

**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<sub>2</sub>CF<sub>2</sub>H groups. Analysis of its <sup>19</sup>F NMR spectrum suggested <10% of this monoester contaminant. <sup>19</sup>F NMR (CDCl<sub>3</sub>): 64.4 (s, 6 F), 85.8 (s, 4 F), 121.4 (s, 4 F) ppm; trace signals at 88.8 (s, OCF<sub>2</sub>), 137.3 (d, J<sub>HF</sub> = 51 Hz, CF<sub>2</sub>H). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 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. <sup>19</sup>F NMR (282.2 MHz, CDCl<sub>3</sub>): 64.48 (s, 6 F), 85.90 (t, J<sub>app</sub> = 4.4 Hz, 4 F), 121.54 (t, J<sub>app</sub> = 4.4 Hz, 4 F) ppm. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.41, 7.23 (approx. AB q, J<sub>AB</sub> = 8.8 Hz, 8 H), 4.00 (s, 6 H). IR (CHCl<sub>3</sub>): 1780 (s), 1510 (m), 1310 (m), 1180 (vs), ~1000 (s), 1020 (m) cm<sup>-1</sup>. MS: *m/e* 652 (M<sup>+</sup>), 583 (M<sup>+</sup> - CF<sub>3</sub>, base), intensity ratio 1:2; two small fragment peaks, 407 (583 - OCF<sub>2</sub>CF<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub> - H), 401 (M<sup>+</sup> - C<sub>6</sub>H<sub>4</sub>OCF<sub>2</sub>CF<sub>2</sub>CO<sub>2</sub>CH<sub>3</sub>). Anal. Calcd for C<sub>23</sub>H<sub>14</sub>O<sub>6</sub>F<sub>14</sub>: 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 <sup>19</sup>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. <sup>19</sup>F NMR (282.2 MHz, CDCl<sub>3</sub>, trace DMSO-*d*<sub>6</sub>): 64.46 (s, 6 F), 86.77 (s, 4 F), 126.12 (tt's, J<sub>HF</sub> = 14.6 Hz, J<sub>FF</sub> = 3 Hz) ppm. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>, trace DMSO-*d*<sub>6</sub>): 7.40, 7.25 (approx. AB q, J<sub>AB</sub> = 8.9 Hz, 8 H), 4.40 (t, J = 7.0 Hz, 2 H), 4.09 (td's, J<sub>HF</sub> = 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<sup>-1</sup>. MS: *m/e* 596 (M<sup>+</sup>), 527 (M<sup>+</sup> - CF<sub>3</sub>, base), intensity ratio 1:2; two small fragment peaks, 379 (527 - OCF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>OH - H), 373 (M<sup>+</sup> - C<sub>6</sub>H<sub>4</sub>OCF<sub>2</sub>CF<sub>2</sub>CH<sub>2</sub>OH). Anal. Calcd for C<sub>21</sub>H<sub>14</sub>O<sub>4</sub>F<sub>14</sub>: 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*<sub>max</sub> ~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 <sup>19</sup>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 <sup>1</sup>H 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*<sub>R</sub> 2.3, 6.0, 8.0, and 12.0 min, respectively. The last *t*<sub>R</sub> 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<sup>+</sup> - CH<sub>3</sub>), 81 ("HOCH<sub>2</sub>CF<sub>2</sub><sup>+</sup>"), 61 ("HOCH<sub>2</sub>CF<sub>2</sub><sup>+</sup> - HF), 59 [{"CH<sub>3</sub>CHO<sup>+</sup>"}], 45 (CH<sub>3</sub>CH=OH<sup>+</sup>, base). B, 2,2-dicyclohexylpropane (16): 208 (M<sup>+</sup>), 193 (M<sup>+</sup> - CH<sub>3</sub>), both very weak; 125 (M<sup>+</sup> - C<sub>6</sub>H<sub>11</sub>), 124, 83 (C<sub>6</sub>H<sub>11</sub><sup>+</sup>), 69 (C<sub>5</sub>H<sub>9</sub><sup>+</sup>, base). C, compound 17: 348 (M<sup>+</sup>), 265 (M<sup>+</sup> - C<sub>6</sub>H<sub>11</sub>, base). D, diol 4: 488 (M<sup>+</sup>), 473 (M<sup>+</sup> - CH<sub>3</sub>, base).

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## Tandem Nucleophilic Additions of Aryloxides

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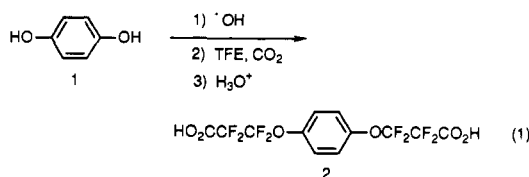
Hydroquinone disodium salt added sequentially to tetrafluoroethylene and carbon dioxide to yield a symmetrical dicarboxylic acid, which was transformed into the corresponding dimethyl ester, diol, diamide, and diamine. Chlorotrifluoroethylene in analogous reactions gave the corresponding diester and 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

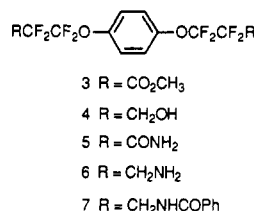
phenolate ion to a fluorinated olefin to yield a carbanion, which was intercepted by carbon dioxide, a transformation developed by Krespan.<sup>1</sup> A continuing interest in creating

useful new monomers has led us to explore further the scope of the Krespan reaction, extending it to a dihydric phenol, a trihydric phenol and a new fluoroolefin.

Hydroquinone (1) was converted to its disodium salt by using aqueous base in dimethyl sulfoxide/chlorobenzene, with azeotropic water removal.<sup>2</sup> The resulting anhydrous suspension of the salt in dimethyl sulfoxide was transferred to a pressure reactor into which tetrafluoroethylene (TFE) and carbon dioxide were then introduced at liquid nitrogen temperature. When the bomb was warmed to near room temperature, the solvent thawed sufficiently for stirring to begin and the reaction immediately became rapid as indicated by a rise in temperature to ~60 °C and a drop in pressure. Aqueous workup with strong acidification gave diacid 2 as the principal product (eq 1).

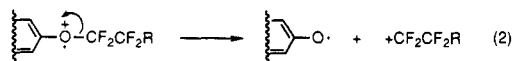


Crude diacid 2 was transformed into crystalline dimethyl ester 3 in 66% overall yield. Lithium aluminum hydride reduction of 3 to diol 4 was nearly quantitative. Ammonia reacted rapidly with diester 3 at 0 °C, giving diamide 5 in excellent yield. Transformation of this diamide to diamine 6 was accompanied by C-N cleavage even with diborane/tetrahydrofuran as the reducing agent, which normally minimizes this side reaction.<sup>3</sup> Both amino alcohol and a small amount of diol 4 were present in the product, as revealed by <sup>19</sup>F NMR and mass spectral analysis. The ratio of hydroxy- to amino-terminated side chains was about 20%. Benzoylation of a portion of this product mixture yielded pure bisbenzamide 7.

