibromo-*p*-xylene under phase-transfer conditions resulted in a 94% yield of the desired material but with a disappointingly low inherent viscosity of 0.13 dL/g. An attempt to prepare a polyester from diol 3 and the highly reactive 2,2-bis(4'-benzoylchloro)-1,1,1,3,3,3-hexafluoropropane in pyridine or under phase-transfer conditions likewise gave only low molecular weight material. One side reaction[7] which the alkoxide form of the 2-aryl-6F-2-propanol group can undergo is loss of a trifluoromethyl group to form the corresponding ketone; this may explain, in part, why high polymer is difficult to obtain directly from the diol 3. Diol 3 was essentially unreactive towards Cl$_2$SiMe$_2$[8] in pyridine.

As mentioned earlier, the dibenzonitrile ether 6c derived from diol 3 and 4-cyanobenzyl bromide was converted into the corresponding diacid chloride 10 (Scheme IV). This monomer proved very useful for preparing high polymers with good thermal properties.

Despite the fact that the 2-arylhexafluoro-2-propanol moiety is tertiary and benzylic, the strong inductive effect of the fluorine atoms apparently disfavors the formation of the corresponding carbonium ion, as the failure of the diol 3 to undergo the Friedel–Crafts reactions attempted in this study demonstrates. Analogously, the dichloride 5 and dimesylate 8 also failed to give access to a carbocation. The failure of these latter two compounds to undergo bimolecular substitution reactions no doubt reflects the steric crowding usually associated with tertiary centers.

(3) Cho, B. R.; Park S. D. *Bulletin of Korean Chemical Society* **1984**, *5*(3), 126. Chang, I. S.; Price, J. T.; Tomlinson, A. J.; Willis C. *J. Can. J. Chem.* **1972**, *50*, 512.

(4) Conditions with **1b**: Shriner, R. L.; Fuson, R. C.; Curtin, D. Y.; Morrill, T. C. *The Systematic Identification of Organic Compounds*, 6th ed.; John Wiley and Sons, Inc.: New York, 1980; p 156. **2d** and **2e**: McGrath, J. E.; Tyaji, D.; Wilkes, G. L. *Polym. Prepr.* **1986**, *27*(1), 100.

(5) Dehmlow, E. V.; Dehmlow, S. S. *Phase Transfer Catalysis*; Verlag Chemie: Weinheim, 1980; p 251.

(6) (a) Ono, Aoi; Sasaki, H.; Yaginuma, F. *Chem. Industry (London)* **1983**, 480. (b) Skiles, J. W.; Cava, M. P. *J. Org. Chem.* **1979**, *44*, 409 (conversion of compound 12 to 16 in that article). (c) Abbayes, H.; Alper, H. *J. Am. Chem. Soc.* **1977**, *91*, 98.

(7) Farah, B. S.; Gilbert, E. E; Sibilia, J. P. *J. Org. Chem.* **1965**, *30*, 998.

(8) Pommier, J. C.; Calas, R.; Valade, J. *Bull. Soc. Chim. Fr.* **1986**, 1475.

Table I. Model Reactions of Bisphthalide 4 with Amines

	amine	conditions	result	ref
1.	PhNH$_2$	NMP, 75 °C, 40 min	NR	12
2.	PhNH$_2$	NMP, TsOH (705%), 245 °C, 72 h	imine[a] formation	–
3.	PhNH$_3$Cl	DMSO, reflux, 2 days	NR	–
4.	PhNH$_3$Cl	DMF, 180 °C, 4 days	NR	13
5.	PhNH$_2$	(1) KH, DMSO; (2) 18F-BP, 25 °C for 2 days; (3) 70 °C, 2 days	NR	14
6.	PhNH$_2$	K$_2$CO$_3$, DMF, 2 days	Dec	–
7.	PhNH$_2$	NaOEt/HMPA, 60 °C, 2 days	slow, dec	15
8.	PhCH$_2$NH$_2$	168 °C, 72 h	NR[b]	12

[a] The lactone 4 vanished but was regenerated upon addition of HCl. [b] Benzylamine decomposed but 4 was unchanged.

## Table II. Attempted Reactions of 4 with Ester-Cleaving Agents

	reagent/conditions	result	ref
1.	ZnCl$_2$, SOCl$_2$, reflux, 2 days	NR	16
2.	(1) Ph$_3$PBr$_2$, 200 °C, 2 days; (2) PhNH$_2$	NR	17
3.	50% HBr, AcOH, reflux, 3 days	NR	18
4.	P$_2$S$_5$, xylene, reflux, 40 h	NR	19

Scheme VI

Scheme VII

Scheme VIII

Scheme IX

Scheme X
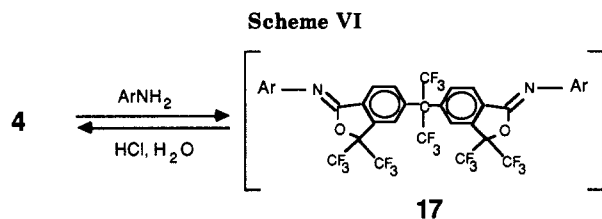
However, the chlorination of the diol 3 with SOCl$_2$ and pyridine presumably must proceed by an S$_N$2 and/or an S$_N$i pathway.[9] Apparently, the best method known for enacting Friedel–Crafts type substitution (probably S$_N$1) at the carbinol carbon of the 2-arylhexafluoro-2-propanol group is use of anhydrous HF at elevated temperature and pressure.[10] There is kinetic evidence that the corresponding tosylates may undergo solvolysis via an S$_N$1 mechanism.[11] The reactivity of these tosylates appears to be related to the steric distortion of the tetrahedral geometry at the carbinol carbon.

