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Synthesis of Polyfluoro Aromatic Ethers: A Facile Route Using Polyfluoroalkoxides Generated from Carbonyl and Trimethysilyl Compounds

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The polyfluoro aromatic ethers $C_6F_5CH_2OR_F$ [R_F = CF_3, C_2F_5, CF_3CH_2, $CF(CF_3)_2$, $C(CF_3)_3$, $C(CF_3)_2(C_6F_5)$, $C(CF_3)_2(OCH_2CF_3)$, $C(C_6F_5)_2(CF_3)$], $(4\text{-}CF_3CH_2O)C_6F_4CH_2OCH_2CF_3$, and $C_6F_5CH_2OCF_2CF_2OCH_2C_6F_5$, were synthesized from $C_6F_5CH_2Br$ in the presence of CsF by reaction with the perfluoro carbonyl compounds COF_2, $CF_3C(O)F$, C_6F_5COF, $(C_6F_5)_2CO$, $(CF_3)_2CO$, and $(COF)_2$; reaction with polyfluoro siloxanes $CF_3CH_2OSi(CH_3)_3$ and $C_6F_5OSi(CH_3)_3$; or reaction with polyfluoroalkoxides generated from the fluorinated silanes $CF_3Si(CH_3)_3$, $C_6F_5Si(CH_3)_3$, and $CF_3CH_2OSi(CH_3)_3$ reacting with the carbonyl compounds listed above. Single-crystal X-ray analysis of $C_6F_5CH_2OC(C_6F_5)_2(CF_3)$ is reported. Reactivities of the carbonyl substrates and the silicon-containing reagents are discussed as a function of the alkyl (aryl) substituents present.

Introduction

Per- and polyfluorinated ethers are of special interest because of their utility as high temperature lubricants and solvent resistant elastomers. The applications of perfluoro polyethers[2] and polymers based on fluorinated monomers have been well reviewed.[3] Direct fluorination using elemental fluorine gas[4,5] and electrochemical fluorination[6] are important synthetic methods for the preparation of perfluoro aliphatic ethers; however, these methods are not suitable for the synthesis of fluorinated aromatic compounds.

For the preparation of per- and polyfluoro aromatic ethers, reactions that make use of fluorinated alcohols and their silyl derivatives are convenient synthetic routes. Polyfluoro alcohols R_FCH_2OH and $HCF_2R_FCH_2OH$ are available by reduction of the corresponding carboxylic acids.[7] These fluoro alcohols are readily converted to siloxanes $R_FCH_2OSi(CH_3)_3$ and $HCF_2R_FCH_2OSi(CH_3)_3$ by reaction with $[(CH_3)_3Si]_2NH$ in the presence of a catalytic amount of saccharin.[8] Reported reactions of $CF_3CH_2OSi(CH_3)_3$ with organic[9−11] as well as inorganic compounds[12−14] are numerous. The fluoro aromatic siloxane $C_6F_5OSi(CH_3)_3$ is prepared by the reaction of C_6F_5OH with $[(CH_3)_3Si]_2NH$, and reactions with SF_4, CF_3SF_3,[15] WF_6,[16] and aryl halides are described.[17] While the perfluoro alcohols R_FCF_2OH and $R_FR_F'CFOH$ are unstable and rapidly decompose to form acid fluorides and ketones,[18,19] perfluoroalkoxides $R_FCF_2O^-$ and $R_FR_F'CFO^-$ are prepared from the corresponding acid fluorides and ketones *via* reaction with a metal fluoride. These alkoxides react with alkyl halides, allyl halides, and acyl fluorides to provide perfluoroalkyl ethers[20−22] and perfluoroalkyl esters.[23]

The chemistry of silanes is currently focused on the synthesis of new fluorinated compounds. It is reported that nucleophilic reactions of $R_FSi(CH_3)_3$ (R_F = CF_3, C_2F_5, C_3F_7) with carbonyl compounds provides fluorinated alcohols and alkoxides.[24−29] Several fluorinated benzyl alcohols are obtained when $C_6F_5Si(CH_3)_3$ is reacted with carbonyl substrates.[29,30] Some papers describe the formation of fluorinated esters;[27,29] however, no reports on the preparation of per- and polyfluoro ethers using these fluorinated silanes have appeared.

We wish to describe here the preparation of per- and polyfluoroalkoxides generated from perfluoro carbonyl compounds with per- and polyfluorosilyl and -siloxyl reagents and their application to the synthesis of new polyfluoro aromatic ethers having one or more pentafluorobenzyl group. We also

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(2) Lagow, R. J.; Bierschenk, T. R.; Juhlke, T. J.; Kawa, H. In *Synthetic Fluorine Chemistry*; Olah, G. A., Chambers, R. D., Prakash, G. K. S., Eds.; John Wiley & Sons, Inc.: New York, 1992; Chapter 5.

(3) Madison, N. L. in *Fluoropolymers*; Wall, L. A., Ed.; John Wiley & Sons, Inc.: New York, 1972; Chapter 7.

(4) Huang, H. N.; Persico, D. F.; Clark, L. C., Jr.; Lagow, R. J. *J. Org. Chem.* **1988**, *53*, 78.

(5) Lin, W. H.; Clark, W. D.; Lagow, R. J. *J. Org. Chem.* **1989**, *54*, 1990.

(6) Simons, J. H. *U.S. Pat.*, 2 500 388, May 14, 1950; *Chem. Abstr.* **1950**, *44*, 5236b.

(7) De, S. K.; Palit, S. R. *Adv. Fluorine Chem.* **1970**, *6*, 69.

(8) Elias, A. J.; Hope, H.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.* **1994**, *33*, 415.

(9) Ykman, P.; Hall, H. K., Jr. *J. Organomet. Chem.* **1976**, *116*, 153.

(10) Tietze, L. F.; Beller, M. *Liebigs Ann. Chem.* **1990**, 587.

(11) Patel, N. R.; Chen, J.; Zhang, Y. F.; Kirchmeier, R. L.; Shreeve, J. M. *Inorg. Chem.*, **1994**, *33*, 5463.

(12) Handy, L. B. *J. Fluorine Chem.* **1976**, *7*, 641.

(13) Jeanneaux, F.; Riess, J. G. *Tetrahedron Lett.* **1978**, *48*, 4845.

(14) Krolevets, A. A.; Prpov, A. G. *Zh. Obshch. Khim.* **1983**, *53*, 2646; *Chem. Abstr.* **1984**, *100*, 156701y.

(15) Darragh, J. I.; Hossain, S. F.; Sharp, D. W. A. *J. Chem. Soc., Dalton Trans.* **1975**, 218.

(16) Majid, A.; Sharp, D. W. A.; Winfield, J. M., Hanley, I. *J. Chem. Soc., Dalton Trans.* **1973**, 1876.

(17) Voronkov, M. G.; Dubinskaya, E. I., Pavlov, S. F.; Gorokhova, V. G. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1976**, 2355.

(18) Hauptschein, M.; Stokes, C. S.; Grosse, A. V. *J. Am. Chem. Soc.* **1952**, *74*, 1974.

(19) Banks, R. E.; Mullen, K. *J. Chem. Soc. C* **1967**, 2333.

(20) Scherer, O.; Millauer, H. *Ger. Offen*, 1 283 820, Nov. 28, 1968; *Chem. Abstr.* **1969**, *70*, 57134w.

(21) Scherer, O.; Millauer, H. *Ger. Offen*, 1 294 949, May 14, 1969; *Chem. Abstr.* **1969**, *71*, 49263t.

(22) Redwood, M. E.; Willis, C. J. *Can. J. Chem.* **1967**, *45*, 389.

(23) De Marco, R. A.; Couch, D. A.; Shreeve, J. M. *J. Org. Chem.* **1972**, *37*, 3332.

(24) Prakash, G. K. S.; Krishnamurti, R.; Olah, G. A. *J. Am. Chem. Soc.* **1989**, *111*, 393.

(25) Krishnamurti, R.; Bellew, D. R.; Prakash, G. K. S. *J. Org. Chem.* **1991**, *56*, 984.

(26) Stahly, G. P.; Bell, D. R. *J. Org. Chem.* **1989**, *54*, 2873.

(27) Kotum, S. P., Anderson, J. D. O.; DesMarteau, D. D. *J. Org. Chem.* **1992**, *57*, 1124.

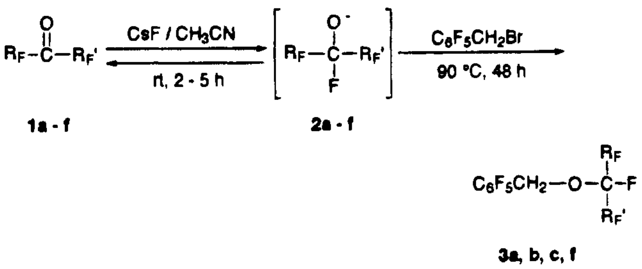
(28) Broicher, V.; Geffken, D. *Tetrahedron Lett.* **1989**, *30*, 5243.

(29) Patel, N. R.; Kirchmeier, R. L. *Inorg. Chem.* **1992**, *31*, 2537.

(30) Fujita, M.; Obayashi, M.; Hiyama, T. *Tetrahedron* **1988**, *44*, 4135.