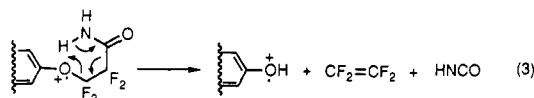


Comparison of the ultraviolet spectra of 2-6 with that of hydroquinone is striking. Both the long- and short-wavelength transitions of hydroquinone in the near UV [ $\lambda_{\text{max}} = 224.5$  (5180), 293.5 nm (2810), methanol]<sup>4a</sup> are shifted hypo- and hypsochromically when the powerfully electron-withdrawing fluorinated side chains are attached to the oxygens. For diol 4, as an example,  $\lambda_{\text{max}} = 214$  (3105), 264 nm (345) in the same solvent. Note that the long-wavelength transition has blue-shifted ~30 nm and diminished in intensity by a factor of ~8, thus markedly attenuating the molecule's absorption of the solar ultraviolet. We have found parallel but smaller shifts in the corresponding derivatives of bisphenols.<sup>2</sup>

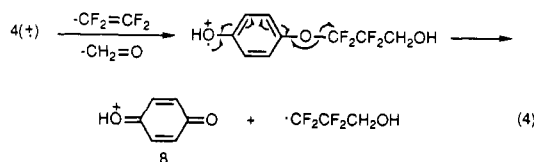
The mass spectra of 3-5 show both similarities and interesting contrasts. All three give a parent peak, which is also the base peak for 3 and 5, and a peak representing loss of one complete side chain. A prominent fragment ion from all three is the side chain minus oxygen, presumably formed as shown in eq 2. In the diol and di-



amide, but not the diester, an important ion is the parent minus all of a side chain except for OH. The McLafferty-like pathway<sup>5</sup> illustrated in eq 3 with the parent ion from 5 rationalizes the observed selectivity in the formation of the fragment ion, for the diester does not have a hydrogen atom well situated for the proposed transfer.

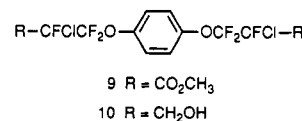


Both diol 4 and diamide 5 display peaks for hydroquinone cation radical and ion 8. The former presumably arises via 2-fold fragmentation as in eq 3. The latter ion, which is much too abundant to arise solely by cleavage of the former,<sup>6</sup> probably originates via the McLafferty-like fragmentation followed by C-O homolysis (eq 4). The ion



8 peak is far more intense in the diol than in the diamide spectrum; it is the base peak, in fact, for the diol. Since the rate of the homolysis step should depend little on the nature of the end group, this observation suggests that the McLafferty-like cleavage is considerably more rapid in the diol than in the diamide.

We substituted chlorotrifluoroethylene (CTFE) for TFE in the Krespan reaction with the disalt from hydroquinone. In this case the dimethyl ester 9 was prepared directly and in very high overall yield by adding dimethyl sulfate to the reaction mixture containing the dicarboxylate salt. The diester melted over a 5 °C range, which was unchanged upon recrystallization because both *dl* and meso forms were present. This mixture was presumably 1:1 since the configuration of the first side chain to be introduced should not have significantly influenced the configuration of the second. Reduction of 9 with lithium aluminum hydride gave the diastereomeric mixture of diols 10 in excellent yield.



Throughout the family of bifunctional molecules 2-7, 9, and 10, features in the infrared and NMR spectra that are characteristic of the side chains parallel those found for the corresponding molecules in the preceding paper and are therefore not discussed here.

In the hope of carrying out a 3-fold Krespan reaction to obtain trifunctional crosslinkers, the trihydric phenol phloroglucinol (11) was chosen for study. The ultraviolet spectrum of 11 shows long-wavelength transitions with very low intensity,  $\lambda_{\text{max}} = 272$  (310) and 268 (354),<sup>4b</sup> and these absorptions were expected to be blue-shifted when fluorinated side chains were attached. The very low solubility of the trisodium salt of 11 in dimethyl sulfoxide made our standard method for salt preparation impractical. This

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

(2) See the preceding paper.

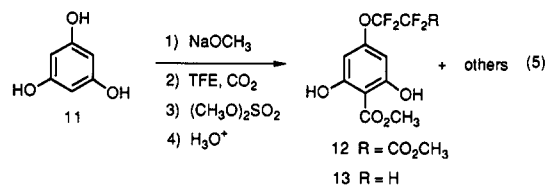
(3) Brown, H. C.; Heim, P. *J. Org. Chem.* 1973, 38, 912-916.

(4) *The Sadtler Handbook of Ultraviolet Spectra*; Sadtler Research Laboratories: Philadelphia, 1979; (a) No. 1912; (b) No. 1947.

(5) McLafferty, F. W. *Interpretation of Mass Spectra*, 3rd ed.; University Science Books: Mill Valley, CA, 1980; pp 63-70.

(6) *Registry of Mass Spectral Data*; Stenhagen, E., Abrahamsson, S., McLafferty, F. W., Eds.; Wiley: New York, 1974; Vol. 1, p 128.

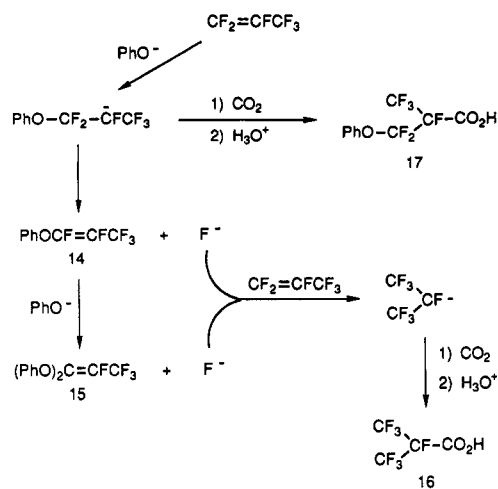
very air-sensitive salt was made by using sodium methoxide in anhydrous methanol and dried to constant weight at  $\sim 200^\circ\text{C}$  in vacuo. The Krespan reaction was carried out with TFE, and the temperature was raised to and maintained at  $100^\circ\text{C}$  until the pressure remained constant. After esterification with dimethyl sulfate at room temperature and aqueous workup, an ether-soluble liquid was obtained in far less than the theoretical amount expected from 3-fold addition of TFE and carbon dioxide. The  $^{19}\text{F}$  NMR spectrum displayed resonances at 85.9 and 121.4 ppm, as expected for the proximal and distal fluorines, respectively, of the desired side chains. Minor peaks at 89.1 and 137.7 ppm (d,  $J \approx 50$  Hz) signified the presence of proton-quenched side chains,  $\text{OCF}_2\text{CF}_2\text{H}$ . The  $^1\text{H}$  NMR spectrum was more complicated, however, with several methyl singlets in the range  $\delta$  3.8–4.1; aromatic singlets at  $\delta$  6.3, 7.0 and 8.2; and exchangeable protons at  $\delta \sim 10$  ppm. Thin-layer chromatography confirmed that the product mixture was indeed very complex, but partial resolution was achieved by flash chromatography. The most mobile fraction, a semicrystalline material comprising 45% of the crude product, displayed an infrared spectrum strongly reminiscent of methyl salicylate<sup>7</sup> and the same four  $^{19}\text{F}$  NMR resonances that were observed originally. Its  $^1\text{H}$  NMR spectrum ( $\text{CDCl}_3$ ) revealed major signals at  $\delta$  4.00 (s,  $\text{CH}_3$ ), 4.06 (s,  $\text{CH}_3$ ), 6.26 (s, ArH),  $\sim 9.8$  (br, OH,  $\text{D}_2\text{O}$ -exchangeable). Mass spectrometry confirmed the structure of the principal component as phenolic diester 12 and identified a second product as the proton-quenched monoester 13 (eq 5).