Returning to the bisphthalide, our original plan (Scheme V) was to condense 4 with various diamines 15 to form highly fluorinated polylactams (polyphthalimidines) 16 as an extension of the growing field of polymers derived from hexafluoroacetone.[1]

In order to investigate this possibility, model reactions between bisphthalide 4 and aniline, aniline hydrochloride,
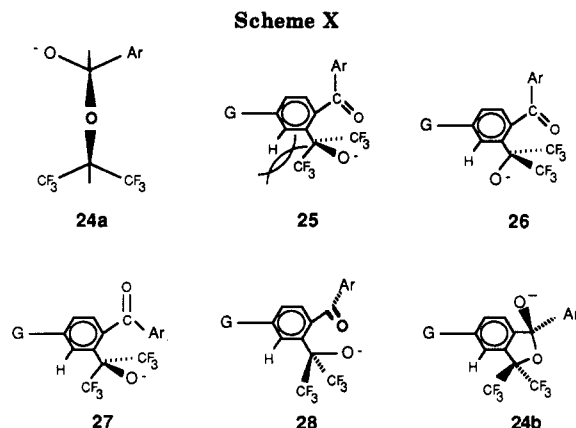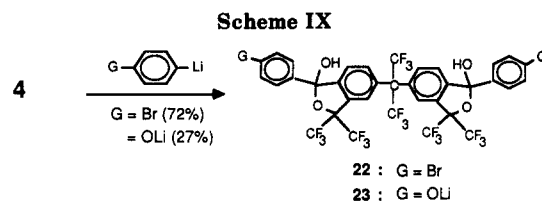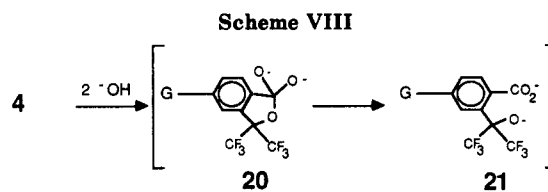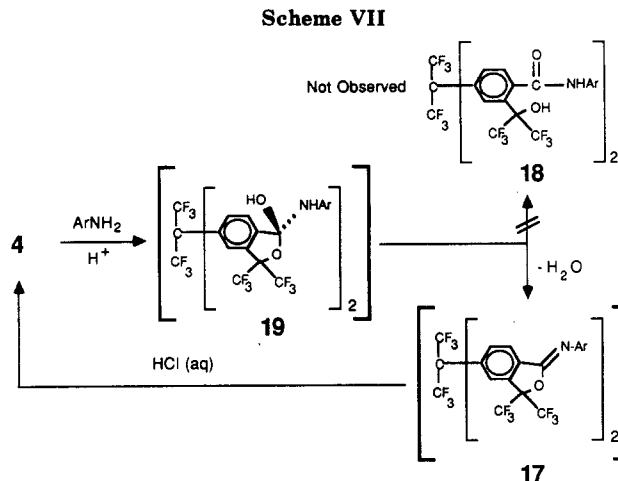
and benzyl amine were performed under a variety of conditions as shown in Table I. Remarkably, only reactions 2 and 6 (Table I) showed any measureable change. During reaction 2, the GC peak corresponding to bisphthalide 4 slowly faded. However, 4 was immediately restored upon the addition of dilute acid. These results suggested the formation of imine intermediate 17 which was hydrolyzed, by acid, back to the starting bisphthalide 4 (Scheme VI).

Having failed to open the lactone with the reactions in Table I, several other reagents/conditions known to cleave or modify esters and lactones were investigated as shown in Table II. Once again, 4 was found surprisingly unreactive toward many standard reaction conditions. Bisphthalide 4 was then heated with a 4-fold excess of KOH in a DMSO/EtOH solvent system at 150 °C for 72 h. At the end of this period, GC showed only traces of 4. However, upon addition of dilute HCl, 4 was regenerated

(9) March, J. *Advanced Organic Chemistry*, 3rd ed.; John Wiley and Sons, Inc.: New York, 1985; pp 286–287.

(10) Private communication from Hoechst Celanese Co. Also see Kosolapoff, G. M. *Chem. Abstr.* **1960**, *54*, 22485e.

(11) Allen, A. D.; Kanagasabapathy, V. M.; Tidwell, Thomas T. *J. Am. Chem. Soc.* **1986**, *108*, 3470 and references therein (especially ref 4).

(12) D'Alelio, G. F.; Reid, E. E. *J. Am. Chem. Soc.* **1937**, *59*, 111.

(13) Lohr, R. A.; Cassidy, P. E.; Kutac, A. *J. Polym. Sci. (Polym. Chem. Ed.)* **1980**, *18*, 1719.

(14) Singh, B. *Tetrahedron Lett.* **1971**, 321.

(15) DeFeoand, R. J.; Strickler, P. D. *J. Org. Chem.* **1963**, *28*, 2915.

(16) Goel, O. P.; Seamans, R. E. *Synthesis* **1973**, 538.

(17) Anderson, A. G.; Kono, D. H. *Tetrahedron Lett.* **1973**, 5121.

(18) Gresham, T. L.; Jansen, J. E.; Shaver, F. W. *J. Am. Chem. Soc.* **1950**, 72.

(19) Fawcett, N. C.; Cassidy, P. E.; Lin, J. C. *J. Org. Chem.* **1977**, *42*, 2929.

(shown by GC). Apparently, the saponification to tetraanion 21 (Scheme VIII) followed by acid-induced reversal had occurred.

In light of the fact that the direct amidation of esters with amines is known to be both acid and base catalyzed,[20] the results shown in Table I are indeed remarkable. The fact that reaction 2 (Table I) consumed 4 (GC) to form a substance (possibly 17, Scheme VII) which could be hydrolyzed back to starting material suggests that ring opening of presumed intermediate 19 to afford amide alcohol 18 is extremely difficult.

Ring opening (Scheme VIII) with hydroxide to afford alkoxide carboxylate 21 may have been successful since a tetrahedral dianion 20, an intermediate proposed[21] to explain the usefulness of "naked hydroxide" in cleaving amides under mild conditions, may have been formed.

The unwillingness of a tetrahedral monoanion intermediate to open was conclusively demonstrated upon the isolation of stable hemiketals 22 and 23 from the reaction of dilactone 4 with aryllithium reagents[22] (Scheme IX).

Inspection of models of the monoanion tetrahedral intermediate 24a and 24b (Scheme X) and the ketoalkoxide (25-28) which would result from ring opening suggests that unfavorable steric and rotamer interactions in the latter may raise its potential energy substantially.