0020-1669/95/1334-6085$09.00/0

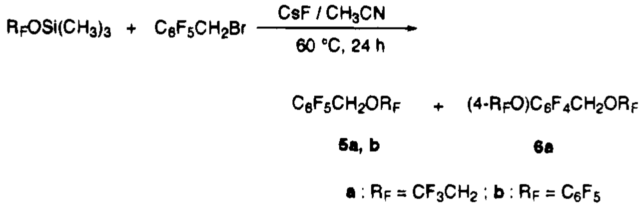
Table 1. Fluoride Ion Induced Perfluoroalkoxylation of Pentafluorobenzyl Bromide



carbonyl compounds	products (yields[a])
COF_2 (**1a**)	$C_6F_5CH_2OCF_3$ (**3a**, 55%)
$CF_3C(O)F$ (**1b**)	$C_6F_5CH_2OCF_2CF_3$ (**3b**, 46%[b]), $C_6F_5CH_2OC(O)CF_3$ (**4b**, 4.7%[b]), $C_6F_5CH_2F$ (3.4%)
$(CF_3)_2C{=}O$ (**1c**)	$C_6F_5CH_2OCF(CF_3)_2$ (**3c**, 82%)
$C_6F_5C(O)F$ (**1d**)	$C_6F_5CH_2OC(O)C_6F_5$ (**4d**, 3.1%[b]), $(C_6F_5)_2C{=}O$ (3.3%[b])
$(C_6F_5)C{=}O$ (**1e**)	recovery of starting material[c]
$(COF)_2$ (**1f**)	$C_6F_5CH_2OCF_2CF_2OCH_2C_6F_5$ (**3f**, 21%)

[a] Isolated yields based on $C_6F_5CH_2Br$. [b] Determined by ^1H and/or ^{19}F NMR. [c] Several fluorinated compounds also formed, of which structures are still under investigation.

Table 2. Reaction of (Polyfluoalkoxy)trimethylsilane with Pentafluorobenzyl Bromide



R_F (equiv)	yield[a] (%)	
	5	**6**
CF_3CH_2 (1.2)	33[b]	24[b]
CF_3CH_2 (2.5)		79
C_6F_5 (1.0)	45	
C_6H_5 (2.5)	72	

[a] Isolated yields based on $C_6F_5CH_2Br$. [b] Determined by ^1H NMR.

report nucleophlic reactions of $CF_3CH_2OSi(CH_3)_3$ with perfluorocarbonyl compounds.

Results and Discussion

Initially, we attempted reactions of CF_3OCs with heteroatom halides (e.g., $(CH_3)_3SiCl$, PCl_3, SF_5Cl, and $P_3N_3Cl_6$); however, the corresponding fluorides ($(CH_3)_3SiF$, PF_3, SF_6, and $P_3N_3F_6$[31]) were obtained instead of trifluoromethoxy heteroatom compounds. Similar reactions of CF_3OCs with perfluoroarenes, C_6F_6 and C_6F_5CN, resulted only in the recovery of starting materials. These results confirmed that α-fluorinated alkoxides ($R_FCF_2O^-$), such as CF_3OCs, are weak nucleophiles and that they readily release fluoride ion. Subsequently, we examined the reaction of perfluoroalkoxides with $C_6F_5CH_2Br$, which is an excellent electrophile because of resonance stabilization of the carbonium ion intermediate. After preparation of the perfluoroalkoxides by the reaction of $R_FC(O)R_F'$ (**1**, R_F, R_F' = F, CF_3, C_6F_5) with CsF at room temperature for 2 h, the resulting perfluoroalkoxides are combined with $C_6F_5CH_2Br$ at 90 °C for 48 h *in situ*.[32] The results are shown in Table 1. The perfluoroalkyl ethers $C_6F_5CH_2OCF_3$ (**3a**), $C_6F_5CH_2OC_2F_5$ (**3b**), and $C_6F_5CH_2OCF(CF_3)_2$ (**3c**) are formed in moderate yields. The products are purified by low temperature trap-to-trap distillation. Neither $C_6F_5C(O)F$ (**1d**) nor $(C_6F_5)_2CO$ (**1e**) gives $C_6F_5CH_2OCF_2C_6F_5$ or $C_6F_5CH_2OCF(C_6F_5)_2$, respectively. Only small amounts of fluorinated byproducts are formed. It is believed that the aromatic carbonyl compounds **1d** and **1e** have significant conjugation between the benzene ring and carboxyl group so that only small amounts of intermediates **2d** and **2e** exist in equilibrium between **1** and **2**. Although oxalyl fluoride $(COF)_2$ (**1f**) is an interesting carbonyl compound because of the two reaction sites no reports on the reaction of **1f** with organic halides appear with the exception of one with very reactive allyl bromide.[33] Interestingly, the reaction of **1f** with $C_6F_5CH_2Br$ gives the polyfluoro diether, $C_6F_5CH_2OCF_2CF_2OCH_2C_6F_5$ (**3f**), however, in lower yield (21%) than the perfluoroalkyl ethers **3a**–**3c**. This result suggests that the dianion $^-OCF_2CF_2O^-$ is rather unstable and of low reactivity when combined with organic halides, but $C_6F_5CH_2Br$ is reactive enough to give rise to the ether **3f**.

The siloxanes $CF_3CH_2OSi(CH_3)_3$ and $C_6F_5OSi(CH_3)_3$ are easily converted to the alkoxides $CF_3CH_2O^-$ and $C_6F_5O^-$ by reaction with fluoride ion. Reactions of $CF_3CH_2OSi(CH_3)_3$ and $C_6F_5OSi(CH_3)_3$ with $C_6F_5CH_2Br$ in the presence of CsF are performed at 60 °C and the results are shown in Table 2. When using 1.2 equiv of $CF_3CH_2OSi(CH_3)_3$, both the monosubstituted ether $C_6F_5CH_2OCH_2CF_3$ (**5a**) and the disubstituted ether $(4\text{-}CF_3CH_2O)C_6F_4CH_2OCH_2CF_3$ (**6a**) are obtained in 33% and 24%, yields, respectively. An excess (2.5 equiv) of $CF_3CH_2OSi(CH_3)_3$ results only in the formation of the disubstituted ether **6a** in 79% yield, while reactions of $C_6F_5OSi(CH_3)_3$ give only the monosubstituted ether $C_6F_5CH_2OC_6F_5$ (**5b**) even with an excess of 2.5 equiv of $C_6F_5OSi(CH_3)_3$.

We also prepared perfluoroalkoxides $(R_F)_2R_F'CO^-$ (**7**) by the reaction of perfluoroketones $(R_F)_2CO$ (R_F = CF_3, C_6F_5) with the trimethylsilyl reagents $CF_3Si(CH_3)_3$ and $C_6F_5Si(CH_3)_3$, and examined reactivities of these alkoxides with $C_6F_5CH_2Br$ *in situ*. The results are given in Table 3. The alkoxide $(CF_3)_3CO^-$ (**7a**), prepared from $(CF_3)_2CO$ and $CF_3Si(CH_3)_3$ at 60 °C in the presence of CsF, reacts readily with $C_6F_5CH_2Br$ at 90 °C to give $C_6F_5CH_2OC(CF_3)_3$ (**8a**) in 75% yield. Similarly reaction of $C_6F_5(CF_3)_2CO^-$ (**7b**), prepared from $(CF_3)_2CO$ and $C_6F_5Si(CH_3)_3$, provides $C_6F_5CH_2OC(CF_3)_2(C_6F_5)$ (**8b**) in somewhat lower yield (40%). To our knowledge, reactions of $CF_3CH_2OSi(CH_3)_3$ with ketones have not been reported previously. Nucleophilic attack of $CF_3CH_2OSi(CH_3)_3$ on $(CF_3)_2CO$ proceeds easily, and is followed by reaction with $C_6F_5CH_2Br$ to give $C_6F_5CH_2OC(CF_3)_2(OCH_2CF_3)$ (**8c**) in 89% yield. In the case of the addition of $C_6F_5OSi(CH_3)_3$ to $(CF_3)_2CO$, nucleophilic reaction with $C_6F_5CH_2Br$ is more preferable than the addition reaction and as a result $C_6F_5CH_2OC_6F_5$ (**5b**) is obtained in 36% yield. The existence of **5b** and the absence of the desired product, $C_6F_5CH_2OC(CF_3)_2(OC_6F_5)$, is proved by ^1H NMR, ^{19}F NMR, and MS spectral analyses.

Because of steric hinderance and the possiblity of nucleophilic attack on the ring, $(C_6F_5)_2CO$ shows different reactivities with silyl compounds compared with $(CF_3)_2CO$. The successive reaction of $(C_6F_5)_2CO$ with $CF_3Si(CH_3)_3$ and $C_6F_5CH_2Br$ at room temperature gives an unidentified complex mixture and a large amount of tar. When the addition is carried out at −30 °C for 30 min and then allowed to warm to room temperature for 5 h, the alkoxide that forms reacts with $C_6F_5CH_2Br$ *in situ*

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(31) Schmutzler, R. *Inorg. Synth.* **1967**, *9*, 75.

(32) Chen, L. F.; Mohtasham, J.; Gard, G. L. *J. Fluorine Chem.* **1990**, *46*, 21.

(33) Yamamoto, Y.; Koike, N.; Yoshida, A.; Takaai, T. *Jpn. Kokai Tokkyo Koho* JP 63 225 327 [88 225 337], Sep 20, 1988; *Chem. Abstr.* **1989**, *110*, 94512h.

