Synthesis and Chemistry of Acyclic Mono- and Disiloxanes: Useful Precursors to Per- and Polyfluoroethers

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Acyclic polyfluoro mono and disiloxanes $CF_3CH_2OSiMe_3$ (**1**), $CF_3C(CH_3)_2OSiMe_3$ (**2**), $CH_3C(CF_3)_2OSiMe_3$ (**3**), $C_6H_5C(CF_3)_2OSiMe_3$ (**4**), $(CF_3)_2CHOSiMe_3$ (**5**), $(CF_3)_3COSiMe_3$ (**6**), $FCH_2CH_2OSiMe_3$ (**7**), $HCF_2CF_2CH_2OSiMe_3$ (**8**), n-$C_7F_{15}CH_2OSiMe_3$ (**9**), $(CF_2CH_2OSiMe_3)_2$ (**10**), and $CF_2(CF_2CH_2OSiMe_3)_2$ (**11**) are synthesized by the reactions of their respective alcohols with hexamethyldisilazane. Reactions of **1** with CH_2Br_2, $(CNF)_3$, $CFBr_3$, perfluorocyclobutene, and C_6F_5CN proceed readily in the presence of fluoride ion to form $CH_2(R_f)_2$ (**12**), $C_3N_3(R_f)_3$ (**13**), $C(R_f)_4$ (**14**), $\overline{CF_2C(R_f)=C(R_f)CF_2}$ (**15**), $\overline{CF_2C(R_f)=C(F)CF_2}$ (**16**) and 4-$R_fC_6F_4CN$ (**17**) (when reacted 1:1) and $(R_f)_5C_6CN$ (**18**) (when reacted with excess of **1**), respectively ($R_f = OCH_2CF_3$). Reactions of **2** with C_6F_5CN, C_6F_6, $CF_3C_6F_5$, ClC_6F_5, NC_5F_5, 1,2-diiodotetrafluorobenzene and perfluorocyclobutene in the presence of fluoride ion give $R_fC_6F_4CN$ (**19**) or $(R_f)_2C_6F_3CN$ (**20**) (depending on the ratio of reactants), $R_fC_6F_5$ (**21**), $R_fC_6F_4CF_3$ (**22**), $R_fC_6F_4Cl$ (**23**), $R_fC_5F_4N$ (**24**), $R_fC_6F_3I_2$ (**25**), and $\overline{CF_2C(R_f)=C(F)CF_2}$ (**26**), respectively ($R_f = CF_3C(CH_3)_2O$). Reactions of **3** with C_6F_5CN, C_6F_6 and 1,2-diiodotetrafluorobenzene with fluoride ion as catalyst form $R_fC_6F_4CN$ (**27**), $R_fC_6F_5$ (**28**) and $R_fC_6F_3I_2$ (**29**), respectively ($R_f = CH_3C(CF_3)_2O$). Reactions of **4** with $CF_3C_6F_5$, C_6F_5CN, perfluorocyclobutene, $C_6H_5CH_2Br$ and CH_3I give $R_fC_6F_4CF_3$ (**30**), $R_fC_6F_4CN$ (**31**), $\overline{CF_2C(R_f)=C(F)CF_2}$ (**32**), $R_fCH_2C_6H_5$ (**33**) and R_fCH_3 (**34**), respectively ($R_f = C_6H_5C(CF_3)_2O$). Reactions of **5** with C_6F_5CN and $CF_3C_6F_5$ result in $R_fC_6F_4CN$ (**35**) and $R_fC_6F_4CF_3$ (**36**), respectively ($R_f = (CF_3)_2CHO$). Siloxanes **6**, **7**, **8** and **9** with C_6F_5CN form $CNC_6F_4OC(CF_3)_3$ (**37**), $FCH_2CH_2OC_6F_4CN$ (**38**), $HCF_2CF_2CH_2OC_6F_4CN$ (**39**) and n-C_7F_{15}-$CH_2OC_6F_4CN$ (**40**). Disiloxane **10** with CH_2Br_2, $Br_2CHCHBr_2$, SOF_2, SO_2Cl_2, COF_2, C_6F_5CN, $(COF)_2$, $POCl_3$, C_5F_5N, CF_3SO_2F, 1,2-diiodotetrafluorobenzene, $I(CF_2)_2O(CF_2)_2SO_2F$, $FC(O)(CF_2)_3C(O)F$ and 1,4-dibromotetrafluorobenzene gives polyfluorinated cyclic or acyclic ethers $\overline{CF_2CH_2OCH_2OCH_2CF_2}$ (**41**), $\overline{CF_2CH_2OCHOCH_2(CF_2)_2CH_2OCHOCH_2CF_2}$ (**42**), $\overline{CF_2CH_2OS(O)OCH_2CF_2}$ (**43**), $\overline{CF_2CH_2OSO_2OCH_2CF_2}$ (**44**), $FC(O)OCH_2CF_2CF_2CH_2OC(O)F$ (**45**), 4-$CNC_6F_4OCH_2CF_2CF_2CH_2OC_6F_4CN$-4 (**46**), $\overline{CF_2CH_2OC(O)C(O)OCH_2CF_2}$ (**47**), $\overline{CF_2CH_2OP(O)FOCH_2CF_2}$ (**48**), $NC_5F_4OCH_2CF_2CF_2CH_2OC_5F_4N$ (**49**), $CF_3SO_2OCH_2CF_2CF_2CH_2OSO_2CF_3$ (**50**), $\overline{F_2CH_2CO(3,6\text{-difluoro-}4,5\text{-diiodo-}o\text{-phenylene})OCH_2CF_2}$ (**51**), $I(CF_2)_2O(CF_2)_2SO_2OCH_2(CF_2)_2CH_2OSO_2(CF_2)_2O(CF_2)_2I$ (**52**), $\overline{CF_2CH_2OC(O)(CF_2)_3C(O)OCH_2CF_2}$ (**53**), and $(-F_2CH_2CO)_2(3,6\text{-dibromo-}1,2,4,5\text{-benzenetetrayl})(OCH_2CF_2-)_2$ (**54**), respectively. Reactions of **11** with CH_2Br_2, COF_2, SOF_2, and SO_2Cl_2 also give cyclic and acyclic ethers $\overline{CF_2CF_2CH_2OCH_2OCH_2CF_2}$ (**55**), $FC(O)OCH_2(CF_2)_3CH_2OC(O)F$ (**56**), $\overline{CF_2CF_2CH_2OS(O)OCH_2CF_2}$ (**57**), and $\overline{CF_2CF_2CH_2OSO_2OCH_2CF_2}$ (**58**), respectively. Ethers **17**, **38**−**40** and $CH_3CH(CF_3)OC_6F_4CN$ (**59**) are also prepared by reacting the corresponding alcohols with pentafluorobenzonitrile in the presence of alkali carbonate as the HF-acceptor. Reaction of $C_6H_5OSiMe_3$ with C_6F_5CN yields the polyether $(C_6H_5O)_5C_6CN$ (**60**). When ethers **17**, **38**−**40** and **59** are hydrolyzed in alkaline hydrogen peroxide (30%), the corresponding benzamides $CF_3CH_2OC_6F_4CONH_2$ (**61**), $FCH_2CH_2OC_6F_4CONH_2$ (**62**),$HCF_2CF_2CH_2OC_6F_4CONH_2$ (**63**), n-$C_7F_{15}CH_2OC_6F_4$-$CONH_2$ (**64**) and $CH_3CH(CF_3)OC_6F_4CONH_2$ (**65**), respectively, are formed.

Introduction

The demand for materials that may be useful as stable high temperature fluids in a variety of environments encourages the research for methodologies to form highly fluorinated ethers or per or polyfluoroalkoxy derivatives. Silicon−oxygen bond characteristics result in many useful organic and inorganic synthetic applications of siloxanes.[1−3] Although cleavage of a silicon−oxygen bond frequently requires more rigorous conditions[4] or highly reactive reagents[5] than those for Si−X (X = halogen, nitrogen or chalcogen), it does occur under rather mild conditions in, for example, the reactions of silyl enol ethers[2] or of siloxanes with moieties which have a variety of main group element−fluorine bonds.[6] Others have demonstrated that in the presence of anionic catalysts, silyl ethers can be caused to react

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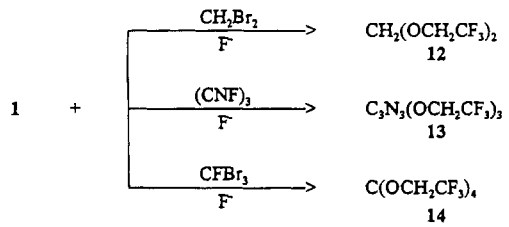
with perfluorinated alkenes to produce partially fluorinated vinyl ethers in exceptionally high yields.[7] However, until recently organosilicon reagents were employed only rarely in the synthesis of highly fluorinated materials.[7-10] In our continuing search for efficacious routes for the introduction of fluoroalkoxy substituents into fluorinated substrates, as well as our ongoing studies of polyfluorinated diols, we have extended markedly the synthesis and chemistry of polyfluoroalkoxysilanes.[6,11] While earlier we reported the reactions of dilithium and disodium derivatives of diols with various S,[12] P,[6,13] and C[11,14] -containing compounds, we note a marked difference in reactivity and product formation as a function of the length of the fluoroalkyl chain and the method used to activate the hydroxy group.

In this work, the synthesis of acyclic mono and disiloxane derivatives of various alcohols and their reactions with a variety of halogenated compounds is carried out to prepare new cyclic and acyclic polyfluoro and perfluoroethers. Both mono and disiloxanes are found to react readily with halogenated compounds in the presence of fluoride ion as catalyst via facile elimination of the respective silyl fluorides.

Results and Discussion

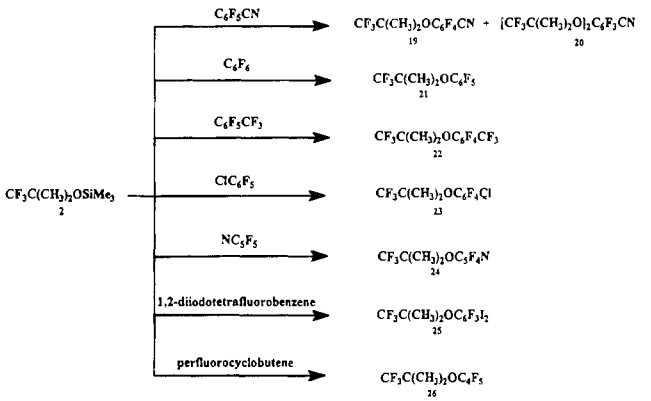
The siloxanes $CF_3CH_2OSiMe_3$ (**1**), $CF_3C(CH_3)_2OSiMe_3$ (**2**), $CH_3C(CF_3)_2OSiMe_3$ (**3**), $C_6H_5C(CF_3)_2OSiMe_3$ (**4**), $(CF_3)_2CHOSiMe_3$ (**5**), $(CF_3)_3COSiMe_3$ (**6**), $FCH_2CH_2OSiMe_3$ (**7**), $HCF_2CF_2CH_2OSiMe_3$ (**8**), n-$C_7F_{15}CH_2OSiMe_3$ (**9**), $Me_3SiOCH_2(CF_2)_2CH_2OSiMe_3$ (**10**), and $Me_3SiOCH_2(CF_2)_3CH_2OSiMe_3$ (**11**) are obtained conveniently in relatively high yields by the controlled treatment of the corresponding alcohols with hexamethyldisilazane in the presence of a catalytic amount of sodium saccharin.[6,11,15,16]

Reactions of **1** with CH_2Br_2, $(CNF)_3$, and $CFBr_3$ proceed rapidly in the presence of fluoride ion to give the polyfluorinated ethers which are a stable liquid (**12**) or solids (**13**, **14**) melting below 95 °C. The methylene **12** or triazene **13** ether is also

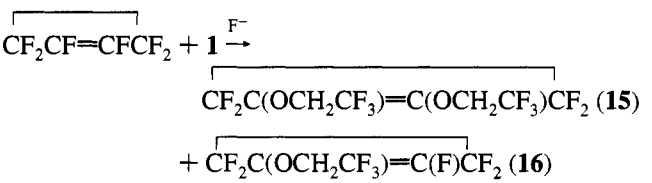


obtained either from the reaction of 2,2,2-trifluoroethanol with formaldehyde in the presence of 90% H_2SO_4[17] or with triazene in the presence of KOH,[18] respectively. However, the use of silylated precursors has the advantage in that these reagents can be employed under mild conditions (heating at 70 °C in presence of fluoride ion with acetonitrile as solvent) without using highly acidic or basic solutions. The reaction with $CFBr_3$ to form **14** stresses the increasing electrophilicity of the carbon center as the bromine atoms are displaced by polyfluorinated alkoxide which aids the displacement of the sole fluorine atom.

