Inorg. Chem. **1992**, *31*, 2537-2540

used. Prolonged heating seems to favor the formation of **7**. However, both compounds are easily deprotected by hydrogen chloride in ether. The overall yield of **1** calculated from **6** was 27%.

The amine salt **2** was also prepared by this route starting with 1-iodopent-4-yne (**13**). In this case the yield was 13%.

The phase transfer alkylation route to *N,N-tert*-butyloxycarbonyl(aminoalkyl)carboranes should be quite general and useful not only for the synthesis of primary *o-closo*-carboranyl(12)amines but also for the synthesis of corresponding protected nido amines. The stability of the protected amines, such as **9**, toward base allows the degradation to the nido analogues without deprotection of the amino group.[15]

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Registry No. **1**, 140662-84-6; **2**, 140662-87-9; **3**, 141120-02-7; **4**, 141120-03-8; **5**, 141120-04-9; **6**, 51779-32-9; **7**, 141120-05-0; **8**, 141120-06-1; **9**, 141120-07-2; **10**, 12072-30-9; **11**, 23835-93-0; **12**, 141120-08-3; **13**, 2468-55-5; **14**, 51276-07-4; **15**, 17815-32-6; **16**, 141120-09-4; **17**, 141120-10-7; **18**, 75611-01-7; **19**, 141120-11-8; propargyl bromide, 106-96-7; bis(acetonitrile) complex of decaborane, 28377-97-1.

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Trifluoromethylation and Pentafluorophenylation of Sulfur and Carbon Centers Using (Trifluoromethyl)- and (Pentafluorophenyl)trimethylsilane

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Trifluoromethyl and pentafluorophenyl moieites are easily transferred to a variety of fluorinated inorganic and organic sulfur and carbon centers by using (trifluoromethyl)trimethylsilane and (pentafluorophenyl)trimethylsilane in the presence of catalytic amounts of fluoride ion. This methodology is readily applied to the simple, efficient preparation of known, previously difficult to obtain molecules, as well as a number of new perfluoroalkyl and perfluoroaryl sulfuranes, sulfoxides, ketones, esters, and alcohols. In addition, the first stable oxysulfurane containing more than two sulfur–carbon bonds has been prepared.

Introduction

The importance of methods for the introduction of perfluorinated moieties into molecules is well-known, but such perfluoroalkylations have historically been extremely difficult to achieve, primarily because of the dearth of transfer reagents with general applicability. Methods to place per- or polyfluoroalkyl groups on sulfur are often fraught with problems, such as multistep syntheses, extreme conditions of temperature and pressure, and low-yield reactions.

While there are a variety of easily accessible and quite stable MR_f alkylating reagents where M = Hg, Ag, Cd, Cu, or Zn,[2-5] the formation of sulfonium salts from the reaction of S(IV) sulfuranes with most of these reagents rather than covalent products is observed.[6,7] Some investigators have examined the potential of selected sulfonium salts for use as perfluoroalkylating reagents.[8] However, the usefulness of these reagents for fluoroalkylation of carbon centers is limited to nonfluorinated or polyfluorinated compounds containing labile halogen atoms, e.g., CH_3I, $R_fCH_2CH_2I$, or $C_6H_5(Br, I)$.

While lithium poly- and perfluoroalkoxides, e.g., CF_3CH_2O and $(CF_3)_2CHO$,[9] and (pentafluorophenyl)lithium[10] have been used extensively to alkylate sulfur, lithium salts of perfluoroalkyls are subject to decomposition by elimination of lithium fluoride at ambient temperatures. Thus, the utility of this method for the general introduction of perfluoroalkyl moieties is limited to low-temperature conditions.

The focus of the work described in this paper is the application of (trifluoromethyl)- and (pentafluorophenyl)trimethylsilane to the trifluoromethylation and pentafluorophenylation of a variety of sulfur and carbon centers. Since the reactions of (trifluoromethyl)trimethylsilane with per- or polyfluorinated inorganic substrates (e.g., COF_2, $SOCl_2$, SOF_2, SO_2F_2, and $C_2O_2F_2$) or other classes of perfluoroalkyl compounds such as perfluoroalkyl sulfoxides, perfluoroalkyl sulfones, or perfluoroalkyl aldehydes have not been reported, we have examined the reactions of these substrates in detail. Much of the arylation chemistry achieved with (pentafluorophenyl)trimethylsilane in reactions with per- and polyfluorinated substrates has been reviewed.[11] Recently, trifluoromethylation reactions of (trifluoromethyl)trimethylsilane with nonfluorinated aldehydes, ketones, alkyl nitroso compounds, esters, sulfonyl fluorides, acid halides, and aryl halides have been studied in some detail.[12-20] Perfluoroalkyl ketones and acid halides

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are converted to silylated alcohols or ketones, respectively.[21-23] We report here, new, convenient, and high-yield synthetic methods for the preparation of previously difficult to obtain products, as well as routes to a variety of new and unusual compounds.