Scheme 1

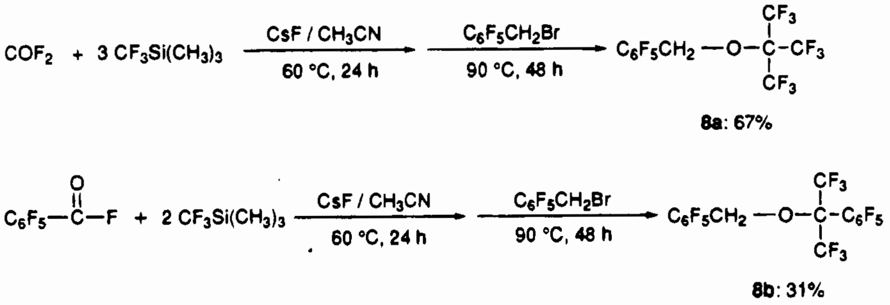
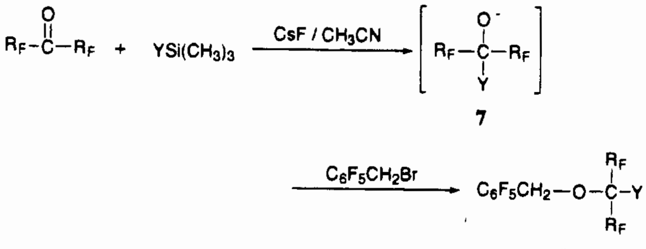


Table 3. Preparation and Reaction of Polyfluoroalkoxides Generated from Silyl Compounds and Perfluorocarbonyl Compounds



R_F	Y	products (yields[a])
CF_3	CF_3	$C_6F_5CH_2OC(CF_3)_3$ (**8a**, 75%)
CF_3	C_6F_5	$C_6F_5CH_2OC(CF_3)_2(C_6F_5)$ (**8b**, 40%)
CF_3	CF_3CH_2O	$C_6F_5CH_2OC(CF_3)_2(OCH_2CF_3)$ (**8c**, 89%)
CF_3	C_6F_5O	$C_6F_5CH_2OC_6F_5$ (**5b**, 34%[b]), $(C_6F_5CH_2O)_2C(CF_3)_2$ (**9**, 2.1%[b])
C_6F_5	CF_3	$C_6F_5CH_2OC(C_6F_5)_2(CF_3)$ (**8d**, 53%)
C_6F_5	C_6F_5	recovery of starting material[c]
C_6F_5	CF_3CH_2O	$CF_3CH_2OC_6F_4C(O)C_6F_5$ (**10**, 11%[d]), $[(4\text{-}CF_3CH_2O)C_6F_4]_2CO$ (**11**, 32%[d])

[a] Isolated yields based on $C_6F_5CH_2Br$. [b] Determined by ^1H NMR. [c] Although several fluorinated compounds also formed, there were no peaks in ^1H NMR assignable to $C_6F_5CH_2$. [d] Determined by ^{19}F NMR.

Table 4. Boiling and Melting Points of Polyfluoro Aromatic Ethers[a]

polyfluoroaryethers	bp (°C)[b]	mp (°C)
$C_6F_5CH_2OCF_3$ (**3a**)	143–144	
$C_6F_5CH_2OCF(CF_3)_2$ (**3c**)	162–163	
$C_6F_5CH_2OCH_2CF_3$ (**5a**)	159–160	
$(4\text{-}CF_3CH_2O)C_6F_4CH_2OCH_2CF_3$ (**6a**)	195–196	
$C_6F_5CH_2OC_6F_5$ (**5b**)	247–248	53–54
$C_6F_5CH_2OC(CF_3)_3$ (**8a**)	173–174	
$C_6F_5CH_2OC(CF_3)_2(C_6F_5)$ (**8b**)	260–261	61.5–62.5
$C_6F_5CH_2O(CF_3)_2(OCH_2CF_3)$ (**8c**)	197–198	
$C_6F_5CH_2OC(C_6F_5)_2(CF_3)$ (**8d**)	307–308[c]	73–74
$C_6F_5CH_2OCF_2CF_2OCH_2C_6F_5$ (**3f**)	277–278	80.5–81.5

[a] Presented values are not corrected. [b] Compounds were stable in air below boiling points otherwise noted. [c] Compound partly turned dark above 300 °C.

to give $C_6F_5CH_2OC(CF_3)(C_6F_5)_2$ (**8d**) in 53% yield. In the reaction of $C_6F_5Si(CH_3)_3$ with $(C_6F_5)_2CO$, most of the $(C_6F_5)_2CO$ is recovered and only small amounts of an unknown tarry product is obtained. The addition reaction of C_6F_5 to the carbonyl group is hindered by the presence of the two bulky C_6F_5 groups. The oxygen nucleophile $CF_3CH_2OSi(CH_3)_3$ attacks at the *para*-position of the C_6F_5 ring in $(C_6F_5)_2CO$ rather than at the carbonyl group. The analogous reaction of $CF_3CH_2OSi(CH_3)_3$ with $(C_6F_5)_2CO$ gives a mixture of the monosubstituted ether $(4\text{-}CF_3CH_2O)C_6F_4C(O)C_6F_5$ (**10**, 11%) and the disubstituted ether $[(4\text{-}CF_3CH_2O)C_6F_4]_2CO$ (**11**, 32%). Melting points and boiling points for several of the fluorinated ethers described above are given in Table 4.

Silyl compounds also react readily with $C_6F_5C(O)F$ and COF_2, in a 1:1, 1:2, or 1:3 mole ratio. A mixture of $C_6F_5C(O)F$ with 2 equiv of $CF_3Si(CH_3)_3$, similar to the reaction of $(CF_3)_2C{=}O$ with $C_6F_5Si(CH_3)_3$, reacts with $C_6F_5CH_2Br$ to give $C_6F_5CH_2OC(CF_3)_2(C_6F_5)$ (**8b**) in 31% yield. Further, COF_2 reacts with 3 equiv of $CF_3Si(CH_3)_3$, and successively *in situ* with $C_6F_5CH_2Br$ to give $C_6F_5CH_2OC(CF_3)_3$ (**8a**) in 67% yield (Scheme 1). Neither $C_6F_5CH_2OCF(CF_3)(C_6F_5)$ nor $C_6F_5CH_2OCF_2CF_3$, which would form if only 1 equiv of the silyl compound reacts, is detectable by ^1H or ^{19}F NMR spectra.

The reaction of $CF_3CH_2OSi(CH_3)_3$ with the acyl fluorides $CF_3C(O)F$ and $C_6F_5C(O)F$ are performed for the purpose of preparing the polyfluoroaryl ethers $C_6F_5CH_2OCR_F(OCH_2CF_3)_2$ (R_F = CF_3, C_6F_5) (Scheme 2). The successive reaction of $CF_3C(O)F$ with $CF_3CH_2OSi(CH_3)_3$ and $C_6F_5CH_2Br$ gives $C_6F_5CH_2OC(CF_3)(OCH_2CF_3)_2$ (**12**) and $(4\text{-}CF_3CH_2O)C_6F_4CH_2OC(CF_3)(OCH_2CF_3)_2$ (**13**) only in 4.0% and 3.9% yields, respectively. Because of the very low yields, these polyfluoroaryl ethers (**12 and 13**) could not be isolated from the main product, $(4\text{-}CF_3CH_2O)C_6F_4CH_2OCH_2CF_3$ (**6a**, 21%), formed by reaction of $C_6F_5CH_2Br$ with unreacted $CF_3CH_2OSi(CH_3)_3$. In the reaction of $C_6F_5C(O)F$ with $CF_3CH_2OSi(CH_3)_3$, as in the reaction of $CF_3CH_2OSi(CH_3)_3$ with $(C_6F_5)_2CO$, nucleophilic attack on the benzene ring is predominant, rather than at the carbonyl group. This gives a mixture of $(4\text{-}CF_3CH_2O)C_6F_4C(O)OCH_2CF_3$ (**14**) and $(2,4\text{-}CF_3CH_2O)_2C_6F_3C(O)OCH_2CF_3$ (**15**) in 67% and 11% yields, respectively.

In the reaction of COF_2 with $CF_3CH_2OSi(CH_3)_3$ and $C_6F_5CH_2Br$, two $CF_3CH_2OSi(CH_3)_3$ molecules react with one COF_2 molecule to give $(CF_3CH_2O)_2CO$[34] in 44% yield. Also formed in this reaction are $C_6F_5CH_2F$ (23%), $C_6F_5CH_2OCH_2CF_3$ (**5a**, 29%) and $(4\text{-}CF_3CH_2O)C_6F_4CH_2OCH_2CF_3$ (**6a**, 25%) (Scheme 3), which are obtained by reaction of $C_6F_5CH_2Br$ with excess CsF and $CF_3CH_2OSi(CH_3)_3$, respectively.

In order to investigate the influence of the CF_3CH_2O group on the stability of the alkoxide intermediate, reactions of $(CF_3CH_2O)_2CO$ with silyl compounds were carried out. Reaction of $(CF_3CH_2O)_2CO$ with $CF_3Si(CH_3)_3$ and $C_6F_5CH_2Br$ gives a 53% yield of $C_6F_5CH_2OC(CF_3)_2(OCH_2CF_3)$ (**8c**), 14% $C_6F_5CH_2OCH_2CF_3$ (**5a**), and $(4\text{-}CF_3CH_2O)C_6F_4CH_2OCH_2CF_3$ (**6a**) in 15% yield, instead of the expected product $C_6F_5CH_2OC(CF_3)(OCH_2CF_3)_2$. On the other hand, the reaction of $(CF_3CH_2O)_2CO$ with $C_6F_5Si(CH_3)_3$ and $C_6F_5CH_2Br$ results in the formation of $(4\text{-}CF_3CH_2O)C_6F_4C(O)OCH_2CF_3$ (**14**) in 27% yield and unknown fluorinated products. Plausible mechanisms for these reactions are given in Scheme 4. The silyl compounds $CF_3Si(CH_3)_3$ and $C_6F_5Si(CH_3)_3$ add to $(CF_3CH_2O)_2CO$ to give the intermediates $(CF_3)(CF_3CH_2O)_2CO^-$ (**16**) and $(C_6F_5)(CF_3CH_2O)_2CO^-$ (**18**) in the presence of CsF. These two intermedi-

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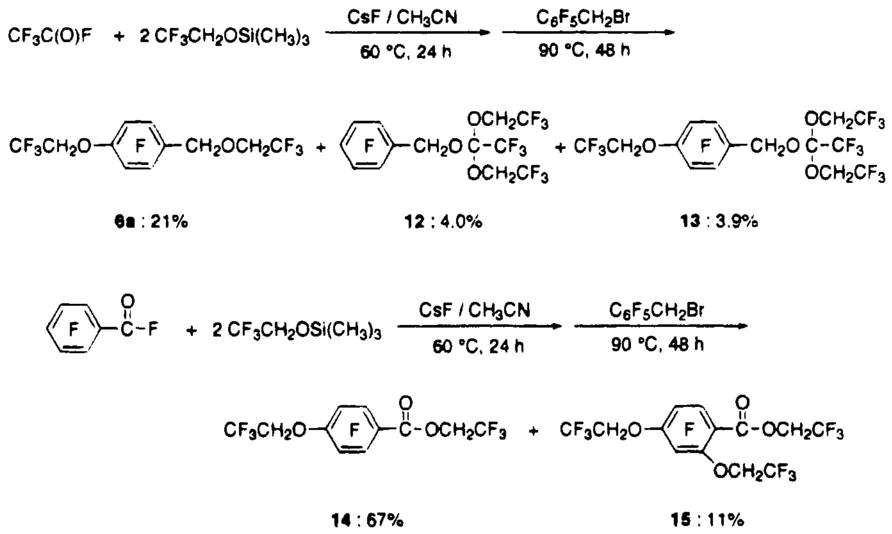
(34) Krespan, C. G.; Smart, B. E. *J. Org. Chem.* **1986**, *51*, 320.