Scheme 1



The products obtained when **1** is reacted with perfluorocyclobutene in a ratio of 2:1 in the presence of fluoride ion are solid (**15**) and liquid (**16**).



Ethers **15** and **16** were both previously prepared in a stainless steel pressure reactor by using 2,2,2-trifluoroethanol and perfluorocyclobutene in presence of 85% KOH.[19] This reaction again demonstrates that siloxane reactions are possible under less vigorous conditions.

The ease with which the carbon−fluorine bonds in a variety of perfluoro or polyfluoroaromatic materials can be substituted to introduce one or more per or polyfluoroalkoxide group(s) primarily as a function of stoichiometry provides a powerful route to multiple families of stable, highly fluorinated aromatic polyethers. Reaction of **1** with an aromatic ring C_6F_5CN gives rather low yields of 4-$CF_3CH_2OC_6F_4CN$ (**17**) (when reacted 1:1) and $(CF_3CH_2O)_5C_6CN$ (**18**) (when reacted with excess of **1**). The pentaether is a white, crystalline solid whose structure is expected to be similar to that of $(CF_3CH_2O)_6C_6$ that is synthesized from **1** with hexafluorobenzene.[11]

In changing from **1** to **2** where the methylene protons are replaced by methyl groups, reactions with C_6F_5CN, C_6F_6, $C_6F_5CF_3$, C_6F_5Cl, C_5F_5N, 1,2-diiodotetrafluorobenzene as well as perfluorocyclobutene proceed in the presence of fluoride ion to give monoethers **19**, **21**−**26** and diether **20** (Scheme 1). Although not as many reactions are successful with **3** where the alkoxide is bis(trifluoromethyl)-*tert*-butoxy, similar reactions occur with the most electrophilic reagents, pentafluorobenzonitrile, hexafluorobenzene and diiodotetrafluorobenzene to form the monosubstituted derivatives $CH_3C(CF_3)_2OC_6F_4CN$ (**27**), $CH_3C(CF_3)_2OC_6F_5$ (**28**), and $CH_3C(CF_3)_2OC_6F_3I_2$ (**29**), respectively. Further modification of the alkoxy group to phenylbis(trifluoromethyl)-*tert*-butoxy (**4**) causes no problems in the subsequent formation of $CF_3C_6F_4OR_f$ (**30**), $NCC_6F_4OR_f$ (**31**), c-$C_4F_5OR_f$ (**32**), $C_6H_5CH_2OR_f$ (**33**), and CH_3OR_f (**34**) (R_f =

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$C_6H_5C(CF_3)_2$) from $CF_3C_6F_5$, C_6F_5CN, $CF_2CF{=}CFCF_2$, $C_6H_5CH_2Br$ and CH_3I. Using a reaction stoichiometry of 1:1 silyl ether to substrate, only in the case of **2** with C_6F_5CN is evidence found that disubstitution occurs to form **20** which suggests a slightly greater nucleophilic character for **2**. This is not surprising since the nucleophilicity of the alkoxide should be related inversely to the number of trifluoromethyl substituents.

Of the electrophiles attempted, reactions of **5** proceed only with C_6F_5CN and $C_6F_5CF_3$ to form $(CF_3)_2CHOC_6F_4CN$ (**35**) and $(CF_3)_2CHOC_6F_4CF_3$ (**36**). Finally, under the same mild conditions, perfluoro-*tert*-butylsilyl ether (**6**) reacted only with the most active electrophile used in this study, C_6F_5CN, to form $(CF_3)_3COC_6F_4CN$ (**37**) in ~70% yield. This is in keeping with the effect of the reduced nucleophilicity of the alkoxide since the inductive effect of the trifluoromethyl groups decreases the basicity of the oxygen. Not surprisingly when the reactant is iodomethane, metathesis with **4** occurs readily to displace the iodine. However, when the iodine is found in an electron deficient environment, as in 1,2-diiodotetrafluorobenzene, the carbon bonded to fluorine is significantly more electrophilic and therefore more likely to undergo nucleophilic attack by **2**, e.g., to form **25**.

With the highly electrophilic C_6F_5CN, silylethers, such as **7**–**9**, that have polyfluoroalkyl groups containing two, three and eight carbon atoms, respectively, produce stable polyfluoroethers in yields between 54–74%, *viz.* While ethers **17**, **38**–**40** and

$$\underset{\mathbf{7}}{+\ FCH_2CH_2OSiMe_3} \rightarrow \underset{\mathbf{38}}{FCH_2CH_2OC_6F_4CN}$$

$$C_6F_5CN + \underset{\mathbf{8}}{HCF_2CF_2CH_2OSiMe_3} \rightarrow \underset{\mathbf{39}}{HCF_2CF_2CH_2OC_6F_4CN}$$

$$\underset{\mathbf{9}}{+\ n\text{-}C_7F_{15}CH_2OSiMe_3} \rightarrow \underset{\mathbf{40}}{n\text{-}C_7F_{15}CH_2OC_6F_4CN}$$

59 are stable to their melting points and beyond, and to acqueous hydrolysis, they are hydrolyzed when dissolved in 5% KOH in ethanol and treated with 30% hydrogen peroxide at 25 °C to form the stable benzamides **61**–**65** that melt without decomposition over the range 140–174 °C. These amides may have

$$\underset{\mathbf{17,\ 38-40,\ 59}}{ROC_6F_4CN} + 2H_2O_2 \xrightarrow{OH^-} \underset{\mathbf{61-65}}{ROC_6F_4CONH_2}$$

practical value in the preparation of modified benzoylurea herbicides. The presence of the groups FCH_2CH_2O- and $HCF_2CF_2CH_2O$-, may be effective as biologically active groups while n-$C_7F_{15}CH_2O$- could increase the surfactant characteristics of the molecule.

Earlier we used metallated polyfluorodiols to form cyclic diethers with a variety of simple inorganic species.[6,12–14] Polyfluorinated disiloxanes are much easier to use, react under milder conditions, and are much more versatile synthetic reagents. At ~70 °C, in the presence of fluoride ion, and with the concomitant formation of $(Me)_3SiF$ as the driving force, disiloxane $Me_3SiOCH_2(CF_2)_2OSiMe_3$ (**10**) readily reacts with CH_2Br_2, $Br_2CHCHBr_2$, SOF_2, SO_2Cl_2, COF_2, C_6F_5CN, $(COF)_2$, $POCl_3$, C_5F_5N, CF_3SO_2F, 1,2-diiodotetrafluorobenzene, $ICF_2CF_2OCF_2CF_2SO_2F$, perfluoroglutaryl fluoride, and 1,4-dibromotetrafluorobenzene to give diethers **41**–**54** as shown in Table 1. With the exception of **45**, **46**, **49** and **52**, the products are cyclic diethers. The yields of the ethers range between 60 and 80%. Although acetonitrile is normally the solvent of choice, the reactions of $ICF_2CF_2OCF_2CF_2SOF_2$, perfluoroglutaryl fluoride, and 1,4-dibromotetrafluorobenzene with **10** are found to proceed smoothly under the same conditions in THF as well. Diglyme is particularly useful as solvent for the reaction of **10** with 1,2-diiodotetrafluorobenzene.

The products obtained are a function of the stoichiometry of the reactants used. For example, in order to synthesize cyclic diethers **41**, **43**, **44**, **47**, **48** and **53**, reactions of CH_2Br_2, SOF_2, SO_2Cl_2, $(COF)_2$, $POCl_3$ and $FC(O)(CF_2)_3C(O)F$ with **10** should be carried out by using a ratio of 1:1 to avoid mixtures of products. Because of the presence of only a single reactive site, e.g., in CF_3SO_2F and $ICF_2CF_2OCF_2CF_2SO_2F$, or a strong para-directing tendency as in C_6F_5CN and C_5F_5N, a stoichiometry of 2:1 reactant to **10** is required to obtain the acyclic polyfluoro diethers **50**, **52**, **46** and **49**, respectively. Not surprisingly, nucleophilic attack occurs only at the S-F bond in $ICF_2CF_2OCF_2CF_2SO_2F$, to form acyclic **52**, and at the C-F bonds in 1,2-diiodotetrafluorobenzene to give bicyclic **51** as well as in 1,4-dibromotetrafluorobenzene to result in tricyclic **54**. This was also observed when **2** was reacted with the diiodobenzene.

While the geometry of oxalyl fluoride is such that it is possible to easily form the cyclic diether **47**, planar COF_2 with bond angles of ~120° precludes the formation of the strained seven or eight membered rings with **10** or **11**. This is in contrast to the stable cyclic sulfites (**43**, **57**) or sulfates, (**44**, **58**) that result when **10** or **11** are reacted with pyramidal SOF_2 or tetrahedral SO_2Cl_2.

Similarly $Me_3SiOCH_2(CF_2)_3CH_2OSiMe_3$ (**11**) is reacted with CH_2Br_2, COF_2, SOF_2, and SO_2Cl_2, in a ratio of 1:1 to form cyclic and acyclic polyfluoro diethers $CF_2CF_2CH_2OCH_2OCH_2CF_2$ (**55**), $FC(O)OCH_2(CF_2)_3CH_2OC(O)F$ (**56**), $CF_2CF_2CH_2OS(O)OCH_2CF_2$ (**57**), and $CF_2CF_2CH_2OSO_2OCH_2CF_2$ (**58**) in high yields. Of the diethers that are reported here only **41** and **55** are in the literature having resulted from the reaction of the respective diols with formaldehyde in the presence of H_2SO_4.[20] No spectral data are reported for these compounds.

Ethers **17** and **38**–**40** as well as $CH_3CH(CF_3)OC_6F_4CN$, **59**, are prepared by reacting the corresponding polyfluoroalcohol with C_6F_5CN in the presense of alkali carbonate as an HF-acceptor. However, the yields obtained when siloxanes are used as the nucleophile are superior. The nonfluorinated analogue of **18** results when an excess of $C_6H_5OSiMe_3$ is reacted with C_6F_5CN forming $(C_6H_5O)_5C_6CN$, **60**.

