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# Fluorinated Bifunctional Derivatives of Bisphenol A

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Bisphenol A reacted as its disodium salt with tetrafluoroethylene and carbon dioxide followed by dimethyl sulfate to give in high yield a symmetrical dimethyl ester assembled from seven structural elements. This diester was transformed into the corresponding diol, diamide, diamine, diisocyanate, and bis(methyl carbamate). Analogous diesters were prepared by using bisphenol A and chlorotrifluoroethylene as well as hexafluorobisphenol A and tetrafluoroethylene. Both of these esters were transformed into other bifunctional derivatives. Catalytic hydrogenation of the diol derived from bisphenol A and tetrafluoroethylene was accompanied by hydrogenolysis of the aryl-oxygen bonds.

As part of a program to create useful new monomers, we have synthesized a family of bisphenol derivatives with fluorinated side chains. Our approach was based on a reaction developed by Krespan: tandem addition of a suitable nucleophile to a fluorinated olefin and carbon dioxide.[1] Krespan demonstrated that phenoxide ion, for example, reacts with tetrafluoroethylene (TFE) and carbon dioxide in dimethyl sulfoxide to give the salt of a carboxylic acid, which is conveniently isolated as its methyl ester after reaction with dimethyl sulfate (eq 1).

$$\mathrm{PhO^- + CF_2{=}CF_2 + CO_2 \xrightarrow{DMSO} PhO\text{-}CF_2\text{-}CF_2\text{-}CO_2^-}$$

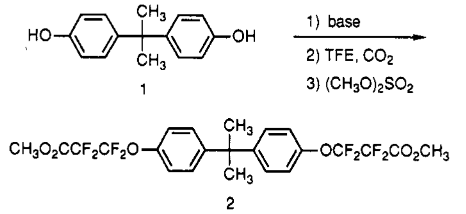
$$\mathrm{\xrightarrow{(CH_3O)_2SO_2} PhO\text{-}CF_2\text{-}CF_2\text{-}CO_2CH_3} \qquad (1)$$

A priori, a reaction in which two electrophiles and a nucleophile are combined could produce a complex mixture. The success of this clever reaction depends upon several fortunate features. Since one of the electrophiles, carbon dioxide, reacts *reversibly* with the nucleophile, the other electrophile, the fluoroolefin, has an opportunity to react ultimately with all of the nucleophile. The resulting carbanion could attack another molecule of olefin and/or eliminate fluoride ion were it not for the ability of the carbon dioxide to trap it efficiently and irreversibly, giving so stable an anion that no further reaction occurs.

We have been able to perform dual Krespan reactions on diphenoxides. The transformation is remarkable in the sense that seven structural elements are assembled in a single laboratory step, in good to excellent yield. Our work began with preparation of the disodium salt of 4,4′-isopropylidenediphenol (bisphenol A, **1**). Initial attempts at the Krespan reaction with this salt failed completely because of the presence of tenaciously bound water. We solved the problem by preparing the salt with sodium hydride in anhydrous tetrahydrofuran. Though dry, the salt obtained in this way was unreactive until heated in vacuo at temperatures over 100 °C. The resulting reactive powder, which darkened in the air, performed very well in the Krespan reaction.

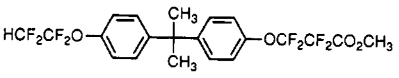
An equally effective and far more convenient procedure reported by Johnson and co-workers[2] uses aqueous sodium hydroxide to make the salt and azeotropic distillation to obtain it in anhydrous form. A mixture of the diphenol, aqueous base, chlorobenzene, and dimethyl sulfoxide is heated under a combination water separator and fractionating column. The pot temperature gradually rises as water and chlorobenzene are removed; when it reaches 180 °C the pot contains an anhydrous solution of the salt in dimethyl sulfoxide, which is ready to be poured into a pressure reactor for use in the Krespan reaction.

Our experimental setup required that the bomb be cooled in order to introduce the fluoroolefin and carbon dioxide by static vacuum transfers. Therefore the addition of the nucleophile to the olefin could only begin when the solvent thawed and the mixture became stirrable at about 20 °C. At that point a moderate exotherm and a steady pressure drop were observed. In one run the diacid was isolated from the product after strong acidification, but in general the dimethyl ester, which was more useful for our purposes, was prepared directly at room temperature by addition of dimethyl sulfate to the reaction mixture (eq 2). Aqueous workup gave the crude diester **2** in 90% yield.



(2)

$^{19}$F NMR analysis revealed the presence of about 10% of monoester **3**, the quenching product of an intermediate anion by an adventitious proton source. The diester could be purified by distillation but was often used directly in further reactions.



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We were interested in preparing monomers from which polyurethanes could be fashioned: diols, diisocyanates, and protected diisocyanates. Lithium aluminum hydride reduction of distilled diester **2** gave crystalline diol **4** in 91% yield (Scheme I). Ammonolysis of the highly electron-deficient diester occurred very rapidly even at 0 °C in methanol solution. Crude **2** served well in this reaction, as trituration of the product with chloroform removed the monoamide derived from the impurity **3**; the remaining crystals (73% yield) of diamide **5** were quite pure, even before recrystallization.

For reduction of **5** to the diamine **6**, the borane-tetrahydrofuran complex was chosen in order to minimize C-N bond cleavage and thus alcohol formation.[3] The *crude* yield of diamine was quantitative, but $^{19}$F NMR revealed the presence of 10-20% of the amino alcohol resulting from C-N cleavage on one side of the molecule. Diamine **6**

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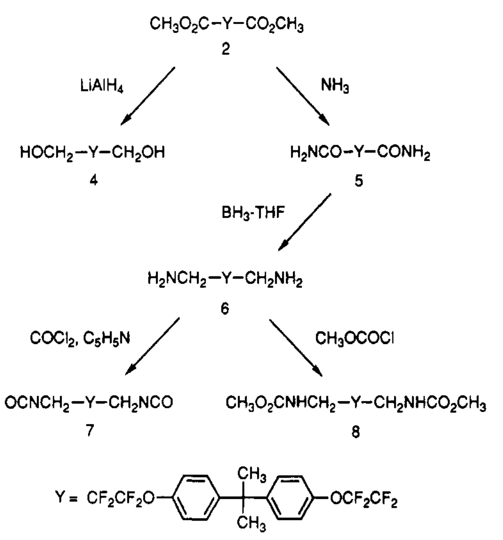
[1] Krespan, C. G.; Van-Catledge, F. A.; Smart, B. E. *J. Am. Chem. Soc.* **1984**, *106*, 5544-5546.

[2] Johnson, R. N.; Farnham, A. G.; Clendinnig, R. A.; Hale, W. F.; Merriam, C. N. *J. Polym. Sci., Part A-1* **1967**, *5*, 2375-2378.