Since the three unsubstituted ring positions in the phloroglucinol trianion are each triply activated for electrophilic substitution, it is not surprising that the Kolbe-Schmitt carboxylation reaction intervened here and precluded the proposed 3-fold Krespan reaction. The fact that ring carboxylation was not observed in the Krespan reactions on hydroquinone and monohydric phenols indicates that the ring must be powerfully activated for the Kolbe-Schmitt reaction to compete.<sup>8</sup> Formation of diester 12 obviously required both Kolbe-Schmitt and Krespan reactions, and it is a good surmise that the former was the first to occur. The ensuing Krespan reaction would be expected to take place at the least hindered of the oxygen atoms, as observed. If one assumed that the Krespan reaction on the trianion were faster than the Kolbe-Schmitt, it would be difficult to explain why a second Krespan reaction would not be favored relative to carboxylation of a ring that was now significantly less activated. Note that the Kolbe-Schmitt reaction frees a ring proton to neutralize an aryloxy anion. The availability of phenolic hydrogens makes the origin of the proton-quenched product 13 easy to understand.

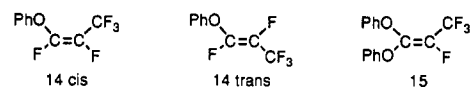
In an attempt to extend the range of fluoroolefins that can be used in the Krespan reaction, we allowed hydroquinone disodium salt to react with hexafluoropropene and carbon dioxide. The complex mixture that resulted per-

Scheme I

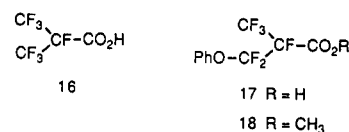


sued us to explore the simplest example of the reaction. Thus, anhydrous sodium phenoxide in dimethyl sulfoxide was prepared and combined with hexafluoropropene and carbon dioxide in the usual manner. After a moderate exotherm raised the temperature to  $40^\circ\text{C}$ , the mixture was stirred at room temperature until the pressure became constant. The pale yellow reaction solution contained a multicomponent mixture, as revealed by  $^{19}\text{F}$  NMR. Aqueous workup gave two ether-soluble liquid fractions of similar size; one was obtained at neutral pH, the other was extracted after strong acidification.

Bulb-to-bulb distillation of the neutral fraction gave a colorless volatile fraction composed principally of *cis*- and *trans*-1,2,3,3,3-pentafluoro-1-phenoxypropene (14) in the approximate ratio 2:1.  $^{19}\text{F}$  NMR chemical shifts and coupling constants for the two isomers agreed very well with literature values.<sup>9</sup> Distillation of the residue yielded a pale yellow liquid, which was mainly 2,3,3,3-tetrafluoro-1,1-diphenoxypropene (15). Again comparison of chemical shifts and coupling constants with literature data<sup>9</sup> confirmed the structure assignment.



$^{19}\text{F}$  NMR analysis in ether of the acidic fraction revealed a mixture of two carboxylic acids, perfluoroisobutyric acid (16) and its phenoxy derivative 17, the principal component. The former displayed signals at 75.0 (d, 6 F) and 180.8 ppm (septet, 1 F), consistent with literature values.<sup>10</sup> The new acid 17 had resonances at 74.2 (q, 3 F), 77.2 (m, 2 F), and 179.0 ppm (m, 1 F), which showed its close relationship to 16. Further proof of structure was provided by data obtained on its methyl ester 18, described in the Experimental Section.



Formation of the array of neutral and acidic compounds 14–17 is rationalized in Scheme I. Carboxylation of the carbanion formed by addition of phenoxide to hexafluoropropene (HFP) gave upon acidification the desired acid 17, but elimination of fluoride ion from the carbanion to yield 14 competed on a roughly equal footing with

(7) *The Aldrich Library of Infrared Spectra*, 3rd ed.; Aldrich Chemical Co.: Milwaukee, 1981; No. 1029 C.

(8) Phenol 11 has been carboxylated in aqueous potassium hydrogen carbonate at  $100^\circ\text{C}$  and atmospheric pressure. Holmes, P.; White, D. E.; Wilson, I. H. *J. Chem. Soc.* 1950, 2811.

(9) Ishikawa, N.; Harada, H. *Nippon Kagaku Kaishi* 1975, 2, 311–315.

(10) Graham, D. P.; McCormack, W. B. *J. Org. Chem.* 1966, 31, 958.

carboxylation. A second addition/elimination sequence transformed 14 into diphenoxy olefin 15. The fluoride ion released in both elimination steps captured a significant amount of the HFP, giving 16 after acidification. Clearly, the secondary carbanion intermediate formed when a phenoxide adds to HFP has a far greater tendency to suffer elimination in competition with carboxylation than is the case for the primary carbanion intermediates formed in Krespan reactions with TFE or CTFE.

The activation entropy for the initial (unimolecular) elimination reaction should be far more positive than that of the (bimolecular) carbon dioxide trapping reaction. That the two processes have nearly equal free energies of activation under our reaction conditions thus implies that the elimination has a higher activation enthalpy than trapping. It follows that lowering the temperature should favor the trapping reaction. We therefore repeated the reaction maintaining the temperature below 5 °C and using a larger excess of carbon dioxide to accelerate the carboxylation step. 1-Methyl-2-pyrrolidinone was added as a cosolvent to the dimethyl sulfoxide (mp 18 °C) to prevent it from freezing.

The result was a dramatic improvement. <sup>19</sup>F NMR analysis of the reaction mixture revealed that the salt of 17 was the dominant product, contaminated with only ~5 mol % of 14, ~1.5 mol % of 15, and ~10 mol % of the salt of 16. The reaction mixture was treated with dimethyl sulfate, and methyl ester 18<sup>11</sup> was isolated in 46% yield. No further attempt was made to optimize this Krespan reaction, but significant additional improvement is probably possible. Whether this type of reaction with HFP can be improved sufficiently to become practical with a bisphenol or dihydric phenol has not been investigated.

In this paper we have shown that the Krespan reaction with TFE and CTFE can be extended very successfully to a dihydric phenol, yielding diesters from which a variety of other bifunctional derivatives can be prepared. With the trihydric phenol phloroglucinol, on the other hand, an attempt to carry out a 3-fold reaction of this type was frustrated by intervention of the Kolbe-Schmitt reaction. We have found that HFP can function as the fluorolefin in a Krespan reaction if the temperature is kept low and the carbon dioxide pressure high to minimize the formation of elimination products.