As shown in 24a, the CF_3 groups are completely staggered with respect to the fused aromatic ring in the tetrahedral intermediate. Upon ring opening, an alkoxide moiety and an aromatic ketone function are formed. In order that the diaryl ketone may remain completely conjugated (coplanar) and to minimize steric interactions with the bulky tertiary alkoxide group, structures 25 and 26 are clearly preferrable to 27, where the Ar group and the alkoxide moiety are in close proximity. However, in order that the substituents on the carbinol carbon may avoid the carbonyl, a rotamer where either a CF_3 group or the alkoxide oxygen is more or less eclipsed with the aromatic ring must be formed (25 and 26). This latter problem can be obviated if the ketone rotates out of conjugation as in 28; the alkoxide group can now more easily adopt a staggered rotamer. Although conjugation would be lost in 28 relative to, say, 25, coordination of the alkoxide and carbonyl moieties with lithium cation would favor 28. However, structure 28 is properly arranged for ring closure to structure 24b. The other rotamers of 28, which are formed upon rotation of the alkoxide function, would still suffer from the steric congestion between the CF_3 groups and the ketone moiety. Hence, rotamers 25-28 suffer from either steric compression between the ketone and alkoxide moieties (27), eclipsing between the alkoxy group and the aromatic ring (25-27), or loss of conjugation in the diaryl ketone (28). Staggering the alkoxy group with respect to the benzene ring (as in 28) results in its eclipsing with the ketone moiety. Staggering the alkoxy group with respect to the ketone group results in its eclipsing with the benzene ring (as in 25 and 26). Apparently, the closed structure 24, with its totally staggered arrangement, is the low point on the potential surface. That 24 is preferred suggests steric and rotameric influences on the system's potential energy outweigh the enthalpic stabilization available via carbonyl formation.

The reactions of an ester 25 (Scheme XI), under the first three conditions in Table II, presumably have a common

Scheme XI
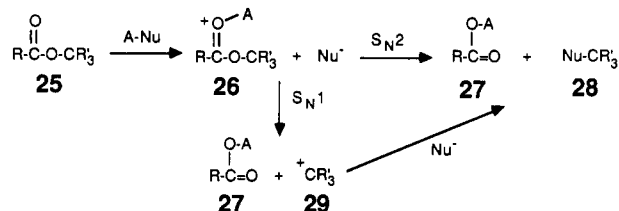
mechanism. A Lewis acid component A^+ complexes with the ester's carbonyl oxygen to afford intermediate 26, thereby making the carboxyl moiety a good leaving group. Then a nucleophile Nu^- may attack the carbinol carbon in 26 via an S_N2 fashion to afford carboxylate 27 or combine with carbocation 29 (if formed) after S_N1 cleavage.

The failure of these reagents to effect the usual result in the case of 4 no doubt reflects the insusceptibility of the 2-arylhexafluoro-2-propanol moiety to S_N2 and S_N1 processes. Hence, the lactone moieties of 4 are remarkable in their unreactivity: neither the carbonyl carbon–alcohol oxygen bond nor the carbinol carbon–oxygen bond can be broken easily.

Experimental Section

Instrumentation and Analysis. All GC analyses were conducted with a Varian Model 3700 gas chromatograph utilizing a flame ionization detector, a 25-m OV-1701 on vitreous silica capillary column, and an argon carrier gas, in conjuction with a Hewlett-Packard 3390A integrator. GCMS analyses were performed on a Finnigan 4023 mass spectrometer with a 25-m DB-1 (0.25 μm film) capillary column and helium carrier gas. HRMS analyses were accomplished with a Dupont (CEC) 21-110 mass spectrometer. Combustion analyses were performed by Desert Analytics, Tucson, AZ. NMR spectra were recorded on a 90-MHz IBM FTNMR spectrometer and are reported in ppm relative to a TMS reference. NMR samples were dissolved in $CDCl_3$ unless otherwise indicated. IR spectra were recorded in either a Perkin-Elmer 1310 or 683 IR spectrophotometer. Melting points were determined with either a Thomas Hoover Capillary Melting Point Apparatus or a MEL-TEMP and are uncorrected. The thermal gravimetric analyses (TGA) and the glass transition temperatures (T_g) were determined on a Dupont 9900 Thermal Analyzer by Texas Research Institute, Inc., Austin, TX. Dielectric constants were measured at the NASA Langley Research Center, Hampton, VA.

^{13}**C NMR Spectra.** Due to C–F coupling, signal to noise ratio considerations, and/or the complexity of the spectra in the aromatic region of most of the compounds of this study, the lines corresponding to the carbons of the CF_3 groups and some aliphatic quaternary centers were difficult to identify and have not, therefore, been reported. The C–F coupling in the dibenzoate 7b, where fluorine atoms are directly attached to aromatic rings, was so extensive (long-range coupling) that identification of the true adsorption frequencies was impractical. In this isolated case, all the observed lines, including those resulting from coupling, are reported.

Synthesis of Dibromide 2. To 25.01 g (75.2 mmol) of ditoluene 1 (Hoechst Celanese), 924 mg (16.6 mmol) of iron powder, and 38 mL of dry CCl_4 in a round-bottom flask, equipped with a magnetic stirring bar, a constant-pressure addition funnel, and a gas (HBr) trap, was added with stirring 9.48 mL (29.6 g, 185 mmol) of neat Br_2 (from the addition funnel) dropwise over 10 min at ambient conditions. After being stirred for 1 h, the reaction mixture showed only one peak by GC. The product solution was washed with dilute $NaHSO_3$ solution to remove unreacted Br_2, and the aqueous wash was extracted with CH_2Cl_2. The combined organic layers were washed with saturated $NaHCO_3$, filtered through a cotton plug in a powder funnel, and concentrated. The light-orange oil crystallized under high vacuum. A total of 36.78 g (74.7 mmol, 99%) of 98% pure (GC) dibromide 2 was obtained. Mp: 78–82 °C. ^{1}H NMR: δ 2.414 (s, 6 H, CH_3), 7.216–7.555 (m, 6 H, aromatic). ^{13}C NMR: δ 22.56, 124.82, 128.98, 130.49, 132.18,

(20) Reference 9, pp 375–376.
(21) Gassman, P. G.; Schenk, W. N. *J. Org. Chem.* 1977, *42*, 918.
(22) (a) Preparation of 4-BrPh-Li: Gilman, H.; Langham, W.; Moore, F. W. *J. Am. Chem. Soc.* 1940, *62*, 2327. (b) Preparation of 4-LiO-Ph-Li: Davidsohn, W. *J. Organomet. Chem.* 1972, *36*, 283.