[3] Brown, H. C.; Heim, P. *J. Org. Chem.* **1973**, *38*, 912-916.

0022-3263/91/1956-0146$02.50/0 © 1991 American Chemical Society

**Scheme I**



decomposed upon attempted distillation, probably as a result of dehydrofluorination brought about by its amino groups.

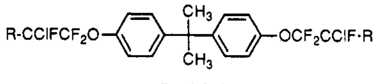
For diisocyanate preparation, the most promising method appeared to be a "unique chlorocarbonylation technique" reported[4] for the synthesis of fluorinated diisocyanates. The reagent was described as a crystalline pyridine/phosgene (1:1) adduct that formed readily in diethyl ether. After our first attempts at that reaction failed, we adjusted the stoichiometry of the reactants, since the crystalline material formed from pyridine and phosgene is known to be a 1:2 adduct.[5] Although the modified method worked well as judged by $^{19}$F NMR, isolated yields of the reactive diisocyanate **7** were very poor. In part the impurity present in the crude diamine **6** was to blame.

It proved to be much more practical to prepare the stable bis(methyl carbamate) **8** using methyl chloroformate. Since carbamates can fragment at elevated temperatures[6] to yield isocyanates and alcohol, **8** can be regarded as a protected form of **7** from which the latter can be released under curing conditions with loss of methanol. Dicarbamate was obtained in 82% crude yield, but about 20% of this product was carbamate/alcohol derived from the impurity in the diamine. Repeated recrystallizations gave pure dicarbamate **8**, mp 92–93 °C. These transformations are summarized in Scheme I.

Throughout this series of symmetrical compounds, $^{19}$F NMR spectra comprised signals of equal area at 86 ± 1.5 ppm for the fluorines geminal to oxygen and at 124 ± 2.6 ppm for the other pair. The two sets of fluorines are coupled weakly enough that, except under high resolution, the low field set appears as a broad singlet; the high field pair is observed as a broad singlet or triplet, depending on whether a pair of vicinal protons is present. In both dimethyl sulfoxide and acetonitrile the $^{1}$H NMR spectrum of diamide **5** displayed two widely separated signals for the protons on nitrogen, suggesting that both intermolecular exchange and C–N bond rotation are slow. Even in the dicarbamate **8**, C–N bond rotation is slow on the NMR time scale, as revealed by the $^{19}$F NMR spectrum. A small unresolved triplet shifted 0.3 ppm upfield from the main triplet for the high-field pair of fluorines corresponds to the minor rotational isomer.[7]

The mass spectra of all of these compounds displayed parent peaks but were dominated by ($M^+ - 15$) peaks corresponding to loss of one of the central methyls to give tertiary benzhydryl cations. The single exception was dicarbamate **8**, whose mass spectrum depended strongly on the conditions for its measurement. When the solid probe, initially at 100 °C, was rapidly heated the spectrum displayed molecular ion peaks corresponding to **8**, carbamate/isocyanate, and diisocyanate **7**, together with fragment peaks derived from each. The base peak had the composition $C_5H_5F_3NO_2$, representing a side chain of **8** minus HF and the ring oxygen. With slow heating of the probe from room temperature, the spectrum was dominated by the signals arising from carbamate/isocyanate and diisocyanate. Now the base peak was the diisocyanate ($M^+ - 15$) signal. Clearly, pyrolytic loss of methanol from **8** was occurring in the spectrometer prior to ionization.

Chlorotrifluoroethylene (CTFE) was substituted for TFE in the dual Krespan reaction with bisphenol A disodium salt. This olefin is less hazardous to work with, and we were interested in both the practicality of our syntheses and the potential for scale-up. The new diester **9**, obtained as a dark amber, viscous liquid, was nonetheless clean by both $^{19}$F and $^{1}$H NMR (81% yield). It could not be distilled without decomposition. Lithium aluminum hydride reduction of **9** gave crystalline diol **10** in 96% yield. Ammonolysis of **9** in cold methanol was almost instantaneous, giving diamide **11** in spectroscopically pure form after a wash with chloroform (72% yield). Since the compounds in this series contain a pair of identical chiral centers, both *dl* and meso isomers are present.



9 R = $CO_2CH_3$
10 R = $CH_2OH$
11 R = $CONH_2$

The $^{19}$F NMR spectra of these three CTFE derivatives display subsplit AB quartets for the pair of fluorines geminal to oxygen at roughly 80 ppm, $J$ = ~139 Hz; the remaining fluorine appears in the 130 ppm region. Side-chain conformer populations differ between carbonyl derivatives **9** and **11** on the one hand and diol **10** on the other, as revealed by the vicinal F–F spin–spin coupling. In **9** and **11** the fluorine geminal to chlorine is coupled to only one member of the AB pair ($J$ = ~12 Hz), but in **10** it is coupled almost equally to both ($J$ = 8.1, 10.0 Hz). Mass spectra of all three compounds show parent peaks as isotopic clusters appropriate for two chlorines, and again ($M^+ - 15$) is the base peak.

We were interested in monomers with the potential to yield durable materials upon polymerization. It is known that bisphenol A polycarbonate, a widely used polymer, suffers photodegradation. The literature on this subject is plentiful.[8] A photooxidative process involving one of the bisphenol A methyl groups appears to be a major contributor to the degradation.[8d] The question arose as to whether polymers derived from hexafluorobisphenol A (**12**) could be more durable. Information found in a patent[9]

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(4) Gosnell, R.; Hollander, J. *J. Macromol. Sci.-Phys.* **1967**, *B1*, 831–850.

(5) (a) Dyson, G. M. *Chem. Rev.* **1927**, *4*, 163. (b) Hyden, German Patent 109933, Mar 9, 1900; *Chem. Zentralbl.* **1900**, Part 2, 460.

(6) Barton, D.; Ollis, W. D. *Comprehensive Organic Chemistry*; Pergamon Press: Oxford, 1979; Vol. 2, pp 1085–1086.

(7) In a very closely related carbamate, variable temperature NMR measurements confirmed that the minor signals were attributable to a rotational isomer.

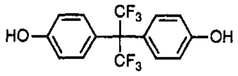
(8) (a) Factor, A.; Chu, M. L. *Polym. Degrad. Stab.* **1980**, *2*, 203–223. (b) Rivaton, A.; Sallet, D.; Lemaire, J. *Polymer Photochem.* **1983**, *3*, 463–481. (c) Lemaire, J.; Gardette, J.-L.; Rivaton, A.; Roger, A. *Polym. Degrad. Stab.* **1986**, *15*, 1–13. (d) Factor, A.; Ligon, W. V.; May, R. J. *Macromolecules* **1987**, *20*, 2461–2468.