Scheme 2



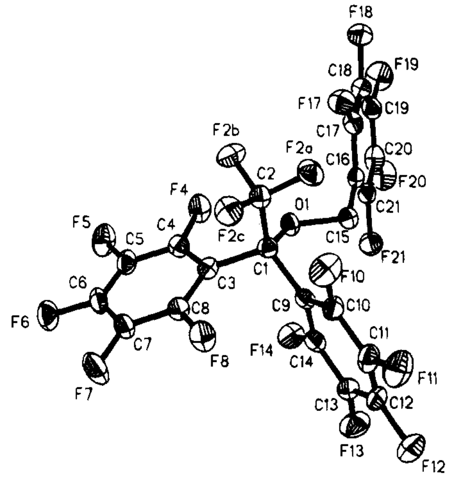


Figure 1. Molecular structure of $C_6F_5CH_2OC(C_6F_5)_2(CF_3)$ (**8d**) with thermal ellipsoids at 30% probability.

Scheme 3

$$COF_2 + 3\ CF_3CH_2OSi(CH_3)_3 \xrightarrow[60\ °C,\ 24\ h]{CsF\ /\ CH_3CN} \xrightarrow[90\ °C,\ 48\ h]{C_6F_5CH_2Br}$$

$$\underset{44\%}{(CF_3CH_2O)_2CO} + \underset{23\%}{C_6F_5CH_2F} + \underset{\mathbf{5a}:\ 29\%}{C_6F_5CH_2OCH_2CF_3} +$$

$$\underset{\mathbf{6a}:\ 25\%}{(4\text{-}CF_3CH_2O)C_6F_4CH_2OCH_2CF_3}$$

ates **16** and **18** readily release $CF_3CH_2O^-$ anion to give esters $CF_3C(O)OCH_2CF_3$ (**17**) and $C_6F_5C(O)OCH_2CF_3$ (**19**), respectively. In the former case, additional $CF_3Si(CH_3)_3$ reacts with ester **17** to give $CF_3CH_2O(CF_3)CO^-$ (**7c**) which then reacts with $C_6F_5CH_2Br$ to give $C_6F_5CH_2OC(CF_3)_3(OCH_2CF_3)$ (**8c**). The ethers **5a** and **6a** are obtained by the reaction of $C_6F_5CH_2Br$ with the loss of the $CF_3CH_2O^-$ anion. In the latter case, the $CF_3CH_2O^-$ eliminated attacks at the *para* ring position of ester **19** to give the diether **8c**. Consequently, in the reaction of COF_2 with $CF_3CH_2OSi(CH_3)_3$, even if $(CF_3CH_2O)_3CO^-$ (**20**) is formed, the anion **20** is not stable enough to react with $C_6F_5CH_2Br$ but, instead, gives $(CF_3CH_2O)_2CO$ by elimination of $CF_3CH_2OSi(CH_3)_3$.

The molecular structure of $C_6F_5CH_2OC(CF_3)(C_6F_5)_2$ (**8d**) obtained by X-ray crystallographic analysis is shown in Figure 1 together with the atomic numbering scheme. Some selected bond lengths, bond angles, and torsion angles are listed in Table 6. As a consequence of steric crowding on C1, the C_{sp^2}-C_{sp^3} bonds i.e., C1–C3 and C1–C9, are elongated to a value of ~1.537 Å, which is longer than the corresponding C15–C16 distance of 1.496 Å but similar to the C_{sp^3}-C_{sp^3} distance in C1–C2 of 1.539(8) Å. The C–O bond distance found in the structure of $C_6F_5CH_2OC(CF_3)(C_6F_5)_2$ is quite similar to that reported for a structure containing a similar nonfluorinated benzyl–O– fragment (1.437 Å).[35] These C–O distances are, however, longer than those calculated theoretically for perfluorinated ethers. Surprisingly, the trifluoromethyl group shows no disorder in the molecular structure of **8d**. This can be explained by considering the Newman projection along the C1–C2 axis (Figure 2). It is clear that the molecule adopts a staggered conformation with the two *gem*-pentafluorophenyl groups on C1 positioned almost perpendicular to each other (84.6°). X-ray diffraction studies of monofluoro-substituted mandelic acids[36] reveal that attractive electrostatic interactions between carbon and fluorine atoms in the case of these *o*- and

Table 5. X-ray Crystallographic Data/Parameters for $C_6F_5CH_2OC(C_6F_5)_2(CF_3)$ (**8d**)

empirical formula	$C_{21}H_2F_{18}O$
cryst size (mm)	0.25 × 0.20 × 0.20
fw	612.2
color, habit	colorless, chunk
cryst syst	monoclinic
space group	$P2_1/c$
unit cell dimens	a = 15.770 (2) Å; b = 15.363 (3) Å; c = 8.525 (2) Å; β = 95.610 (2)°
volume (Å³)	2055.5 (6) Å³
Z	4
ρ_{calc} (g cm⁻³)	1.978
absorption coeff (mm⁻¹)	0.234
2θ range (deg)	3.5–45.0
no. of data collcd	3602
no. of unique data	2675 (R_{int} = 6.32%)
no. of data with $F > 2.5\ \sigma(F)$	1772
weighting scheme $w^{-1} = \sigma^2(F) + xF^2$	x = 0.0005
no. of param refined	367
final R indices (%)	R = 5.73; R_w = 5.51
goodness-of-fit	1.17
largest and mean Δ/σ	0.001, 0.000
largest difference peak/hole e Å⁻³	0.57/–0.38

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(35) Vitagliano, L.; Zagart, A.; Capasso, S. *Acta Crystallogr.* **1994**, *C50*, 1135.

(36) Larsen, S.; Marthi, K. *Acta Crystallogr.* **1994**, *B50*, 373.

Scheme 4

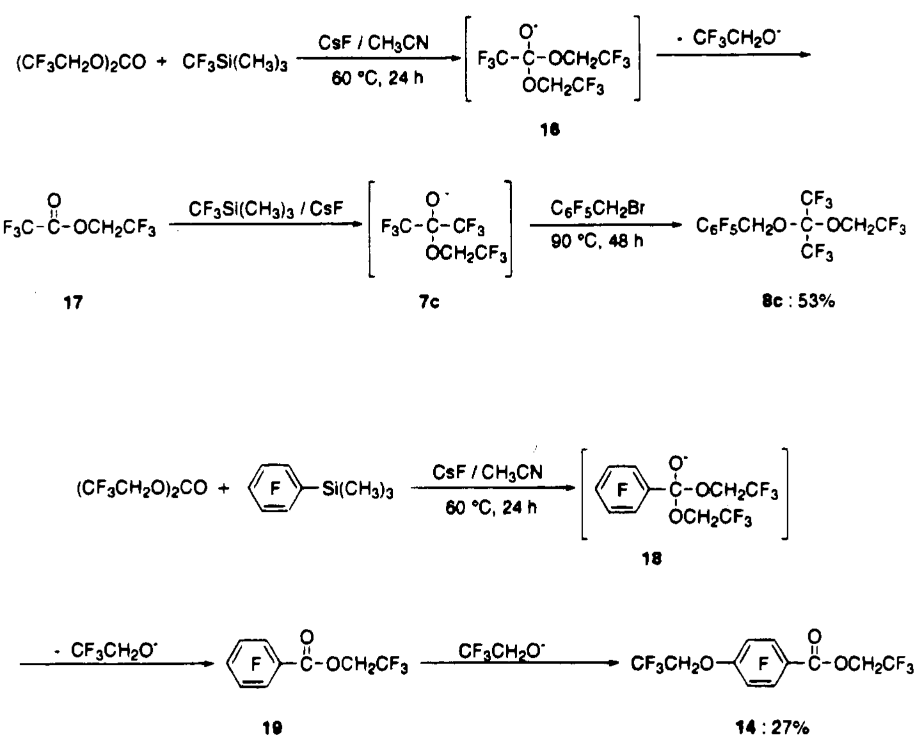

Table 6. Selected Bond Lengths (Å), Bond Angles (deg) and Torsion Angles (deg) for $C_6F_5CH_2OC(C_6F_5)_2(CF_3)$ (**8d**) with Esds in Parentheses

	Bond Lengths		
C1–O1	1.411(7)	C15–O1	1.440(8)
C1–C2	1.539(8)	C1–C3	1.538(8)
C1–C9	1.535(7)	C15–C16	1.496(9)
	Bond Angles		
C1–O1–C15	119.3(4)	O1–C1–C9	109.7(4)
O1–C1–C3	107.3(4)	C9–C1–C3	110.8(4)
O1–C1–C2	106.6(4)	C9–C1–C2	116.0(5)
C3–C1–C2	105.9(4)	O1–C15–C16	107.2(5)
	Torsion Angles		
O1–C1–C2–F2c	170.4(4)	C9–C1–C2–F2c	−67.4(5)
C3–C1–C2–F2c	56.2(2)	O1–C1–C2–F2a	−65.8(5)
C9–C1–C2–F2a	56.5(6)	C3–C1–C2–F2a	180.0(4)
O1–C1–C2–F2b	52.3(5)	C9–C1–C2–F2b	174.6(4)
C3–C1–C2–F2b	−61.9(5)		