Although there are many methods for introducing polyfluoroalkoxy groups into active halogenated compounds, such as direct reaction of the appropriate alcohol in the presence of a base, or metallation of the alcohol to form sodium or lithium salts, these methods, although widely used, are not free from disadvantages. The procedures involve filtration and purification of products from the salts which form or often the metallated alkoxides are only moderately stable. To overcome these difficulties, silicon mediated synthesis of polymers was attempted initially on silylated diphenols.[21] The method was later extended to polyfluorodiols and used to prepare macrocyclic polyfluoroethers in a stepwise manner.[22] The stable, easily synthesized, somewhat less reactive siloxy compounds

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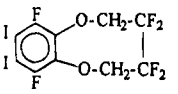
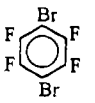
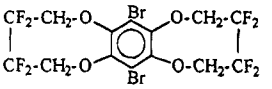
Table 1. Reactions of $(Me_3SiOCH_2CF_2)_2$, **10**

Reactant	Product	Reactant	Product
CH_2Br_2	$CF_2CH_2OCH_2OCH_2CF_2$ **41**	$POCl_3$	$CF_2CH_2OP(O)FOCH_2CF_2$ **48**
$Br_2CHCHBr_2$	$CF_2CH_2OCHOCH_2CF_2CF_2CH_2OCHOCH_2CF_2$ **42**	C_5F_5N	$NC_5F_4OCH_2(CF_2)_2CH_2OC_5F_4N$ **49**
SOF_2	$CF_2CH_2OS(O)OCH_2CF_2$ **43**	CF_3SO_2F	$CF_3SO_2OCH_2(CF_2)_2CH_2OSO_2CF_3$ **50**
SO_2Cl_2	$CF_2CH_2OSO_2OCH_2CF_2$ **44**		 **51**
COF_2	$FC(O)OCH_2CF_2CF_2CH_2OC(O)F$ **45**	$ICF_2CF_2OCF_2CF_2SO_2F$	$(ICF_2CF_2OCF_2CF_2SO_2OCH_2CF_2\rightarrow_2$ **52**
C_6F_5CN	p-$CNC_6F_4OCH_2CF_2CF_2CH_2OC_6F_4CN$-p **46**	$C(O)F(CF_2)_3C(O)F$	$CF_2CH_2OC(O)(CF_2)_3C(O)OCH_2CF_2$ **53**
$(COF)_2$	$CF_2CH_2OC(O)C(O)OCH_2CF_2$ **47**		 **54**

coupled with the ease of purification of the reaction products make this alternative route very attractive.

Experimental Section

Materials. $[CF_2CH_2OH]_2$ (gift from 3M), and $CF_2(CF_2CH_2OH)_2$ (PCR) are purified by sublimation prior to use. CsF, SOF_2, COF_2, $(COF)_2$, C_5F_5N, perfluoroglutaryl fluoride, perfluorocyclobutene, C_6F_6, and all starting alcohols are purchased from (PCR). Hexamethyldisilazane, C_6F_5CN, $POCl_3$, $CF_3C_6F_5$, CH_3I, SO_2Cl_2 (Aldrich), CH_2Br_2, $Br_2CHCHBr_2$ (Eastman Kodak), $(CNF)_3$, 1,2-diiodotetrafluorobenzene (Alfa), 1,4-dibromotetrafluorobenzene (SCM Chemicals), and CF_3SO_2F (gift from 3M) are used as received. $ICF_2CF_2OCF_2CF_2SO_2F$ is made by the literature method.[23] The preparation of siloxanes is described elsewhere.[6,11,15] The solvents THF, acetonitrile and diglyme are dried and distilled prior to use according to standard procedures.

General Procedure. A conventional vacuum system comprised of a Pyrex glass vacuum line equipped with Heise Bourdon tube and Televac thermocouple gauges is used to handle gases and volatile liquids. Reactions are performed in thick-walled 100 mL round-bottomed flasks fitted with Teflon stopcocks.

Products are separated and purified by distillation or crystallization. Infrared spectra are recorded on a Perkin-Elmer 1710 FTIR spectrometer equipped with an IBM PS-2 data station by using KBr disks or a 10 cm gas cell equipped with KBr disks. The ^1H and ^{19}F NMR spectra are obtained with Bruker AC 200 or AC 300 Fourier transform NMR spectrometers using $CDCl_3$ or CD_3CN as solvent and Me_4Si and $CFCl_3$ as references. Mass spectra are obtained with a VG 7070HS GC/MS spectrometer by using electron impact or chemical ionization techniques. Elemental analyses are performed by Beller Mikroanalytisches Laboratorium, Göttingen, Germany.

Preparation of Siloxanes (1−11). Siloxanes **1** to **11** are prepared by the reaction of the respective alcohols (40 mmol) with $(Me_3Si)_2NH$ (45 mmol) in a 100 mL round-bottomed flask fitted with a reflux condenser. A pinch of sodium saccharin is added as catalyst to drive the reaction to completion. After the initial evolution of ammonia subsides, the mixture is heated to 80 °C and maintained at that temperature for 8−10 h. The siloxanes are obtained as colorless air stable liquids upon vacuum distillation. They are characterized by comparing their spectral data with the literature.[6,11,15]

General Procedure for the Preparation of Ethers (12−58). In a typical reaction, 5 mL of acetonitrile or THF or diglyme, a catalytic amount of CsF and siloxane **1−11** (6−10 mmol) are combined in a 100 mL round-bottomed Pyrex flask equipped with a Teflon stopcock. The mixture is frozen at −196 °C and the vessel is evacuated. Five to10 mmol of respective substrate is then condensed into the flask and the mixture is allowed to warm slowly to 25 °C. The mixture is stirred for 10−12 h at 60−70 °C. The products are separated by low temperature trap-to-trap distillation or by extracting the residue with diethyl ether. The yields of the products (**12−58**) range from 35−80%.

Properties of $CH_2(OCH_2CF_3)_2$ (12). The preparation of **12** is reported[17] but no details are given nor are spectral data presented. Spectral data obtained are as follows. IR (neat): 2961 m, 1438 m, 1377 m, 1284 s, 1256 s, 1159 vs, 1098 m, 1065 s, 965 s, 919 w, 872 s, 850 s, 754 m, 665 w, 642 w cm^{-1}; NMR: ^{19}F, δ −75 (CF_3, t, $^3J_{H-F}$ = 7.7 Hz); ^1H, δ 4.67 (OCH_2O, 2H, s); 3.7 (OCH_2, 4H, q); CI MS [*m/e* (species) intensity]: 211 ($M^+ - H$) 1.6; 193 ($M^+ - F$) 7.8; 174 ($M^+ - 2F$) 3.1; 143 ($M^+ - CF_3$) 1.7; 113 ($M^+ - OCH_2CF_3$) 73.9; 101 ($CF_3CH_2OH^+ + 1$) 6.3; 93 ($COCH_2CF_2^+ + 1$) 6.5; 83 ($C_2F_3H_2^+$) 11.4; 81 ($C_2F_3^+$) 61.3; 75 ($CH_2OCH_2CF^+$) 86; 73 ($C_3H_2FO^+$) 100; 69 (CF_3^+) 9.4.

Properties of $C_3N_3(OCH_2CF_3)_3$ (13). The preparation of **13** is reported[18] but no details are given nor are spectral data presented (mp 45 °C). Spectral data obtained are as follows. IR (KBr disk): 3003 m, 2945 m, 1620 s, 1583 m, 1567 s, 1499 m, 1445 m, 1413 s, 1376 vs, 1290 s, 1273 w, 1242 w, 1177 s, 1131 s, 1085 s, 1040 s, 963 w, 919 s, 815 m, 750 m, 621 w cm^{-1}; NMR: ^{19}F, δ −74.6 (CF_3, t, $^3J_{H-F}$ = 7.8 Hz); ^1H, δ 4.88 (CH_2, q); CI MS [*m/e* (species) intensity]: 376 ($M^+ + 1$) 1.8; 356 ($M^+ - F$) 1.6; 315 ($M^+ - 3HF$) 13.2; 307 ($M^+ - CF_3 + 1$) 2.2; 293 ($M^+ - CH_2CF_3 + 1$) 2.7; 276 ($M^+ - OCH_2CF_3$) 10.8; 268 ($M^+ - CF_3 - 2F$) 5.1; 263 ($M^+ - COCH_2CF_3 - H$) 1.4; 250 ($M^+ - NCOCH_2CF_3$) 2.2; 237 ($M^+ - 2CF_3$) 5.7; 231 ($M^+ - NCOCH_2CF_3 - F$) 10.7; 212 ($M^+ - NCOCH_2CF_3 - 2F$) 73.8; 193 ($M^+ - OCH_2CF_3 - CH_2CF_3$) 4.3; 177 ($M^+ - 2OCH_2CF_3$) 37.9; 159 ($MH^+ - 2OCH_2CF_3 - F$) 21.2; 149 ($MH^+ - NCOCH_2CF_3 - CH_2CF_3 - F$) 44.4; 133 ($C_4H_2F_2N_2O^+ + 1$) 12.8; 119 ($C_3HF_2N_2O^+$) 49.3; 99 ($CF_3CH_2O^+$) 15.2; 90 ($C_3H_2F_2O^+$) 100; 83 ($CH_2CF_3^+$) 11.1; 81 ($C_2F_3^+$) 11; 69 ($CF_3^+$) 12.9.

(23) Persulfonic Acid Group, Shanghai Institute of Organic Chemistry, *Acad. Sin. Sci. Sin. (Engl. Ed.)* **1978**, *21*, 773.

Properties of $C(OCH_2CF_3)_4$ (14). This compound melts at 90–92 °C. Spectral data are as follows. IR (KBr disk): 2968 m, 1440 m, 1380 m, 1290 s, 1261 s, 1160 s, 1091 m, 1060 s, 961 m, 925 w, 874 s, 852 s, 750 w cm^{-1}; NMR: ^{19}F, δ −75.3 (CF_3, t, $^3J_{H-F}$ = 7.8 Hz); ^1H, δ 4.1 (CH_2, q) CI [*m/e* (species) intensity]: 319 ($M^+ - CF_3 - HF$) 2.9; 309 ($M^+ - OCH_2CF_3$) 4.9; 291 ($MH^+ - OCH_2CF_3 - F$) 2.3; 281 ($M^+ - CF_3 - 3F - H$) 1.5; 269 ($M^+ - 2CF_3 - H$) 1.5; 254 ($M^+ - 2CF_3 - CH_2 - 2H$) 3.3; 229 ($M^+ - 2CF_3 - 2HF - H$) 14.1; 226 ($M^+ - OCH_2CF_3 - CH_2CF_3$) 22.1; 211 ($M^+ - 2OCH_2CF_3 + 1$) 57.6; 188 ($C_5H_4F_4O_3^+$) 2.9; 173 ($C_5H_5F_4O_2^+$) 8.2; 169 ($C_5HF_4O_2^+$) 5.6; 147 ($C_5HF_2O_3^+$) 100; 126 ($C_3HF_3O_2^+$) 20.1; 100 ($CF_3CH_2OH^+$) 2.8; 83 ($CH_2CF_3^+$) 62.5; 81 ($CF_2CH_2OH^+$) 68.9; 69 ($CF_3^+$) 31.3.

Properties of $\overline{CF_2C(OCH_2CF_3)=C(OCH_2CF_3)CF_2}$ (15). This compound melts at 141 °C. Spectral data compared with literature[19] are as follows. IR (KBr disk): 2973 m, 1749s, 1459 m, 1416 m, 1377 vs, 1300 s, 1377 vs, 1300 s, 1281 s, 911 vs, 838 m, 736 vs, 651 s, 554 w cm^{-1}; NMR: ^{19}F, δ −75.2 (CF_3, 6F, t, $^3J_{H-F}$ = 7.6 Hz); −114.5 (CF_2, 4F, s); ^1H, δ 4.44 (CH_2, 4H, q); CI MS [*m/e* (species) intensity]: 322 (M^+) 16.4; 303 ($M^+ - F$) 55.7; 83 ($CH_2CF_3^+$) 100. Anal. Calcd for $C_8H_4F_{10}O_2$: C, 29.81; F, 59.0; H, 1.24. Found: C, 30.1; F, 58.7; H, 1.31.

Properties of $\overline{CF_2C(OCH_2CF_3)=C(F)CF_2}$ (16). Spectral data compared with literature[19] are as follows. IR (neat): 2960 m, 2901 w, 1769 s, 1446 s, 1420 s, 1377 vs, 1283 vs, 1255 s, 1176 vs, 1130 s, 1116 s, 1062.5 vs, 999 s, 985 m, 971 m, 889 m, 848 s, 758 w, 689 w, 671 w, 660 m cm^{-1}; NMR: ^{19}F, δ −75.1 (CF_3, 3F, t, $^3J_{H-F}$ = 7.8 Hz); −117.2 (CF_2, 2F, m); −119.1 (CF_2, 2F, m); −137.0 (CF, 1F, m); ^1H, δ 4.5 (CH_2, 2H, q); CI MS [*m/e* (species) intensity]: 242 (M^+) 4.2; 223 ($M^+ - F$) 12.7; 173 ($M^+ - CF_3$) 2.7; 147 ($C_3F_5O^+$) 100.