Results and Discussion

The synthesis of perfluoroalkyl and perfluoroaryl sulfides, sulfoxides, or sulfur oxydifluorides is generally a difficult task. Methods for the preparation of perfluoroalkyl sulfides are multistep procedures, purification is difficult at best, and yields vary widely depending on the perfluoroalkyl group attached to sulfur.[24-27] Perfluoroalkyl sulfoxides and (perfluoroalkyl)sulfur oxydifluorides are prepared by derivatization of the perfluoroalkyl sulfides referenced above.[28,29] We find that reactions of (trifluoromethyl)trimethylsilane or (pentafluorophenyl)trimethylsilane with a variety of readily available and inexpensive sulfur substrates provide a new, vastly improved method for the preparation of perfluoroalkyl or -aryl sulfinyl fluorides, sulfonyl fluorides, sulfoxides, and sulfuranes, leading subsequently to (perfluoroalkyl)- or (perfluoroaryl)sulfur oxydifluorides.[28,29]

$$\begin{array}{llcl} & OSCl_2 & & R_fS(O)F \\ & OSF_2 & & R_fS(O)F \\ R_fSi(CH_3)_3 \ + & CF_3S(O)F & \xrightarrow[CH_3CN]{KF} & CF_3(R_f)S(O) \\ & SO_2Cl_2 & \begin{array}{l}25\ ^\circ C, \\ 1\ to\ 8\ h\end{array} & R_fSO_2F \\ & CF_3SO_2Cl & & CF_3SO_2R_f \\ & SO_2F_2 & & R_fSO_2F \end{array}$$

$$R_f = CF_3,\ C_6F_5$$

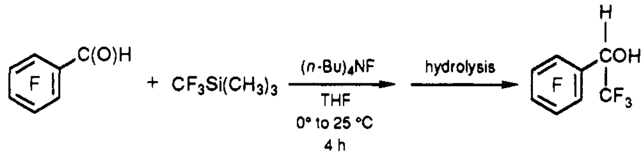
Product yields range from 75 to 95%, and purification by low-temperature trap-to-trap distillation or preparative gas chromatography is easily accomplished. In some cases, the product yield and the actual product obtained are dependent on the stoichiometry of the starting materials used. For example, while SOF_2 can be reacted with either 1 or 2 molar equiv of $CF_3Si(CH_3)_3$ to give $CF_3S(O)F$ or $(CF_3)_2SO$ in a single step, with $SOCl_2$ or SO_2Cl_2, a 2:1 molar ratio of $CF_3Si(CH_3)_3$ to $SOCl_2$ or SO_2Cl_2 results primarily in the formation of CF_3Cl. The products $(CF_3)_2SO$ and $(CF_3)_2SO_2$ must be formed stepwise when using $SOCl_2$ or SO_2Cl_2 as substrate.

With only three exceptions, i.e., $(C_6F_5)_4S$,[30] $(CF_3)_2S(CN)_2$, and $CF_3SF_2(CN)_2Cl$,[31] no (fluoroalkyl)sulfurane or -oxysulfurane containing more than two sulfur–carbon bonds has been reported in the literature. Other four- and six-coordinate sulfuranes and persulfuranes are limited to those containing two sulfur–carbon bonds and two or four alkoxy ligands[32-37] or two alkoxy ligands and two or four halogen (chlorine or fluorine) ligands[38,39] and to those containing sulfur–nitrogen bonds.[40] We now report the synthesis of the first stable, mixed (perfluoroalkyl)alkyloxysulfurane that contains three carbon–sulfur bonds and one sulfur–oxygen single bond. When dimethyl sulfoxide is combined in a 1:1 mole ratio with (trifluoromethyl)trimethylsilane in tetrahydrofuran in the presence of catalytic amounts of $(n\text{-}C_4H_9)_4NF$, the product $(CH_3)_2CF_3SOSi(CH_3)_3$ is formed after 2 h at room temperature.

$$(CH_3)_2SO + CF_3Si(CH_3)_3 \xrightarrow[THF]{(n\text{-Bu})_4NF} (CH_3)_2CF_3SOSi(CH_3)_3$$

No evidence is obtained for the formation of any other products, i.e., alkyl sulfides or trimethylsilyl fluoride. No unreacted dimethyl sulfoxide is found. The successful synthesis of this material is highly dependent on solvent and fluoride ion source. In acetonitrile or benzonitrile, regardless of the source of fluoride ion, no reaction occurs. Similarly, when potassium fluoride is used, regardless of the solvent, no $(CH_3)_2CF_3SOSi(CH_3)_3$ is obtained.