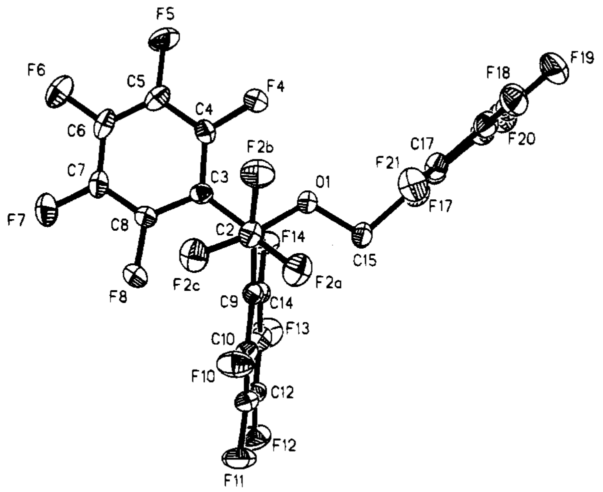

Figure 2. Newman projection along the C1–C2 axis (looking down the C2–C1 bond) showing the staggered conformation of $C_6F_5CH_2OC(C_6F_5)_2(CF_3)$.

p-substituted acids result in higher melting entropy and enthalpy vis-a-vis the *m*-derivative. A C···F intramolecular van der Waals contact between C2···F10 (2.775(7) Å) is much shorter than the sum of the van der Waals radii for carbon (1.77 Å)[37] and fluorine (1.47 Å).[37] This contact bisects the angle F2a–C2–F2c almost equally with angles F10–C2–F2a and F10–C2–F2c at 66.4 and 67.2°, respectively, and F2b is positioned at a maximum distance from F10. Furthermore, there are two van der Waals F···F contacts between F10···F2a (2.552 (5) Å) and F10···F2c (2.571 (5) Å) which also help "lock" the trifluoromethyl group.

The crystal structure of $C_6F_5CH_2OC(CF_3)(C_6F_5)_2$ shows no long range H··· F or H··· O interactions. However, there are numerous C···F and F···F van der Waals interactions. The packing diagram (Figure 3) shows some of these interactions which lie in the range 2.817–2.880 Å, leading to the formation of a layered structure. Intermolecular repulsions are reduced by twisting of the $C_6F_5CH_2O$ groups belonging to adjacent molecules to positions where they are nearly perpendicular to each other (82.3°).

Experimental Section

Materials. The silanes $CF_3Si(CH_3)_3$ and $C_6F_5Si(CH_3)_3$ are prepared by the reaction of the corresponding bromides with $(CH_3)_3SiCl$ and hexaethylphosphorous triamide (HEPT) in C_6H_5CN.[25,29] The siloxanes $CF_3CH_2OSi(CH_3)_3$ and $C_6F_5OSi(CH_3)_3$ are prepared by the reaction of the corresponding alcohols with $[(CH_3)_3Si]_2NH$ in the presence of saccharin as catalyst.[8] The fluorocarbonate $(CF_3CH_2O)_2CO$ is prepared by the reaction of COF_2 with $CF_3CH_2OSi(CH_3)_3$. The acyl fluorides $CF_3C(O)F$ and $C_6F_5C(O)F$ are prepared by the reaction of the corresponding acyl chloride with CsF in the absence of solvent. All other materials are purchased as indicated: $C_6F_5CH_2Br$, C_6F_5Br, CF_3Br, COF_2, $(COF)_2$, $CF_3C(O)Cl$, $C_6F_5C(O)Cl$ (PCR); $(C_6F_5)_2CO$ (Aldrich); $(CF_3)_2CO$ (Daikin Chemicals). The solvent CH_3CN is dried over P_4O_{10} and distilled prior to use according to standard procedures.

General Procedure. The reaction vessel for each run consists of a 100 mL Pyrex-glass flask equipped with a Teflon stopcock and a

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(37) Bondi, A. *J. Chem. Phys.* **1964**, *68*, 441.

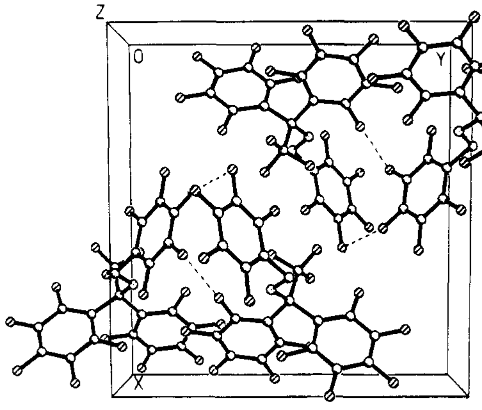

Figure 3. Crystal packing diagram of $C_6F_5CH_2OC(C_6F_5)_2(CF_3)$ showing some intermolecular F−F van der Waals contacts (view along *c* axis).

Teflon-covered stirring bar. Gases and volatile liquids are handled in a conventional Pyrex glass vacuum system equipped with a Heise-Bourdon tube gauge and a Televac thermocouple gauge. Volatile compounds are measured quantitatively by using PVT techniques. Infrared spectra are recorded with a Perkin-Elmer Model 1710 FT-IR spectrometer using KBr disks. ^1H and ^{19}F NMR spectra are obtained with a Bruker AC 200/300 FT-NMR spectrometer by using dry $CDCl_3$ as a solvent. Chemical shifts are referenced to $(CH_3)_4Si$ (^1H) or $CFCl_3$ (^{19}F). Mass spectra are obtained on a Varian VG 7070 HS mass spectrometer. Elemental analyses are performed by Beller Microanalytisches Laboratorium, Göttingen, Germany.

Preparation of $C_6F_5CH_2OCF_3$ (3a). Into a 100 mL reaction vessel is added 0.91 g (6.0 mmol) of dried CsF; 0.40 g (6.0 mmol) of COF_2 and 5 mL of CH_3CN are vacuum transferred into the reaction vessel at −196 °C. After the reaction mixture is stirred at room temperature for 2 h, a clear solution is obtained. The vessel is cooled to −196 °C and 1.04 g (4.0 mmol) of $C_6F_5CH_2Br$ is added under nitrogen. The reaction mixture is heated at 90 °C for 48 h. The product is collected in a trap cooled at −40 °C. It is obtained in 55% yield as a clear liquid. Spectral data are as follows. IR (neat) (cm^{-1}): 1661 m, 1527 s, 1514 vs, 1474 w, 1438 w, 1408 w, 1320 s, 1272 vs, 1224 s, 1160 s, 1059 s, 978 m, 938 s, 879 w, 839 w, 753 w. ^1H NMR: δ 5.80 (s). ^{19}F NMR: δ −61.9 (3F, s, CF_3), −142.5 (2F, m, *o*-C_6F_5), −151.2 (1F, m, *p*-C_6F_5), −161.7 (2F, m, *m*-C_6F_5). MS (EI, 70 eV) [*m/e* (species) intensity]: 266 (M^+) 46; 181 ($M^+ - OCF_3$) 100.

Preparation of $C_6F_5CH_2OCF_2CF_3$ (3b). In a similar procedure to that described for compound **3a**, 0.30 g (2.6 mmol) of $CF_3C(O)F$, 0.40 g (2.6 mmol) of dried CsF, 3 mL of CH_3CN, and 0.57 g (2.2 mmol) of $C_6F_5CH_2Br$ are reacted at room temperature for 2 h and then at 90 °C for 48 h. The product is collected in a trap cooled at −40 °C. Compound **3b** is obtained in 46% yield accompanied with 3.4% of $C_6F_5CH_2F$[38] and 4.7% of $C_6F_5CH_2OC(O)CF_3$ (**4b**).[39] These two impurities could not be removed from compound **3b** completely, and their structures are confirmed by ^1H NMR, ^{19}F NMR, and MS. Spectral data of compound **3b** are as follows. IR (neat) (cm^{-1}): 1660 m, 1511 vs, 1318 s, 1219 vs, 1106 s, 1055 s, 991 m, 938 s. ^1H NMR: δ 5.15 (s). ^{19}F NMR: δ −86.8 (3F, s, CF_3), −92.2 (2F, s, CF_2), −142.7 (2F, m, *o*-C_6F_5), −151.4 (1F, m, *p*-C_6F_5), −161.7 (2F, m, *m*-C_6F_5). MS (EI, 70 eV) [*m/e* (species) intensity]: 316 (M^+) 17; 181 ($M^+ - OCF_2CF_3$) 100. Spectral data of compound **4b** are as follows. IR (neat) (cm^{-1}): 1797 s. ^1H NMR: δ 5.58 (s). ^{19}F NMR: δ −75.6 (3F, s, CF_3), −142.2 (2F, m, *o*-C_6F_5), −154.3 (1F, m, *p*-C_6F_5), −162.2 (2F, m, *m*-C_6F_5). MS (EI, 70 eV) [*m/e* (species) intensity]: 294 (M^+) 1.

Preparation of $C_6F_5CH_2OCF(CF_3)_2$ (3c). In a manner similar to that for compound **3a**, 0.60 g (3.6 mmol) of $(CF_3)_2CO$, 0.55 g (3.6 mmol) of dried CsF, 5 mL of CH_3CN, and 0.78 g (3.0 mmol) of $C_6F_5CH_2Br$ are reacted at room temperature for 2 h and then at 90 °C for 48 h. With heating, the reaction mixture is passed through a U-trap cooled at −20 °C to give compound **3c** in 82% yield as a clear liquid. Spectral data are as follows. IR (neat) (cm^{-1}): 1661 m, 1515 vs, 1438 w, 1405 w, 1318 m, 1238 vs, 1176 s, 1138 w, 1114 w, 1056 m, 1007 s, 938 s, 733 m. ^1H NMR: δ 5.11 (s). ^{19}F NMR: δ −79.7 (6F, s, CF_3), −143.0 (2F, m, *o*-C_6F_5), −144.8 (1F, s, CF), −151.4 (1F, m, *p*-C_6F_5), −161.6 (2F, m, *m*-C_6F_5). MS (EI, 70 eV) [*m/e* (species) intensity]: 366 (M^+) 29; 181 ($M^+ - OCF(CF_3)_2$) 100.