**Table I. Ultraviolet Data for Bisphenols and Derived Diols**[a]

| compound | $\lambda_{max}$ [nm] ($\epsilon$) | $\lambda_{max}$ [nm] ($\epsilon$) |
|---|---|---|
| bisphenol A (BPA, **1**)[b] | 117 (26 900) | 278.5 (6300) |
| BPA/TFE diol (**4**) | 214 (16 230) | 266 (910) |
| BPA/CTFE diol (**10**) | 214 (15 130) | 266 (820) |
| hexafluorobisphenol A (HFBPA, **12**)[c] | 229 (19 400) | 274 (2720)<br>281 (2490) |
| HFBPA/TFE diol (**14**) | 216 (13 060) | 260 (532) |

[a] Solvent is methanol. [b] *The Sadtler Handbook of Ultraviolet Spectra*, No. 1908. [c] *Sadtler Standard Spectra*, Ultraviolet Collection, No. 22247.

pointed in that direction: polyesters derived from **12** showed better weather resistance than their counterparts derived from bisphenol A.



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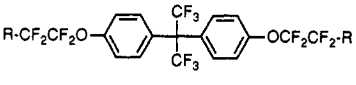
We have therefore carried out the dual Krespan reaction with TFE on bisphenol **12**. Its disodium salt was prepared as described for bisphenol A and the reaction was carried out in parallel fashion, giving diester **13** as a very viscous liquid in 81% yield. The $^{19}$F NMR spectrum indicated the presence of <10% proton-quenched monoester analogous to **3**. Crystals of **13** were obtained from methanol. Lithium aluminum hydride reduction of the diester gave diol **14** in 87% yield after recrystallization. The mass spectra of both **13** and **14** display parent peaks and, analogously to their bisphenol A counterparts, the base peaks correspond to loss of $CF_3$. The parent peaks are weak in the bisphenol A derived compounds, the intensity being about 10% of the base peak intensity. Not surprisingly, the parent peaks of **13** and **14** are considerably stronger, 50–60% of base peak intensity.



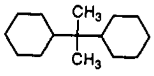
13 $R = CO_2CH_3$
14 $R = CH_2OH$

Attaching fluorinated side chains to bisphenol A and hexafluorobisphenol A, thereby withdrawing electron density from the oxygens, has quite a dramatic effect on the ultraviolet spectra of these compounds, as shown in Table I. Both long- and short-wavelength bands are shifted hypo- and hypsochromically. The intensity decrease is especially marked at long wavelengths. Solar UV light absorption by these molecules is thus very small relative to that of the parent bisphenols.

Bisphenol A is rapidly hydrogenated at 75° and 365 psi in 2-propanol with 5% rhodium/carbon as catalyst.[10] Attempts to saturate the bisphenol A derived diol **4** under these conditions failed; the diol was recovered unchanged. Under more vigorous conditions (145 °C, ~700 psi) in the same catalyst/solvent system hydrogenation did take place, but not without destruction of the molecular skeleton. Gas chromatography after workup revealed, in addition to starting material, the presence of three compounds differing widely in volatility. GC/MS analysis identified the three products as isopropyl 2,2-difluoro-3-hydroxypropionate (**15**), 2,2-dicyclohexylpropane (**16**), and the partially hydrogenated/hydrogenolyzed alcohol **17**. Additional evidence for the structure of **15** was provided by its $^{19}$F NMR spectrum, which comprised a triplet at 115.6 ppm, $J = 12.3$ Hz.

$HOCH_2CF_2CO_2CH(CH_3)_2$

15



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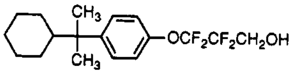

17

The formation of **15**–**17** and the fact that the reaction mixture contained much hydrogen fluoride can be accounted for by the following mechanistic hypothesis. Hydrogenation begins on one of the aromatic rings, but at a stage when the side chain occupies an allylic position hydrogenolysis ensues. Saturation of the ring is then completed and the second ring is subsequently attacked in a similar fashion. Unstable diol **18**, formed in the hydrogenolysis step, loses HF to give acid fluoride **19**, which acylates the solvent to yield **15**.

$$\underset{18}{HOCH_2CF_2CF_2OH} \xrightarrow{-HF} \underset{19}{HOCH_2CF_2COF} \xrightarrow{i\text{-}PrOH} 15$$

In conclusion, dual Krespan reactions can be carried out on bisphenols in very good yields with tetrafluoroethylene and chlorotrifluoroethylene. The resulting diesters can be transformed into a diverse array of bifunctional derivatives.

## Experimental Section

Melting points were determined in open capillary tubes and are uncorrected. Routine $^{19}$F NMR spectra were obtained at 56.2 MHz on a JEOL FX60Q Fourier transform instrument. The higher field data were obtained at 282.2 MHz on a Varian XL-300 spectrometer. Trichlorofluoromethane was used as the internal standard and chemical shifts are reported in parts per million upfield from the reference. $^1$H NMR spectra were recorded either on a Varian EM-360 (60 MHz) spectrometer or at 300 MHz on the Varian XL-300 with tetramethylsilane as internal standard. The high-field NMR data are specifically marked in the text. Infrared spectra were determined on a Perkin-Elmer 599 infrared spectrophotometer. Mass spectra were obtained with a Finnigan Model 4023 quadrupole mass spectrometer; the ionizing voltage was 70 eV. A Hewlett-Packard Model 5880A gas chromatograph was used to obtain analytical gas chromatograms. Ultraviolet spectra were recorded on a Hewlett-Packard diode array spectrophotometer. Microanalyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI.

4,4′-Isopropylidenediphenol (97%) (bisphenol A) was purchased from Aldrich. Tetrafluoroethylene (TFE) and chlorotrifluoroethylene (CTFE) were obtained from PCR. Hexafluorobisphenol A was supplied by American Hoechst Corporation. Tetrahydrofuran was distilled from benzophenone ketyl prior to use. All other solvents and reagents were reagent grade.

**Equipment and General Procedure for Pressure Reactions.** Reactions were run in (a) a 200-mL pressure vessel (Parr Model No. 4755) fitted with a gauge block assembly and an internal thermocouple [the bomb was wrapped in a heating sleeve and mounted in a rocker for agitation] or (b) a 450-mL Mini Reactor (Parr Model No. 4562) equipped with a pressure gauge, an internal thermocouple, a stirrer with a magnetic drive, and a bomb heater. For remote pressure readout a pressure transducer (OMEGA PX-105-2KG-5V) and a digital pressure indicator (OMEGA Model DP 202) were used. Temperatures were measured and maintained with an OMEGA temperature controller (Model 149). Both pressure vessels were made of Monel 400.

