

Reaction of hexafluorobenzene with trimethylsilyl ethers

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Abstract

Hexafluorobenzene reacts readily with a variety of trimethylsilyl ethers ROSiMe_3 ($\text{R} = \text{CF}_3\text{CH}_2$, FCH_2CH_2 , $\text{H}(\text{CF}_2)_n\text{CH}_2$ ($n = 2, 4$), $\text{CF}_3(\text{CF}_2)_6\text{CH}_2$, $\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2$, $\text{Me}_3\text{SiOCH}_2\text{CH}_2$, $\text{C}_6\text{F}_5\text{OCH}_2\text{CH}_2$, C_6H_5 , 4- FC_6H_4) to give from mono- to hexapolyfluoroalkoxy- and polyfluoroaryloxy-benzenes. The structure of $\text{C}_6(\text{OCH}_2\text{CF}_3)_6$ has been confirmed by single-crystal X-ray analysis. The perfluorinated ether $\text{C}_6\text{F}_5\text{OCF}_2\text{CF}_3$ may be synthesized from $\text{C}_6\text{F}_5\text{OCH}_2\text{CF}_3$ by chlorination and subsequent fluorination with $\text{SbF}_3/\text{SbCl}_5$. The chlorination of 5,6,7,8-tetrafluoro-1,4-benzodioxane is also discussed.

Introduction

The search for fluids which function effectively as lubricants and hydraulic fluids under extremely harsh conditions, and which simultaneously pose little or no threat to safety in terms of flammability or toxicity, has been ongoing for many years. Advanced high-performance aerospace systems require the development of fluids exhibiting a liquid range from -65°F to $+700^\circ\text{F}$ (-54°C to 372°C) as well as thermal and oxidative stability at these temperatures. In addition, good lubricating properties and low-temperature flow are necessary attributes for these materials.

Although a large number of compound classes have been studied in this regard, to date no single class of compounds has met all of the above requirements satisfactorily. Perfluorinated polyethers, including branched, linear and perfluoroalkylether *s*-triazines, have been and are being studied in great detail [1–10], but all of these classes of perfluorinated polyethers are limited in their applicability [2, 11]. In the design of any new base fluid that is expected to display high thermal and oxidative stability, while showing good low-temperature flow properties, a high viscosity index and good lubricating properties, it is necessary to include in a single molecule a variety of structural and chemical features. In the case of polyperfluoroalkyl ethers, one logical objective might be, for example, the inclusion of both a straight-chain perfluoroalkyl ether functionality to enhance viscosity/temperature behavior and a branched-chain perfluoroalkyl ether functionality to

maximize oxidative stability. Some results have been reported along this line of investigation utilizing *s*-triazine and phospho-*s*-triazine rings derivatized with perfluoroalkyl ether pendant chains [1, 8].

In the work reported here, perfluoroaryl derivatives have been synthesized for study as potential stable fluids. This is a class of compounds that, whilst well known and studied extensively, has not been explored or developed for its potential as stable fluids. Since there are six sites available for derivatization when using hexafluorobenzene as starting material, aromatic products composed of a variety of functional and structural moieties can be synthesized. These structural and functional groups, as well as their substitution pattern, can be selectively chosen to impart high thermal and oxidative stabilities, good low-temperature flow characteristics and good lubricating properties.

Results and discussion

Fluoroaromatic substrates are quite susceptible to attack by nucleophiles and, under appropriate conditions, perfluorocycloalkanes are as well [12–15]. We have developed an easy method for the polyfluoroalkoxidation of fluoroaromatic substrates utilizing fluorinated silyl ethers.