Properties of 4-$CF_3CH_2OC_6F_4CN$ (17). This compound boils at 95–97 °C/6 Torr (35% yield). Spectral data are as follows. IR (KBr): 2247 cm^{-1} (CN). NMR: ^{19}F, −75.4 (3F); −132.4 (2F); −153.7 (2F); ^1H, 4.61 (q, $^3J_{H-F}$ = 8 Hz). CI MS [*m/e* (species) intensity]: 274 ($M^+ + 1$) 7.3; 273 (M^+) 2.1; 254 ($M^+ - F$) 0.8; 204 ($M^+ - CF_3$) 0.4; 99 ($CF_3CH_2O^+$) 1.34; 83 ($CF_3CH_2^+$) 4.6; 79 (CF_2CHO^+) 2.8; 69 (CF_3^+) 22.9; 59 ($CFCO^+$) 100. A small amount of higher boiling product (b.p. 125–130 °C/6mm) was identified by EI MS ($M^+ + 1$, 354, 100%) to be bis(trifluoroethoxy)trifluorobenzonitrile.

Properties of $(CF_3CH_2O)_5C_6CN$ (18). This compound melts at 70–72 °C (40% yield). Spectral data are as follows. IR (KBr): 2241 cm^{-1} (CN). NMR: ^{19}F, δ −74.7 (t, $^3J_{H-F}$ = 8 Hz); −75.0 (t, $^3J_{H-F}$ = 8 Hz); 1H, 4.39 (q); 4.53 (q, J_{H-F} = 8 Hz); 4.54 (q, J_{H-F} = 8 Hz); EI MS [*m/e* (species) intensity]: 593 (M^+) 75; 574 ($M^+ - F$) 4; 510 ($M^+ - CF_3CH_2$) 99.9; 83 ($CF_3CH_2^+$) 100. Anal. Calcd for $C_{17}H_{10}F_{15}O_5N$: C, 34.4; H, 1.69; N, 2.36; F, 48.04. Found: C, 34.86; H, 1.71; N, 2.50; F, 46.2.

Properties of $NCC_6F_4OC(CH_3)_2CF_3$ (19). This compound is recrystallized from heptane (33% yield, mp 62–64 °C). Spectral data are as follows. IR (film): 2243 m, 1646 m, 1495 s, 1439 s, 1401 m, 1381 m, 1331 m, 1169 s, 1125 s, 991 s, 968 s cm^{-1}; NMR: ^{19}F, δ −82.8 (CF_3, 3F, s); −133.0 (Ar−F, 2F, m); −147.6 (Ar−F, 2F, m); ^1H, δ 1.52 (CH_3, 6H, s); CI MS [*m/e* (species) intensity]: 301 (M^+) 0.4; 286 ($M^+ - CH_3$) 2.5; 232 ($M^+ - CF_3$) 7.4; 191 ($NCC_6F_4O^+ + 1$) 100; 174 ($NCC_6F_4^+$) 2.7; 162 ($NCC_5F_4^+$) 4.7; 143 ($NCC_5F_3^+$) 9.4; 91 ($C_4H_5F_2^+$) 58.8; 69 (CF_3^+) 5.9.

Properties of $NCC_6F_3[OC(CH_3)_2CF_3]_2$ (20). This compound is recrystallized from hexane (34% yield, mp 100–102 °C). Spectral data are as follows. IR (film): 2926 m, 2243 m, 1646 m, 1494 s, 1438 m, 1401 m, 1169 s, 1125 s, 992 s, 968 s cm^{-1}; NMR: ^{19}F, δ −82.0 (CF_3, 3F, s); −82.6 (CF_3, 3F, s); −132.6 (Ar−F, 1F, m); −134.3 (Ar−F, 1F, m); −146.0 (Ar−F, 1F, m); ^1H, δ 1.50 (CH_3, s); 1.53 (CH_3, s); CI MS [*m/e* (species) intensity]: 410 ($M^+ + 1$) 5.8; 409 (M^+) 41.8; 340 ($M^+ - CF_3$) 2.4; 314 ($M^+ - CF_3 - CN$) 1.9; 299 ($M^+ - C_4H_6F_3 + 1$) 15.4; 280 ($M^+ - C_4H_6F_4 + 1$) 11.6; 230 ($M^+ - C_4H_6F_3 - CF_3 + 1$) 1.9; 204 ($M^+ - C_4H_6F_3 - CF_3 - CN + 1$) 7.3; 91($C_4H_5F_2^+$) 19.5. Anal. Calcd for $C_{15}H_{12}F_9O_2N$: C, 44.01; H, 2.93; F, 41.81. Found: C, 44.26; H, 2.94; F, 41.4.

Properties of $C_6F_5OC(CH_3)_2CF_3$ (21). This compound is distilled at 112–114 °C (71.1% yield). Spectral data are as follows. IR (film): 2881 m, 1639 m, 1515 s, 1474 m, 1398 m, 1380 m, 1233 m, 1171 s, 1128 s, 1029 s, 995 s, 952 m, 845 m, 837 m, cm^{-1}; NMR: ^{19}F, δ −82.9 (CF_3, 3F, s); −151.4 (p-F, 2F, m); −160.1 (m-F, 1F, m); −162.5 (o-F, 2F, m); ^1H, δ 1.53 (CH_3, s); EI MS [*m/e* (species) intensity]: 294 (M^+) 0.6; 279 ($M^+ - CH_3$) 2.0; 275 ($M^+ - F$) 27.5; 225 ($M^+ - CF_3$) 6.2; 184 ($C_6F_5OH^+$) 100; 183 ($C_6F_5O^+$) 7.3; 167 ($C_6F_5^+$) 3.1; 155 ($C_5F_5^+$) 10.9; 136 ($C_5F_4^+$) 16.4; 117 ($C_5F_3^+$) 11.3; 111 ($C_4H_6F_3^+$) 30.5; 96 ($C_3H_3F_3^+$) 1.6; 81 ($C_2F_3^+$) 58.8; 69 (CF_3^+) 15.0.

Properties of $CF_3C_6F_4OC(CH_3)_2CF_3$ (22). This compound is distilled at 88–90 °C (73.5% yield). Spectral data are as follows. IR (film): 1655 m, 1505 s, 1430 m, 1400 m, 1382 m, 1345 s,1238 s, 1172 s, 1129 s, 995 s, 888 m, 718 m, cm^{-1}; NMR: ^{19}F, δ −56.8 ($ArCF_3$, 3F, s); −83.2 (CF_3, 3F, s); −141.8 (Ar−F, 2F, m); −149.6 (Ar−F, 2F, m); ^1H, δ 1.53 (CH_3, s); EI MS [*m/e* (species) intensity]: 329 ($M^+ - CH_3$) 3.1; 325 ($M^+ - F$) 17.3; 275 ($M^+ - CF_3$) 8.6; 234 ($C_7F_7OH^+$) 100; 217 ($C_7F_7^+$) 5.1; 215 ($C_7F_6OH^+$) 62.3; 214 ($C_7F_6O^+$) 4.4; 117 ($C_5F_3^+$) 9.0; 111 ($C_4H_6F_3^+$) 15.0; 91 ($C_4H_5F_2^+$) 35.5; 69 (CF_3^+) 10.4.

Properties of $ClC_6F_4OC(CH_3)_2CF_3$ (23). This compound is distilled at 145 °C (53.5% yield). Spectral data are as follows. IR (film): 2956 w, 1504 s, 1489 m, 1399 m, 1380 m, 1391 m,1232 s, 1171 s, 1128 s, 982 s, 953 m, 894 s, 888 m cm^{-1}; NMR: ^{19}F, δ 82.6 (CF_3, 3F, s); −141.8 (Ar−F, 2F, m); −150.2 (Ar−F, 2F, m); ^1H, δ 1.47 (CH_3, s); CI MS [*m/e* (species) intensity]: 312/310 (M^+) 1.2/3.1; 293/291 ($M^+ - F$) 22.3/68.1; 243/241 ($M^+ - CF_3$) 5.3/11.1; 202/200 ($ClC_6F_4OH^+$) 26.9/100; 185/183 ($ClC_6F_4^+$) 1.5/3.7; 111 ($C_4H_6F_3^+$) 47.1; 91 ($C_4H_5F_2^+$) 66.3; 69 (CF_3^+) 9.4.

Properties of $NC_5F_4OC(CH_3)_2CF_3$ (24). This compound is distilled at 107–109 °C (76.4% yield). Spectral data are as follows. IR (film): 2884 m, 1633 m, 1555 s, 1485 m, 1417 m, 1381 m, 1352 s, 1281 s, 1248 m, 1148 s, 1058 s, 953 s cm^{-1}; NMR: ^{19}F, δ −82.9 (CF_3, 3F, s); −89.4 (Py-F, 2F, m); −156.2 (Py-F, 2F, m); ^1H, δ 1.50 (CH_3, s); CI MS [*m/e* (species) intensity]: 278 ($M^+ + 1$) 3.5; 277 (M^+) 3.6; 258 ($M^+ - F$) 24.8; 208 ($M^+ - CF_3$) 5.5; 167 ($NC_5F_4OH^+$) 100; 166 ($NC_5F_4O^+$) 94.4; 148 ($NC_5F_3OH^+$) 32.1; 111 ($C_4H_6F_3^+$) 6.7; 91 ($C_4H_5F_2^+$) 24.4; 71 ($C_4H_4F^+$) 11.7; 69 (CF_3^+) 14.2.

Properties of $C_6F_3I_2OC(CH_3)_2CF_3$ (25). This compound is distilled at 102 °C/4 × 10^{-4} Torr (21.6% yield). Spectral data are as follows. IR (film): 2955 m, 1598 m, 1459 s, 1398 s, 1380 s, 1329 s, 1310 s, 1258 s, 1150 s, 1024 s, 953 m, 940 m, 853 s, 813 s, 782 s cm^{-1}; NMR: ^{19}F, δ −82.4 (CF_3, 3F, s); −92.6 (Ar−F, 1F, m); −105.6 (Ar−F, 1F, m); −140.8 (Ar−F, 1F, m); ^1H, δ 1.46 (CH_3, s); CI MS [*m/e* (species) intensity]: 511 ($M^+ + 1$) 1.5; 510 (M^+) 11.5; 441 ($M^+ - CF_3$) 1.5; 400 ($C_6F_3I_2OH^+$) 100; 399 ($C_6F_3I_2O^+$) 5.5, 371 ($C_6F_3I_2O^+ - CO$) 4.5; 273 ($C_6F_3IOH^+$) 21.0; 146 ($C_6F_3OH^+$) 25.2; 145 ($C_6F_3O^+$) 1.7; 117 ($C_5F_3^+$) 22.4; 98 ($C_5F_2^+$) 10.1.

Properties of c-$C_4F_5OC(CH_3)_2CF_3$ (26). This compound is collected in a trap cooled to −40 °C (46.8% yield). Spectral data are as follows. IR (film): 3005 m, 1757 m, 1479 m, 1389 s, 1384 s, 1320 m, 1188 s, 1146 s, 1024 s, 981 m, 731 m cm^{-1}; NMR: ^{19}F, δ −83.0 (CF_3, 3F, s); −117.4 (CF_2, 2F, m); −120.3 (CF_2, 2F, m); −130.4 (C=CF, 1F, m); ^1H, 1.59 (CH_3, s); CI MS [*m/e* (species) intensity]: 251 ($M^+ - F$) 17.0; 231 ($M^+ - HF_2$) 4.2; 160 ($M^+ - C(CF_3)(CH_3)_2 + 1$) 1.3; 143 ($C_4F_5^+$) 1.3; 141 ($C_4F_4O^+ + 1$) 25.2; 111 ($C(CF_3)(CH_3)_2^+$) 14.7; 91 ($C_4H_5F_2^+$) 100; 89 ($CF_2CO^+ + 1$) 11.4; 69 ($CF_3^+$) 4.4; 59 ($CFCO^+$) 8.0.