For the transfer of gases a pressure/vacuum manifold was constructed from $^1/_4$ in. stainless steel tubing with Swagelok connections, five Nupro "H" series bellows seal valves (No. SS-4H), and a pressure gauge. The reactor was connected to the manifold

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[9] Howerton, W. W. U.S. Patent 3,824,211, July 16, 1974; *Chem. Abstr.* **1975**, *82*, 18780g.

[10] Sasa, C.; Hirai, H. Japanese Patent 70 35,300, Nov 11, 1970; *Chem. Abstr.* **1971**, *74*, P141098c.

[11] Kirk-Othmer. *Encyclopedia of Chemical Technology*, 3rd. ed.; Wiley: New York, 1980; Vol. 11, p 4.

via a pressure hose (Parr A495HC). Gaseous reagents were added into the reactor by static vacuum transfers from the gas cylinders to the bomb cooled in liquid nitrogen. For carbon dioxide and chlorotrifluoroethylene, the amount was measured by following the weight loss of the cylinder. Tetrafluoroethylene was measured by condensing the required volume (density = 1.7 g/mL) into a heavy-walled glass trap cooled to −125 °C in an ether/liquid nitrogen slush bath. From there TFE was vacuum transferred into the bomb. A small excess of fluoroolefin was usually employed, and the number of moles of carbon dioxide was typically about 1.5 times the number of moles of the fluoroolefin. Maximum pressures ranged from 400 to 500 psi. A moderate exotherm and an initially rapid pressure drop were usually observed as soon as the contents of the bomb became stirrable at an internal temperature of 20–25 °C.

*WARNING*: As received from PCR, tetrafluoroethylene contains an inhibitor, but it becomes much more dangerous when it is condensed as the pure monomer. As a referee has pointed out, care should be taken to exclude oxygen when working with TFE, and the amounts added to the pressure reactor should be controlled to avoid pressures in excess of 500–600 psi unless special barricades are in use.

**Anhydrous Disodium Salt of Bisphenol A in DMSO.** A 500-mL three-necked flask equipped with a mechanical stirrer, a thermometer, and a gas inlet tube was charged with 26 g (0.11 mol) of bisphenol A (1), 140 mL of DMSO, and 220 mL of chlorobenzene. The solution was purged with nitrogen for 0.5 h; then the inlet tube was replaced by an addition funnel and 0.22 mol of sodium hydroxide (18.15 g of a 50.2% solution) was added dropwise with vigorous stirring at 35–40 °C. The addition funnel was replaced by a custom-made water separator (recycle type) that incorporated a column packed with glass helices. The reaction mixture was heated. At a pot temperature of about 120 °C the chlorobenzene/water azeotrope started to distill. When the temperature reached 145–150 °C, the distillate was free of water. The water separator was replaced by a short-path distilling head and the excess chlorobenzene was rapidly removed while the internal temperature climbed to 180–185 °C. At this point an amber viscous solution of anhydrous disalt in DMSO remained. The hot solution was quickly poured into the metal bomb, the bomb was closed, and its contents were allowed to cool under nitrogen. A nitrogen atmosphere was maintained in the apparatus throughout the disalt preparation.

**Dimethyl 3,3′-[(1-Methylethylidene)bis(4,1-phenyleneoxy)]bis(2,2,3,3-tetrafluoropropionate) (2).** The 450-mL pressure reactor was charged with the disodium salt solution prepared from 26 g (0.11 mol) of bisphenol A. Carbon dioxide (15 g, 0.34 mol) followed by TFE (23 g, 0.23 mol) was introduced via static vacuum transfer. The contents of the bomb was allowed to reach room temperature. At about 25 °C and 400 psi it became possible to start the stirrer. The internal temperature rose to 40 °C while the pressure dropped steadily. The reaction mixture was kept at 45 °C for several hours until the pressure remained constant; then it was allowed to cool to room temperature. After the residual gases had been carefully vented, the bomb contents were transferred to a flask. Foaming was a problem! Dimethyl sulfate (20.8 mL, 0.22 mol) was added dropwise. After being stirred for 3 h at room temperature, the reaction mixture was poured into 600 mL of ice water. Additional water was added and the mixture was allowed to stand until a good separation of the product layer was achieved. The aqueous layer was decanted; the brown oily product was dissolved in ether, washed with brine, and dried over magnesium sulfate. The ether was removed on a rotary evaporator. The residual light amber, viscous liquid was warmed to reduce the viscosity and stirred under vacuum until all trapped solvent was removed. $^{19}$F NMR analysis showed that crude diester 2 (53.8 g, 0.099 mol, 90%) contained about 10% of monoester 3 (minor resonances stemming from $OCF_2CF_2H$ portion): 88.6 (s, 2 F), 137.9 (d, $J_{HF}$ = 56 Hz, 2 F) ppm. Fractional distillation gave 2 as a colorless viscous liquid, bp 190–195 °C (0.035 Torr). $^{19}$F NMR ($CDCl_3$): 85.5 (s, 4 F), 121.4 (s, 4 F) ppm. $^1$H NMR ($CDCl_3$): δ 7.23 (m, 8 H), 3.97 (s, 6 H), 1.67 (s, 6 H). IR (neat): 2960 (m), 1780 (vs), 1590 and 1600 (w), 1500 (s), 1440 (m), 1300 (s), 1190 (vs), ~1100 (s), 1020 (s) cm$^{-1}$. MS: *m/e* 544 ($M^+$), 529 ($M^+ - CH_3$, base). Anal. Calcd for $C_{23}H_{20}F_8O_6$: F, 27.94. Found: F, 27.74.

Distillation on a ~25-g scale gave the ester in 59% yield, but distillation on a large scale led to some thermal decomposition. $^1$H NMR (300 MHz) analysis of the product from a large scale run revealed new minor resonances at δ 7.06, 6.74 (approx. AB q, $J_{AB}$ = 8.7 Hz), and 1.63 (s) attributable to the cleavage product $H_3CO_2CCF_2CF_2OC_6H_4C(CH_3)_2C_6H_4OH$. Therefore undistilled diester was used in subsequent reactions whenever possible.