Reaction of $C_6F_5C(O)F/CsF$ with $C_6F_5CH_2Br$. In a procedure similar to that for compound **3a**, 0.54 g (2.5 mmol) of $C_6F_5C(O)F$, 0.38 g (2.5 mmol) of dried CsF, 3 mL of CH_3CN, and 0.65 g (2.5 mmol) of $C_6F_5CH_2Br$ are reacted at room temperature for 5 h and then at 90 °C for 48 h. A white precipitate is removed by decantation and extracted with ether (20 mL × 2). The collected organic layer is evaporated and distilled in a glass tube oven to give 3.3% of $(C_6F_5)_2CO$ and 3.1% of $C_6F_5C(O)OCH_2C_6F_5$ (**4d**), structures of which are proven by ^1H NMR, ^{19}F NMR, and MS. Spectral data of **4d** are as follows. IR (neat) (cm^{-1}): 1749 s, 1500 vs, 1424 w, 1331 s, 1217 s, 1135 m, 1058 w, 941 m. ^1H NMR: δ 5.47 (s). ^{19}F NMR: δ −137.8 (2F, m, *o*-C_6F_5), −141.8 (2F, m, *o*-C_6F_5), −147.6 (1F, m, *p*-C_6F_5), −151.8 (1F, m, *p*-C_6F_5), −160.4 (2F, m, *m*-C_6F_5), −161.5 (2F, m, *m*-C_6F_5). MS (EI, 70 eV) [*m/e* (species) intensity]: 392 (M^+) 31.

Preparation of $C_6F_5CH_2OCF_2CF_2OCH_2C_6F_5$ (3f). In a similar procedure to that for compound **3a**, 0.14 g (1.5 mmol) of $(COF)_2$, 0.46 g (3.0 mmol) of dried CsF, 3 mL of CH_3CN, and 0.78 g (3.0 mmol) of $C_6F_5CH_2Br$ are reacted at room temperature for 5 h and then at 90 °C for 48 h. The reaction mixture is poured into water and extracted with ether (20 mL × 2). The organic layer is washed and dried over Na_2SO_4 and then evaporated to give compound **3f** as white needles in 21% yield (recrystallized from hexane/ether solution). Spectral data are as follows. IR (Nujol) (cm^{-1}): 1660 m, 1529 s, 1506 vs, 1403 w, 1319 s, 1306 s, 1275 m, 1228 s, 1185 m, 1138 m, 1123 s, 1102 s, 1083 s, 1050 vs, 980 m, 931 vs, 909 m, 780 w, 747 w. ^1H NMR: δ 5.07 (s). ^{19}F NMR: δ −91.7 (4F, s, CF_2), −142.4 (2F, m, *o*-C_6F_5), −151.6 (1F, m, *p*-C_6F_5), −161.6 (2F, m, *m*-C_6F_5). MS (EI, 70 eV) [*m/e* (species) intensity]: 494 (M^+) 5; 313 ($M^+ - CH_2C_6F_5$) 20; 197 ($C_6F_5CH_2O^+$) 6; 181 ($C_6F_5CH_2^+$) 100. Anal. Calcd for $C_{16}H_4F_{14}O_2$: C, 38.89; H, 0.82; F, 53.82. Found: C, 39.18; H, 0.90; F, 53.5.

Preparation of $C_6F_5CH_2OCH_2CF_3$ (5a) and $(4\text{-}CF_3CH_2O)\text{-}C_6F_4CH_2OCH_2CF_3$ (6a). Into a 100 mL reaction vessel are added, 0.55 g (3.6 mmol) of dried CsF, 3 mL of CH_3CN, and 0.78 g (3.0 mmol) of $C_6F_5CH_2Br$, and 1.00g (3.6 mmol) of $CF_3CH_2OSi(CH_3)_3$ is vacuum transferred into the reaction vessel at −196 °C. The reaction vessel is heated at 60 °C for 24 h. The reaction mixture is separated by trap-to-trap distillation to give compound **5a** (clear liquid, 33% yield) in a trap cooled at −30 °C. The residual material is poured into water and extracted with ether (20 mL × 2). The organic layer is washed and dried over Na_2SO_4, and then distilled in a glass tube oven to give compound **6a** (clear liquid, 24% yield). A similar reaction of 0.86 g (5.0 mmol) of $CF_3CH_2OSi(CH_3)_3$, 0.76g (5.0 mmol) of dried CsF, and 5 mL of CH_3CN with 0.52 g (2.0 mmol) of $C_6F_5CH_2Br$ gives only compound **6a** in 72% yield. Spectral data of **5a** are as follows. IR (neat) (cm^{-1}): 2949 w, 1658 s, 1526 vs, 1510 vs, 1436 w, 1416 w, 1383 w, 1282 vs, 1171 vs, 1137 vs, 1058 s, 978 s, 938 s, 851 w, 830 m, 760 w, 685 m, 660 m. ^1H NMR: δ 3.88 (2H, q, $J = 8.5$ Hz, CF_3CH_2), 4.60 (2H, s, $C_6F_5CH_2$). ^{19}F NMR: δ −74.5 (3F, br s, CF_3), −142.9 (2F, m, *o*-C_6F_5), −152.6 (1F, m, *p*-C_6F_5), −161.6 (2F, m, *m*-C_6F_5). MS (EI, 70 eV) [*m/e* (species) intensity]: 280 (M^+) 15; 181 ($M^+ - OCH_2CF_3$) 100. Spectral data of **6a** are as follows. IR (neat) (cm^{-1}): 2970 w, 1656 s, 1505 vs, 1460 m, 1447 w, 1433 m, 1416 m, 1377 m, 1278 vs, 1180 vs, 1057 s, 975 s, 933 s, 852 m, 832 m, 763 w, 664 m. ^1H NMR: δ 3.87 (2H, q, $J = 8.5$ Hz, CF_3CH_2), 4.47 (2H, m, CF_3CH_2), 4.74 (2H, s, $C_6F_5CH_2$). ^{19}F NMR: δ −74.6 (3F, br s, CF_3), −75.4 (3F, br s, CF_3), −143.7 (2F, m, *o*-C_6F_5), −156.6 (2F, m, *m*-C_6F_5). MS (EI, 70 eV) [*m/e* (species) intensity]: 360 (M^+) 23; 341 ($M^+ - F$) 5; 277 ($M^+ - CH_2CF_3$) 11, 260 ($M^+ - OCH_2CF_3$) 100.

Preparation of $C_6F_5CH_2OC_6F_5$ (5b). In a procedure similar to that for compound **5a**, 1.28 g (5.0 mmol) of $C_6F_5OSi(CH_3)_3$, 0.76 g (5.0 mmol) of dried CsF, 5 mL of CH_3CN, and 0.52 g (2.0 mmol) of $C_6F_5CH_2Br$ are reacted at 60 °C for 24 h. The reaction mixture is poured into water and extracted with ether (20 mL × 2). The organic layer is washed and dried over Na_2SO_4, and evaporated to give a light orange solid. The crude solid is distilled in a glass tube oven to give compound

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(38) Olah, G. A.; Comisarow, M. B. *J. Am. Chem. Soc.* **1969**, *91*, 2955.

(39) Claussen, U.; Kroeck, F. W.; Oeller, M.; Rudolph, H.; Renner, O.; Kops, E. F. *Ger. Offen.* DE 3 526 235, May 22, 1986; *Chem. Abstr.* **1987**, *106*, P41721m.

5b in 79% yield as white plates (recrystallized from hexane/ether solution). Spectral data are as follows. IR (neat) (cm^{-1}): 1660 m, 1516 vs, 1377 m, 1317 w, 1149 m, 1131 s, 1060 m, 1029 s, 1015 w, 999 s, 927 w, 938 s, 916 w, 773 w. ^1H NMR: δ 5.25 (s). ^{19}F NMR: δ −142.4 (2F, m), −150.9 (1F, m), −156.1 (2F, m), −161.1 (3F, m), −162.3 (2F, m). MS (EI, 70 eV) [*m/e* (species) intensity]: 364 (M^+) 3; 345 ($M^+ - F$) 6; 197 ($M^+ - C_6F_5$) 15; 184 ($M^+ - CH_2C_6F_5$) 23; 181 ($M^+ - OC_6F_5$) 100.

Preparation of $C_6F_5CH_2OC(CF_3)_3$ (8a). Into a 100 mL reaction vessel is added, 0.55 g (3.6 mmol) of dried CsF, and 0.50 g (3.0 mmol) of $(CF_3)_2CO$, 0.43 g (3.0 mmol) of $CF_3Si(CH_3)_3$, and 5 mL of CH_3CN are vacuum transferred into the reaction vessel at −196 °C. The reaction mixture is stirred for 20 h at 60 °C. The vessel is cooled to −196 °C, and 0.78 g (3 mmol) of $C_6F_5CH_2Br$ is added under nitrogen and the mixture is heated at 90 °C for 48 h. With heating, the reaction mixture is passed through a U-trap cooled at −20 °C to give compound **8a** in 75% yield as a clear liquid. This compound is also obtained in 67% yield by the reaction of 0.11 g (1.7 mmol) of COF_2, 0.75 g (5.3 mmol) of $CF_3Si(CH_3)_3$, 0.81 g (5.3 mmol) of dried CsF, and 0.44 g (1.7 mmol) of $C_6F_5CH_2Br$ in a procedure similar to that described above. Spectral data are as follows. IR (neat) (cm^{-1}): 1661 m, 1511 vs, 1479 w, 1406 w, 1255 vs, 1181 m, 1148 vs, 1056 s, 1017 s, 975 s, 939 s, 785 m, 736 s, 728 s. ^1H NMR: δ 5.15 (s). ^{19}F NMR: δ −70.8 (9F, s, CF_3), −143.2 (2F, m, *o*-C_6F_5), −151.6 (1F, m, *p*-C_6F_5), −161.8 (2F, m, *m*-C_6F_5). MS (EI, 70 eV) [*m/e* (species) intensity]: 416 (M^+) 11; 181 ($M^+ - OC(CF_3)_3$) 100. Anal. Calcd for $C_{11}H_2F_{14}O$: C, 31.75; H, 0.49; F, 63.92. Found: C, 32.47; H, 0.62; F, 63.3.