Trimethylsilyl ethers are used for the alkoxidation of some reactive halogeno compounds, e.g. AsF_3 , $\text{R}_n\text{PF}_{5-n}$ and POCl_3 [16–19]. In the presence of fluoride ion, trimethylsilyl ethers react with benzenesulfonyl fluoride and perfluoroalkanesulfonyl fluoride to give benzenesulfonates and perfluoroalkanesulfonates [20,

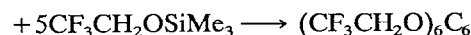
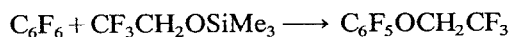
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21]. Recently, the reaction of the bis(trimethylsilyl)ether, $\text{Me}_3\text{SiOCH}_2(\text{CF}_2)_3\text{CH}_2\text{OSiMe}_3$, with perfluorocyclobutene to give fluorinated macrocyclic ethers has been reported [22]. In our present work, we find that hexafluorobenzene reacts smoothly with a variety of trimethylsilyl ethers, such as polyfluoroalkoxy- and polyfluoroaryloxy-trimethylsilanes, to give a series of mono- and polyfluoroalkoxy- and polyfluoroaryloxy-substituted benzenes.

Several methods are available for the conversion of alcohols and phenols to the corresponding trimethylsilyl ethers by using various silylating agents. Of these, hexamethyldisilazane (HMDS) is a good choice because it is an inexpensive reagent and ammonia is the sole reaction byproduct, thus permitting easy purification of the desired product. Although the poor silylating power of HMDS is a drawback, its effectiveness can be improved by using a suitable catalyst such as sodium saccharin. HMDS thereby becomes a convenient and effective silylating agent for the preparation of the trimethylsilyl ethers [23]. The ethers used in this work were prepared by this catalytic method in very good yield (Table 1). With this technique, all of the alcohols and phenols listed were rapidly silylated without the necessity of solvent. The resulting silyl ethers were purified by simple distillation.

The reactions of hexafluorobenzene with these trimethylsilyl ethers take place in the presence of a catalytic amount of cesium fluoride and with anhydrous dimethoxyethane, tetrahydrofuran or dimethylformamide as solvent. The driving force in these reactions is the formation of the strong Si-F bond in $(\text{CH}_3)_3\text{SiF}$. In the reaction of hexafluorobenzene with alkali metal alkoxides, it is difficult to form di- and polyalkoxy-substituted benzenes, even when the alkoxides are used in large excess. With trimethylsilyl ethers, the molar ratio of the reactants is the key factor that determines the degree of substitution found in the products; for example, in the reaction of $\text{CF}_3\text{CH}_2\text{OSiMe}_3$ (**Ia**) with

C_6F_6 , all six fluorine atoms can be replaced stepwise with the $\text{CF}_3\text{CH}_2\text{O}$ group as the molar ratio of **Ia** to C_6F_6 is changed from 1:1 to more than 6:1.



Crystal data for $(\text{CF}_3\text{CH}_2\text{O})_6\text{C}_6$ are given in Table 2. Data collection was carried out on a Siemens R3m/V diffractometer using Cu $K\alpha$ ($\lambda = 154.178$) radiation at 293 K. A highly oriented graphite crystal was used as the monochromator. The structure has been solved by direct methods and refined by the full-matrix least-squares method using the Siemens SHELXTL Plus (VMS) program [24]. Selected bond lengths and angles are given in Table 3. The observed bond lengths and bond angles are consistent with expected values. Two of the six CF_3 groups are disordered due to packing effects. The crystal structure is shown in Fig. 1.

Aryltrimethylsilyl ethers can be used for the preparation of hexakis(aryloxy)benzenes. These compounds provide a basis for interesting studies in clathrate chemistry [25]. Polyfluoroaryltrimethylsilyl ethers react with hexafluorobenzene more readily than metal aryl-oxides even in the absence of solvent. For example,

TABLE 2. Crystal data and structure refinement for $(\text{CF}_3\text{CH}_2\text{O})_6\text{C}_6$