In many cases, the preparation of poly- and perfluorinated tertiary alcohols by reacting (trifluoromethyl)trimethylsilane with fluorinated ketones or aldehydes provides a simple, inexpensive, high-yield route to these materials.[22] When (trifluoromethyl)trimethylsilane is reacted in a 1:1 mole ratio with pentafluorobenzaldehyde, followed by hydrolysis, the corresponding tertiary alcohol is obtained in 60–70% yield.



With a 1:3:9 molar ratio of COF_2:$CF_3Si(CH_3)_3$:KF, an 85% yield of perfluoro-*tert*-butyl alcohol was obtained following acid hydrolysis of the solid residue.[1,22] It is interesting to note that, in our hands, reaction of $CF_3Si(CH_3)_3$ with COF_2, in a 3:1 mole ratio as well as the reaction of $CF_3Si(CH_3)_3$ with $(CF_3)_2CO$ in a 1:1 mole ratio or $CF_3Si(CH_3)_3$ with $CF_3C(O)X$ (X = F or Cl) in a 2:1 mole ratio in the presence of catalytic amounts of potassium fluoride did not result in the formation of large amounts of perfluoro-*tert*-butyl alcohol. The major product isolated in every case was the ester shown below. This product is believed to be formed in the following series of reactions, where silylated perfluoro-*tert*-butyl alcohol is an intermediate in the reaction sequence:

$$COF_2 + 3CF_3Si(CH_3)_3 \xrightarrow[CH_3CN]{KF} (CF_3)_3COSi(CH_3)_3$$

$$CF_3C(O)F + CF_3Si(CH_3)_3 \rightarrow (CF_3)_2C{=}O$$

$$\begin{array}{l}(CF_3)_2C{=}O + CF_3Si(CH_3)_3 \rightarrow \\ \quad [(CF_3)_3COSi(CH_3)_3] + CF_3C(O)F \rightarrow (CF_3)_3COC(O)CF_3\end{array}$$

Apparently, the reactions between the siloxane $(CF_3)_3COSi(CH_3)_3$ and $CF_3C(O)F$ and between COF_2 and $CF_3Si(CH_3)_3$ are much more rapid than the reaction between $CF_3C(O)F$ and $CF_3Si(CH_3)_3$. Even when a 5-fold excess of $CF_3Si(CH_3)_3$ is used, the major product is $(CF_3)_3COC(O)CF_3$. In each case, a 15–20% yield of $(CF_3)_3COH$ is isolated by treatment of the solid residue remaining

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in the reaction vessel with hydrochloric acid. This is a product of the acid hydrolysis of $(CF_3)_3COK$, which is formed from the reaction between $(CF_3)_3COSi(CH_3)_3$ and potassium fluoride. Similarly, no silylated alcohol was formed when $CH_3C(O)F$ was combined with (trifluoromethyl)trimethylsilane in acetonitrile in the presence of small amounts of KF, with the ester $CH_3(CF_3)_2COC(O)CH_3$ being the only product formed.

Attempts to synthesize $CF_3C(O)C(O)CF_3$ from the reaction between (trifluoromethyl)trimethylsilane and oxalyl fluoride in the presence of KF resulted in the quantitative formation of $CF_3C(O)F$. Nucleophilic attack evidently occurs at the carbonyl carbon followed by severing of the carbon–carbon bond in oxalyl fluoride to form $CF_3C(O)F$, rather than loss of $(CH_3)_3SiF$ and formation of $CF_3C(O)C(O)CF_3$.

Interestingly, when large excesses of both $(CH_3)_3SiCF_3$ and KF are reacted with oxalyl fluoride (3 or 4 to 1), a new oligomer(s) $(CF_3)_3CO(C(CF_3)_2O)_nC(O)CF_3$ (n = 2–4), is obtained. This exciting molecule(s) is a colorless, viscous liquid easily purified by low-temperature distillation. A moderately intense carbonyl stretch at 1877 cm^{-1} is found in the infrared spectrum. The complex ^{19}F NMR spectrum is indicative of three types of fluorines present in varying ratios depending on the stoichiometry of the reaction ($(CF_3)_3C$, $(CF_3)_2CO$, and $CF_3C(O)$). No resonance is observed for $-C(O)F$. This compound is expected to exhibit highly useful physical properties and is the subject of further study in this laboratory. The synthesis of these symmetrical, branched-chain polyethers is difficult by other means.

The reaction of (pentafluorophenyl)trimethylsilane with carbon centers occurs under mild reaction conditions, similar to those used for (trifluoromethyl)trimethylsilane. With $CH_3C(O)F$, in acetonitrile in the presence of catalytic amounts of KF, the ester $CH_3(C_6F_5)_2COC(O)CH_3$, is obtained in 65% yield. When the bifunctional acid fluoride $FC(O)(CF_2)_3C(O)F$ is combined with (pentafluorophenyl)trimethylsilane in acetonitrile in the presence of KF, the perfluorinated diketone $C_6F_5C(O)(CF_2)_3C(O)C_6F_5$ is isolated in 55% yield.