Preparation of $C_6F_5CH_2OC(CF_3)_2(C_6F_5)$ (8b). In a procedure similar to that for compound **8a**, 0.22g (1.3 mmol) of $(CF_3)_2CO$, 0.31 g (1.3 mmol) of $C_6F_5Si(CH_3)_3$ in C_6H_5CN solution, 0.24 g (1.6 mmol) of dried CsF, 2 mL of CH_3CN, and 0.34 g (1.3 mmol) of $C_6F_5CH_2Br$ are reacted at 60 °C for 12 h and then at 90 °C for 48 h. The reaction mixture is poured into water and extracted with ether (20 mL × 2). The organic layer is washed and dried over Na_2SO_4, and evaporated and distilled in a glass tube oven at 70−80 °C. Silica gel chromatography of the resulting light yellow liquid (eluent: petroleum ether) gives compound **8b** in 40% yield as white needles (recrystallized from warm hexane solution). This compound is also formed in 31% yield by the reaction of 0.43 g (2.0 mmol) of $C_6F_5C(O)F$, 0.57 g (4.0 mmol) of $CF_3Si(CH_3)_3$, 0.73 g (4.8 mmol) of dried CsF, and 0.52 g (2.0 mmol) of $C_6F_5CH_2Br$ in a procedure similar to that described above. Spectral data are as follows. IR (neat) (cm^{-1}): 1658 m, 1510 vs, 1396 m, 1312 w, 1286 m, 1252 s, 1224 vs, 1154 m, 1143 m, 1117 m, 1054 m, 1025 m, 971 s, 937 s, 818 m, 747 w, 731 m, 719 m. ^1H NMR: δ 4.75 (s). ^{19}F NMR: δ −71.9 (6F, m, CF_3), −133.9 (2F, br s, *o*-C_6F_5), −142.3 (2F, m, *o*-C_6F_5), −147.0 (1F, m, *p*-C_6F_5), −151.5 (1F, m, *p*-C_6F_5), −159.0 (2F, m, *m*-C_6F_5), −161.5 (2F, m, *m*-C_6F_5). MS (EI, 70 eV) [*m/e* (species) intensity]: 514 (M^+) 5; 181 ($M^+ - OC(CF_3)_2(C_6F_5)$) 100. Anal. Calcd for $C_{16}H_2F_{16}O$: C, 37.38; H, 0.39; F, 59.12. Found: C, 37.49, H, 0.38, F, 59.2.

Preparation of $C_6F_5CH_2OC(CF_3)_2(OCH_2CF_3)$ (8c). In a procedure similar to that for compound **8a**, 0.50 g (3.0 mmol) of $(CF_3)_2CO$, 0.52 g (3.6 mmol) of $CF_3CH_2OSi(CH_3)_3$, 0.55 g (3.6 mmol) of dried CsF, 5 mL of CH_3CN, and 0.78 g (3.0 mmol) of $C_6F_5CH_2Br$ are reacted at 60 °C for 12 h and then at 90 °C for 48 h. With heating, the reaction mixture was passed through a U-trap cooled at −20 °C to give compound **8c** in 89% yield as a clear liquid. Spectral data are as follows. IR (neat) (cm^{-1}): 2977 w, 1661 m, 1515 vs, 1431 w, 1403 m, 1305 vs, 1230 vs, 1181 vs, 1132 vs, 1055 s, 1003 m, 986 m, 971 m, 939 s, 859 m, 808 w, 754 w, 735 s, 689 m. ^1H NMR: δ 4.17 (2H, q, *J* = 7.8, CF_3CH_2), 4.94 (2H, s, $C_6F_5CH_2$). ^{19}F NMR: δ −75.1 (3F, m, CF_3CH_2), −75.6 (6F, m, CF_3), −143.3 (2F, m, *o*-C_6F_5), −151.3 (1F, m, *p*-C_6F_5), −161.4 (2F, m, *m*-C_6F_5). MS (EI, 70 eV) [*m/e* (species) intensity]: 446 (M^+) 5; 181 ($M^+ - OC(CF_3)_2(OCH_2CF_3)$) 100. Anal. Calcd for $C_{12}H_4F_{14}O_2$: C, 32.30; H, 0.90; F, 59.62. Found: C, 32.40; H, 0.85; F, 59.6.

Reaction of $(CF_3)_2CO/C_6F_5OSi(CH_3)_3$/CsF with $C_6F_5CH_2Br$. In a procedure similar to compound **8a**, 0.28 g (2 mmol) of $(CF_3)_2CO$, 0.51 g (2 mmol) of $C_6F_5OSi(CH_3)_3$, 0.36 g (2.4 mmol) of dried CsF, 3 mL of CH_3CN, and 0.44 g (1.7 mmol) of $C_6F_5CH_2Br$ are reacted at 60 °C for 12 h and then at 90 °C for 48 h. The reaction mixture is poured into water and extracted with ether (20 mL × 2). The organic layer is washed and dried over Na_2SO_4, and evaporated to give an orange solid. The crude solid is distilled in a glass tube oven to give a mixture of 36% of compound **5b** and 2.1% of $(C_6F_5CH_2O)_2(CF_3)_2C$ (**9**), the structures of which were confirmed by ^1H NMR, ^{19}F NMR, and MS analysis. Spectral data of **9** are as follows. IR (Nujol) (cm^{-1}): 1230 s. ^1H NMR: δ 4.97 (s). ^{19}F NMR: δ −74.7 (s, 3F, CF_3), −142.6 (m, 4F, *o*-C_6F_5), −151.3 (m, 2F, *p*-C_6F_5), −161.1 (m, 4F, *m*-C_6F_5). MS (EI, 70 eV) [*m/e* (species) intensity]: 544 (M^+) 4.

Preparation of $C_6F_5CH_2OC(C_6F_5)_2(CF_3)$ (8d). Into a 100 mL reaction vessel are added, 0.91 g (2.5 mmol) of $(C_6F_5)_2CO$ and 0.38 g (2.5 mmol) of dried CsF, and 0.36 g (2.5 mmol) of $CF_3Si(CH_3)_3$ and 3 mL of CH_3CN are vacuum transferred into the reaction vessel cooled to −196 °C. The reaction vessel is stirred at −30 °C for 30 min and at room temperature for 5 h. The vessel is cooled to −196 °C, and 0.65 g (1.3 mmol) of $C_6F_5CH_2Br$ is added under nitrogen. The reaction mixture is heated at 90 °C for 48 h. The reaction mixture is poured into water and extracted with ether (20 mL × 2). The organic layer is washed and dried over $NaSO_4$ and evaporated and distilled in a glass tube oven at 60−110 °C. Silica gel chromatography of the resulting light brown liquid (eluent: petroleum ether) provides compound **8d** in 53% yield as white plates (recrystallized from warm hexane solution). Spectral data are as follows. IR (neat) (cm^{-1}): 1652 s, 1526 vs, 1494 vs, 1417 w, 1398 m, 1341 w, 1312 m, 1251 s, 1202 vs, 1150 s, 1133 s, 1091 m, 1056 s, 1016 m, 1000 s, 967 vs, 936 s, 829 s, 793 w, 778 s, 745 m, 723 m, 705 m, 683 w. ^1H NMR: δ 4.65 (s). ^{19}F NMR; δ −73.3 (3F, m, CF_3), −135.0 (4F, m, *o*-C_6F_5), −143.9 (2F, m, *o*-C_6F_5), −149.7 (2F, m, *p*-C_6F_5), −152.0 (2F, m, *p*-C_6F_5), −160.3 (4F, m, *m*-C_6F_5), −161.6 (2F, m, *m*-C_6F_5). MS (EI, 70 eV) [*m/e* (species) intensity]: 612 (M^+) 0.8; 543 ($M^+ - CF_3$) 10; 415 ($M^+ - OCH_2C_6F_5$) 4; 346 ($[(C_6F_5)_2C]^+$) 5; 327 ($[C_6F_5CC_6F_4]^+$) 8; 197 ($[C_6F_5CH_2O]^+$) 18; 181 ($[C_6F_5CH_2]^+$) 100.

Reaction of $(C_6F_5)_2CO/CF_3CH_2OSi(CH_3)_3$/CsF with $C_6F_5CH_2Br$. In a procedure similar to that for compound **8a**, 0.91 g (2.5 mmol) of $(C_6F_5)_2CO$, 0.43 g (2.5 mmol) of $CF_3CH_2OSi(CH_3)_3$, 0.38 g (2.5 mmol) of dried CsF, 5 mL of CH_3CN, and 0.65 g (2.5 mmol) of $C_6F_5CH_2Br$ are reacted at −20 °C to room temperature for 8 h and then at 90 °C for 48 h. The reaction mixture is poured into water and extracted with ether (20 mL × 2). The organic layer is washed and dried over Na_2SO_4 and evaporated to give an orange liquid. The crude liquid is distilled in a glass tube oven to give a mixture of 11% of $(4\text{-}CF_3CH_2O)C_6F_4C(O)C_6F_5$ (**10**) and 32% of $[(4\text{-}CF_3CH_2O)C_6F_4]_2CO$ (**11**) and 0.19 g of recovered $(C_6F_5)_2CO$. The identities of the products are confirmed by ^1H NMR, ^{19}F NMR, and MS. Spectral data of **10** are as follows. IR (Nujol) (cm^{-1}): 1700 s, 1460 vs, 1378 m, 1296 s, 1274 s, 1171 vs, 1095 m, 997 vs. ^1H NMR: δ 4.65 (q, *J* = 7.9 Hz); ^{19}F NMR: δ −75.6 (3F, br s, CF_3CH_2), −142.2 (2F, m, *o*-C_6F_5), −146.6 (F, m, *p*-C_6F_5), −160.0 (2F, m, *m*-C_6F_5). MS (EI, 70 eV) [*m/e* (species) intensity]: 442 (M^+) 2. Spectral data of **11** are as follows. IR (Nujol) (cm^{-1}): 1651 s, 1505 vs, 1407 s, 1334 s, 1182 vs, 1066 m, 1000 vs, 938 m. ^1H NMR: δ 4.64 (q, *J* = 7.9 Hz); ^{19}F NMR: δ −75.6 (6F, br s, CH_2CF_3), −142.4 (2F, m, *o*-C_6F_5), −155.56 (2F, m, *m*-C_6F_5). MS (EI, 70 eV) [*m/e* (species) intensity]: 522 (M^+) 7.