Empirical formula	$\text{C}_{18}\text{H}_{12}\text{F}_{18}\text{O}_6$
Formula weight	666.28
Temperature	293(2) K
Wavelength	1.54178 Å
Crystal system	monoclinic
Space group	$C2/c$
Unit cell dimensions	$a = 18.504(3)$ Å $\alpha = 90^\circ$ $b = 15.773(2)$ Å $\beta = 110.990(10)^\circ$ $c = 8.682(2)$ Å $\gamma = 90^\circ$
Volume	2365.8(7) Å ³
Z	4
Density (calculated)	1.871 mg m ⁻³
Absorption coefficient	2.099 mm ⁻¹
$F(000)$	1320
Crystal size	0.01 × 0.15 × 0.15 mm
Range for data collection	$3.79^\circ < \theta < 56.83^\circ$
Index ranges	$-20 < h < 18, 0 < k < 17, 0 < l < 9$
Reflections collected	1734
Independent reflections	1592 [$R(\text{int}) = 0.0201$]
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	1592/42/222
Goodness-of-fit on F^2	2.498
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0546, R_w = 0.0784$
R indices (all data)	$R1 = 0.0806, R_w = 0.0807$
Largest diff. peak and hole	0.359 e Å ⁻³ and -0.292 e Å ⁻³

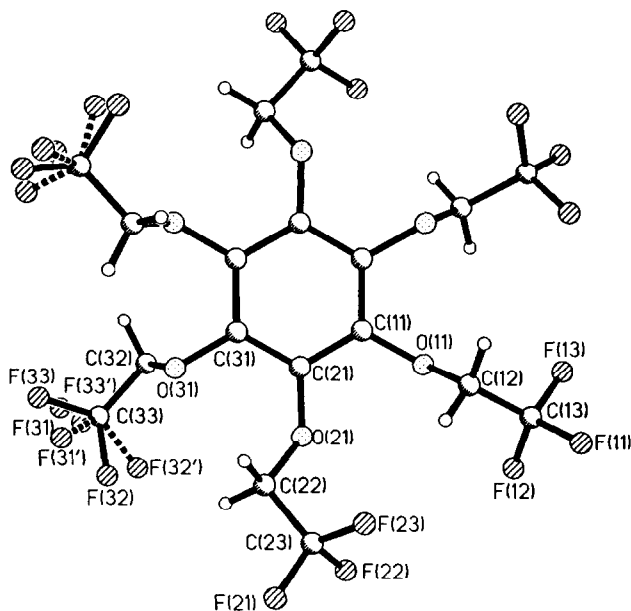
TABLE 1. Preparation of trimethylsilyl ethers

ROSiMe_3 R =	Yield (%)	B.p. [°C (mmHg)]
CF_3CH_2 (Ia)	94	78
FCH_2CH_2 (Ib)	96	94–96
$\text{HCF}_2\text{CF}_2\text{CH}_2$ (Ic)	88	105–108
$\text{H}(\text{CF}_2)_4\text{CH}_2$ (Id)	93	132–134
$\text{CF}_3(\text{CF}_2)_6\text{CH}_2$ (Ie)	87.5	166
$\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2$ (If)	95.5	86–88 (28)
$\text{Me}_3\text{SiOCH}_2\text{CH}_2$ (Ig)	85	70 (25)
$\text{C}_6\text{F}_5\text{OCH}_2\text{CH}_2$ (Ih)	90	65–68 (3)
C_6H_5 (Ii)	81	172
4- FC_6H_4 (Ij)	90	46 (3)

*Reference 30. The alcohol precursor was prepared via the literature method.

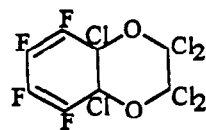
TABLE 3. Selected bond lengths (Å) and angles (°) for (CF₃CH₂O)₆C₆

Bond	Length	Bond	Angle
C(21)–O(21)	1.370(5)	O(21)–C(21)–C(11)	117.8(4)
O(21)–C(22)	1.421(5)	C(22)–O(21)–C(21)	117.8(4)
C(22)–C(23)	1.458(6)	C(31)–C(21)–C(11)	119.4(3)
C(21)–C(31)	1.383(6)	C(23)–C(22)–O(21)	109.8(4)

Fig. 1. Crystal structure of (CF₃CH₂O)₆C₆.

hexakis(phenoxy)benzene is obtained by the reaction of C₆F₆ with 18 molar equivalents of PhONa for 4 d at 120 °C with dimethylethylenurea as solvent [26]. With 18 mmol of (CH₃)₃SiOC₆H₅, reaction with 2 mmol of C₆F₆ at 90–120 °C for 12 h in the absence of solvent gives a 52% yield of hexakis(phenoxy)benzene.