The mechanism by which (trifluoromethyl)trimethylsilane is formed in the reaction between phosphorus tris(diethylamide), bromotrifluoromethane, and chlorotrimethylsilane has been postulated to proceed through the phosphonium salt $[(Et_2N)_3PBr]^+CF_3^-$, although no evidence is presented for the formation of this intermediate.[41]

$$[(CH_3CH_2)_2N]_3P + CF_3Br \rightarrow$$
$$[([(CH_3CH_2)_2N]_3PBr)^+CF_3^-] \xrightarrow{(CH_3)_3SiCl} (CH_3)_3SiCF_3$$

While the synthesis of (pentafluorophenyl)trimethylsilane from bromopentafluorobenzene works well by this method, when pentafluorobenzyl bromide is used, no (pentafluorobenzyl)trimethylsilane is isolated. Instead, the stable phosphonium salt, $([(CH_3CH_2)_2N]_3PCH_2C_6F_5)^+Br^-$, is obtained nearly quantitatively, and chlorotrimethylsilane is recovered unreacted. Presumably the difference in charge separation in comparing C_6F_5Br with $C_6F_5CH_2Br$ (where the bromine is partially positive in C_6F_5Br and partially negative in $C_6F_5CH_2Br$) is the cause of the change in the course of this reaction. The isolation of this material lends some credence to the mechanism proposed for the formation of $CF_3Si(CH_3)_3$ from CF_3Br. This salt should prove to be a useful reagent in Wittig reactions for the synthesis of a variety of alkenes that contain the pentafluorobenzyl moiety.

In summary, we have shown that (perfluoroalkyl)silanes are highly useful for alkylation and arylation not only at carbon but, more importantly, at sulfur to give high yields of (perfluoroalkyl)- and (perfluoroaryl)sulfuranes. Versatile and highly useful methods have been developed for the synthesis of previously difficult to obtain compounds, new and potentially useful reagents for synthetic sulfur and polymer chemistry, and for the preparation of a new class of polyfluorinated alkyloxysulfuranes. The chemistry of those compounds which were previously not readily obtained, for example sulfurane oxides and their derivatives, can now be easily expanded. In addition, it is expected that new and exciting techniques which make use of $CF_3(CH_3)_2SOSi(CH_3)_3$ as a catalyst or reagent in a variety of additional synthetic schemes will provide the basis for unusual sulfur chemistry.

Experimental Section

Materials. The starting materials chlorotrimethylsilane, benzonitrile, acetonitrile, potassium fluoride, phosphorus tris(diethylamide) (Aldrich), bromotrifluoromethane, bromopentafluorobenzene, $CH_3C(O)F$, $CF_3C(O)Cl$, COF_2, $C_2O_2F_2$ (PCR), $SOCl_2$, and SO_2Cl_2 (MCB) were purchased and used as received. (Trifluoromethyl)trimethylsilane was prepared by the literature method.[41]

General Procedures. Both JEOL FX-90Q and Bruker NR200 Fourier transform NMR spectrometers were used to obtain ^{19}F and ^1H NMR spectra with $CFCl_3$ and $(CH_3)_4Si$ as external references, respectively. A VG 7070HS mass spectrometer was used to record chemical ionization and electron impact ionization mass spectra. Infrared spectral data were obtained with a Perkin-Elmer model 1700 Fourier transform infrared spectrometer equipped with an IBM PS/2 Model 50Z data station. Volatile compounds were manipulated using standard *PVT* vacuum-line techniques. The vacuum system was composed of standard Pyrex glass and equipped with a Heise-Bourdon tube gauge and a Televac micron thermocouple vacuum meter.

Preparation of $C_6F_5Si(CH_3)_3$. The preparation of $C_6F_5Si(CH_3)_3$ has been reported,[11] but no details were given nor were spectral data presented. In a 500-mL flask fitted with a rubber septum were combined bromopentafluorobenzene (2.4 g, 10 mmol), chlorotrimethylsilane (1.08 g, 10 mmol), and 8 mL of benzonitrile. The contents of the flask were kept at −196 °C, and air was evacuated. The flask and its contents were then placed in a −30 °C slush bath, and phosphorus tris(diethylamide) (2.4 g, 10 mmol) was added dropwise with stirring. The temperature was raised slowly to 25 °C, and stirring was continued for 15 h. The product, (pentafluorophenyl)trimethylsilane, was subsequently isolated via low-temperature distillation in a trap cooled to −50 °C as a colorless liquid in 70% yield. Spectral data obtained are as follows. ^{19}F NMR: ϕ −127.9 (2 F, m), −162.4 (2 F, m), −153.3 (1 F, m). ^1H NMR: δ 0.27. MS (CI) [m/e (species) intensity]: 240 (M^+) 14.9, 225 ($M^+ - CH_3$) 45.2, 168 ($C_6F_5^+ + 1$), 2.6, 118 ($(CH_2)_2SiC_2F_2^+$) 31.2, 104 ($(CH_3)_3SiCF^+$) 100, 91 ($SiC_2F_2^+ + 1$) 15.9, 73 ($(CH_3)_3Si^+$) 17. IR (gas): 2969 s, 2914 w, 1650 m, 1582 vs, 1565 s, 1263 s, 1181 m, 1143 w, 1075 vs, 958 s, 912 vs, 903 s, 854 vs, 757 m, 723 w cm^{-1}.