**3,3′-[(1-Methylethylidene)bis(4,1-phenyleneoxy)]bis(2,2,3,3-tetrafluoropropanol) (4).** A solution of distilled diester 2 (15.0 g, 27.6 mmol) in 40 mL of THF was added dropwise to a suspension of lithium aluminum hydride (1.5 g, 39.5 mmol) in 70 mL of THF at such a rate as to keep the reaction mixture at reflux. Efficient stirring with a mechanical stirrer is essential. More solvent had to be added to keep the thickening suspension manageable. After the addition was complete, the mixture was refluxed for 1 h. A sample was withdrawn, hydrolyzed, and analyzed by $^{19}$F NMR; it showed that reduction was complete. Ethyl acetate (~5 mL) was added to the cold grey suspension followed by careful addition of 15% sodium hydroxide and water. Vigorous stirring was continued until all precipitates were white. The supernatant liquid was decanted and evaporated, and the residue from evaporation was partitioned between ether and brine. The white solids were washed with ether and the combined ethereal solutions were dried over magnesium sulfate. Evaporation gave a colorless, clear syrup (13.7 g) that was freed from residual solvent by heating (~60 °C) and stirring under vacuum. The result was soft white crystals (12.2 g, 25 mmol, 91%) of diol 4, mp 63–64 °C. $^{19}$F NMR ($CDCl_3$): 86.6 (s, 4 F), 126.6 (t, $J_{HF}$ = 14 Hz, 4 F) ppm. $^1$H NMR ($CDCl_3$): δ 7.20 (m, 8 H), 4.13 (t, $J_{HF}$ = 14 Hz, 4 H), 2.86 (br, 2 H), 1.67 (s, 6 H). $^1$H NMR (300 MHz, $CDCl_3$): δ 7.21, 7.10 (approx. AB q, $J_{AB}$ = 8.6 Hz), 4.13 (td's, $J_{HF}$ = 14 Hz, $J$ = 7.4 Hz), 2.07 (t, $J$ = 7.4 Hz), 1.67 (s). IR (KBr): 3340 (s), 2970 (m), 1590 (w), 1500 (s), 1180 (vs), ~1100 (s), 1000 (s) cm$^{-1}$. MS: *m/e* 488 ($M^+$), 473 ($M^+ - CH_3$, base). Anal. Calcd for $C_{21}H_{20}F_8O_4$: C, 51.64; H, 4.10; F, 31.15. Found: C, 51.82; H, 4.08; F, 31.23.

**3,3′-[(1-Methylethylidene)bis(4,1-phenyleneoxy)]bis(2,2,3,3-tetrafluoropropanamide) (5).** Liquid ammonia (~20 mL) was dissolved in 120 mL methanol at 0 °C. Undistilled diester 2 (26.0 g, 48 mmol) in 60 mL of methanol was added dropwise with stirring to the cold reagent solution. After the solution had been stirred for another hour at room temperature, a sample was withdrawn and evaporated. IR analysis of the residue in methylene chloride showed that no ester functionality remained. Excess ammonia was removed before the residue was evaporated to dryness on a rotary evaporator. The light brown, lumpy crude solid was treated with chloroform at 0 °C until a uniform suspension was obtained. Filtration gave a white solid (17.8 g, 35 mmol, 73%) and a yellow filtrate that contained mostly monoamide derived from monoester 3. In most runs the diamide 5 thus obtained was already pure. Recrystallization from boiling chloroform gave a chalky white solid, mp 120–121 °C. $^{19}$F NMR ($CD_3CN$): 84.5 (s, 4 F), 121.6 (s, 4 F) ppm. $^1$H NMR (DMSO-$d_6$): δ 8.60 (s, 2 H), 8.42 (s, 2 H), 7.32, 7.17 (approx. AB q, $J_{AB}$ = 8.9 Hz, 8 H), 1.66 (s, 6 H). $^1$H NMR ($CD_3CN$): δ 7.30, 7.15 (approx. AB q, $J_{AB}$ = 8.9 Hz, 8 H), 7.15 (br, eclipsed by aromatic res., ~2 H), 6.7 (br, 2 H), 1.67 (s, 6 H). IR (KBr): 3430, 3200 (m), 2970 (w), 1715 (vs), 1610 (w), 1505 (s), 1330 (s), 1190 (vs), ~1100 (s), 1015 (s) cm$^{-1}$. MS: *m/e* 514 ($M^+$), 499 ($M^+ - CH_3$, base). Anal. Calcd for $C_{21}H_{18}F_8N_2O_4$: C, 49.03; H, 3.50; F, 29.57; N, 5.45. Found: C, 49.11; H, 3.42; F, 29.67; N, 5.41.

**3,3′-[(1-Methylethylidene)bis(4,1-phenyleneoxy)]bis(2,2,3,3-tetrafluoropropanamine) (6).** The borane–tetrahydrofuran complex (230 mL, 1 M in THF) was cannula-transferred under nitrogen to a 500-mL three-necked flask equipped with a condenser and an addition funnel. Diamide 5 (13.0 g, 25 mmol) in 100 mL of THF was added dropwise at 0 °C over 1 h. The reaction mixture was allowed to reach room temperature, then it was heated to reflux under nitrogen. The progress of the reduction was monitored by $^{19}$F NMR. Samples were withdrawn periodically, hydrolyzed with a few drops of 3 N hydrochloric acid, and stirred until gas evolution ceased. When $^{19}$F NMR analysis indicated complete consumption of diamide, the excess borane reagent and the borane complexes were decomposed with 3 N hydrochloric acid. This required careful addition of the acid (~36 mL) to the reaction mixture at 0 °C. Frothing was very severe at the outset. Most of the THF was removed by distillation at atmospheric pressure. The residual liquid turned into a white crystalline mass on cooling. Diamine was freed by adding enough 50% sodium hydroxide solution to effect the formation of two liquid phases. The supernatant aqueous layer (pH ~8) was decanted and extracted with ether (2 × 50 mL); the product layer was dissolved in ether (150 mL) and washed with brine. The combined ether solutions were dried over sodium sulfate. Evaporation gave a yellowish viscous liquid (13.5 g) that was stirred while being warmed under vacuum. When the weight reached 12.3 g (25 mmol, 100%), the syrup was solvent free. This crude diamine **6** contained amino alcohol in amounts that usually ranged from 10 to 20%. During an attempted vacuum distillation the diamine decomposed in the pot on heating. $^{19}$F NMR (ether): 86.7 (s, 4 F), 125.2 (t, $J_{HF}$ = 16 Hz, 4 F) ppm; minor resonances at 86.2 (s), 125.9 (t, $J_{HF}$ = 14 Hz) ppm that represent the $OCF_2CF_2CH_2OH$ portion of the mixed product. $^1$H NMR ($CDCl_3$): $\delta$ 7.13 (m, 8 H), 3.30 (t, $J_{HF}$ = 16 Hz, 4 H), 1.83 (br s, 4 H), 1.66 (s, 6 H). Byproduct indicated by a small triplet at $\delta$ 4.06, $J_{HF}$ = 14 Hz. IR (neat): 3380 (m), 3280 (m), 2960 (s), 2850 (m), 1600 and 1580 (m), 1500 (vs), 1330 (s) 1190 (vs), ~1100 (vs) cm$^{-1}$. MS: *m/e* 486 (M$^+$), 485 (M$^+$ - 1), 471 (M$^+$ - $CH_3$, base).