### Experimental Section

Melting points were determined in open capillary tubes and are uncorrected. Routine <sup>19</sup>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. <sup>1</sup>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. In cases where the sample did not dissolve completely in deuteriochloroform, a few drops of deuterated dimethyl sulfoxide were added to achieve a homogeneous solution. 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. Ultraviolet spectra were recorded on a Hewlett-Packard diode array spectrophotometer. Microanalyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI.

Hydroquinone was purchased from Aldrich, phloroglucinol from Fluka. Tetrafluoroethylene (TFE), chlorotrifluoroethylene (CTFE), and hexafluoropropene (HFP) were obtained from PCR.

Tetrahydrofuran was distilled from benzophenone ketyl prior to use. DMSO was distilled from calcium hydride under reduced pressure. 1-Methyl-2-pyrrolidinone was dried by removing water as the benzene azeotrope followed by distillation under reduced pressure. All other solvents and reagents were reagent grade.

**Equipment and General Procedure for Pressure Reactions.** Reactions were run in 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). The bomb was 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 valves (No. SS-4H), and a pressure gauge. The reactor was connected to the manifold via a pressure hose (Parr A495HC). Gaseous reagents were introduced by static vacuum transfers from the gas cylinders to the bomb cooled in liquid nitrogen. For carbon dioxide, CTFE, and HFP 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)<sup>12</sup> 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.

**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 Hydroquinone in DMSO.** The experimental setup for the preparation of an anhydrous solution of the disalt of bisphenol A has been described previously.<sup>2</sup> Thus hydroquinone (11.4 g, 103 mmol) was dissolved in DMSO (180 mL) and chlorobenzene (170 mL). After the solution had been purged with nitrogen, aqueous sodium hydroxide (16.5 g of a 50.2% solution, 206 mmol) was added dropwise with vigorous stirring. With a water separator/fractionating column in place, the mixture was heated and stirred (mechanical stirrer!) under a protective nitrogen atmosphere. Removal of the azeotrope was followed by distillation of excess chlorobenzene. During this step the temperature inside the pot rose gradually to 183 °C. A uniform suspension of sand-colored disalt in a brown DMSO solution was obtained.<sup>13</sup> The hot suspension was quickly poured into the metal bomb, the bomb was closed, and its contents were allowed to cool under nitrogen. Rapid transfer was essential because the hydroquinone salt darkened instantaneously upon exposure to air. Therefore any solid left behind in the flask could not be salvaged. The dark brown solid was washed with ether and dried under vacuum to assess the amount of disalt not transferred. Its weight (3.8 g) represented 24% of the theoretical amount of disodium hydroquinone.

**3,3'-(1,4-Phenylenedioxy)bis(2,2,3,3-tetrafluoropropanoic acid) (2).** The 450-mL pressure reactor charged with the disodium salt suspension described above was cooled in liquid nitrogen. Carbon dioxide (13.2 g, 300 mmol) followed by TFE (20 g, 200 mmol) was introduced by static vacuum transfer. While the reactor warmed to room temperature, the pressure rose to 370 psi. When the stirrer could be activated, the reaction started as evidenced by a temperature rise to ~60 °C and a concomitant pressure drop. The reaction mixture was kept at 50 °C until the pressure remained constant. After the reactor had cooled, the residual gases were vented. The reaction mixture, a thick brown liquid, was poured into ice water (350 mL). The solution thus obtained (pH ~6) was extracted with ether (2 × 60 mL); evaporation of the solvent gave a very small amount of material that

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

(13) The reaction was also tried with potassium hydroxide in the hope of obtaining a more soluble salt. However, the dipotassium salt did not form a manageable suspension. Most of the solid was caked to the flask and, due to its rapid oxidation, was very difficult to transfer.

(11) Preparation of this ester by a different route is claimed in Japanese patent no. 56/25133, Mar. 10, 1981; *Chem. Abstr.* 1981, 95, 97094f.

contained proton-quenched end groups,  $\text{ArOCF}_2\text{CF}_2\text{H}$ .  $^{19}\text{F}$  NMR analysis: 88.8 (s,  $\text{ArOCF}_2$ ), 138.2 (d,  $J = 56$  Hz,  $\text{CF}_2\text{H}$ ) ppm. Upon strong acidification of the reaction mixture with 40 mL of concentrated hydrochloric acid, a dark brown oily product layer separated. It was dissolved in ether and washed with brine. The original aqueous solution (pH <2) was extracted with ether ( $2 \times 60$  mL), and the combined ethereal solutions were dried over magnesium sulfate. Evaporation of the solvent gave crude diacid 2, a brown crystalline mass (28 g, 90%), that was free of fluorine-containing impurities as shown by  $^{19}\text{F}$  NMR.

A small sample of the crude diacid (320 mg) was dissolved in 25 mL of boiling toluene. The hot solution was decanted from some brown insoluble residue, concentrated, and allowed to crystallize in the cold to yield off-white crystals (220 mg) of diacid 2, mp 134–135 °C.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ , trace DMSO- $d_6$ ): 85.8 (s, 4 F), 121.8 (s, 4 F) ppm.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , trace DMSO- $d_6$ ):  $\delta$  7.20 (s, 4 H), 10.15 (s, 2 H). Anal. Calcd for  $\text{C}_{12}\text{H}_8\text{F}_8\text{O}_6$ : C, 36.18; H, 1.51; F, 38.19. Found: C, 36.22; H, 1.44; F, 38.22.

**Dimethyl 3,3'-(1,4-Phenylenedioxy)bis(2,2,3,3-tetrafluoropropionate) (3).** For the esterification of the diacid with methanol, a technique<sup>14</sup> was chosen that uses molecular sieves to remove water.

Crude diacid 2 (27.6 g) in methanol (300 mL) and a catalytic amount of sulfuric acid (0.3 mL) were placed in a flask fitted with a Soxhlet extractor, which was charged with 3-Å molecular sieves. After this mixture had been refluxed overnight, the catalyst was neutralized with sodium carbonate (530 mg). A small amount of solid (sodium sulfate) was removed by filtration and the brown filtrate was concentrated on the rotary evaporator, whereupon a crystalline solid precipitated. Evaporation was stopped before dryness and a few milliliters of water were added to enhance the crystallization. The product was collected by suction filtration, washed with cold methanol-water (3:1), and dried to yield tan crystals (21.9 g, 51 mmol) of diester 3, mp 62–63 °C. The yield over two steps based on diacid transferred was 66%. For an analytical sample the diester was recrystallized from methanol-water (3:1), mp unchanged.  $^{19}\text{F}$  NMR (282.2 MHz,  $\text{CDCl}_3$ ): 85.98 (t,  $J_{\text{app}} = 4.5$  Hz, 4 F), 121.51 (t,  $J_{\text{app}} = 4.5$  Hz, 4 F) ppm.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.21 (s, 4 H), 4.00 (s, 6 H). IR (KBr): 1790 (s), 1500 (m), 1440 (m), 1340 (m), 1300 (s), 1160 and 1090 (vs), 1020 (s)  $\text{cm}^{-1}$ . MS:  $m/e$  426 ( $\text{M}^+$ , base), 251 ( $\text{M}^+ - \text{OCF}_2\text{CF}_2\text{CO}_2\text{CH}_3$ ), 159 ( $^+\text{CH}_3\text{O}_2\text{CCF}_2\text{CF}_2^+$ ), 59 ( $\text{CH}_3\text{O}_2\text{C}^+$ ). Anal. Calcd for  $\text{C}_{14}\text{H}_{10}\text{F}_8\text{O}_6$ : C, 39.44; H, 2.35; F, 35.68. Found: C, 39.47; H, 2.29; F, 35.60.