The trimethylsilyl ether, C₆F₅OCH₂CH₂OSiMe₃ (**1h**), reacts with an excess of hexafluorobenzene to give the product C₆F₅OCH₂CH₂OC₆F₅ (**11h**). Compound **1h** also undergoes an intramolecular rearrangement in the presence of KF in DMF to form 5,6,7,8-tetrafluoro-1,4-benzodioxane [27]. This dioxane is photolytically chlorinated in a quartz flow cell; however, the reaction cannot be controlled to give the desired product 5,6,7,8-tetrafluoro-2,2,4,4-tetrachloro-1,4-benzodioxane. Mass spectral analysis indicates that the major product is



Although hexafluorobenzene undergoes radical addition with chlorine under UV radiation to produce

the saturated chlorofluorocyclohexane [26, 28], the –CH₂– group in C₆F₅OCH₂CF₃ can be chlorinated without benzene ring destruction. This is a result of the fact that the methylene adjacent to oxygen is more reactive toward chlorine, so that chlorination can be achieved under milder conditions, i.e. with low-intensity UV illumination and at temperatures below 150 °C [28]. Thus, the chlorofluoroalkoxybenzene C₆F₅OCCL₂CF₃ (**111a**) is easily synthesized. This chlorinated compound can be readily converted to the perfluoroalkoxybenzene with Swarts reagent, i.e. perfluoroethoxybenzene, C₂F₅OC₆F₅ (**111b**), is prepared by the fluorination of **111a** with SbF₃/SbCl₅ in 65% yield.

The ultimate objective of this work was to design functional fluids exhibiting the best possible combined characteristics of lubricity, low-temperature flow, high viscosity index and maximized thermal/oxidative stability by the incorporation of all necessary functional moieties into a single molecule. Aryl substrates were chosen for this study because of their innate high thermal and oxidative or reductive stability, and the ease with which a variety of alkyl-substituted derivatives may be synthesized.

Supplementary material available

Tables of observed and calculated structure factors, atomic coordinates, anisotropic thermal parameters and a complete list of bond distances and bond angles are available from the authors (University of Idaho) on request.

Experimental

General procedures

¹H and ¹⁹F NMR spectra were recorded on a Bruker NR 200 FT spectrometer and chemical shifts are reported in ppm from (CH₃)₄Si and CCl₄, respectively. Positive shifts are downfield from the reference. Mass spectral data were obtained with a VG 7070-HS mass spectrometer. Elemental analyses were performed by Beller Laboratories in Göttingen, Germany.

Cesium fluoride was dried at 300 °C for more than 48 h. Dimethoxyethane was distilled from sodium benzophenone before use. All reactions were carried out in an atmosphere of dry nitrogen.

The starting materials, C₆F₆ and the polyfluorinated alcohols (PCR), as well as sodium saccharin and hexamethyldisilazane (Aldrich) were purchased and used as received.

Preparation of trimethylsilyl ethers

Hexamethyldisilazane (0.12 mol) was added to a mixture of alcohol (0.2 mol) or phenol (0.1 mol) or ethylene glycol (0.1 mol) and sodium saccharin (0.01

mol). The mixture was heated slowly to 80–90 °C and stirred for 2 h. Distillation at reduced pressure gave the pure trimethylsilyl ether (Table 1) in yields of 80%–90%.

General procedure for the preparation of polyfluoroalkoxybenzenes

A mixture consisting of hexafluorobenzene (2–60 mmol), ROSiMe_3 (3–46 mmol) and a catalytic amount of CsF (0.2 g or less) in 5–20 ml of dimethoxyethane was stirred and heated from 80 °C to 140 °C for 12–24 h. Vacuum distillation was used to purify the silyl ether. Boiling points were determined under reduced pressure and ^{19}F and ^1H NMR data were obtained using CDCl_3 as solvent. Reaction stoichiometries, times and temperatures are given in Table 4.