133.71, 139.47. HRMS: *m/e* calculated ($C_{17}H_{12}F_6Br_2$) 487.920 99, *m/e* found 487.920 58.

Synthesis of Diol 3. This procedure must be carried out in an efficient fume hood since HFA is a developmental and reproductive toxin; in addition, it will fog the cornea of the eye. An oven-dried, 250-mL, round-bottom flask was equipped with a magnetic stir bar, a reflux condenser, a 500-mL constant pressure addition funnel, and rubber stoppers so that the system was gas tight. To the flask was added 10.55 g (0.434 mol) of Mg ribbon. The system was then flame dried while being purged with dry Ar. Upon cooling, the addition funnel was charged with 80.22 g (0.163 mol) of dibromide 2 in 250 mL of anhydrous ether (the solution had been dried over $CaCl_2$). While under a blanket of Ar, about 25 mL of the dibromide solution was added to the Mg. After initiation (this sometimes required the addition of I_2, ethylene bromide, etc.), the rest of the dibromide solution was added at such a rate so as to maintain a gentle reflux. After 2h, GC analysis of a small reaction aliquot quenched with 1 N HCl revealed essentially only ditoluene 1, indicating formation of the dianion was complete. The now dark tan solution was cooled to −78 °C. Then, HFA (SCM Specialty Chemicals; dried by passing over $CaSO_4$) was introduced into the stirred Grignard solution via a long hypodermic needle which penetrated the liquid surface. Addition was continued until the solution was pale yellow. The formation of diol 3 can be conveniently monitored by GC (order of elution: 1, mono alcohol, 3): a reaction aliquot was quenched with 1 N HCl, extracted with EtOAc, and analyzed. An upper limit of 86% diol (composition) was obtained; addition of more HFA did not increase the relative amount of diol. At this point, the reaction mixture was allowed to warm to ambient conditions and then opened to the atmosphere. After an hour (when most of the HFA had evaporated), the crude mixture was poured into a 1-L separatory funnel containing saturated NH_4Br. Then, 200 mL of ice-cold 6 N HCl was added. After shaking, the organic layer was separated and then washed successively with $NaHCO_3$ (saturated) and brine. The organic layer was then filtered through cotton, concentrated, and dried under high vacuum for 18 h, during which the product crystallized. A total of 99.56 g of 86% pure diol 3 (0.13 mol, 80%) was obtained. The crude diol sublimes at 75–80 °C (<1.0 Torr), affording a chemically pure (GC) white powder, mp 83–84 °C. The diol can also be purified by washing the original material with pentane; this method allowed isolation of 98% pure diol. GC/MS analysis of the product revealed a peak with M^+ = 664 and a base peak m/e = 595 ($M^+ - CF_3$). ^1H NMR: δ 2.63 (s, 6 H, CH_3), 3.37 (s, 2 H, OH), 7.0–7.7 (m, 6 H, aromatic). ^{13}C NMR: δ 22.47, 115.85, 117.00, 127.22, 129.81, 130.13, 130.79, 131.28, 133.69, 140.91. HRMS: *m/e* calculated 664.070 64, *m/e* measured 664.069 41.

Synthesis of Bisphthalide 4. To a 250-mL, round-bottom flask equipped with a mechanical stirrer, reflux condenser, and an addition funnel was added 6.08 g (9.152 mmol) of sublimed diol 3, 26.78 g (89.87 mmol) of $Na_2Cr_2O_7$, and 39 mL of H_2O. With stirring, 38 mL (20.64 g, 0.210 mol) of concentrated H_2SO_4 was added dropwise from the addition funnel over 15 min. The mixture was then heated to a gentle feflux for 48 h, during which the color changed from burnt orange to a deep green. After the crude product was cooled, it was poured into 200 mL of H_2O and extracted with 3 × 35-mL portions of EtOAc. The combined organic extracts were washed with 2 × 250 mL of H_2O, 1 × 150 mL of $NaHCO_3$ (saturated), and brine, filtered through cotton, and concentrated. GC analysis revealed that the product was 94% bisphthalide 4. The crude material was recrystallized from EtOAc and then sublimed to afford 5.20 g (7.56 mmol, 83%) of a fine white powder which was analytically pure by GC, mp 168–169 °C. GC/MS of the material showed m/e 619 ($M^+ - CF_3$). The IR spectrum lacked a hydroxyl stretch but did exhibit strong absorption bands at 1811 and 1220 cm^{-1}, which are indicative of a γ lactone structure. The very weak band at 3120 cm^{-1}, corresponding to an aromatic C–H stretch, was the only absorption between 2000 and 4000 cm^{-1}, ruling out any aliphatic C–H moieties (methyl groups). IR (KBr): 3120, 1811, 1611, 1220 cm^{-1}. Anal. Calculated for $C_{23}H_6F_{18}O_4$: C, 40.10; H, 0.88; F, 49.70. Found: C, 40.39; H, 0.84; F, 51.22.