**3,3′-[(1-Methylethylidene)bis(4,1-phenyleneoxy)]bis(2,2,3,3-tetrafluoropropyl isocyanate) (7).** A solution of pyridine (1.9 mL, 23.5 mmol) in 35 mL of anhydrous ether was cooled to -78 °C in a dry ice/acetone bath. Phosgene (1.2 g, 12.1 mmol) was delivered through a gas inlet tube positioned just above the stirred solution. Immediately a pale yellow precipitate formed. The suspension was warmed to 0 °C under nitrogen. Diamine **6** (2.7 g, 5.6 mmol) in 15 mL of ether was added dropwise over 20 min. After removal of the ice bath the reaction mixture, a white suspension, was stirred for another hour. A small amount of acidic ion exchange resin (Amberlyst XN-1010) was added to remove free pyridine that could catalyze isocyanate di- or trimerizations. The suspension was filtered through Celite in a Schlenk funnel under nitrogen overpressure. Evaporation of solvent gave a viscous turbid residue that was treated with Freon 113 and again filtered through Celite. Removal of Freon 113 left a yellowish liquid (2.3 g) that was predominantly the diisocyanate by $^{19}$F NMR. However, on storage at -5 °C in a closed container the product quickly deteriorated as indicated by several new resonances in its $^{19}$F NMR spectrum. A short-path vacuum distillation yielded a few drops of diisocyanate **7**, bp 160–162 °C (0.050 Torr). Once purified, the diisocyanate dissolved in methylene chloride was stable in the cold for weeks. $^{19}$F NMR ($CH_2Cl_2$): 86.4 (s, 4 F), 122.4 (t, $J_{HF}$ = 13.5 Hz, 4F) ppm. IR ($CH_2Cl_2$): 2960 (w), 2270 (vs, N=C=O), 1505 (m), 1340 (w), 1200 (s), ~1100 (m) cm$^{-1}$. MS: *m/e* 538 (M$^+$), 523 (M$^+$ - $CH_3$, base).

**Dimethyl 3,3′-[(1-Methylethylidene)bis(4,1-phenyleneoxy)]bis[(2,2,3,3-tetrafluoropropyl)carbamate] (8).** A solution of diamine **6** (11.7 g, 24 mmol) in 130 mL of ether was cooled in an ice bath, and methyl chloroformate (3.7 mL, 48 mmol) was added dropwise. A voluminous precipitate formed immediately. After about one-third of the reagent had been added, dropwise addition of aqueous base (48 mL of 1 M NaOH) was started. The reaction mixture was stirred vigorously (mechanical stirrer!) and kept at 8–10 °C while the simultaneous additions continued. At the conclusion of this step no solids remained. The two-phase mixture was allowed to come to room temperature, the aqueous layer (pH ~8) was separated, and the ether layer was washed with brine and dried over magnesium sulfate. After solvent removal on a rotary evaporator, the residual syrup had to be freed from trapped ether by heating and stirring under vacuum. The very viscous product (13.1 g) was triturated with pentane to give an off-white solid (11.8 g, 19.6 mmol, 82%). Because of amino alcohol present in the starting diamine, this crude solid contained ~21% carbamate/alcohol based on $^{19}$F NMR analysis. Successive recrystallizations from methanol–water (4:1) at -28 °C gave white crystals of analytically pure dicarbamate **8**, mp 92–93 °C. $^{19}$F NMR (282.2 MHz, $CDCl_3$): 87.30 (s, 4 F), 122.89 (t, $J_{HF}$ = 14.4 Hz, 4 F) ppm. Small unresolved triplet at 123.2 ppm can be attributed to a conformational isomer. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.21, 7.10 (approx. AB q, $J_{AB}$ = 8.8 Hz, 8 H), 5.05 (br, ~2 H), 3.96 (td's, $J_{HF}$ = 14.4 Hz, $J$ = 6.4 Hz, 4 H), 3.73 (s, 6 H), 1.67 (s, 6 H). IR (KBr): 3310 (m), 2970 (w), 1715 (vs), 1560 (m), 1510 (m), 1150 (m), 1280 (s), 1190 (vs), ~1100 (s) cm$^{-1}$. Anal. Calcd for $C_{25}H_{26}F_8N_2O_6$: C, 49.83; H, 4.32; F, 25.25; N, 4.65. Found: C, 49.90; H, 4.38; F, 25.32; N, 4.54.

The mass spectral fragmentation pattern was strongly dependent on the conditions under which the spectrum was run. Initial probe temperature 100 °C, rapid heating: *m/e* 602 (M$^+$, dicarbamate), 587 (M$^+$ - $CH_3$), 567 (M$^+$ - $CH_3$-HF), 547 (M$^+$ - $CH_3$ - 2HF), 168 ($C_5H_5F_3NO_2^+$, base); 570 (M$^+$, carbamate/isocyanate), 555 (M$^+$ - $CH_3$), 535 (M$^+$ - $CH_3$ - HF), 168; 538 (M$^+$, diisocyanate), 523 (M$^+$ - $CH_3$). Initial probe temperature 25 °C, slow heating: *m/e* 602 (M$^+$, dicarbamate), 587 (M$^+$ - $CH_3$); 570 (M$^+$, carbamate/isocyanate), 555 (M$^+$ - $CH_3$); 538 (M$^+$, diisocyanate), 523 (M$^+$ - $CH_3$, base).

**Dimethyl 3,3′-[(1-Methylethylidene)bis(4,1-phenyleneoxy)]bis(2-chloro-2,3,3-trifluoropropionate) (9).** The procedure described for diester **2** was followed closely. The bomb was charged with disalt from 26 g (0.11 mol) of bisphenol A, CTFE (29.5 g, 0.25 mol), and carbon dioxide (17 g, 0.38 mol). Cooling the bomb to -78 °C during the gas transfers was sufficient. The maximum pressure in this experiment was 190 psi at 25 °C. After methylation with dimethyl sulfate (20.8 mL, 0.22 mol) and the usual aqueous workup, a dark amber viscous liquid was obtained. This product was, according to $^{19}$F NMR, the diester **9** (53.3 g, 0.09 mol, 81%) free of fluorine-containing contaminants. Its $^1$H NMR spectrum looked equally clean. Extraction of the aqueous solution with ether gave another 2.9 g of diester that contained a minor impurity, monoester with proton-quenched side chain analogous to **3**, and was therefore not used. $^{19}$F NMR (ether): 79.3, 83.4 (AB q, $J_{AB}$ = 139 Hz, B portion subsplit into doublets, $J$ = 12.4 Hz, 4 F), 129.5 (d, $J$ = 12.4 Hz, 2 F) ppm. $^1$H NMR ($CDCl_3$): $\delta$ 7.17 (m, 8 H), 3.96 (s, 6 H), 1.66 (s, 6 H). IR (neat): 2960 (s), 1780 (vs), 1600 and 1590 (w), 1510 (s), 1440 (m), ~1300 (vs), 1190 (vs) cm$^{-1}$. MS: *m/e* 576 (M$^+$), 561 (M$^+$ - 15, base). Isotope peaks: 578 (M + 2), 563 (M + 2 - $CH_3$), 580 (M + 4), 561 (M + 4 - $CH_3$).