**3,3'-(1,4-Phenylenedioxy)bis(2,2,3,3-tetrafluoropropanol) (4).** A solution of diester 3 (18.1 g, 43 mmol) in ether (150 mL) was added dropwise to a suspension of lithium aluminum hydride (2.4 g, 63 mmol) in 200 mL of anhydrous ether. After the addition a sample was withdrawn and hydrolyzed at 0 °C with a few drops of acid.  $^{19}\text{F}$  NMR analysis of the ether solution showed that the reduction was still incomplete. Therefore refluxing and monitoring was continued until, after 5 h, the reduction was finished. The reaction mixture was cooled in an ice bath while hydrochloric acid (200 mL, 6 N solution) was added dropwise to the vigorously stirred suspension. Another 50 mL of water provided two homogeneous liquid layers. After separation of the ether solution, the aqueous phase was extracted with ether ( $2 \times 50$  mL). The combined ether solutions were washed and dried over magnesium sulfate. Evaporation to dryness gave a white solid (15.7 g) that was dissolved in the minimum amount of boiling chloroform. On cooling the product crystallized as white shiny wafers. The yield after filtration and drying was 14.7 g (40 mmol, 93%) of diol 4, mp 104–105 °C.  $^{19}\text{F}$  NMR ( $\text{CD}_3\text{CN}$ ): 85.7 (s, 4 F), 124.9 (t,  $J_{\text{HF}} = 14.6$  Hz, 4 F) ppm.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ ):  $\delta$  7.26 (s, 4 H), 4.00 (t,  $J_{\text{HF}} \approx 15$  Hz) and 3.76 (br s) overlapping signals,  $\sim 6$  H.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , trace DMSO- $d_6$ ):  $\delta$  7.23 (s, 4 H), 5.13 (t,  $J = 6.9$  Hz, 2 H), 4.06 (t d,  $J_{\text{HF}} = 14.7$  Hz,  $J = 6.9$  Hz, 4 H). IR (KBr): 3320 (s), 2960 (w), 1500 (s), 1350 (m), 1170 and 1090 (vs), 1000 (s)  $\text{cm}^{-1}$ . MS:  $m/e$  370 ( $\text{M}^+$ ), 240 ( $\text{M}^+ - \text{CF}_2\text{CF}_2\text{CH}_2\text{O}$ ), 223 ( $\text{M}^+ - \text{OCF}_2\text{CF}_2\text{CH}_2\text{OH}$ ), 131 ( $^+\text{HOCH}_2\text{CF}_2\text{CF}_2^+$ ), 110 ( $\text{HOC}_6\text{H}_4\text{OH}^+$ ), 109 ( $\text{HOC}_6\text{H}_4\text{O}^+$ , base). Anal. Calcd for  $\text{C}_{12}\text{H}_{10}\text{F}_8\text{O}_4$ : C, 38.92; H, 2.70; F, 41.08. Found: C, 38.74; H, 2.74; F, 41.13.

**3,3'-(1,4-Phenylenedioxy)bis(2,2,3,3-tetrafluoropropanamide) (5).** A solution of diester 3 (3.0 g, 7 mmol) was added dropwise at 0 °C to a freshly prepared solution of liquid ammonia ( $\sim 5$  mL) in methanol (25 mL). During the addition, the product started to precipitate and the reaction mixture turned into a thick white suspension. Filtration under suction gave a snow-white chalky solid (1.0 g). The filtrate was concentrated to afford another crop (1.44 g) of diamide. A small third crop was less pure and was therefore discarded. Combined yield was 2.44 g (6.2 mmol, 89%) of diamide 5, mp 212–213 °C.  $^{19}\text{F}$  NMR ( $\text{CH}_3\text{OH}$ ): 85.2 (s, 4 F), 121.9 (s, 4 F) ppm.  $^1\text{H}$  NMR ( $\text{CD}_3\text{CN}$ , trace DMSO- $d_6$ ):  $\delta$  7.88, 7.80 (two br s, 4 H), 7.35 (s, 4 H). IR (KBr): 3400 (s), 3200 (m), 1700 (vs), 1620 (w), 1500 (m), 1320 (m), 1180 and 1160 (vs), 1080 (s), 1010 (m)  $\text{cm}^{-1}$ . MS:  $m/e$  396 ( $\text{M}^+$ , base), 253 ( $\text{M}^+ - \text{CF}_2\text{CF}_2\text{CONH}$ ), 236 ( $\text{M}^+ - \text{OCF}_2\text{CF}_2\text{CONH}_2$ ), 144 ( $^+\text{H}_2\text{NCOCF}_2\text{CF}_2^+$ ), 126 ( $^+\text{NCCF}_2\text{CF}_2^+$ ), 110 ( $\text{HOC}_6\text{H}_4\text{OH}^+$ ), 109 ( $\text{HOC}_6\text{H}_4\text{O}^+$ ). Anal. Calcd for  $\text{C}_{12}\text{H}_8\text{F}_8\text{N}_2\text{O}_4$ : C, 36.36; H, 2.02; F, 38.38; N, 7.07. Found: C, 36.32; H, 2.04; F, 38.18; N, 7.08.

**3,3'-(1,4-Phenylenedioxy)bis(2,2,3,3-tetrafluoropropanamine) (6).** The usual order of addition, i.e., substrate to the borane reagent, was reversed because of the low solubility of diamide 5 in THF. The reduction was carried out under nitrogen.

Diamide 5 (2.0 g, 5 mmol) partially dissolved in anhydrous THF (70 mL). The borane-tetrahydrofuran complex (25 mL, 1 M in THF) was transferred via cannula to an addition funnel and then added dropwise to the suspension. The reaction mixture became homogeneous during the addition. The progress of the reduction was monitored by  $^{19}\text{F}$  NMR. Samples were withdrawn periodically, hydrolyzed with a few drops of 3 N hydrochloric acid, and stirred until gas evolution ceased. The reduction was sluggish even at reflux temperature. More borane complex ( $\sim 10$  mL) was added in portions to achieve complete consumption of diamide. Excess reagent and borane complexes were decomposed with 3 N hydrochloric acid. Slow addition of the acid is required due to severe frothing. Most of the THF was distilled off at atmospheric pressure. The diamine was freed by adding enough 50% sodium hydroxide solution to reach pH  $\sim 8$ . The product was extracted with ether ( $3 \times 50$  mL) and the extracts were dried over sodium sulfate. Upon evaporation a white amorphous solid formed, 1.9 g after drying under vacuum. This product proved to be diamine 6 contaminated with amino alcohol and diol 4 (impurity signals marked with asterisks below).  $^{19}\text{F}$  NMR ( $\text{CDCl}_3/\text{DMSO-}d_6$ ): 86.6\* (s), 87.1 (s), 125.0 (t,  $J_{\text{HF}} = 16$  Hz), 125.7\* (t,  $J_{\text{HF}} \approx 15$  Hz) ppm. Relative integration of singlets: 86.6\* ppm (0.20), 87.1 ppm (1.00).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3/\text{DMSO-}d_6$ ):  $\delta$  7.31 (s), 4.00\* (t,  $J_{\text{HF}} = 15$  Hz), 3.28 (t,  $J_{\text{HF}} = 16$  Hz), 1.7 (br). Relative integration of triplets:  $\delta$  4.00\* (0.23), 3.28 (1.00). MS: all three  $\text{M}^+$  peaks, 6  $m/e$  368, amino alcohol  $m/e$  369, and 4  $m/e$  370, were detected.