2,2,2-Trifluoroethoxypentafluorobenzene (**IIa**) was obtained in 71% yield (b.p. 144–146 °C) [29] as a colorless liquid. Spectral data obtained were as follows. ^{19}F NMR δ : –75.3 (m, 3F); –156.5 (m, 2F); –160.8 (m, 1F); –162.4 (m, 2F) ppm. ^1H NMR δ : 4.4 (q) ppm. MS (CI) [m/e (species) intensity]: 266 (M^+) 70.

1,4-Di-2,2,2-trifluoroethoxytetrafluorobenzene (**IIb**) was obtained in 54% yield as a colorless solid (b.p. 196–198 °C; m.p. 63–65 °C). Spectral data obtained were as follows. ^{19}F NMR δ : –76.7 (m, 3F); –157 (m, 4F) ppm. ^1H NMR δ : 4.45 (q) ppm. MS (CI) [m/e (species) intensity]: 346 (M^+) 62; 327 ($\text{M}^+ - \text{F}$) 40; 263 ($\text{M}^+ - \text{CF}_3\text{CH}_2$) 100.

Hexa-2,2,2-trifluoroethoxybenzene (**IIc**) was purified by recrystallization from chloroform (m.p. 90–92 °C). Spectral data obtained were as follows. ^{19}F NMR δ : –75.27 (m) ppm. ^1H NMR δ : 4.38 (q) ppm. MS (CI) [m/e (species) intensity]: 666 (M^+) 58; 647 ($\text{M}^+ - \text{F}$) 5; 583 ($\text{M}^+ - \text{CF}_3\text{CH}_2$) 100. Analysis: Calc. for $\text{C}_{18}\text{H}_{12}\text{F}_{18}\text{O}_6$: C, 32.43; H, 1.80; F, 61.35%. Found: C, 32.48; H, 1.84; F, 50.6%.

2-Fluoroethoxypentafluorobenzene (**IId**) was a colorless liquid boiling at 170–172 °C. Spectral data obtained were as follows. ^{19}F NMR δ : –157 (m, 2F); –163.2 (m, 1F); –163.6 (m, 2F); –224.8 (m, 1F) ppm. ^1H NMR δ : 4.7 (dt, CH_2F); 4.4 (dt, CH_2O) ppm. MS (CI) [m/e (species) intensity]: 230 (M^+) 69; 211 ($\text{M}^+ - \text{F}$) 35.

2,2,3,3-Tetrafluoropropanoxypentafluorobenzene (**IIe**) was obtained as a colorless liquid boiling at 154–156 °C. Spectral data obtained were as follows. ^{19}F NMR δ : –126.4 (m, 2F); –139.7 (m, 2F); –161.8 (m, 1F); –163.2 (m, 2F) ppm. ^1H NMR δ : 6.0 (t, 1H); 4.4 (t, 2H) ppm. MS (CI) [m/e (species) intensity]: 298 (M^+) 100; 279 ($\text{M}^+ - \text{F}$) 35; 197 ($\text{M}^+ - \text{C}_2\text{F}_4\text{H}$) 47.

2,2,3,3,4,4,5,5-Octafluoropentanoxypentafluorobenzene (**IIff**) was a colorless liquid boiling at 114 °C/30 mmHg [30]. Spectral data obtained were as follows. ^{19}F NMR δ : –121.8 (m, 2F); –126.4 (m, 2F); –131.1 (m, 2F); –138.0 (m, 2F); –157 (m, 2F); –162 (m, 1F); –163 (m, 2F) ppm. ^1H NMR δ : 6.0 (t, 1H); 4.6 (t, 2H) ppm.

1*H*,1*H*-Perfluoro-octanoxypentafluorobenzene (**IIg**) was a colorless liquid having a boiling point of 102 °C/0.75 mmHg. Spectral data obtained were as follows. ^{19}F NMR δ : –81.3 (m, 3F); –121.2 (m, 2F); –122.4 (m, 2F); –123.1 (m, 2F); –123.5 (m, 2F); –126.8 (m, 2F); –157.3 (m, 2F); –161 (m, 1F); –162.6 (m, 2F) ppm. MS (CI) [m/e (species) intensity]: 566 (M^+) 100; 547 ($\text{M}^+ - \text{F}$) 47. Analysis: Calc. for $\text{C}_{14}\text{H}_2\text{F}_{20}\text{O}$: C, 29.68; H, 0.35; F, 67.13%. Found: C, 30.06; H, 0.48; F, 67.0%.