**3,3′-[(1-Methylethylidene)bis(4,1-phenyleneoxy)]bis(2-chloro-2,3,3-trifluoropropanol) (10).** The reduction procedure has been described for the TFE-derived diol **4**. Here crude diester **9** (16.1 g, 27.9 mmol) in 60 mL of THF was added to a suspension of lithium aluminum hydride in 60 mL of THF. Reduction was rapid and quantitative as shown by the $^{19}$F NMR spectrum of a sample withdrawn and hydrolyzed ~0.5 h after the addition was complete. The standard workup gave a yellowish syrup that, after being freed from residual solvent under vacuum, turned into a crystalline mass of diol **10** (13.9 g, 26.8 mmol, 96%). Recrystallization from methylene chloride and pentane (1:2) afforded as a first crop 10.7 g (74%) of white crystals, mp 88–90 °C. $^{19}$F NMR ($CDCl_3$): 82.5 (pseudo d, $J$ = 9.5 Hz, 4 F), 134.1 (subsplit septet, 2 F) ppm. $^{19}$F NMR (282.2 MHz, $CDCl_3$): 82.37, 82.81 (AB q, $J_{AB}$ = 139.8 Hz, 4 F; A part, d's, $J$ = 8.1 Hz; B part, d's, $J$ = 10.0 Hz); 134.21 (complex m, 2 F) ppm. $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ 7.21, 7.11 (AB q, $J_{AB}$ = 8.7 Hz, 8 H); 4.21 (complex m, 4 H); 2.29 (t, $J \approx$ 7 Hz, 2 H); 1.67 (s, 6 H). MS: *m/e* 520 (M$^+$), 505 (M$^+$ - $CH_3$, base). Isotope peaks: 522 (M + 2), 507 (M + 2 - $CH_3$), 524 (M + 4), 509 (M + 4 - $CH_3$). Anal. Calcd for $C_{21}H_{20}O_4F_6Cl_2$: C, 48.37; H, 3.84; F, 21.88. Found: C, 48.35: H, 3.94: F, 21.94.

**3,3′-[(1-Methylethylidene)bis(4,1-phenyleneoxy)]bis(2-chloro-2,3,3-trifluoropropanamide) (11).** Ammonolysis of diester has been described for the preparation of the TFE-derived diamide. Diester **9** (28.6 g, 49.6 mmol) in 50 mL of methanol was added to a cold methanolic solution of excess ammonia. Diamide formation was virtually instantaneous. The crude product, a brown-yellow solid (27 g), was treated with ice-cold chloroform (~80 mL). The diamide was isolated as a white brittle solid (19.5 g, 35.6 mmol, 72%). This product was already spectroscopically pure. It can be recrystallized from boiling chloroform to give diamide **11** as a white chalky solid, mp 159–162 °C. $^{19}$F NMR (282.2 MHz, DMSO-$d_6$): 78.53, 81.45 (AB q, $J_{AB}$ = 138.6 Hz, 4 F; B part, d's, $J$ = 11.3 Hz); 127.16 (d, $J$ = 11.3 Hz, 2 F) ppm. $^1$H NMR (300 MHz, DMSO-$d_6$): $\delta$ 8.44 (s, 2 H), 8.32 (br s, 2 H), 7.31, 7.15 (approx. AB q, $J_{AB}$ = 8.6 Hz, 8 H). IR (KBr): 3420 and ~3200 (m), 2960 (w), 1710 (vs), 1600 (w), 1500 (m), 1390 (w), 1280 (s), 1170 (vs) cm$^{-1}$. MS: *m/e* 546 (M$^+$), 531 (M$^+$ - $CH_3$, base). Isotope peaks: 548 (M + 2), 533 (M + 2 - $CH_3$), 535 (M + 4 - $CH_3$). Anal. Calcd for $C_{21}H_{18}N_2O_4F_6Cl_2$: C, 46.07; H, 3.29; F, 20.84; N, 5.12. Found: C, 46.20; H, 3.17; F, 20.80; N, 5.13.

**Dimethyl 3,3′-[[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene]bis(4,1-phenyleneoxy)]bis(2,2,3,3-tetrafluoropropionate) (13).** Anhydrous disalt preparation was carried out according to the method described for bisphenol A. Here 30 g (89 mmol) of hexafluorobisphenol A (**12**), 200 mL of DMSO, and 300 mL of chlorobenzene were used. Upon addition of the aqueous base (14.2 g of 50.2% sodium hydroxide), the reaction mixture underwent a series of vivid color changes: yellow, purple, bluish green, and pink. When chlorobenzene removal was complete, the now burgundy-colored solution was poured hot into the metal bomb. Carbon dioxide (11.7 g, 267 mmol) followed by TFE (18 g, 180 mmol) was introduced as described before. Upon warming, the reactor reached the maximum pressure (~400 psi) at 25 °C just before the stirrer could be activated. A rapid pressure drop occurred while the internal temperature rose to 60 °C. Methylation of the reaction mixture with 16.9 mL (178 mmol) of dimethyl sulfate was followed by the usual aqueous workup. A large amount of water (>1000 mL) was necessary to get a good separation of the product layer, which was then dissolved in ether, washed, and dried. After solvent traces were removed under vacuum at elevated temperature, a dark amber, very viscous product remained. This crude diester **13** (47.0 g, 72 mmol, 81%) contained a small fraction of proton-quenched $OCF_2CF_2H$ groups. Analysis of its $^{19}F$ NMR spectrum suggested <10% of this monoester contaminant. $^{19}F$ NMR ($CDCl_3$): 64.4 (s, 6 F), 85.8 (s, 4 F), 121.4 (s, 4 F) ppm; trace signals at 88.8 (s, $OCF_2$), 137.3 (d, $J_{HF}$ = 51 Hz, $CF_2H$). $^1H$ NMR ($CDCl_3$): $\delta$ 7.33 (m, 8 H), 4.00 (s, 6 H).