**Dibenzamide of 3,3'-(1,4-Phenylenedioxy)bis(2,2,3,3-tetrafluoropropanamine) (7).** A portion of the above product mixture (289 mg) was dissolved in pyridine (5 mL) and treated with excess benzoyl chloride (0.8 mL). The resulting suspension was briefly heated to reflux. Excess reagent was destroyed with aqueous sodium hydroxide (2 N, 2.5 mL). The organic layer was separated and stored in the cold overnight, whereupon the crude product precipitated. The solid was collected by filtration and washed with cold methanol. The yellowish powder (200 mg) thus obtained was recrystallized from ethyl acetate. First crop was white crystals (103 mg) of bisbenzamide 7, mp 196–197 °C. Additional clean product (50 mg) precipitated from the filtrate (pyridine/methanol mixture) made alkaline with 2 N sodium hydroxide.  $^{19}\text{F}$  NMR (282.2 MHz, DMSO- $d_6$ ): 85.96 (unres. t, 4 F), 119.25 (tt,  $J_{\text{HF}} = 16$  Hz,  $J = 4.6$  Hz) ppm.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ ):  $\delta$  9.05 (t,  $J = 6.3$  Hz, NH), 7.9 (subsplit d,  $J = 7.5$  Hz, Ph, o-H), 7.6 (subsplit t,  $J = 7.5$  Hz, Ph, p-H), 7.5 (subsplit t,  $J = 7.5$  Hz, Ph, m-H), 7.48 (s, phenylene H), 4.19 (td,  $J_{\text{HF}} = 16$  Hz,  $J = 6.3$  Hz,  $\text{CH}_2$ ). IR (KBr): 3340 (m), 1650 (vs), 1540 (vs), 1500 (s), 1430 (w), 1340 (m), 1310 (s), 1230 (m), 1170 (vs)  $\text{cm}^{-1}$ . Anal. Calcd for  $\text{C}_{26}\text{H}_{20}\text{F}_8\text{N}_2\text{O}_4$ : C, 54.17; H, 3.47; F, 26.39; N, 4.86. Found: C, 54.18; H, 3.48; F, 26.32; N, 4.80.

**Dimethyl 3,3'-(1,4-Phenylenedioxy)bis(2-chloro-2,3,3-trifluoropropionate) (9).** The initial pressure reaction has been described in detail for the preparation of diacid 2. The bomb was charged with the disalt suspension prepared from 11.4 g (103 mmol) hydroquinone and the gaseous reagents CTFE (27.0 g, 232

(14) Harrison, H. R.; Haynes, W. M.; Arthur, P.; Eisenbraun, E. J. *Chem. Ind. (London)* 1968, 1568.

mmol) and carbon dioxide (14.0 g, 318 mmol). Maximum pressure was 300 psi at room temperature. The reaction mixture was kept at 50–60 °C until there was no further pressure drop.  $^{19}\text{F}$  NMR analysis of the dark amber homogeneous reaction mixture revealed, aside from the dicarboxylate salt, no fluorine-containing products.  $^{19}\text{F}$  NMR (282.2 MHz, DMSO): 77.87, 80.54 (AB q,  $J_{\text{AB}} = 139$  Hz, 4 F), 118.97 (s, 2 F) ppm.

Isolation of the diacid was bypassed in favor of direct methylation of the dicarboxylate. Dimethyl sulfate (19.4 mL 206 mmol) was added dropwise at room temperature. The reaction mixture was stirred for 3 h and then poured into ~500 mL of ice water. The product layer was dissolved in ether, and the solution was washed with brine and dried over magnesium sulfate. Evaporation gave a brown crystalline mass (42 g) that was dissolved in methanol. Upon addition of 10–15% v/v of water, crystallization started and continued in the cold. After filtration, washing, and vacuum drying, tan colored crystals of diester **9** (33.0 g, 72 mmol, 70%) were obtained, mp 53–58 °C.<sup>15</sup> This yield is not adjusted for loss of disalt during transfer. Assuming ~20% loss, as in the previous transfer, the yield was ~88%. For an analytical sample the diester was once more recrystallized from methanol and water without change in the melting range.  $^{19}\text{F}$  NMR (282.2 MHz,  $\text{CDCl}_3$ ): 80.12, 83.96 (AB q,  $J_{\text{AB}} = 138.5$  Hz; A part: d's,  $J = 3.3$  Hz; B part: d's,  $J = 12$  Hz, 4 F), 130.40 (subsplit d,  $J = 12$  Hz, 2 F) ppm.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  7.23 (s, 4 H), 4.00 (s, 6 H). Anal. Calcd for  $\text{C}_{14}\text{H}_{10}\text{Cl}_2\text{F}_6\text{O}_6$ : C, 36.60; H, 2.18; F, 24.84. Found: C, 36.64; H, 2.12; F, 24.79.

**3,3'-(1,4-Phenylenedioxy)bis(2-chloro-2,3,3-trifluoropropanol)** (**10**). The reduction procedure was analogous to the one described for diol **4**. Diester **9** (29.0 g, 63 mmol) in ether (150 mL) was reduced with lithium aluminum hydride (3.6 g, 95 mmol) in ether (200 mL). The usual workup with aqueous acid gave crude diol (25 g) as a white chalky solid. Recrystallization from boiling chloroform, in which the solid dissolved very slowly, afforded white crystals of diol **10** (22.1 g, 54.8 mmol, 87%), mp 120–125 °C.<sup>15</sup>  $^{19}\text{F}$  NMR (56.2 MHz,  $\text{CDCl}_3$ , trace DMSO- $d_6$ ): 82.6 (pseudo d,  $J \approx 11$  Hz, 4 F), 133.5 (subsplit septet, 2 F) ppm.  $^{19}\text{F}$  NMR (282.2 MHz,  $\text{CDCl}_3$ , trace DMSO- $d_6$ ):  $\delta$  82.56, 82.84 (AB q,  $J_{\text{AB}} = 139.7$  Hz, 4 F; A part: d's,  $J = 8.7$  Hz; B part: d's,  $J = 9.6$  Hz), 133.74 (complex m, 2 F) ppm.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ , trace DMSO- $d_6$ ):  $\delta$  7.25 (s, 4 H), 5.40 (t,  $J = 7$  Hz, 2 H), 4.3–4.0 (m, overlapping td's,  $J_{\text{HF}} \approx 14$  Hz,  $J = 7$  Hz, 4 H). Anal. Calcd for  $\text{C}_{12}\text{H}_{10}\text{Cl}_2\text{F}_6\text{O}_4$ : C, 35.73; H, 2.48; F, 28.29. Found: C, 35.86; H, 2.39; F, 28.16.