Synthesis of Dichloride 5. Via a literature procedure,[2] 8.51 g (12.14 mmol) of diol 3 was refluxed with 50 mL (82.75 mmol) of $SOCl_2$ and 3 mL of pyridine under Ar for 7 days, after which

GC analysis showed the reaction was essentially complete. The crude reaction mixture was cooled in an ice bath and then slowly poured into a 2-L separatory funnel one-third full of crushed ice (this process is exothermic and should be done in a hood). The remaining contents in the reaction flask were rinsed into the separatory funnel with CH_2Cl_2 and H_2O. After the phases were separated, the aqueous phase was extracted several times with CH_2Cl_2. The aqueous phase was then saturated with salt and reextracted. The combined extracts were filtered through cotton, washed with $NaHCO_3$ (saturated), concentrated on the rotary evaporator, and dried under high vacuum to afford 6.3 g of 87% pure dichloride 5 (7.8 mmol, 64%). The sublimed pure solid had a melting point of 79–81 °C. GC/MS revealed M^+ = 700 and a base peak of m/e 631 ($M^+ - CF_3$). ^1H NMR: δ 2.72 (s, 6 H, CH_3), 7.2–7.8 (m, 6 H, aromatic). ^{13}C NMR: δ 23.54, 115.47, 116.89, 127.18, 129.73, 130.91, 131.60, 134.74, 141.56. HRMS: *m/e* calculated 700.002 86, *m/e* measured 700.001 68.

Synthesis of Dinitro Diether 6b. Reaction of Diol 3 with 4-Nitrobenzyl Bromide. To a 50-mL round-bottomed flask was added 200 mg (0.30 mmol) of sublimed diol 3, 140 mg (0.65 mmol) of p-NO_2PhCH_2Br, 100 mg (0.31 mmol) of Bu_4NBr, and 4.0 mL of benzene. The mixture was stirred until dissolution of the ingredients. Then 10 mL of pH 11.86 buffer was added. After being stirred at ambient conditions for 6 days, the reaction mixture was diluted with EtOAc and washed with H_2O and brine. The organic solution was filtered through cotton, concentrated, and placed under high vacuum. The crude product was dissolved in a minimal amount of ether. Upon standing, light yellow prisms formed, mp 134–140 °C. The isolated solid (200 mg, 0.214 mmol, 71%) was free of all but traces of the starting bromide according to GC. ^1H NMR: δ 2.49 (s, 6 H, CH_3), 4.77 (s, 4 H, CH_2), 7.1–8.7 (m, 14 H, aromatic). ^{13}C NMR: δ 20.92, 66.80, 115.37, 123.79, 126.76, 127.21, 129.88, 131.09, 131.43, 133.94, 140.51, 142.94, 147.78. HRMS: *m/e* calculated 934.134 70, *m/e* found 934.135 57.

Synthesis of Dinitrile 6c. A 1-L Erlenmeyer flask was charged with 16.80 g (25.2 mmol) of diol 3, 9.92 g (50.5 mmol) of 4-cyanobenzyl bromide (Aldrich), and 3.94 g (12 mmol) of tetra-n-butylammonium bromide. Benzene, 255 mL, was added to the mixture of solid reagents. Then, 410 mL of pH 11.8 buffer was added. The heterogeneous mixture was then allowed to stir under ambient conditions for 5 days. After separation of the phases, the aqueous phase was extracted two times with 50 mL of benzene. The extracts were then combined with the 255 mL of benzene used in the reaction. The combined organic phases were washed with water and brine and dried over anhydrous potassium carbonate. After filtering off the drying agent and removal of the solvent, the resulting residue was crystallized from alcohol to give 17.8 g (78% yield) of dinitrile 6c, mp 123–25 °C. IR (KBr): 2200, 1270–1195, 1125 cm^{-1}. ^1H NMR: δ 2.49 (s, 3 H), 4.73 (s, 2 H), and 7.77–7.74 (m, 7 H). ^{13}C NMR: δ 20.7, 66.89, 85.10, 112.01, 115.33, 116.33, 125.70, 127.07, 129.79, 130.99, 131.31, 132.28, 133.84, 140.44, 140.95. HRMS: *m/e* calculated ($C_{39}H_{24}F_{18}N_2O_2$) 894.155 04, *m/e* found 894.153 76.

Synthesis of Dibenzoate 7b. To a dry round-bottomed flask was added 1.335 g (2.01 mmol) of the sublimed diol 3 and 10 mL of dry pyridine. While under Ar, 0.5 mL of 4-F-PhCOCl was added to the stirred mixture as rapidly as possible. The reaction was then heated at reflux for 16 h. Upon cooling, the mixture was poured into 175 mL of H_2O and extracted with 2 × 40 mL of EtOAc. The aqueous phase was salted and reextracted with 20 mL of EtOAc. The combined organic fractions were washed successively with 100 mL of 10% HCl and 100 mL of $NaHCO_3$ (saturated). The organic solution was dried over $MgSO_4$, filtered, concentrated, and placed under high vacuum. To the resulting oil was added Et_2O, which caused immediate precipitation of fluffy off-white crystals of the desired diester (>90% pure) with a mass of 1.48 g (1.63 mmol, 81%), mp 130–134 °C. ^1H NMR: δ 2.38 (s, 6 H, CH_3), 6.95–8.40 (m, 14 H, aromatic). ^{13}C NMR: δ 21.02, 114.99, 115.75, 116.65, 124.01, 124.14, 126.11, 129.34, 130.19, 130.67, 131.42, 132.75, 133.23, 133.58, 138.57, 160.37, 161.18, 173.12. HRMS: *m/e* calculated 908.104 22, *m/e* found 908.099 54.

Synthesis of the Dimesylate 8. To a dry, round-bottom flask equipped with a constant-pressure addition funnel was added 1.01 g (1.52 mmol) of sublimed diol 3, 0.58 mL (0.423 g, 4.17 mmol) of NEt_3 (distilled from Na), and 5 mL of dry CH_2Cl_2. The solution was cooled to −5 °C in an ice/salt bath. The addition funnel was

charged with 0.45 mL (0.67 g, 5.82 mmol) of MsCl (reagent, Aldrich) in 3.0 mL of CH_2Cl_2. The MsCl was added dropwise over 15 min, during which a slushy mixture formed. The reaction was stirred under Ar for an additional 2 h, during which it warmed to ambient temperature. The organic solution was washed successively with 1 N HCl, $NaHCO_3$ (saturated), and brine, filtered through cotton, and concentrated. The oily residue was placed under vacuum (<1 Torr), where it eventually solidified. The crude product was recrystallized from benzene to afford diamond-shaped crystals, mp 132–136 °C, 9.35 mg (1.14 mmol, 75%) which were pure by GC. ^{1}H NMR: δ 2.7 (s, 6 H, benzylic CH_3), 3.22 (s, 6 H, CH_3 on S), 7.2–7.6 (m, 6 H, aromatic). ^{13}C NMR: δ 21.73, 40.76, 114.30, 125.83, 129.96, 130.44, 131.68, 133.97, 140.79. LRMS: 751 (M^+ – CF_3, base peak 559). Anal. Calculated for $C_{25}H_{18}F_{18}O_6S_2$: C, 36.60; H, 2.21; F, 41.68; O, 11.70; S, 7.81. Found: C, 36.44; H, 2.08; F, 41.69; O, 11.63; S, 7.77.