Properties of $NCC_6F_4OC(CF_3)_2CH_3$ (27). This compound is recrystallized from heptane (74.6% yield, mp 56–58 °C). Spectral data were as follows. IR (film): 2248 m, 1650 m, 1506 s, 1469 m, 1442 m, 1400 m, 1327 s, 1303 s, 1231 s, 1140 s, 1088 s, 996 s, 965 s cm^{-1}; NMR: δ −77.2 (CF_3, 6F, s); −131.5 (Ar−F, 2F, m); −146.3 (Ar−F, 2F, m); ^1H, δ 1.66 (CH_3, 3H, s); CI MS [*m/e* (species) intensity]: 356 ($M^+ + 1$) 100; 355 (M^+) 23.0; 336 ($M^+ - F$) 8.9; 191 ($NCC_6F_4OH^+$) 31.3; 190 ($NCC_6F_4O^+$) 1.2; 162 ($NCC_6F_4O^+ - CO$) 1.6; 143 ($NCC_6F_4O^+ - CO - F$) 2.2; 69 (CF_3^+) 4.6. Anal. Calcd for $C_{11}H_3F_{10}NO$: C, 37.20; H, 0.85; F, 53.50. Found: C, 37.22; H, 0.87; F, 53.5.

Properties of $C_6F_5OC(CF_3)_2CH_3$ (28). This compound is distilled at 78–80 °C (66.8% yield). Spectral data are as follows. IR (film): 2987 w, 1533 s, 1458 m, 1389 m, 1312 s, 1232 s, 1180 s, 1089s, 1019 s, 702 m cm^{-1}; NMR: ^{19}F, δ −77.5 (CF_3, 3F, s); −149.9 (p-F, 2F, m); −156.8 (m-F, 1F, m); −161.9 (o-F, 2F, m); ^1H, δ 1.62 (CH_3, s); EI MS [*m/e* (species) intensity]: 348 (M^+) 5.2; 186 ($C_6F_6^+$) 100; 184 ($C_6F_5OH^+$) 16.3; 183 ($C_6F_5O^+$) 6.9; 167 ($C_6F_5^+$) 16.9; 155 ($C_6F_5O^+ - CO$) 17.2; 136 ($C_5F_4^+$) 12.0; 117 ($C_5F_3^+$) 77.3; 98 ($C_5F_2^+$) 8.2.

Properties of $C_6F_3I_2OC(CF_3)_2CH_3$ (29). This compound is distilled

at 85−88 °C/4 × 10^{-4} Torr (19.5% yield). Spectral data are as follows. IR (film): 2928 w, 1477 s, 1437 s, 1397 s, 1368 s, 1313 s, 1240 s, 1139 s, 1090 s, 1024 s, 907 s, 879 m, 815 s, 788 s cm^{-1}; NMR: ^{19}F, δ −77.2 (CF_3, 6F, s); −92.1 (Ar−F, 1F, m); −104.8 (Ar−F, 1F, m); −140.1 (Ar−F, 1F, m); ^1H, δ 1.59 (CH_3, s); CI MS [*m/e* (species) intensity]: 565 ($M^+ + 1$) 9.9; 564 (M^+) 100; 437 ($M^+ - I$) 2.2; 400 ($C_6F_3I_2OH^+$) 38.8; 399 ($C_6F_3I_2O^+$) 91.4; 371 ($C_6F_3I_2O^+ - CO$) 41.7; 273 ($C_6F_3IOH^+$) 21.9; 272 ($C_6F_3IO^+$) 1.2; 244 ($C_6F_3IO^+ - CO$) 7.7; 146 ($C_6F_3OH^+$) 44.2; 145 ($C_6F_3O^+$) 13.9; 129 ($C_6F_3^+$) 12.1; 117 ($C_5F_3^+$) 78.0; 98 ($C_5F_2^+$) 35.8; 77 ($CH_3CCF_2^+$) 3.8.

Properties of $CF_3C_6F_4OC(CF_3)_2C_6H_5$ (30). This compound is distilled at 69−71 °C/10^{-3} Torr (66.3% yield). Spectral data are as follows. IR (film): 3073 w, 1654 m, 1505 m, 1433 m, 1347 m, 1234 s, 1195 s, 1155 s, 1119 s, 998 s, 942 m, 879 m, 727 m cm^{-1}; NMR: ^{19}F, δ −56.6 (CF_3, 3F, s); −71.2 (CF_3, 6F, s); −131.5 (Ar−F, 2F, m); −146.7 (Ar−F, 1F, m); ^1H, δ 7.66−7.42 (Ar−H, m); CI MS [*m/e* (species) intensity]: 441 ($M^+ - F$) 4.0; 421 ($M^+ - HF_2$) 1.2; 234 ($CF_3C_6F_4OH^+$) 8.5; 227 ($C_6H_5C(CF_3)_2^+$) 100; 217 ($CF_3C_6F_4^+$) 1.06; 215 ($CF_3C_6F_4OH^+ - F$) 20.9; 207 ($C_6H_5C(CF_3)_2^+ - HF$) 16.0; 198 ($CF_3C_6F_4^+ - F$) 1.4; 159 ($C_6H_5C(CF_3)^+ + 1$) 2.0; 69 (CF_3^+) 3.4; 59 ($CFCO^+$) 1.8.

Properties of $NCC_6F_4OC(CF_3)_2C_6H_5$ (31). This compound was distilled at 83−85 °C/10^{-3} Torr (68.6% yield). Spectral data are as follows. IR (film): 3073 w, 2247 m, 1648 m, 1502 m, 1443 m, 1323 m, 1225 s, 1140 s, 1003 s, 943 s, 722 m, cm^{-1}; NMR: ^{19}F, δ −71.0 (CF_3, 3F, s); −132.7 (Ar−F, 2F, m); −145.3 (Ar−F, 1F, m); CI MS [*m/e* (species) intensity]: 418 ($M^+ + 1$) 17.1; 398 ($M^+ - F$) 2.5; 271 ($M^+ - CF_3 - C_6H_5$) 4.7; 227 ($C_6H_5C(CF_3)_2^+$) 100; 208 ($C_6H_5C(CF_3)(CF_2)^+$) 18.5; 207 ($C_6H_4C(CF_3)(CF_2)^+$) 14.1; 190 ($NCC_6F_4O^+$) 2.03; 175 ($NCC_6F_4H^+$) 18.9; 159 ($C_6H_5C(CF_3)^+ + 1$) 2.0; 77 ($C_6H_5^+$) 3.3; 69 (CF_3^+) 12.4.

Properties of c-$C_4F_5OC(CF_3)_2C_6H_5$ (32). This compound was distilled at 66−68 °C (38.2% yield). Spectral data are as follows. IR (film): 3075 w, 1759 s, 1658 m, 1385 s, 1299 s, 1257 s, 1230 s, 1024 s, 1142 s, 1064 s, 1010, s, 970 m, 958 m, 726 m, 705 m cm^{-1}; NMR: ^{19}F, δ −72.3 (CF_3, 6F, s); −118.6 (CF_2, 2F, m); −121.0 (CF_2, 2F, m); −125.6 (C=CF, 1F, m); ^1H, δ 7.51 (C_6H_5, m); CI MS [*m/e* (species) intensity]: 386 (M^+) 0.9; 367 ($M^+ - F$) 11.3; 347 ($M^+ - HF_2$) 31.8; 317 ($M^+ - CF_3$) 1.2; 227 ($C_6H_5C(CF_3)_2^+$) 100; 208 ($C_6H_5C(CF_3)(CF_2)^+$) 8.3; 207 ($C_6H_4C(CF_3)(CF_2)^+$) 11.9; 159 ($C_4F_5O^+$) 1.7; 143 ($C_4F_5^+$) 4.5; 69 (CF_3^+) 9.3.

Properties of $C_6H_5C(CF_3)_2OCH_2C_6H_5$ (33). This compound was distilled at 90 °C/10^{-2} Torr (88.3% yield). Spectral data are as follows. IR (film): 3037 w, 1499 s, 1455 s, 1393 s, 1217 s, 1126 s, 1088 s, 1011 s, 945 s, 764 m, 737 m, 719 s cm^{-1}; NMR: ^{19}F, δ 70.8 (CF_3, 6F, s); ^1H, δ 7.39−7.66 (C_6H_5, 10H, m); 4.66 (CH_2, 2H, s); CI MS [*m/e* (species) intensity]: 257 ($M^+ - C_6H_5$) 1.9; 227 ($M^+ - C_6H_5CH_2O$) 44.6; 208 ($C_6H_5C(CF_3)(CF_2)^+$) 1.8; 159 ($C_6H_5C(CF_3)^+ + 1$) 12.8; 107 ($C_6H_5CH_2O^+$) 84.3; 91 ($C_6H_5CH_2^+$) 100; 77 ($C_6H_5^+$) 9.4, 69 (CF_3^+) 15.2.

Properties of $C_6H_5C(CF_3)_2OCH_3$ (34). This compound was distilled at 76 °C/10^{-3} Torr (77.7% yield). Spectral data are as follows. IR (film): 3070 w, 2994 w, 2959 m, 2854 w, 1454 m, 1289 s, 1201 s, 1149 s, 1126 s, 1086 s, 999 s, 945 s, 720 s cm^{-1}; NMR: ^{19}F, δ 71.3 (CF_3, 6F, s); ^1H, δ 7.41−7.54 (C_6H_5, 5H, m); 3.46 (CH_2, 2H, sept, $J_{H-F} = 1.01$); CI MS [*m/e* (species) intensity]: 258 (M^+) 12.9; 239 ($M^+ - F$) 73.9; 227 ($M^+ - CH_3O$) 100; 190 ($M^+ - CF_3 + 1$) 7.0; 189 ($M^+ - CF_3$) 86.8; 181 ($M^+ - C_6H_5$) 3.9; 105 ($C_6H_5CO^+$) 13.0; 77 ($C_6H_5^+$) 5.2; 69 (CF_3^+) 12.1.

Properties of $NCC_6F_4OC(CF_3)_2H$ (35). This compound was distilled at 121 °C (76.5% yield). Spectral data are as follows. IR (film): 2882 m, 1652 m, 1511 m, 1456 m, 1353 m, 1287 s, 1236 s, 1203 s, 1109 s, 1000 s, 855 m, 729 m cm^{-1}; NMR: ^{19}F, δ −73.9 (CF_3, 6F, s), −131.3 (Ar−F, 2F, m); −152.3 (Ar−F, 2F, m); ^1H, δ 5.00 (OCH, sept, $J_{H-F} = 5.1$); CI MS [*m/e* (species) intensity]: 342 ($M^+ + 1$) 5.9; 341 (M^+) 5.8; 340 ($M^+ - 1$) 8.6; 191 ($NCC_6F_4OH^+$) 30.5; 190 ($NCC_6F_4O^+$) 17.6; 162 ($NCC_6F_4O^+ - CO$) 8.9; 175 ($NCC_6F_4^+ + 1$) 16.5; 149 ($C_6F_4^+ + 1$) 34.0; 79 (CF_2COH^+) 11.8; 69 (CF_3^+) 35.9; 59 ($CFCO^+$) 100.

Properties of $CF_3C_6F_4OC(CF_3)_2H$ (36). This compound was distilled at 115 °C (61.2% yield). Spectral data are as follows. IR (film): 2989 m, 1660 m, 1512 m, 1435 m, 1369 m, 1346 s, 1299 s, 1243 s, 1153 s, 1112 s, 1038 s, 999 s, 852 m, 718 m cm^{-1}; NMR: ^{19}F, δ −56.9 (Ar−CF_3, 3F, s); −74.5 (CF_3, 6F, s); −140.0 (Ar−F, 2F, m); −154.5 (Ar−F, 2F, m); ^1H, δ 4.93 (OCH, sept, $J_{H-F} = 5.3$). CI MS [*m/e* (species) intensity]: 385 ($M^+ + 1$) 7.2, 384 (M^+) 59.5, 366 ($M^+ - F + 1$) 9.2, 365 ($M^+ - F$) 100, 315 ($M^+ - CF_3$) 5.6, 233 ($M^+ - C_3F_6H$) 20.0, 217 ($C_7F_7^+$) 48.9, 205 ($C_7F_7O^+ - CO$) 25.6, 69 (CF_3^+) 37.8.