General Procedure for the Fluoroalkylation (Fluoroarylation) of Acid Fluorides, Aldehydes, Ketones, and Sulfoxides with $CF_3Si(CH_3)_3$ or $C_6F_5Si(CH_3)_3$. The previously reported compounds $(CF_3)_3COSi(CH_3)_3$,[42] $(CF_3)_3COC(O)CF_3$,[43] $CF_3C(O)F$,[44] $CF_3S(O)F$,[45] $(CF_3)_2SO$,[25] CF_3SO_2F,[46] $(CF_3)_2SO_2$,[28] $C_6F_5S(O)F$,[47] and $(C_6F_5)_2SO$[47] were prepared from the substrates $(CF_3)_2CO$, COF_2, $C_2O_2F_2$, SOF_2 (or $SOCl_2$), $CF_3S(O)F$, SO_2F_2 (or SO_2Cl_2), CF_3SO_2F, SOF_2 (or $SOCl_2$), and $C_6F_5S(O)F$ (or SOF_2), respectively. The products were identified by comparison of infrared, NMR, and mass spectral data to the data presented in the literature. In a typical reaction, 8 mL of acetonitrile or benzonitrile, a catalytic amount of potassium fluoride or $(n\text{-}C_4H_9)_4NF$, and from 1 to 30 mmol of (trifluoromethyl)trimethylsilane or (pentafluorophenyl)trimethylsilane were combined in a 300-mL round-bottomed Pyrex flask equipped with a Teflon stopcock and a rubber septum. The mixture was frozen, and the vessel was evacuated. From 1 to 10 mmol of substrate was then condensed into the flask, the flask and its contents were allowed to warm slowly to room temperature, and the mixture was stirred for 2–5 h. The products were then separated by low-temperature trap-to-trap distillation and identified as described above. Yields of the products listed range from 65 to 95%.

Preparation of $(CF_3)_3COH$. A 1-mmol sample of COF_2 and 3 mmol of $CF_3Si(CH_3)_3$ were condensed into a 300-mL round-bottomed Pyrex flask containing 9 mmol of potassium fluoride in 8 mL of acetonitrile. The contents of the flask were allowed to warm slowly to room temperature and stirred at that temperature for 5 h. Subsequently, all volatile materials were removed under vacuum, and 1.5 mmol of HCl was added to the solid residue. After 2 h at room temperature, the products were separated by low-temperature trap-to-trap distillation, and $(CF_3)_3COH$ was isolated in a −90 °C trap in 85% yield. The product alcohol was identified by comparison of its ^{19}F and ^1H NMR and IR

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spectral data to the data collected for a known sample.

Preparation of $C_6F_5CH(CF_3)OH$. This compound has been prepared previously by a different method; however, no spectral data were given.[48] A mixture consisting of 5 mmol of pentafluorobenzaldehyde and 6 mmol of $(n\text{-}C_4H_9)_4NF$ in 6 mL of tetrahydrofuran was placed into a 300-mL Pyrex round-bottomed flask equipped with a Teflon stopcock. The flask and its contents were placed under vacuum at −196 °C, and 5 mmol of (trifluoromethyl)trimethylsilane was added. The reaction mixture was allowed to warm slowly to −30 °C and was stirred at that temperature for 2 h. The temperature was then brought to 25 °C, and stirring was continued for 10 h. All volatile compounds of the reaction mixture were then removed under vacuum. The solid residue was extracted with three 10-mL portions of ether. The ether extracts were combined, washed with two 5-mL portions of water, dried over magnesium sulfate, filtered, and evaporated to leave the solid product, $C_6F_5CH(CF_3)OH$, in 62% yield (mp 94–96 °C). Spectral data obtained are as follows. ^{19}F NMR: ϕ −76.09 (CF_3, d, J_{CF_3-H} = 6.11 Hz), −138.4 (3 F, m), −153.7 (2 F, m). ^1H NMR: δ 5.88 (CH, q). MS (EI) [*m/e* (species) intensity]: 267 (M^+ + 1) 3.5, 249 (M^+ − OH) 79.8, 231 ($C_8F_7H^+$ + 1) 48.7, 230 ($C_8F_7H^+$) 32, 229 ($C_8F_7^+$) 53.5, 211 ($C_8F_6H^+$) 31.4, 199 ($C_7F_6H^+$) 13.8, 181 ($C_7F_5H_2^+$) 24.5, 161 ($C_7F_4H^+$) 17.8, 149 ($C_6F_4H^+$) 40.9, 131 ($C_3F_4H_3O^+$) 30.3, 123 ($C_4F_3H_2O^+$) 8, 95 ($C_3F_3H_2^+$) 17.1, 71 ($CF_3H_2^+$) 43.2, 69 (CF_3^+) 54.9. IR (KBr): 3243 b, m, 1655 m, 1611 m, 1506 vs, 1431 m, 1377 s, 1311 m, 1282 s, 1195 vs, 1157 vs, 1042 w, 1004 s, 969 m, 888 w, 801 w, 679 s cm^{-1}.