Some crystallization was observed within the syrup on prolonged standing. The bulk of the crude diester could not be crystallized successfully. However, a sample in methanol was decolorized with charcoal and concentrated to give diester **13** as a soft off-white solid, mp 49–50 °C. $^{19}F$ NMR (282.2 MHz, $CDCl_3$): 64.48 (s, 6 F), 85.90 (t, $J_{app}$ = 4.(4) Hz, 4 F), 121.54 (t, $J_{app}$ = 4.(4) Hz, 4 F) ppm. $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 7.41, 7.23 (approx. AB q, $J_{AB}$ = 8.8 Hz, 8 H), 4.00 (s, 6 H). IR ($CHCl_3$): 1780 (s), 1510 (m), 1310 (m), 1180 (vs), ~1000 (s), 1020 (m) $cm^{-1}$. MS: *m/e* 652 ($M^+$), 583 ($M^+ - CF_3$, base), intensity ratio 1:2; two small fragment peaks, 407 ($583 - OCF_2CF_2CO_2CH_3 - H$), 401 ($M^+ - C_6H_4OCF_2CF_2CO_2CH_3$). Anal. Calcd for $C_{23}H_{14}O_6F_{14}$: C, 42.33; H, 2.15; F, 40.80. Found: C, 42.41; H, 2.11; F, 40.66.

**3,3′-[[2,2,2-Trifluoro-1-(trifluoromethyl)ethylidene]bis(4,1-phenyleneoxy)]bis(2,2,3,3-tetrafluoropropanol) (14).** In contrast to the procedure described for diol **2**, this reduction was run in ether and aqueous acid was used in the workup. A solution of crude diester **13** (30.0 g, 46.0 mmol) in 150 mL of ether was added to a suspension of lithium aluminum hydride (2.9 g, 76.5 mmol) in 180 mL of ether. The rate of addition governed refluxing. Before workup completeness of the reduction was ascertained by $^{19}F$ NMR analysis. The reaction mixture was hydrolyzed by slowly adding 6 N hydrochloric acid (100 mL) and 50 mL of water until all solids were dissolved. Vigorous stirring was necessary. The ether layer was separated and washed to neutrality; the aqueous phase and the wash liquids were back-extracted with ether. The combined pale yellow ether solutions were dried over magnesium sulfate. Removal of solvent and drying under vacuum gave a sticky solid (27.4 g) that was recrystallized from methylene chloride and pentane (1:1) to give white crystals of diol **14** (23.7 g, 39.8 mmol, 87%), mp 106–107 °C. $^{19}F$ NMR (282.2 MHz, $CDCl_3$, trace DMSO-$d_6$): 64.46 (s, 6 F), 86.77 (s, 4 F), 126.12 (tt's, $J_{HF}$ = 14.6 Hz, $J_{FF}$ = 3 Hz) ppm. $^1H$ NMR (300 MHz, $CDCl_3$, trace DMSO-$d_6$): 7.40, 7.25 (approx. AB q, $J_{AB}$ = 8.9 Hz, 8 H), 4.40 (t, $J$ = 7.0 Hz, 2 H), 4.09 (td's, $J_{HF}$ = 14.5 Hz, $J$ = 7.0 Hz, 4 H). IR (KBr): 3340 (br, m), 1620 (w), 1510 (m), ~1230 (vs), 1180 (vs), ~1110 (vs), 1000 (m) $cm^{-1}$. MS: *m/e* 596 ($M^+$), 527 ($M^+ - CF_3$, base), intensity ratio 1:2; two small fragment peaks, 379 ($527 - OCF_2CF_2CH_2OH - H$), 373 ($M^+ - C_6H_4OCF_2CF_2CH_2OH$). Anal. Calcd for $C_{21}H_{14}O_4F_{14}$: C, 42.28; H, 2.35; F, 44.63. Found: C, 42.22; H, 2.39; F, 44.49.

**Hydrogenation of Diol 4.** The 200-mL metal bomb was charged with 340 mg of 5% rhodium on carbon and 1.6 g (3.3 mmol) of diol **4** in 80 mL of 2-propanol. After two purge cycles the bomb was pressurized with hydrogen to 475 psi. The bomb was heated to 145 °C ($p_{max}$ ~700 psi) and rocked for 12 h; then it was allowed to cool. The net pressure loss at 18 °C was ~30 psi. About twice this amount was expected for complete saturation of the aromatic rings. Initial $^{19}F$ NMR analysis of the acidic (pH <2) reaction mixture showed, in addition to the diol resonances, a triplet at 115.6 ppm ($J$ = 12.3 Hz) and a singlet at 170.7 ppm (HF). Upon workup the intensity of the new triplet decreased, indicating a volatile component. The $^1H$ NMR spectrum of the crude mixture was too complex to be meaningful. An attempt to isolate the most volatile component by distillation failed. The first fraction was a constant boiling 2-propanol/HF mixture.

GC analysis: 25-m dimethylsilicone capillary column; carrier gas 14 psi; injector 325 °C; detector 350 °C; temperature program, 60 °C (1 min), 60–240 °C (30°/min), 240 °C (6 min). Four well-separated components, A–D, were found with $t_R$ 2.3, 6.0, 8.0, and 12.0 min, respectively. The last $t_R$ matched that of the starting diol.

The mixture was further analyzed by GC/MS. Component A, isopropyl 2,2-difluoro-3-hydroxypropionate (**15**): *m/e* 153 ($M^+ - CH_3$), 81 (“$HOCH_2CF_2^+$”), 61 (“$HOCH_2CF_2^+$” − HF), 59 [(“$CH_3)_2CHO^+$”], 45 ($CH_3CH{=}OH^+$, base). B, 2,2-dicyclohexylpropane (**16**): 208 ($M^+$), 193 ($M^+ - CH_3$), both very weak; 125 ($M^+ - C_6H_{11}$), 124, 83 ($C_6H_{11}^+$), 69 ($C_5H_9^+$, base). C, compound **17**: 348 ($M^+$), 265 ($M^+ - C_6H_{11}$, base). D, diol **4**: 488 ($M^+$), 473 ($M^+ - CH_3$, base).

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# Tandem Nucleophilic Additions of Aryloxides

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Hydroquinone disodium salt added sequentially to tetrafluoroethylene and carbon dioxide to yield a symmetrical dicarboxylic acid, which was transformed into the corresponding dimethyl ester, diol, diamide, and diamine. Chlorotrifluoroethylene in analogous reactions gave the corresponding diester and diol in excellent yield. When this kind of transformation was attempted on phloroglucinol, the Kolbe–Schmitt carboxylation reaction intervened. Despite serious competition from addition/elimination processes under typical reaction conditions, the tandem addition of phenoxide ion to hexafluoropropene and carbon dioxide was carried out successfully at lower temperatures and higher carbon dioxide pressures.

As described in the preceding paper, we have synthesized a family of fluorinated bifunctional derivatives of bisphenol A. The key reaction we employed entailed addition of a phenolate ion to a fluorinated olefin to yield a carbanion, which was intercepted by carbon dioxide, a transformation developed by Krespan.[1] A continuing interest in creating

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