Properties of $NCC_6F_4OC(CF_3)_3$ (37). This compound was distilled at 91−93 °C (70.1% yield). Spectral data are as follows. IR (film): 2247 m, 1652 m, 1511 m, 1445 m, 1278 s, 1148 s, 1001 s, 973 s, 854 m, 729 m, cm^{-1}; NMR: ^{19}F, δ −74.5 (CF_3, 9F, s); −131.5 (Ar−F, 2F, m); −146.7 (Ar−F, 2F, m); CI MS [*m/e* (species) intensity]: 410 ($M^+ + 1$) 14.5; 409 (M^+) 8.9; 390 ($M^+ - F$) 1.2; 219 ($(CF_3)_3C^+$) 1.6; 190 ($M^+ - C_4F_9$) 13.0; 162 ($M^+ - C_4F_9 - CO$) 8.9; 143 ($M^+ - C_4F_9 - CO - F$) 1.2; 131 ($C_5F_3N^+$) 3.8; 105 ($C_4F_3^+$) 1.3; 88 ($C_3F_2N^+$) 91.1; 86 ($C_4F_2^+$) 100; 69 (CF_3^+) 35.9.

Preparation of Ethers (38−40). A mixture of C_6F_5CN (5.5 g, 30 mmol), siloxane **7** or **8** or **9** (2.4 g, 18 mmol), cesium fluoride (250 mg) and 1,2-dimethoxyethane (10 g) is stirred and heated at 80−90 °C for 4 h. The products **38−40** are obtained in 54 to 74% yield.

Properties of $FCH_2CH_2OC_6F_4CN$ (38). This compound is distilled at 96 °C/1.5 Torr (74% yield). Spectral data are as follows. IR: 2244 cm^{-1} (CN). NMR: ^{19}F, δ −133.7 (2F), −154.5 (2F), −186.5 (1F); ^1H, δ 4.5(m, 2H), 4.86(2H). Hydrolysis product is more fully characterized. See compound **62**.

Properties of $HCF_2CF_2CH_2OC_6F_4CN$ (39). This compound is distilled at 132 °C/3.5 Torr (55% yield). Spectral data are as follows. IR (film): 2243 cm^{-1}; NMR: ^1H, δ 4.8 (m, 2H), 6.1 (t, $J_{HF} = 32$ Hz). Hydrolysis product is more fully characterized. See compound **63**.

Properties of *n*-$C_7F_{15}CH_2OC_6F_4CN$ (40). This compound is distilled at 126 °C/1.5 Torr (54% yield). Spectral data are as follows. IR: 2248 cm^{-1} (CN). NMR: ^{19}F, −80.9 (3F), −122.9 (6F), −124.7 (2F), −126.6 (2F), −132.4 (2F), −158.5 (2F) ^1H, δ 4.8(m). Hydrolysis product is more fully characterized. See compound **64**.

Properties of $\overline{CF_2CH_2OCH_2OCH_2CF_2}$ (41). Spectral data are as follows. IR (neat): 2986 w, 2948 m, 2912 m, 1447 m, 1392 w, 1377 m, 1293 s, 1236 m, 1206 m, 1145 vs, 1059 s, 970 m, 919 w, 908 w, 710 m, 667 m, 571 w cm^{-1}; NMR: ^{19}F, δ −127.9 (4F, m); ^1H, δ 4.74 (OCH_2O, 2H, s); 3.86 ($CH_2CF_2CF_2CH_2$, 4H, m); CI MS [*m/e* (species) intensity]: 175 ($M^+ + 1$) 1.2; 174 (M^+) 2.8; 155 ($M^+ - F$) 21.9; 145 ($M^+ - OCH_2 + 1$) 21.6; 144 ($M^+ - OCH_2$) 6.6; 125 ($M^+ - CF_2 + 1$) 35.3; 124 ($M^+ - CF_2$) 51.5; 114 ($CF_2CF_2CH_2^+$) 8.9; 113 (CF_2CF_2-CH^+) 20.6; 107 ($M^+ - OCH_2F_2 + 1$) 9.8; 95 ($C_3F_3H_2^+$) 12.9; 86 ($CCFCFC^+$) 100; 77 ($CFCFCH_2^+$) 8.3; 64 ($C_2H_2F_2^+$) 32.8; 56 ($C_3H_4O^+$) 12.4.

Properties of $\overline{CF_2CH_2OCHOCH_2CF_2CF_2CH_2OCHOCH_2CF_2}$ (42). This compound melts at 70−72 °C. Spectral data are as follows. IR (KBr disk): 2976 m, 1404 w, 1333 w, 1266 m, 1235 s, 1220 m, 1195 m, 1122 vs, 1073 vs, 1013 s, 933 s, 908 s, 783 s, 652 s, 611 m, 554 s cm^{-1}; NMR: ^{19}F, δ −123.9 (8F, m); ^1H, δ 5.9 (CHCH, 2H, s); 3.88 (CH_2CF_2, 8H, m); CI MS [*m/e* (species) intensity]: 347 ($M^+ + 1$) 3.9; 327 ($M^+ - F$) 1.1; 265 ($M^+ - OCH_2CF_2 - H$) 2.2; 203 ($M^+ - OCH_2(CF_2)_2CH_2 + 1$) 4; 189 ($C_5H_5F_4O_3^+$) 15.8; 159 ($C_4H_3F_4O_2^+$) 6.4; 145 ($C_4H_4F_4O^+ + 1$) 100; 124 ($C_4F_4^+$) 12.2; 113 ($CF_2CF_2CH^+$) 11.4; 100 ($C_2F_4^+$) 5.3; 64 ($CF_2CH_2^+$) 33.3. Anal. Calcd for $C_{10}H_{10}F_8O_4$: C, 34.68; F, 43.93; H, 2.89. Found: C, 35.1; F, 44.21; H, 3.01.

Properties of $\overline{CF_2CH_2OS(O)OCH_2CF_2}$ (43). Spectral data are as follows. IR (neat): 3009 s, 2968 m, 2946 m, 1448 s, 1378 s, 1352 w, 1275 s, 1230 vs, 1207 vs, 1143 vs, 1106 s, 1031 vs, 991 s, 924 s, 745 s, 707 s, 656 s cm^{-1}; NMR: ^{19}F, δ −127.3 (4F, m); ^1H, δ 4.48 and 4.09 (4H, m); CI MS [*m/e* (species) intensity]: 210 ($M^+ + 2$) 3.1; 209 ($M^+ + 1$) 62.4; 189 ($M^+ - F$) 12; 179 ($M^+ - OCH_2 + 1$) 25.4; 178 ($M^+ - OCH_2$) 34; 169 ($M^+ - 2F - H$) 2.5; 145 ($M^+ - CF_2CH_2 + 1$) 28.1; 144 ($M^+ - SO_2$) 1.2; 131 ($M^+ - CH_2SO_2 + 1$) 2.5; 114 (CF_2-$CF_2CH_2^+$) 26.6; 108 ($M^+ - C_2F_4$) 1.1; 100 ($C_2F_4^+$) 6.9; 81 ($C_2F_3^+$) 5.8; 64 ($CF_2CH_2^+$) 100. Anal. Calcd for $C_4H_4F_4SO_3$: C, 23.07; H, 1.9. Found: C, 22.9; H, 2.10.

Properties of $\overline{CF_2CH_2OSO_2OCH_2CF_2}$ (44). Spectral data are as follows. IR (neat): 3003 m, 2945 m, 1445 m, 1422 m, 1397 w, 1376

s, 1255 w, 1228 w, 1188 m, 1152 s, 1060 s, 1040 m, 955 w, 919 w, 748 m cm^{-1}; NMR: ^{19}F, δ −123.6 (4F, m); ^{1}H, 3.92 (4H, m); CI MS [*m/e* (species) intensity]: 224 (M^+) 5.2; 223 ($M^+ - H$) 1.2; 186 ($M^+ - 2F$) 1.1; 174 ($M^+ - CF_2$) 6.9; 161 ($M^+ - SO_2 + 1$) 2.2; 159 ($M^+ - SO_2 - H$) 2.3; 145 ($M^+ - SO_3 + 1$) 12.2; 144 ($M^+ - SO_3$) 7.7; 131 ($M^+ - CH_2SO_3 + 1$) 5.6; 125 ($M^+ - C_2F_4 + 1$) 39.4; 113 ($C_3F_4H^+$) 10.2; 105 ($C_4F_3^+$) 12.2; 93 ($C_3F_3^+$) 10.8; 81 ($C_2F_3^+$) 13.1; 64 (CF_2-CH_2^+) 100.

Properties of $FC(O)OCH_2CF_2CF_2CH_2OC(O)F$ (45). Spectral data are as follows. IR (neat): 3004 m, 2945 m, 1847 vs, 1446 s, 1411 m, 1377 s, 1264 s, 1189 w, 1147 s, 1084 w, 1041 s, 979 m, 919 s, 773 m, 752 m cm^{-1}; NMR: ^{19}F, δ −19.9 (COF, 2F, s); −122.4 (CF_2, 4F, m); ^{1}H, δ 4.55 (4H, m); CI MS [*m/e* (species) intensity]: 235 ($M^+ - F$) 4.5; 192 ($M^+ - CO_2F + 1$) 3.5; 191 ($M^+ - CO_2F$) 58.6; 189 ($M^+ - OCOF - 2H$) 18.2; 177 ($M^+ - CH_2OCOF$) 4.9; 169 ($M^+ - COF - 2F$) 1.9; 155 ($C_5H_3F_4O^+$) 6.1; 145 ($C_4H_5F_4O^+$) 2.7; 127 ($C_4H_3F_4^+$) 18.1; 113 ($CF_2CF_2CH^+$) 6.7; 95 ($C_3H_2F_3^+$) 4.2; 83 ($C_2H_2F_3^+$) 14.8; 81 ($C_2F_3^+$) 5.9; 64 ($CF_2CH_2^+$) 100. Anal. Calcd for $C_6H_4F_6O_4$: C, 28.34; F, 44.88; H, 1.57. Found: C, 28.20; F, 45.21; H, 1.90.

Properties of *p*-$CNC_6F_4OCH_2(CF_2)_2CH_2OC_6F_4CN$-*p* (46). Spectral data are as follows. IR (neat): 2979 m, 2247 s, 1651 s, 1503 s, 1443 s, 1403 s, 1303 m, 1248 m, 1198 s, 1136 s, 998 s, 958 m, 784 w, 756 w cm^{-1}; NMR: ^{19}F, δ −122.1 (CF_2, 4F, m); −132.1 (CF ortho to CN, 4F, m); −153.6 (CF meta to CN, 4F, m); CI MS [*m/e* (species) intensity]: 537 ($M^+ + 29$) 3.3; 523 ($M^+ + 15$) 32.4; 509 ($M^+ + 1$) 21.5; 508 (M^+) 100; 317 ($M^+ - OC_6F_4CN - H$) 92.1; 297 ($MH^+ - C_6F_4CN - 2F$) 2.7; 254 ($CF_2CH_2OC_6F_4CN^+$) 25; 204 ($CH_2OC_6F_4CN^+$) 18.6; 190 ($OC_6F_4CN^+$) 64.2; 174 ($C_6F_4CN^+$) 8.7; 162 ($C_5F_4CN^+$) 25.8; 143 ($C_5F_3CN^+$) 3.6; 124 ($C_5F_2CN^+$) 10.6; 108 ($C_4H_3F_3^+$) 15.6; 93 ($C_3F_3^+$) 5.6; 64 ($CF_2CH_2^+$) 19. Anal. Calcd for $C_{18}H_4F_{12}N_2O_2$: C, 42.51; H, 0.78. Found: C, 43.01; H, 1.1.