Preparation of $[C_6F_5CH_2P(NEt_2)_3^+]Br^-$. To a two-necked round-bottomed flask equipped with a Teflon stopcock and a rubber septum were added 8 mmol of pentafluorobenzyl bromide and 5 mL of benzonitrile. The flask was evacuated after freezing at −196 °C, and 8 mmol of chlorotrimethylsilane was added. The temperature of the reaction mixture was then allowed to increase to −30 °C, at which temperature stirring was initiated and phosphorus tris(diethylamide) was added dropwise with a syringe. After 1 h, the temperature was increased to 25 °C, and the mixture was stirred for an additional 12 h. All volatiles were then removed under vacuum to leave the white, solid product, $[C_6F_5CH_2P(NEt_2)_3^+]Br^-$. Spectral data obtained are as follows. ^{19}F NMR: ϕ − 138.4 (2 F, m), −153.3 (1 F, m), −160.7 (2 F, m). ^1H NMR: δ 3.66 (CH_2P, d, J_{P-CH_2} = 16 Hz), 2.5 (CH_2, q), 0.61 (CH_3, t). $^{31}P\{H\}$ NMR: δ +52.8 (b). MS (CI) [*m/e* (species) intensity]: 439 ($C_6F_5CH_2P(NEt_2)_3^+$ + $2CH_3$ − F) 0.5, 362 ($C_6F_5CH_2P(NEt_2)_3^+$ + 1 − C_2H_5 − 2F) 1.1, 345 ($C_6F_5CH_2P(NEt_2)_3^+$ − C_2H_5 − CH_3 − H − 2F) 0.6, 263 ($CH_2P(NEt_2)_3^+$ + 2) 10.3, 261 ($CH_2P(NEt_2)_3^+$) 7.4, 226 ($C_6F_5CH_2PN^+$) 2.0, 203/201 ($C_4H_9FPNBr^+$) 2.1/2.9, 195 ($C_5F_4CH_2PN^+$) 7.8, 167 ($C_6F_5^+$) 1.9, 153/151 ($C_4H_9NBr^+$) 3.3/5.3, 103 ($PN(C_2H_5)_2^+$) 30.8, 88 ($PNC_2H_5(CH_2)^+$) 41.7, 70 ($C_4H_8N^+$) 90.4, 61 ($C_2H_4NF^+$) 100. IR (KBr): 2979 s, 2937 s, 1657 m, 1525 vs, 1505 vs, 1474 s, 1387 vs, 1298 s, 1257 m, 1207 m, 1154 vs, 1127 s, 1103 m, 1059 m, 1018 s, 984 vs, 926 s, 801 s, 768 m, 728 vs, 693 m, 639 m, 658 w, 639 m, 598 w, 570 w, 552 m, 521 m cm^{-1}.

Preparation of $CF_3(CH_3)_2SOSi(CH_3)_3$. The reactants, 5 mmol of $(n\text{-}C_4H_9)_4NF$ (1 M in tetrahydrofuran) and 5 mmol of dimethyl sulfoxide, were combined in a 500-mL Pyrex round-bottomed flask equipped with a Teflon stopcock. The mixture was held at −196 °C, and the flask was evacuated. A 5-mmol portion of $CF_3Si(CH_3)_3$ was condensed into this system, and the mixture was warmed to −30 °C. Stirring was started at −30 °C and continued for 2 h, before warming the reactants to 25 °C. Stirring at 25 °C was continued for 12 h, after which the product mixture was separated by low-temperature trap-to-trap distillation. Both $CF_3(CH_3)_2SOSi(CH_3)_3$ and tetrahydrofuran were obtained together in the −78 °C trap, having passed a trap at −40 °C. The product could not be completely separated from tetrahydrofuran. Spectral data obtained are as follows. ^{19}F NMR: ϕ −44.7 (CF_3, s). ^1H NMR: δ 2.34 (CH_3, s), 0.11 (CH_3Si, s). MS (EI) [*m/e* (species) intensity]: 219 (M^+ − H) 4.5, 163 (M^+ − 3F) 9.1, 147 (M^+ − $Si(CH_3)_3$) 100, 107 (M^+ − TMS − 2HF) 13.7, 93 (M^+ − TMS − 2HF − CH_2) 22.4, 77 ($C_2H_2FS^+$) 100, 73 ($(CH_3)_3Si^+$) 100. IR (gas): 2982 s, 2967 s, 1263 s, 1176 w, 1138 w, 1079 vs, 913 s, 855 m, 757 m, 575 w, 481 w cm^{-1}.