Hydrolysis of Dinitrile 6c To Form the Corresponding Diether Diacid. A 1-L round-bottom flask was charged with 20.0 g (22.4 mmole) of dinitrile **6c**, 100 mL of alcohol, and 450 mL of 15% (w/v) aqueous NaOH. The flask was fitted with a reflux condenser and a heating mantle. The mixture was heated at reflux until homogeneous (ca. 20 h). After cooling slightly, the reaction apparatus was rearranged for simple distillation; ca. 200 mL of distillate were then collected during which a white solid formed in the still-pot. After cooling to ambient temperature, 1 mL of the reaction mixture was acidified with dilute H_2SO_4; however, no solid (no turbidity) was observed. The reaction pot was placed in the refrigerator overnight. Then, after decanting the liquid, the solid (presumably the disodium salt of the desired diacid) was suspended in 750 mL of water, acidified with dilute H_2SO_4, and extracted into 3 × 100 mL of ether. The combined ether extracts were dried over anhydrous magnesium sulfate, filtered, and concentrated. The residue weighed 19.5 g (93%). Recrystallization from glacial acetic acid afforded 18.6 g (89% yield) of the desired diacid, mp 224–25 °C. IR (KBr): 3000, 1690, 1280–1190, 1120 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 2.58 (s, 3 H), 4.83 (s, 2 H), 7.54–8.17 (m, 7 H), 10.35 (bs, 1 H). ^{13}C NMR (acetone-d_6): δ 21.26, 68.79, 116.57, 126.72, 127.62, 130.82, 131.30, 132.28, 135.34, 141.63, 142.11, 167.63, 206.11. Anal. Calculated for $C_{39}H_{26}F_{18}O_6$: C, 50.23; H, 2.81; F, 36.67. Found: C, 49.88; H, 2.90; F, 35.87.

Synthesis of Diacid Chloride 10. A dry, 100-mL, round-bottom flask was charged with 5.33 g (5.7 mmol) of the di(ether acid) described above, 30 mL of technical thionyl chloride, and 2 drops of dry DMF. The flask was fitted with a reflux condensor and a calcium chloride drying tube. The mixture was then heated at reflux for 2 h, whereupon a homogeneous, pale yellow solution was obtained. The excess thionyl chloride was removed by distillation under reduced pressure. The resulting solid residue was crystallized from dry hexanes to afford 4.2 g (76% yield) of **10**, mp 110–12 °C. IR (KBr): 1750, 1290–1170, 1130 cm^{-1}. ^{1}H NMR: δ 2.79 (s, 3 H), 4.75 (s, 2 H), 7.52–8.18 (m, 7 H). ^{13}C NMR: δ 20.95, 67.02, 115.45, 125.86, 126.68, 129.93, 131.67, 133.00, 133.96, 140.59, 143.69, 167.83. Anal. Calculated for $C_{39}H_{24}F_{18}Cl_2O_4$: C, 48.32; H, 2.50. Found: C, 48.38; H, 2.10.

Synthesis of Poly(ether ester) 12. A 10-mL, round-bottom flask was charged with 336.2 mg (1.0 mmol) of bisphenol **11** (Scheme IV), 6 mg (1.9 × 10^{-2} mmol) of tetra-*n*-butylammonium bromide, and 2 mL of 1 N NaOH. While the mixture was stirred at ambient conditions, 1 N NaOH was added dropwise until solution was achieved (ca. 0.3 mL). Diacid chloride **10** (969.5 mg, 1.0 mmol) was dissolved in 2 mL of nitrobenzene and added in one portion to the vigorously stirred bisphenol **11** solution. More nitrobenzene (0.5 mL) was used to rinse the residual diacid chloride **10** into the reaction flask. After 30 min of stirring at ambient conditions, 5 mL of $CHCl_3$ was added. Then, the entire mixture was slowly poured into 350 mL of methanol, resulting in the precipitation of a stringy white solid. The solid was collected by suction filtration, washed with methanol, and dried under high vacuum at 85 °C overnight. The polymer weighed 106.2 mg (86% yield). The dielectric constant was 2.27 at 10 GHz. Inherent viscosity, η_{inh} ($CHCl_3$): 1.1 dL/g. T_g: 129 °C. TGA (10% weight loss in air/nitrogen): 377 °C/430 °C. IR (thin-film): 3020, 2910, 1735, 1600, 1455, 1275–1155, 1130 cm^{-1}. ^{1}H NMR: δ 2.50 (s, 3 H), 4.74 (s, 2 H), 7.22–8.28 (m, 11 H). ^{13}C NMR: δ 21.03, 67.35, 115.42, 116.63, 121.59, 125.98, 126.78, 129.01, 129.95, 130.53, 130.63,

131.09, 131.57, 133.66, 140.58, 141.69, 151.41, 164.32. Anal. Calculated for $C_{54}H_{32}F_{24}O_6H$: C, 52.61; H, 2.62; F, 36.98. Found: C, 52.33; H, 2.53; F, 36.90.