**Anhydrous Trisodium Salt of Phloroglucinol**. A sodium methoxide solution freshly prepared from sodium (3.0 g, 130 mmol) and anhydrous methanol (45 mL) was added dropwise to phloroglucinol (5.0 g, 40 mmol) in 35 mL of methanol. At the end of the addition the trisalt solution had a purplish color. All operations were carried out under a nitrogen atmosphere. Methanol was removed on the vacuum line to leave a tan solid. This solid was heated in vacuo (bath temperature ~200 °C, 0.01 mm) until its weight remained constant. The trisalt (9.0 g) was stored under nitrogen and used as soon as possible.

**Reaction of Phloroglucinol Trisodium Salt with TFE and Carbon Dioxide**. The bomb was charged with the trisalt (9.0 g) and 100 mL of anhydrous DMSO in a glove bag under nitrogen. The gases were introduced by static vacuum transfers: TFE (15 g, 150 mmol) and carbon dioxide (9 g, 205 mmol). At 20 °C and  $p_{\text{max}} \sim 300$  psi, the bomb contents became stirrable and the reaction started with a moderate temperature rise to 45 °C and a slow pressure drop. The bomb was heated to 100 °C and kept at that temperature until the pressure was steady. The brown homogeneous reaction mixture was treated with dimethyl sulfate (11.2 mL, 118 mmol) and stirred for 3 h at room temperature. Aqueous workup led to the separation of a product layer that was dissolved in ether washed with brine, dried, and evaporated to leave a viscous amber liquid (6.0 g). Its  $^{19}\text{F}$  NMR spectrum looked clean with major peaks at 85.9 and 121.4 ppm, consistent with  $\text{ArOCF}_2\text{CF}_2\text{CO}_2\text{CH}_3$ , and two minor resonances 89.1 and 137.5 (d,  $J \approx 50$  Hz) ppm stemming from  $\text{ArOCF}_2\text{CF}_2\text{H}$ . However, the  $^1\text{H}$  NMR spectrum showed several methyl singlets at  $\delta$  3.8–4.1, aromatic singlets at  $\delta$  6.3, 7.0, 8.2, and exchangeable protons at

$\delta \sim 10.0$  TLC on silica with various eluents confirmed that the crude product was a very complex mixture. Partial separation was achieved by flash chromatography on silica with petroleum ether and ethyl acetate (1:1). The most mobile products were isolated as a semicrystalline material (0.86 g from 1.9 g). IR ( $\text{CH}_2\text{Cl}_2$ ): 3420 (m), ~3100 (w, br), 2960 (w), 1780 (vs), 1680 (s), 1640 (s), 1600 (s)  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ): major resonances  $\delta$  4.00 (s,  $\text{CH}_3$ ), 4.06 (s,  $\text{CH}_3$ ), 6.26 (s, Ar H), ~9.8 (br, OH,  $\text{D}_2\text{O}$  exchangeable). The  $^{19}\text{F}$  NMR spectrum was unchanged except for a small intensity increase of the minor peaks. The structure of the major component, the phenolic diester **12**, was confirmed by mass spectrometry. MS:  $m/e$  342 ( $\text{M}^+$ ), 310 ( $\text{M}^+ - \text{CH}_3\text{OH}$ , base), 282 ( $\text{M}^+ - \text{CH}_3\text{OH} - \text{CO}$ ), 251 (282 -  $\text{OCH}_3$ ), 123 (282 -  $\text{CF}_2\text{CF}_2\text{CO}_2\text{CH}_3$ ), 59 ( $\text{CO}_3\text{CH}_3^+$ ). In the same manner, another product was identified, methyl 4-(1,1,2,2-tetrafluoroethoxy)-2,6-dihydroxybenzoate (**13**). MS:  $m/e$  284 ( $\text{M}^+$ ), 252 ( $\text{M}^+ - \text{CH}_3\text{OH}$ , base), 224 ( $\text{M}^+ - \text{CH}_3\text{OH} - \text{CO}$ ), 101 ( $\text{CF}_2\text{CF}_2\text{H}^+$ ).

**Reaction of Sodium Phenolate with Hexafluoropropene and Carbon Dioxide**. An anhydrous solution of phenolate in DMSO was prepared by the earlier described method of azeotropic water removal.

Phenol (5.3 g, 56 mmol) in a mixture of DMSO (120 mL) and chlorobenzene (160 mL) was treated with sodium hydroxide (4.48 g of a 50.2% solution, 56 mmol). After removal of the auxiliary solvent was complete, the light brown salt solution was poured hot into the 450-mL metal bomb and allowed to cool under nitrogen. Hexafluoropropene (10.0 g, 66 mmol) followed by carbon dioxide (8.50 g, 193 mmol) was introduced via static vacuum transfers. The bomb was allowed to warm to 20 °C; at that temperature the stirrer could be activated. The pressure ( $p_{\text{max}} \sim 150$  psi) dropped rapidly and the temperature rose to 40 °C. Stirring was continued until room temperature was reached and the residual pressure remained constant. The pale yellow product solution proved to be a multicomponent mixture by  $^{19}\text{F}$  NMR. This solution was poured into ice water, whereupon a product layer separated. The aqueous layer (pH ~6) was extracted with ether (3  $\times$  60 mL). The combined extracts were dried over magnesium sulfate and evaporated to give a yellow liquid (8.6 g). The aqueous solution was made strongly acid (pH <2) with concentrated hydrochloric acid. Extraction with ether as above gave a yellow liquid (7.3 g).

**Analysis of Products Extracted at pH ~6**. Volatiles were vacuum transferred at 25°/1 mm into a trap cooled to -78 °C. The colorless liquid contained predominantly a mixture of *cis*- and *trans*-1,2,3,3,3-pentafluoro-1-phenoxypropene (**14**) in about a 2:1 ratio.  $^{19}\text{F}$  NMR (neat): *cis* olefin 67.6 (dd), 90.6 (dq), 179.4 (dq,  $J \approx 19$  Hz,  $J \approx 9.5$  Hz) ppm; *trans* olefin 67.7 (dd), 106.6 (dq,  $J = 121$  Hz,  $J \approx 22$  Hz), 186.1 (dq,  $J = 121$  Hz,  $J \approx 12$  Hz). The residue from the vacuum transfer was distilled, yielding a yellowish liquid (1.1 g) collected at 87–97°/1.4 mm. The main component in this fraction was 2,3,3,3-tetrafluoro-1,1-diphenoxypropane (**15**).  $^{19}\text{F}$  NMR (neat): 66.4 (d, 3 F) 173.7 (q, 1 F) ppm. Chemical shifts and coupling constants agree very well with literature values.<sup>9</sup> No attempt was made to recover the olefins quantitatively.