Preparation of $CH_3(CF_3)_2COC(O)CH_3$. To a 300-mL round-bottomed Pyrex flask was added 4 mmol of potassium fluoride. The flask was held at −196 °C and evacuated, after which 5 mmol of acetonitrile, 4 mmol of acetyl fluoride, and 4 mmol of (trifluoromethyl)trimethylsilane were condensed into the vessel. The reaction mixture was stirred at −30 °C for 1 h and then at 25 °C for 9 h. The product, $CH_3(CF_3)_2COC(O)CH_3$, was isolated in a −78 °C trap as a colorless liquid in 80% yield, having passed through a trap cooled to −50 °C. Spectral data obtained are as follows. ^{19}F NMR: ϕ −76.4 (s). ^1H NMR δ 2.05 (CH_3, CH_3, b). MS (CI) [*m/e* (species) intensity]: 225 (M^+ + 1) 56.2, 224 (M^+) 1.0, 220 (M^+ + CH_3 − F) 66.6, 205 (M^+ − F) 59.6, 200 (M^+ + CH_3 − F) 29.3, 191 (M^+ + 1 − F − CH_3) 10.7, 190 (M^+ − F − CH_3) 10.9, 163 ($C_4F_6H^+$) 3.5, 145 ($C_4F_5H_2^+$) 12.3, 135 ($C_5F_2H_5O_2^+$) 8.4, 95 ($C_3F_3H_2^+$) 3.8, 86 ($C_4H_6O_2^+$) 8.4, 77 ($C_3H_3F_2^+$) 7.3, 69 (CF_3^+) 17.3, 56 ($C_2O_2^+$) 100. IR (gas): 2966 w, 1801 s, 1375 w, 1314 s, 1240 vs, 1204 m, 1154 s, 1098 s, 1016 m, 962 s, 891 w, 851 w, 762 w, 721 w, 686 w, 588 w, 517 w cm^{-1}.

Preparation of $CH_3(C_6F_5)_2COC(O)CH_3$. A 6-mmol sample of $C_6F_5Si(CH_3)_3$ and 6 mmol of potassium fluoride were added to a 300-mL round-bottomed Pyrex flask equipped with a Teflon stopcock. The flask and its contents were held at −196 °C, and the flask was evacuated, after which 6 mmol of acetonitrile and 6 mmol of acetyl fluoride were condensed into the flask. The reaction mixture was stirred at −30 °C for 1 h and at 25 °C for an additional 9 h. All volatile materials were removed under vacuum, and the oily residue remaining was extracted with three 10-mL portions of ether. The ether layers were combined, washed with two 10-mL portions of water, dried over magnesium sulfate, and filtered. The ether was evaporated to give $CH_3(C_6F_5)_2COC(O)CH_3$ as an oily, clear liquid in 65% yield. Spectral data obtained are as follows. ^{19}F NMR: ϕ −139.3 (4 F, m), −162.0 (4 F, m), −153.8 (2 F, m). ^1H NMR: δ 2.15 (CH_3, s), 2.09 (CH_3, s). MS (EI) [*m/e* (species) intensity]: 420 (M^+) 0.6, 361 (M^+ − $OC(O)CH_3$) 16.8, 360 (M^+ − $OC(O)CH_3$ − H) 22.6, 341 (M^+ − $OC(O)CH_3$ − F − H) 1, 252 (M^+ − C_6F_5 − H) 9.8, 211 ($C_6F_5(CH_3)CO^+$ + 1), 64.3, 195 ($C_6F_5CO^+$) 74, 181 ($C_7F_5H_2^+$) 9.7, 167 ($C_6F_5^+$) 14.1 117 ($C_5H_6FO_2^+$) 17.3, 104 ($C_4FH_5O_2^+$) 52.1, 103 ($C_4FH_4O_2^+$) 50.4, 59 ($CH_3C(O)O^+$) 100. IR (gas): 2962 m, 1768 s, 1754 s, 1718 m, 1652 s, 1525 vs, 1500 vs, 1471 m, 1432 w, 1412 w, 1373 m, 1322 s, 1231 s, 1196 vs, 1126 s, 1093 s, 1020 m, 996 s, 984 s, 935 m, 915 m, 899 s, 862 w, 835 m, 789 w, 758 m, 739 w, 726 w, 708 w, 670 w, 628 w, 604 m, 534 w cm^{-1}.