Synthesis of Poly(ether amide) 14. A dry 15-mL three-neck round-bottom flask was charged with 200.2 mg (1.0 mmol) of dianiline **13** and 3 mL of NMP. After flushing the reaction flask with argon, the apparatus was brought to −20 °C. Then 969.5 mg (1.0 mmol) of diacid chloride **10** in a total of 3 mL of NMP were added in one portion. The reaction was maintained at −20 °C for 3 h, and then allowed to warm to ambient temperature over 1.5 h. The viscous colorless solution was diluted with an additional 8 mL of NMP and then slowly poured into 350 mL of briskly stirred methanol. The resulting off-white solid was collected by suction filtration, washed with methanol, and dried under high vacuum at 85 °C overnight. The polymer weighed 956.0 mg (87% yield). Inherent viscosity, η_{inh} (NMP): 0.74 dL/g. TGA (10% weight loss in air/nitrogen): 404 °C/419 °C. IR (thin-film): 3280, 3020, 2935, 1668, 1285–1160, 1125 cm^{-1}. ^{1}H NMR (acetone-d_6): δ 2.59 (s, 3 H), 4.82 (s, 2 H), 6.95–8.10 (m, 11 H). ^{13}C NMR (acetone-d_6): δ 21.29, 66.58, 116.73, 119.65, 122.78, 126.71, 127.97, 128.67, 131.53, 132.30, 135.40, 135.68, 136.20, 140.17, 142.13, 154.59, 165.82. Anal. Calculated for $C_{51}H_{34}F_{18}N_2O_5$: C, 55.85; H, 3.12; N, 2.55; F, 31.18. Found: C, 55.95; H, 2.93; N, 2.78; F, 30.98.

Synthesis of Bishemiketal 22. Preparation[22a] of 4-BrPhLi. While at ambient conditions and under argon, 1.3 mL of 2.5 M BuLi in hexanes was added via syringe over 1 min to 1.028 g (4.36 mmol) of 1,4-dibromobenzene (Aldrich; dried over $CaCl_2$ in ether) in 10 mL of Et_2O with stirring. **Reaction.** After 50 min, the aryllithium reagent was canulated into an addition funnel attached to a round-bottom flask containing 1.029 g (1.50 mmol) of the bisphthalide **4** (dried over K_2CO_3 in THF) in 20 mL of THF. After the stirred bisphthalide solution was cooled to −78 °C, the 4-BrPh-Li solution was added over 5 min, during which the initially cloudy bisphthalide mixture turned into a clear amber solution. The reaction was allowed to warm to ambient temperature. One hour after the addition was complete, the orange solution was poured into saturated NH_4Br; the orange color disappeared upon mixing and more ether was added. After shaking vigorously, the aqueous layer was separated. The organic layer was washed with $NaHCO_3$ (saturated) and then brine. The resulting clear solution was filtered through cotton and concentrated, affording 1.5 g of crude material which contained a small amount of Ph-Br according to GC. Column chromatography (150 g silica gel; 40:1 benzene-Et_2O) afforded 1.08 g (1.08 mmol, 72%) of white crystalline **22**, which was pure by TLC (silica; 40:1 Ph-H-Et_2O) and had mp 88–90 °C. The IR spectrum lacked the carbonyl stretch but did show an O–H absorption. IR (CH_3CN, AgCl): 3360, 2995, 1372, 1210 cm^{-1}. The 1H NMR showed a multiplet in the aromatic region and a singlet at 4.19 ppm in a 7.5:1.0 ratio. Twelve lines were observed in the ^{13}C NMR spectrum between 110 and 145 ppm, a fact consistent with the proposed structure. ^{1}H NMR: δ 4.19 (s, 2 H, OH), 7.3–7.8 (m, 7 H, aromatic). ^{13}C NMR: δ 111.24, 115.0, 124.20, 125.71, 127.70, 128.33, 130.77, 131.88, 133.69, 135.66, 138.36, 144.50. LRMS: M^+ 1003 (1), 846 (50), 829 (100), 765 (35), 689 (46), 619 (71), 569 (34), 185 (72). HRMS: m/e calculated 1002.900 87, m/e measured 1002.906 63.

Synthesis of Bishemiketal 23. Preparation[22b] of 4-LiOPhLi. To a three-necked, 500-mL, dry, round-bottom flask equipped with an addition funnel, a mechanical stirrer, and a thermometer was added, while under Ar, 23 mL of 2.5 M BuLi in hexanes. After the solution was cooled to −78 °C, 5.13 g (29.65 mmol) of 4-BrPhOH (Aldrich) in 80 mL of THF was added with stirring at such a rate so as to maintain the temperature of the solution below −50 °C. After the addition was complete, the mixture was warmed to 0 °C (at which time a white slush ensued), cooled to −10 °C, and stirred for 30 min more. **Reaction.** After again cooling the mixture to −78 °C, 5.2 g (7.55 mmol) of the bisphthalide **4** in 110 mL of THF was added over a 5-min period. After being warmed to ambient conditions, the reaction mixture was stirred for an additional 30 min. Then 3.5 mL of glacial acetic acid was added to the clear orange solution, resulting in a lightening of the color and the formation of a milky white precipitate. The crude mixture was transferred to a clean flask with EtOAc washes and concentrated. The orange oil was placed under high vacuum for 3 days. The resulting orange white solid was

partially soluble in EtOAc. The material was transferred to a separatory funnel containing aqueous NH₄Br (saturated) and shaken, whereupon the orange color appeared in the organic layer while a white flock precipitated in the aqueous phase. The aqueous phase was extracted with EtOAc, but the solid remained in the aqueous layer. The combined EtOAc extracts were washed (3×) with brine, filtered through cotton, concentrated, and placed under high vacuum. Column chromatography (750 g silica gel, 1:1 EtOAc–ligroin [60–80 °C]) afforded 1.8 g (2.054 mmol, 27%) of white solid 23, which was chemically pure by TLC. The IR spectrum (AgCl, CH₃CN) showed an OH stretch (3375 cm⁻¹), a C–O stretch (1205 cm⁻¹), but no lactone carbonyl stretch. ¹H NMR (acetone-d_6): δ 3.34 (bs, 2 H, alcoholic OH), 6.7–7.9 (m, 14 H, aromatic), 8.72 (bs, 2 H, phenolic OH). ¹³C NMR (acetone-d_6): δ 114.55, 116.74, 126.70, 129.18, 130.94, 131.0, 132.29, 133.0, 133.60, 135.37, 136.24, 147.92, 159.98. The lines at 131.0 and 133.0 were very small. LRMS: M⁺ 876 (9), 859 (76), 857 (100). HRMS: m/e calculated 876.081 60, m/e observed 876.078 87.