Properties of $\overline{CF_2CH_2OC(O)C(O)OCH_2CF_2}$ (47). This compound melts at 120 ° C. Spectral data are as follows. IR (KBr disk): 2986 m, 1767 s, 1446 s, 1386 s, 1135 vs, 1021 m, 988 m, 887 m, 787 w, 722 m, 647 w cm^{-1}; NMR: ^{19}F, δ −121.3 (4F, m); ^{1}H, δ 3.9 (4H, m); CI MS [*m/e* (species) intensity]: 217 ($M^+ + 1$) 2; 216 (M^+) 3.1; 215 ($M^+ - H$) 3.6; 203 ($M^+ - CH_2 + 1$) 22.3; 202 ($M^+ - CH_2$) 6.9; 197 ($M^+ - F$) 2.9; 185 ($M^+ - OCH_2 - H$) 3.9; 167 ($M^+ - CF_2 + 1$) 11.7; 166 ($M^+ - CF_2$) 7.4; 153 ($M^+ - CH_2CF_2 + 1$) 4.1; 145 ($CH_2CF_2CF_2$-CH_2OH^+) 100; 135 ($M^+ - OCH_2CF_2 - H$) 6.7; 125 ($C_4H_4F_3O^+$) 57.2; 112 ($C_3H_3F_3O^+$) 24.7; 104 ($C_4H_2F_2O^+$) 13.8; 91 ($C_4H_5F_2^+$) 7.4; 85 ($C_4H_2FO^+$) 13.1; 64 ($CF_2CH_2^+$) 4.4. Anal. Calcd for $C_6H_4F_4O_4$: C, 33.3; F, 35.18; H, 1.85. Found: C, 34.0; F, 35.5; H, 2.0.

Properties of $\overline{CF_2CH_2OP(O)FOCH_2CF_2}$ (48). Spectral data are as follows. IR (neat): 2871 m, 1480 m, 1462 m, 1394 m, 1354 w, 1245 s, 1160 s, 1080 s, 925 s, 852 m, 782 m, 738 m, 708 w, 674 s cm^{-1}; NMR: ^{19}F, δ −84.2 (PF, 1F, d, J_{P-F} = 955.6 Hz); −127.5 (CF_2, 4F, m); ^{1}H, δ 4.5 (4H, m); ^{31}P, δ −10.19 (PF, d); CI MS [*m/e* (species) intensity]: 226 (M^+) 1.4; 225 ($M^+ - H$) 9.2; 204 ($M^+ - HF - 2H$) 57.1; 185 ($M^+ - 2HF - H$) 12.5; 161 ($C_3H_2F_4PO^+$) 9.3; 141 ($C_3H_4F_2$-PO_2^+) 3.8; 131 ($C_3H_3F_4O^+$) 2.2; 114 ($C_2F_4CH_2^+$) 17; 113 ($C_2F_4CH^+$) 19.3; 108 ($C_2H_2FPO_2^+$) 15.6; 101 ($C_2F_4^+ + 1$) 9.1; 100 ($C_2F_4^+$) 3.5; 95 ($C_3H_2F_3^+$) 100; 91 ($C_2H_4PO_2^+$) 25.2; 81 ($C_2F_3^+$) 22.2; 80 (CF_2-CH_2O^+) 28.7; 64 ($CF_2CH_2^+$) 59.5; 62 ($C_2F_2^+$) 34.

Properties of $NC_5F_4OCH_2(CF_2)_2CH_2OC_5F_4N$ (49). Spectral data are as follows. IR (neat): 2978 m, 2895 w, 1645 s, 1603 m, 1511 s, 1484 vs, 1455 s, 1423 m, 1387 m, 1278 m, 1245 s, 1122 vs, 1062 m, 999 m, 964 m, 912 m, 815 w, 788 w, 737 m cm^{-1}; NMR: ^{19}F, δ −89.9 (CF ortho to N, 4F, m); −158.5 (CF meta to N, 4F, m); −122.8 (4F, m); ^{1}H, δ 4.8 (4H, m); CI MS [*m/e* (species) intensity]: 461 ($M^+ + 1$) 13.5; 460 (M^+) 82.3; 441 ($M^+ - F$) 1.6; 421 ($M^+ - F - HF$) 1.9; 294 ($M^+ - OC_5F_4N$) 53.3; 274 ($M^+ - OC_5F_4N - HF$) 10.3; 260 ($M^+ - OC_5F_4N - CH_2 - HF$) 3.1; 230 ($NC_5F_4OCH_2CF_2^+$) 65.6; 180 ($NC_5F_4$-$OCH_2^+$) 100; 167 ($C_5F_4NOH^+$) 8.6; 150 ($C_5F_4N^+$) 73.2; 138 ($C_4F_4N^+$) 28.3; 132 ($C_5F_3NH^+$) 27; 119 ($C_4F_3N^+$) 4.6; 108 ($C_3F_3NH^+$) 13.5; 100 ($C_2F_4^+$) 28.4; 95 ($C_3F_3H_2^+$) 9.6; 93 ($C_3F_3^+$) 13.4; 64 ($CF_2CH_2^+$) 47.5. Anal. Calcd for $C_{14}H_4F_{12}N_2O_2$: C, 36.5; F, 49.56. Found: C, 36.9; F, 49.12.

Properties of $CF_3SO_2OCH_2(CF_2)_2CH_2OSO_2CF_3$ (50). This compound melts at 56−58 °C. Spectral data are as follows. IR (KBr disk): 3049 w, 2926 m, 1454 w, 1424 s, 1408 s, 1306 s, 1249 m, 1204 s, 1134 vs, 1032 s, 959 s, 926 m, 822 m, 719 m cm^{-1}; NMR: ^{19}F, δ −70.0 (CF_3, 6F, s); −116.1 (CF_2, 4F, m); ^{1}H, δ 5.0 (4H, m); CI MS [*m/e* (species) intensity]: 427 ($M^+ + 1$) 1.5; 389 ($M^+ - 2F + 1$) 1.3; 317 ($M^+ - CF_3 - 2HF$) 1.5; 297 ($M^+ - CF_3 - 3HF$) 1.2; 277 ($M^+ - OSO_2CF_3$) 3.9; 263 ($M^+ - CH_2OSO_2CF_3$) 1.9; 251 ($C_3H_2F_7SO_3^+$) 2.7; 213 ($C_3H_2F_5SO_3^+$) 2.1; 195 ($C_3H_2F_4SO_3^+ + 1$) 5.1; 177 ($C_4H_4F_4SO^+ + 1$) 10.5; 149 ($CF_3SO_2O^+$) 100; 133 ($CF_3SO_2^+$) 3.4; 113 ($C_2F_4CH^+$) 99.5; 101 (SCF_3^+) 15.3; 82 (SCF_2^+) 3; 69 (CF_3^+) 27.9. Anal. Calcd for $C_6H_4F_{10}S_2O_6$: C, 16.9; F, 44.6; H, 0.94. Found: C, 17.1; F, 45.1; H, 1.1.

Properties of $F_2\overline{CH_2CO(3,6\text{-difluoro-}4,5\text{-diiodo-}O\text{-phenylene})OCH_2CF_2}$ (51). This compound melts at 96 °C. Spectral data are as follows. IR (KBr disk): 3093 m, 2962 m, 1635 m, 1464 s, 1432 s, 1400 m, 1359 w, 1307 m, 1254 m, 1194 s, 1138 s, 1118 s, 1079 s, 1040 s, 989 w, 833 s, 689 m cm^{-1}; NMR: ^{19}F, δ −122.8 (CF_2, 4F, m); −99.6 (aromatic CF, 2F, m); ^{1}H, δ 4.6 (4H, m); CI MS [*m/e* (species) intensity]: 525 ($M^+ + 1$) 12.5; 524 (M^+) 100; 398 ($M^+ - I + 1$) 8.1; 368 ($M^+ - OCH_2I + 1$) 14.4; 349 ($M^+ - OCH_2FI + 1$) 8.1; 270 ($M^+ - 2I$) 8.1; 241 ($M^+ - OCH_2I_2 + 1$) 29.2; 213 ($M^+ - 2I - 3F$) 11.8; 178 ($M^+ - 2I - COCH_2CF_2$) 10; 147 ($C_6H_4F_2O_2^+ + 1$) 33.1; 127 ($C_6F_2OH^+$) 9.4; 110 ($C_6F_2^+$) 6.7; 98 ($C_5F_2^+$) 17.9; 86 ($C_4F_2^+$) 58.4; 77 ($C_3H_2F_2^+ + 1$) 10.6. Anal. Calcd for $C_{10}H_4F_6I_2O_2$: C, 22.90; F, 21.75; H, 0.76. Found: C, 23.1; F, 22.08; H, 0.54.

Properties of $ICF_2{}^aCF_2{}^bOCF_2{}^cCF_2{}^dSO_2OCH_2(CF_2)_2{}^eCH_2OSO_2$-$CF_2{}^dCF_2{}^cOCF_2{}^bCF_2{}^aI$ (52). This compound melts at 52−53 °C. Spectral data are as follows. IR (KBr disk): 2985 m, 1428 vs, 1340 s, 1298 s, 1174 vs, 1095 s, 1028 s, 988 s, 955 m8, 912 s, 805 m, 761 m, 736 s, 652 m cm^{-1}; NMR: ^{19}F, δ −65.6 (a, 4F, m); −82.4 (b, 4F, m); −85.5 (c, 4F, m); −114.2 (d, 4F, m); −120.8 (e, 4F, m); ^{1}H, δ 4.7 (4H, m); CI MS [*m/e* (species) intensity]: 975 ($M^+ + 1$) 23.5; 974 (M^+) 8.8; 955 ($M^+ - F$) 1.7; 731 ($M^+ - OCF_2CF_2I$) 1; 615 ($M^+ - OCF_2CF_2OCF_2CF_2I$) 31.1; 551 ($M^+ - OSO_2CF_2CF_2OCF_2CF_2I$) 69.9; 487 ($ICF_2CF_2OCF_2CF_2SO_2OCH_2CF_2^+$) 15.1; 407 ($ICF_2CF_2OCF_2CF_2$-$SO_2^+$) 14; 369 ($ICFCFOCF_2CF_2SO_2^+$) 1; 343 ($ICF_2CF_2OCF_2CF_2^+$) 100.

Properties of $\overline{CF_2CH_2OC(O)(CF_2)_3C(O)OCH_2CF_2}$ (53). Spectral data are as follows. IR (neat): 1791 vs, 1455 m, 1403 m, 1325 s, 1146 s, 1140 s, 1078 m, 969 w, 917 m, 782 w, 747 w cm^{-1}; NMR: ^{19}F, δ −118.5 (4F, s); −122.0 (2F, s); −123.8 ($CH_2(CF_2)_2CH_2$, 4F, m); ^{1}H, δ 4.8 (4H, m); CI MS [*m/e* (species) intensity]: 367 ($M^+ + 1$) 11.4; 334 ($M^+ - CH_2F + 1$) 3.9; 241 ($M^+ - C_4F_4H$) 100; 223 ($M^+ - C_2F_4CO_2 + 1$) 18.1; 209 ($M^+ - C_2F_4CO_2CH_2 + 1$) 16.9; 195 (C_3F_6-$CO_2^+ + 1$) 36; 163 ($C_4F_6^+ + 1$) 15; 145 ($C_2F_4CO_2^+ + 1$) 35.2; 131 ($C_3F_5^+$) 8.4; 125 ($C_4F_4^+ + 1$) 32.6; 119 ($C_2F_5^+$) 9.5; 113 ($C_2F_4CH^+$) 6.3; 100 ($C_2F_4^+$) 5.1; 77 ($C_3H_2F_2^+ + 1$) 11; 64 ($CF_2CH_2^+$) 5.3. Anal. Calcd for $C_9H_4F_{10}O_4$: C, 29.51; F, 51.91. Found: C, 28.9; F, 51.5.