**Analysis of Products Extracted at pH <2**. The  $^{19}\text{F}$  NMR spectrum in ether revealed a mixture of 2-(trifluoromethyl)-2,3,3,3-tetrafluoropropanoic acid (**16**), 75.0 (d, 6 F), 180.8 (septet, 1 F) ppm and, as the major component, 2-(difluorophenoxy)methyl-2,3,3,3-tetrafluoropropanoic acid (**17**), 74.2 (q, 3 F), 77.2 (m, 2 F), 179.0 (m, 1 F) ppm.

**Methyl 2-(Difluorophenoxy)methyl-2,3,3,3-tetrafluoropropanoate** (**18**). An anhydrous solution of phenolate in DMSO (75 mL) was prepared from 5.3 g (56 mmol) of phenol. The hot solution was poured into the metal bomb charged with anhydrous 1-methyl-2-pyrrolidinone (75 mL). Hexafluoropropene (10.0 g, 66 mmol) and carbon dioxide (16.5 g, 375 mmol) were vacuum transferred into the bomb cooled in liquid nitrogen. Upon warming, the stirrer could be activated at <0 °C. An immediate pressure drop from  $p_{\text{max}} \sim 120$  psi indicated a rapid reaction. The internal temperature was held below 5 °C by cooling with an ice bath until the pressure remained constant. The crude product mixture was examined by high field  $^{19}\text{F}$  NMR, and the distinctive  $\text{CF}_3$  resonances of olefins and carboxylates served to assess the composition of the mixture. The major product was the sodium salt of **17**.  $^{19}\text{F}$  NMR: 72.2 (m, 3 F), 75.0, 75.9 (subsplit AB q,

(15) The melting range is due to the existence of different stereoisomers, a meso form and a *d,l* pair.

$J_{AB} = 143$  Hz, 2 F), 170.0 (m, 1 F) ppm. In addition, ~5% of monosubstituted olefins 14, ~1.5% of disubstituted olefin 15, and ~10% of carboxylate of 16 were present. Percentages are relative to the major product. Methylation with dimethyl sulfate (5.3 mL, 56 mmol) at room temperature was followed by workup with ice water (~400 mL). The product layer that separated was dissolved in ether, washed, and dried. The brownish liquid thus obtained was fractionated to yield 7.8 g (25.8 mmol, 46%) of ester 18, bp 45–47°/0.01 mm.  $^{19}\text{F}$  NMR (282.2 MHz,  $\text{CDCl}_3$ ): 74.30 (q,  $J = 8.6$  Hz, 3 F), 76.87, 77.99 (subsplit AB q,  $J_{AB} = 142$  Hz,

2 F), 180.45 (m, 1 F) ppm.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.42–7.16 aromatic m, 5 H), 4.00 (s, 3 H). IR ( $\text{CHCl}_3$ ): 3030 (w), 2960 (w), 1780 (s), 1600 (w), 1500 (m), 1450 (w), 1270 (vs), 1190 (s), 1160 (s), ~1100 (s), 1030 (s)  $\text{cm}^{-1}$ . MS:  $m/e$  302 ( $\text{M}^+$ ), 209 ( $\text{M}^+ - \text{C}_6\text{H}_5\text{O}$ ), 131 ( $\text{CF}_2\text{CFCF}_2^+$ ), 81 ( $\text{CF}_2\text{CF}^+$ ), 77 ( $\text{C}_6\text{H}_5^+$ ), 59 ( $\text{CO}_2\text{CH}_3^+$ , base). Anal. Calcd for  $\text{C}_{11}\text{H}_8\text{F}_6\text{O}_3$ : C, 43.71; H, 2.65. Found: C, 44.24; H, 2.72.

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## Carbonyl Chemistry of Tetrafluorocyclopentadienone

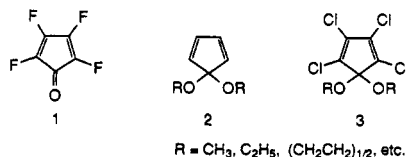
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In order to control the Diels–Alder reactivity of the very labile title compound 1, experiments designed to modify the carbonyl group have been carried out. With methanol a hemiketal (4) is formed reversibly at low temperatures, but conjugate addition to give 3-methoxy derivatives 5 and 6 occurs at ordinary temperatures. Diazomethane reacts with 1 in cold methanol to give a spirooxirane (9) which undergoes Diels–Alder dimerization orders of magnitude slower than dienone 1 at room temperature. Hydrogen cyanide gives a cyanohydrin (15) with 1 at low temperatures, but the compound decomposes at 0 °C. Trimethylsilyl cyanide yields the trimethylsilyl cyanohydrin 16, a stable derivative of 1 that dimerizes only at elevated temperatures, yet retains reactivity as a Diels–Alder diene.

When tetrafluorocyclopentadienone (1) was first synthesized in our laboratory,<sup>2</sup> we hoped that it could serve as a building block for incorporating the 1,2,3,4-tetrafluorobutadienediyl unit ( $-\text{CF}=\text{CFCF}=\text{CF}-$ ) into various perfluoroannulenes and their valence isomers. In principle this could be accomplished via Diels–Alder addition across the diene followed by extrusion of carbon monoxide from the resulting 7-norbornenones. Not surprisingly, 1 undergoes very facile Diels–Alder dimerization, which makes addition of most other dienophiles impractical. Dimerization of 1 is much slower than that of the extraordinarily labile parent cyclopentadienone,<sup>3</sup> however. The orange vapor can be stored for hours at room temperature at pressures below 1 Torr, and it is thus feasible to carry out reactions with the compound in cold, dilute solution.



Since the diene's tendency to dimerize is attributable to a very narrow HOMO–LUMO gap, and since the carbonyl is largely responsible for the low-lying LUMO, we anticipated that derivatization of the carbonyl group could dramatically inhibit dimerization and brighten the prospects for carrying out other Diels–Alder reactions.<sup>4</sup> The Diels–Alder chemistry of ketals of cyclopentadienone (2)<sup>5</sup>

and tetrachlorocyclopentadienone (3)<sup>6</sup> constitutes excellent precedent for this idea. Ketals 2 and 3 were prepared by routes that bypassed the labile dienones;<sup>7</sup> unfortunately, these routes do not seem adaptable to the synthesis of the corresponding derivatives of 1. Treatment of hexachlorocyclopentadiene with alkoxides leads smoothly to 3, for example, but nucleophilic attack on hexafluorocyclopentadiene tends to give products of addition/elimination in which the geminal difluoro group remains intact.<sup>8</sup> This is a consequence of the mutual bond-strengthening effect characteristic of two or more fluorines linked to the same carbon.<sup>9</sup>

Here we describe experiments designed to derivatize directly the carbonyl group of tetrafluorocyclopentadienone. At the outset there was no assurance that this could be accomplished, as all five carbons are highly electron deficient and activated for attack by nucleophilic reagents.

## Results and Discussion

Attempts to prepare the semicarbazone and hydrazones of 1 by treatment of cold solutions of the dienone with various hydrazine derivatives yielded unpromising mixtures. Initial observations of the reaction of dienone 1 with methanol revealed only addition of the alcohol across one of the carbon–carbon double bonds. Closer scrutiny of the

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