Registry No. 1, 1095-77-8; 2, 127002-41-9; 3, 127002-42-0; 4, 127002-43-1; 5, 127002-44-2; 6a, 127002-45-3; 6b, 127002-46-4; 6c, 127002-47-5; 6c diacid derivative, 127002-48-6; 7a, 127002-49-7; 7b, 127002-50-0; 8, 127002-51-1; 9, 127002-52-2; 10, 127002-57-7; (10) (11) (copolymer), 127002-58-8; (10) (13) (copolymer), 127032-66-0; 11, 1478-61-1; 12, 127002-55-5; 13, 101-80-4; 14, 127002-56-6; 22, 127002-53-3; 23, 127002-54-4; HFA, 684-16-2; p-NO₂PhCH₂Br, 100-11-8; 4-FPhCOCl, 403-43-0; 4-BrPhOH, 106-41-2; 4-cyanobenzyl bromide, 17201-43-3; 1,4-dibromobenzene, 106-37-6.

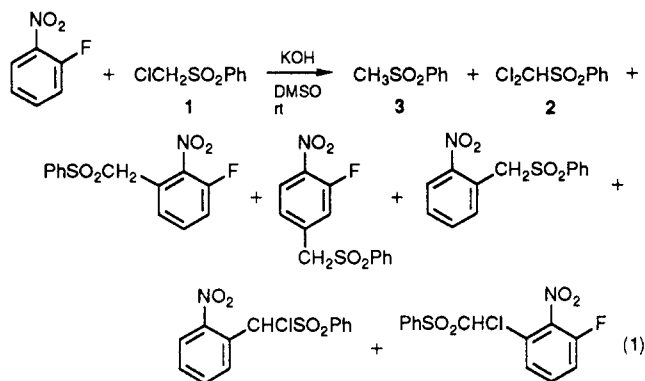# Base-Induced Disproportionation of Halomethyl Phenyl Sulfones to Methyl and Dihalomethyl Phenyl Sulfones

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Due to steric hindrance at the tetrahedral carbon, α-halomethyl sulfones are relatively inert toward intermolecular nucleophilic substitution,[1] a feature that renders these compounds especially suited for the alkylation of nitroarenes via the vicarious nucleophilic substitution (VNS) reaction.[2] Thus, chloromethyl phenyl sulfone (1) has been used as a model nucleophile in many applications of the VNS reaction since it has no tendency to self-condensation.[2] In an attempt to perform the VNS reaction between 2-fluoronitrobenzene and 1 with KOH in DMSO, we observed a very fast and exothermic reaction; 1 was consumed in only a few minutes and led to a complex product mixture, which included dichloromethyl phenyl sulfone (2) and methyl phenyl sulfone (3), as well as several nitrobenzene derivatives conceivably resulting from S$_N$Ar and VNS reactions involving the anions of 1–3 (eq 1). These observations prompted the present investigation which revealed a so far unreported reactivity of α-halomethyl phenyl sulfones in strongly basic media.

Treatment of 1 with excess KOH in DMSO at room temperature (typical conditions used for the VNS reac-

tion)[2b] resulted in complete reaction after 1 h and led to the isolation of 2 and 3 in 22% and 26% yields, respectively (eq 2, X = Cl). The bromo-substituted analogue,
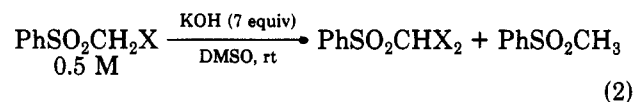
bromomethyl phenyl sulfone, when subjected to the same conditions, underwent the same process with greater efficiency: the reaction was complete in 1 min, methyl phenyl sulfone and dibromomethyl phenyl sulfone being recovered in 57% and 31% yields, respectively (eq 2, X = Br).

To further investigate this interesting disproportionation of a monohalo derivative to the corresponding dihalo and hydrogenated derivatives, experiments were conducted under homogeneous conditions, using t-BuOK as a base. The results with 0.31 M t-BuOK were not significantly different from those obtained with KOH. The progress of a typical reaction, monitored by GLC analysis, is shown in Figure 1. In this as in all other experiments, it was noted that the concentration of the dihalo derivative reached a maximum and then decreased, an effect which was more evident for the bromo-substituted compound. Independent experiments proved that the dihalomethyl phenyl sulfones are reactive in the basic media used to study reaction 2.[3]

The effects of added nitroarenes are also of interest. While, as mentioned earlier, 2-fluoronitrobenzene activates the disproportionation reaction, nitrobenzene and other halonitrobenzenes, like 4-chloronitrobenzene, react more slowly with 1 to give the product of VNS substitution in high yields.[2b]

It was also found that the substrate initial concentration has an effect on the efficiency of reaction 2, which occurs to a significant extent only at high substrate concentration, as indicated by the data of Table I. From the curves of Figure 2, half-life times were roughly 5 and 190 min for initial substrate concentrations of 0.30 and 0.10 M, respectively. It should be also noted that reaction 2 is in competition with at least one other process, prevailing at low substrate concentrations, which consumes 1 and base, as shown, for example, by the drop in base concentration from 0.31 to 0.05 M in the experiment with [1] = 0.1 M.

As for the mechanism of reaction 2, which displays a kinetic order greater than 1 for the substrate, an attractive possibility is shown in Scheme I. The key step in this mechanism is an X-philic reaction,[4] which involves nu-

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(1) Bordwell, F. G.; Cooper, G. D. *J. Am. Chem. Soc.* 1951, 73, 5184.
(2) (a) Makosza, M.; Winiarski, J. *Acc. Chem. Res.* 1987, 20, 282. (b) Makosza, M.; Goliński, J.; Baran, J. *J. Org. Chem.* 1984, 49, 1488.
(3) For a possible fate of the dihaloderivative, see: Hine, J.; Porter, J. J. *J. Am. Chem. Soc.* 1960, 82, 6178.
(4) Zefirov, N. S.; Makhon'kov, D. I. *Chem. Rev.* 1982, 82, 615.