Properties of $(-F_2CH_2CO)_2$(3,6-dibromo-1,2,4,5-benzenetetra-yl)$(OCH_2CF_2-)_2$ (54). This compound melts at 152−154 °C. Spectral data are as follows. IR (KBr disk): 2968 m, 1469 vs, 1452 vs, 1397 m, 1291 m, 1256 m, 1228 m, 1188 m, 1137 s, 1073 s, 978 s, 956 m, 899 m, 826 m, 721 m, 651 w cm^{-1}; NMR: ^{19}F, δ −121.3 (8F, m); ^{1}H, δ 4.8 (8H, m); CI MS [*m/e* (species) intensity]: 473/471 ($M^+ - Br$) 10.9/10.6; 435/433 ($M^+ - Br - 2F$) 68/67.5; 415/413 ($C_{14}H_7F_5O_4$-Br^+) 28.2/27.5; 353 ($C_{14}H_7F_6O_4^+$) 12.3; 335 ($C_{14}H_8F_5O_4^+$) 3.8; 319 ($C_{14}H_8F_5O_3^+$) 5.8; 306 ($C_{13}H_7F_5O_3^+$) 15.1; 275 ($C_{12}H_7F_4O_3^+$) 6.9; 255 ($C_{12}H_6F_3O_3^+$) 2.7; 226 ($C_8H_6F_4O_3^+$) 11.7; 197 ($C_7H_4F_4O_2^+ + 1$) 1.5; 185 ($C_6H_4F_4O_2^+ + 1$) 2.5; 161 ($C_4H_4F_4O_2^+ + 1$) 6.2; 143 ($C_4H_3F_4O^+$) 34.6; 125 ($C_4HF_4^+$) 18.7; 114 ($C_2F_4CH_2^+$) 11.8; 95 ($C_3H_2F_3^+$) 10.5; 81 ($C_2F_3^+$) 100; 64 ($CF_2CH_2^+$) 20.4.

Properties of $\overline{CF_2CF_2CH_2OCH_2OCH_2CF_2}$ (55). Spectral data are as follows. IR (neat): 2960 m, 1257 w, 1152 s, 1064 s, 1007 w, 974 m, 914 w, 849 w, 738 m, 707 w, 605 m cm^{-1}; NMR: ^{19}F, δ −115.4 (terminal CF_2, 4F, m); −128.8 (center CF_2, 2F, s); ^{1}H, δ 4.65 (OCH_2O, 2H, s); 4.0 (4H, m); CI MS [*m/e* (species) intensity]: 225 ($M^+ + 1$) 1.5; 210 ($M^+ - CH_2$) 1.2; 205 ($M^+ - F$) 11.6; 195 ($M^+ - OCH_2 + 1$) 4.4; 194 ($M^+ - OCH_2$) 1.9; 184 ($M^+ - 2HF$) 3; 175 ($M^+ - CF_2 + 1$) 26.4; 174 ($M^+ - CF_2$) 10.4; 145 ($M^+ - OCH_2CF_2 + 1$) 3.9; 131 ($C_3F_5^+$) 1.2; 125 ($M^+ - C_2F_4 + 1$) 3.5; 119 ($C_2F_5^+$) 2.4; 113 ($C_3F_4H^+$) 2.4; 105 ($C_4F_3^+$) 3.5; 100 ($C_2F_4^+$) 5.9; 86 ($C_4F_2^+$) 100; 64 ($CF_2CH_2^+$) 7.6. Anal. Calcd for $C_6H_6F_6O_2$: C, 32.14; F, 50.89. Found: C, 32.7; F, 51.1.

Properties of $FC(O)OCH_2(CF_2)_3CH_2OC(O)F$ (56). Spectral data are as follows. IR (neat): 3004 m, 2945 m, 1848 s, 1633 m, 1446 s, 1377 s, 1272 m, 1168 m, 1040 s, 919 s, 751 s cm^{-1}; NMR: ^{19}F, δ −120.6 (4F, m); −125.9 (2F, s); −19.3 (C(O)F, 2F, s); ^1H, δ 4.69 (4H, m); CI MS [*m/e* (species) intensity]: 285 (M^+ − F) 3.5; 241 (M^+ − OC(O)F) 100; 221 (M^+ − OC(O)F − HF) 4.7; 175 ($C_5H_4F_5O^+$) 17.7; 150 ($C_3F_6^+$) 4.7; 127 ($C_3H_2F_3O_2^+$) 18.2; 119 ($C_2F_5^+$) 4.3; 100 ($C_2F_4^+$) 6.4; 77 ($C_3H_2F_2^+$ + 1) 29.

Properties of $\overline{CF_2CF_2CH_2OS(O)OCH_2CF_2}$ (57). Spectral data are as follows. IR (neat): 2970 m, 2945 m, 1446 s, 1376 s, 1314 w, 1295 m, 1241 s, 1171 s, 1136 s, 1111 m, 1040 s, 996 s, 962 s, 752 s cm^{-1}; NMR: ^{19}F, δ −115.6 (4F, m); −127.6 (2F, s); ^1H, δ 3.95 (4H, m); CI MS [*m/e* (species) intensity]: 273 (M^+ + 15) 2.6; 259 (M^+ + 1) 83.3; 239 (M^+ − F) 17.1; 228 (M^+ − OCH_2) 13.5; 219 (M^+ − 2F − H) 1.2; 209 (M^+ − CF_2 + 1) 1.1; 202 (M^+ − 3F + 1) 4.4; 195 (M^+ − SO_2 + 1) 30.6; 175 (M^+ − SO_2 − F) 100; 161 (M^+ − SO_2 − CH_2 − F) 73.4; 155 (M^+ − SO_2 − HF − F) 11; 145 ($C_4H_4F_4O^+$ + 1) 9.9; 131 ($C_2F_4CH_2O^+$ + 1) 7.1; 113 ($C_2F_4CH^+$) 12.9; 100 ($C_2F_4^+$) 33.9; 79 (CF_2CHO^+) 15.7; 64 ($CF_2CH_2^+$) 50.6.

Properties of $\overline{CF_2CF_2CH_2OSO_2OCH_2CF_2}$ (58). Spectral data are as follows. IR (KBr): 3004 m, 2945 m, 1633 m, 1444 s, 1404 s, 1376 s, 1261 w, 1040 s, 919 m, 831 w, 750 m cm^{-1}; NMR: ^{19}F, δ −116.9 (4F, m); −124.6 (2F, s); ^1H, δ 3.97 (4H, m); CI MS [*m/e* (species) intensity]: 211 (M^+ − SO_2 + 1) 7.4; 209 (M^+ − SO_2 − H) 10.7; 195 (M^+ − OCH_2CF_2 + 1) 3; 191 (M^+ − SO_2 − F) 3.3; 181 ($C_4H_2F_6O^+$ + 1) 3.6; 175 (M^+ − C_2F_4 + 1) 11.1; 155 ($C_5H_3F_4O^+$) 2.4; 130 ($C_2F_4CH_2O^+$) 4.3; 114 ($C_2F_4CH_2^+$) 10.3; 107 ($C_3F_3CH_2^+$) 44.7; 95 ($C_2F_3CH_2^+$) 4.8; 65 ($CF_2CH_2^+$ + 1) 100. Anal. Calcd for $C_5H_4F_6SO_4$: C, 21.90; F, 41.6. Found: C, 22.2; F, 40.97.

Properties of $CH_3CH(CF_3)OC_6F_4CN$ (59). A mixture of C_6F_5CN (5 g, 26 mmol), $CH_3CH(CF_3)OH$ (2.6 g, 26 mmol) and sodium carbonate (3.5 g) is stirred and heated at 70−80 °C for 12 h. Distillation gives the product **59** which boils at 105−110 °C/2 mm (52.8% yield). Spectral data are as follows. IR: 2248 cm^{-1}; NMR: ^{19}F, δ −79.4 (3F), −140.8 (2F), −154.5 (2F); ^1H, δ 1.62 (d), 4.72 (m). Hydrolysis product is more fully characterized. See compound **65**.

Properties of $(C_6H_5O)_5C_6CN$ (60). The reaction of C_6F_5CN (0.97 g, 5 mmol) with siloxane $C_6H_5OSiMe_3$ (5.5 g, 30 mmol) in the presence of cesium fluoride (250 mg) and 1,2-dimethoxyethane (10 mL) at 120 °C for 12 h gives the product **60** which melts at 162−166 °C (48% yield). IR (KBr): 2241 cm^{-1} (CN). EI MS [*m/e* (species) intensity]: 563 (M^+) 100; 470 (M^+ − C_6H_5O) 10. NMR: ^1H, δ 6.9−7.3 (m). Anal. Calcd for $C_{37}H_{25}NO_5$: C, 78.84; H, 4.47; N, 2.49. Found: C, 79.08; H, 5.34; N, 2.34.

Preparation and Properties of 61−65. To **17** or **38−40** or **59** (1.0 g) in ethanol (20 mL) and 5% potassium hydroxide (10 mL) is added 30% hydrogen peroxide (5 mL). The mixture is stirred at room temperature for 8 h. Ethanol was evaporated under reduced pressure. The solid is filtered off, dried in air and recrystallized from petroleum ether/methylene chloride to yield 65−69%.

Properties of $CF_3CH_2OC_6F_4CONH_2$ (61). This compound melts at 156−158 °C (85% yield). Spectral data are as follows. NMR: ^{19}F, δ −75.1 (3F); −140.4 (2F); −155.1 (2F); ^1H, δ 4.8 (m); 7.0 (d); EI MS [*m/e* (species) intensity]: 272 (M^+ − F) 100. Anal. Calcd for $C_9H_4F_7NO_2$: C, 37.11; H, 1.37; N, 4.81; F, 45.70. Found: C, 37.28; H, 1.00; N, 4.78; F, 45.70.

Properties of $FCH_2CH_2OC_6F_4CONH_2$ (62). This compound melts at 173−174 °C (74% yield). Spectral data are as follows. NMR: ^{19}F, δ −141.4 (2F); −155.7 (2F); −190.4 (1F); ^1H, δ 4.6 (m), 4.8 (m), 6.0 (m); E IMS [*m/e* (species) intensity]: 255 (M^+) 34.3; 209 (M^+ − FCH_2CH_2 + 1) 23.5; 193 ($C_6F_4CONH_2^+$ + 1) 100. Anal. Calcd for $C_9H_6F_5NO_2$: C, 42.36; H, 2.35. Found: C, 41.18; H, 2.24.

Properties of $HCF_2CF_2CH_2OC_6F_4CONH_2$ (63). This compound melts at 140−142 °C (78% yield). Spectral data are as follows. NMR: ^{19}F, δ −122.3 (2F); −135.1 (2F); −139.3 (2F); −152.5 (2F); ^1H, δ 4.85 (t,2H); 6.49 (tt,1H); 7.5 (d, 2H); EI MS [*m/e* (species) intensity]: 323 (M^+) 53; 307 (M^+ − NH_2) 100; 193 ($C_6F_4CONH_2^+$ + 1) 100. Anal. Calcd for $C_{10}H_5F_8NO_2$: C, 37.17; H, 1.55; N, 4.34. Found: C, 37.33; H, 1.78; N, 4.46.

Properties of n-$C_7F_{15}CH_2OC_6F_4CONH_2$ (64). The compound melts at 144−149 °C (69% yield). Spectral data are as follows. NMR: ^{19}F, δ −76.7 (3F); −116.5 (2F); −117.6 to −118.6 (8F); −121.8 (2F); −139.3 (2F); −152.3 (2F); ^1H, δ 5.1 (t); 7.5 (d); EI MS [*m/e* (species) intensity]: 591 (M^+) 33; 575 (M^+ − NH_2) 100. Anal. Calcd for $C_{15}H_4F_{19}NO_2$: C, 30.47; H, 0.68; N, 2.37. Found: C, 30.45; H, 0.77; N, 2.53.

Properties of $CH_3CH(CF_3)OC_6F_4CONH_2$ (65). This compound melts at 173−174 °C (85% yield). Spectral data are as follows. NMR: ^{19}F, δ −74.7 (d); −145.3 (2F); −153.2 (2F); ^1H, δ 1.59 (d); 4.63 (m); 7.3 (d). Anal. Calcd for $C_{10}H_6F_7NO_2$: C, 39.34; H, 1.97; N, 4.59; F, 43.61. Found: C, 39.40; H, 2.04; N, 4.58; F, 43.8.

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