Preparation of $(CF_3)_3CO(C(CF_3)_2O)_nC(O)CF_3$ (n = 2–4). To a 300-mL Pyrex round-bottomed flask was added 12–14 mmol of potassium fluoride. The flask was held at −196 °C and evacuated, and 8–10 mmol of acetonitrile, 3 mmol of oxalyl fluoride, and 12–14 mmol of (trifluoromethyl)trimethylsilane were condensed into the vessel. The reaction mixture was stirred at 25 °C for 8–10 h. The mixture was distilled by low-temperature trap-to-trap distillation. The −30 °C trap contained the colorless, thick liquid product. Spectral data obtained for a typical sample are as follows. ^{19}F NMR: ϕ −76.5 (m, 3 F), −78.5 (m, 12 F), −81.1 (m, 9 F). MS (CI) [*m/e* (species) intensity]: 533 (M^+ − F − $OCOCF_3$ + 1) 0.4, 483 ($(CF_3)_2COC(CF_3)_2OC(CF_3)_2^+$ + 1) 4.1, 407 ($OC(CF_3)_2OC(CF_2)_2OC(CF_3)O^+$) 1.6, 391 ($(CF_3)_3COC(CF_2)_2OCO^+$) 4.6, 363 ($(CF_3)_3COC(CF_2)_2O^+$) 0.3, 353 ($(CF_2)COC(CF_3)OC(CF_3)OC(CF_3)^+$) 0.7, 339 ($OC(CF_3)_2OC(CF_2)_2OCO^+$ + 1) 1.8, 325 ($(CF_2)_2C(CF_3)OC(CF_2)_2O^+$) 1.3, 311 ($OC(CF_3)_2OC(CF_2)_2O^+$ + 1) 6.8, 291 ($OC(CF_3)(CF_2)OC(CF_2)_2O^+$) 1.0, 275 ($CF_3(CF_2)COC(CF_2)_2O^+$) 2.8, 261 ($OC(CF_3)_2OC(CF_2)O^+$ + 1) 5.5, 247 ($(CF_3)_2COC(CF_3)^+$) 1.3, 225 ($(CF_2)_2CO(O)CCF_3^+$) 3.9, 203 ($CF_3COC(CF_2)OCO^+$) 3.0, 185 ($C_3F_7O^+$) 4.1, 175 ($CF_3(CF_2)COCO^+$) 3.7, 147 ($CF_3(CF_2)CO^+$) 3.7, 131 ($CF_3CCF_2^+$) 3.8, 97 (CF_3CO^+) 24, 69 (CF_3^+) 100. IR (liquid): 1877 m, 1378 w, 1351 m, 1325 w, 1296 vs, 1200 m, 1177 m, 1163 m, 1136 m, 1112 w, 1084 m, 1042 m, 914 w, 738 m, 481 w cm^{-1}.

Preparation of $C_6F_5C(O)(CF_2)_3C(O)C_6F_5$. To a 300-mL Pyrex round-bottomed flask were added 10 mmol of potassium fluoride and 10 mmol of $C_6F_5Si(CH_3)_3$. The flask was evacuated while being held at −196 °C. Then 8 mmol of acetonitrile and 5 mmol of $FC(O)(CF_2)_3C(O)F$ were condensed into the flask. The reaction mixture was stirred at −30 °C for 2 h and at 25 °C for 10 h. A thick, oily residue remaining after all volatiles were removed under vacuum was extracted with three 10-mL portions of ether. The ether extracts were combined, washed with two 10-mL portions of water, dried over magnesium sulfate, filtered, and evaporated to dryness. The residue was recrystallized from petroleum ether to give the white solid product, $C_6F_5C(O)(CF_2)_3C(O)C_6F_5$ (mp = 75–77 °C), in 70% yield. Spectral data obtained are as follows. ^{19}F NMR: ϕ −115.4 (4 F, m), −125.5 (2 F, m), −136.4 (4 F, m), −154.0 (2 F, m), −163.0 (4 F, m). MS (CI) [*m/e* (species) intensity]: 541 (M^+ + 1) 19.3, 521 (M^+ − F) 5.7, 345 (M^+ − C_6F_5CO) 9.1, 195 ($C_6F_5CO^+$) 100, 168 ($C_6F_5^+$ + 1) 51.2, 167 ($C_6F_5^+$) 36.4, 148 ($C_6F_4^+$) 10.2, 137 ($C_5F_4^+$ + 1) 11.6, 117 ($C_5F_3^+$) 31.5, 70 (CF_3^+ + 1) 49.9. IR (KBr): 1810 s, 1680 s, 1512 vs, 1402 s, 1331 m, 1311 m, 1235 s, 1158 vs, 1033 m, 1008 s, 970 m, 944 w, 815 m, 807 s, 763 s, 719 m, 685 m, 619 m, 579 w, 484 w cm^{-1}.

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(48) Wall, L. A.; Antonucci, J. M. U.S. Pat. 3,880,943, Apr 29, 1975.