Reaction of $CF_3C(O)F/CF_3CH_2OSi(CH_3)_3$/CsF with $C_6F_5CH_2Br$. In a procedure similar to that for compound **8a**, 0.29 g (2.5 mmol) of $CF_3C(O)F$, 0.86 g (5.0 mmol) of $CF_3CH_2OSi(CH_3)_3$, 0.91 g (6.0 mmol) of dried CsF, 3 mL of CH_3CN, and 0.65 g (2.5 mmol) of $C_6F_5CH_2Br$ are reacted at 60 °C for 12 h and then at 90 °C for 48 h. The white precipitate formed is removed by decantation and extracted with ether (20 mL × 2). The collected organic layer is evaporated and distilled in a glass tube oven to give a mixture of 21% of compound **6a**, 4.0% of $C_6F_5CH_2OC(CF_3)_2(OCH_2CF_3)$ (**12**), and 3.9% of $(4\text{-}CF_3CH_2O)C_6F_4\text{-}CH_2OC(CF_3)_2(OCH_2CF_3)$ (**13**), the structures of which are confirmed by ^1H NMR, ^{19}F NMR, and MS analysis. Spectral data of **12** are as follows. ^1H NMR: δ 4.13 (2H, q, *J* = 8.1 Hz, CF_3CH_2), 4.94 (2H, s, $C_6F_5CH_2$). ^{19}F NMR: δ −74.8 (6F, m, CH_2CF_3), −80.4 (3F, s, CF_3), −142.9 (2F, m, *o*-C_6F_5), −151.7 (1F, m, *p*-C_6F_5), −161.3 (2F, m, *m*-C_6F_5). MS (EI, 70 eV) [*m/e* (species)]: 476 (M^+). Spectral data of **13** are as follows. ^1H NMR: δ 4.13 (4H, q, *J* = 8.1 Hz, CF_3CH_2), 4.52 (2H, q, *J* = 9.1 Hz, CF_3CH_2), 4.94 (2H, s, $C_6F_5CH_2$). ^{19}F NMR: δ −74.8 (6F, m, CH_2CF_3), −75.3 (3F, m, CH_2CF_3), −80.4 (3F, s, CF_3), −143.6 (2F, m, *o*-C_6F_5), −156.2 (2F, m, *m*-C_6F_5). MS (EI, 70 eV) [*m/e* (species) intensity]: 556 (M^+) 1.

Reaction of $C_6F_5C(O)F/CF_3CH_2OSi(CH_3)_3/CsF$ with $C_6F_5CH_2Br$. In a procedure similar to that for compound **8a**, 0.52 g (2.4 mmol) of $C_6F_5C(O)F$, 0.83 g (4.8 mmol) of $CF_3CH_2OSi(CH_3)_3$, 0.88 g (5.8 mmol) of dried CsF, 5 mL of CH_3CN, and 0.63 g (2.4 mmol) of $C_6F_5CH_2Br$ are reacted at 60 °C for 12 h and then at 90 °C for 48 h. The white precipitate formed is removed by decantation and extracted with ether (20 mL × 2). The collected organic layer is evaporated and distilled in a glass tube oven to give a mixture of 67% of $(4\text{-}CF_3CH_2O)C_6F_4C(O)OCH_2CF_3$ (**14**) and 11% of $(2,4\text{-}CF_3CH_2O)C_6F_3C(O)OCH_2CF_3$ (**15**). The products are identified by ^1H NMR, ^{19}F NMR, and MS. Spectral data of **14** are as follows. ^1H NMR: δ 4.5−4.8 (m). ^{19}F NMR: δ −74.3 (3F, m, CH_2CF_3), −75.5 (3F, m, CH_2CF_3), −138.0 (2F, m, *o*-C_6F_5), −155.7 (2F, m, *m*-C_6F_5). MS (EI, 70 eV) [*m/e* (species) intensity]: 374 (M^+) 28; 355 ($M^+ - F$) 3. Spectral data of **15** are as follows. ^1H NMR: δ 4.3−4.8 (m). ^{19}F NMR: δ −74.1 (3F, m, CH_2CF_3), −75.3 (6F, m, CH_2CF_3), −138.9 (1F, m, *o*-C_6F_5), −148.5 (1F, m, *m*-C_6F_5), −153.0 (1F, m, *m*-C_6F_5). MS (EI, 70 eV) [*m/e* (species) intensity]: 454 (M^+) 10; 435 ($M^+ - F$) 1.

Reaction of $COF_2/CF_3CH_2OSi(CH_3)_3/CsF$ with $C_6F_5CH_2Br$. In a procedure similar to that for compound **8a**, 0.13 g (2.5 mmol) of COF_2, 1.03 g (6.0 mmol) of $CF_3CH_2OSi(CH_3)_3$, 0.91 g (6.0 mmol) of dried CsF, 3 mL of CH_3CN, and 0.52 g (2.0 mmol) of $C_6F_5CH_2Br$ are reacted at 60 °C for 24 h and then at 90 °C for 48 h. With heating, the reaction mixture is passed through a U-trap cooled at −20 °C and a mixture consisting of 44% (based on COF_2) of $(CF_3CH_2O)_2CO$,[34] 23% of $C_6F_5CH_2F$, 29% of compound **5a**, and 25% of compound **6a** is obtained. The products formed are identified by ^1H NMR, ^{19}F NMR, and MS.

Reaction of $(CF_3CH_2O)_2CO/CF_3Si(CH_3)_3/CsF$ with $C_6F_5CH_2Br$. In a procedure comparative to that for compound **8a**, 0.68 g (3.0 mmol) of $(CF_3CH_2O)_2CO$, 0.43 g (3.0 mmol) of $CF_3Si(CH_3)_3$, 0.46 g (3.0 mmol) of dried CsF, and 0.78 g (3.0 mmol) of $C_6F_5CH_2Br$ are reacted at 60 °C for 12 h and then at 90 °C for 48 h. With heating, the reaction mixture is passed through a U-trap cooled at −20 °C to give 53% of compound **8c**, 14% of compound **5a**, 15% of compound **6a**, and 0.09 g of recovered $(CF_3CH_2O)_2CO$. The products are identified by comparative IR, ^1H NMR, and ^{19}F NMR.

Reaction of $(CF_3CH_2O)_2CO/C_6F_5Si(CH_3)_3/CsF$ with $C_6F_5CH_2Br$. In a procedure similar to that for compound **8a**, 0.37 g (1.6 mmol) of $(CF_3CH_2O)_2CO$, 0.38 g (1.6 mmol) of $C_6F_5Si(CH_3)_3$ in C_6H_5CN solution, 0.24 g (1.6 mmol) of dried CsF, and 0.42 g (1.6 mmol) of $C_6F_5CH_2Br$ are reacted at −30 to −10 °C for 1 h and then at 90 °C for 48 h. The white precipitate formed is removed by decantation and extracted with ether (20 mL × 2). The collected organic layer is evaporated and distilled in a glass tube oven to give 27% of compound **14** and 0.13 g of a mixture of high boiling liquids, the structures of which are under investigation.

Single-Crystal X-ray Analysis of $C_6F_5CH_2OC(C_6F_5)_2(CF_3)$ (8d). Suitable crystals of $C_6F_5CH_2OC(C_6F_5)_2(CF_3)$ (**8d**) are obtained by recrystallization from a 2:1 mixture of 1,1,1-trichlorotrifluoroethane and cyclohexane. A well formed single crystal with dimension 0.25 × 0.20 × 0.20 mm was mounted on a Siemens R3m/V four circle diffractometer (upgraded to P4) at 294 K. A summary of data collection is given in Table 5. Unit cell parameters were determined by least squares refinement of 36 computer-centered reflections (11 reflections with $9.1 < 2\theta < 29.9$ and 25 reflections with $27.3 < 2\theta < 29.9$). Intensity measurements employed graphite monochromatized MoKα radiation (λ = 0.710 73 Å) in ω scan mode with on-line profile fitting and variable scan speeds. During data collection, the intensities of three standard reflections; 122, 224, and 214, monitored every 97 reflections, showed almost no crystal decay. The raw data was corrected for Lorentz and polarization effects. Systematically absent refections with $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$ confirmed the space group as $P2_1/c$ (No. 14). The structure was solved by the direct method using SHELX-86[40] which provides the ordinates of all non-hydrogen atoms. This model was then refined by the full-matrix least-squares procedure initially with isotropic and in the last cycles with anisotropic thermal parameters to minimize the quantity $\Sigma w(F_o - F_c)^2$. The hydrogen atoms of the methylene group were localized from difference Fourier syntheses and then incorporated in refinement in isotropic approximation. A final difference Fourier map reveals no significant peaks greater than 0.31 e Å^{-3}. Scattering factors were taken from the literature.[41] All computation was performed on an IBM 486 PC using SHELXTL PLUS V-4.2[42] software at the University of Pittsburgh during the 3rd ACA summer school in crystallography.

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Supporting Information Available: For compound **8d** a full listing of data collection and processing parameters, bond lengths and angles, atomic coordinates, equivalent isotropic and anisotropic displacement coefficients, and hydrogen atom coordinates and isotropic displacement coefficients is available (8 pages). Ordering information is given on any current masthead page.

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(40) Sheldrick, G. M. SHELXS-86 Program for the Solution of Crystal Structures, University of Göttingen, 1986.

(41) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(42) Sheldrick, G. M. SHELXTL V-4.2, Siemens Analytical Instrument Division, Madison, WI.