1*H*,1*H*,2*H*,2*H*-Perfluoro-octanoxypentafluorobenzene (**IIh**) was a liquid having a boiling point of 102–104 °C/2 mmHg. Spectral data obtained were as follows. ^{19}F NMR δ : –81.5 (m, 3F); –144 (m, 2F); –122.4 (m, 2F); –123.4 (m, 2F); –124.1 (m, 2F); –126.8 (m, 2F); –157.3 (m, 2F); –162.9 (m, 1F); –163.6 (m, 2F) ppm. ^1H NMR δ : 4.4 (t, 2H); 2.6 (m, 2H) ppm. MS

TABLE 4. Reaction of trimethylsilyl ethers with hexafluorobenzene

ROSiMe_3 , (I) R = (mmol)	C_6F_6 (mmol)	Molar ratio I/ C_6F_6	Temperature (°C)	Time (h)	Product (yield, %)
CF_3CH_2 (20)	20	1:1.3	90	12	$\text{C}_6\text{F}_5\text{OCH}_2\text{CF}_3$ (IIa) (71)
CF_3CH_2 (45.7)	22.8	2:1	90	12	1,4-($\text{CF}_3\text{CH}_2\text{O}$) $_2\text{C}_6\text{F}_4$ (IIb) (54)
CF_3CH_2 (30)	3	10:1	120	24	$\text{C}_6(\text{OCH}_2\text{CF}_3)_6$ (IIc) (75)
FCH_2CH_2 (30)	45	1:1.5	90	12	$\text{C}_6\text{F}_5\text{OCH}_2\text{CH}_2\text{F}$ (IId) (66)
$\text{HCF}_2\text{CF}_2\text{CH}_2$ (20)	30	1:1.5	90	12	$\text{C}_6\text{F}_5\text{OCH}_2\text{CF}_2\text{CF}_2\text{H}$ (IIe) (84)
$\text{H}(\text{CF}_2)_4\text{CH}_2$ (19)	25	1:1.3	90	12	$\text{C}_6\text{F}_5\text{OCH}_2(\text{CF}_2)_4\text{H}$ (IIff) (74)
$\text{CF}_3(\text{CF}_2)_6\text{CH}_2$ (3.3)	4.3	1:1.3	100	12	$\text{C}_6\text{F}_5\text{OCH}_2(\text{CF}_2)_6\text{CF}_3$ (IIg) (53)
$\text{CF}_3(\text{CF}_2)_5\text{CH}_2\text{CH}_2$ (5)	7.5	1:1.5	100	12	$\text{C}_6\text{F}_5\text{OCH}_2\text{CH}_2(\text{CF}_2)_5\text{CF}_3$ (IIh) (57)
$\text{Me}_3\text{SiOCH}_2\text{CH}_2$ (20)	60	1:4.3	80	12	$\text{C}_6\text{F}_5\text{OCH}_2\text{CH}_2\text{OC}_6\text{F}_5$ (IIi) (71)
$\text{C}_6\text{F}_5\text{OCH}_2\text{CH}_2$ (3)	10.5	1:3.5	80	12	$\text{C}_6\text{F}_5\text{OCH}_2\text{CH}_2\text{OC}_6\text{F}_5$ (IIi) (53)
C_6H_5 (20)	2	10:1	120	24	$\text{C}_6(\text{OC}_6\text{H}_5)_6$ (IIj) (72)
4- FC_6H_4 (25)	2.5	10:1	120	24	$\text{C}_6\text{F}_n(\text{OC}_6\text{H}_4\text{F})_{6-n}$ ($n=0, 1, 2$) (IIk)

(CI) [*m/e* (species) intensity]: 530 (M^+) 12; 184 ($C_6F_5O^+ + 1$) 100.

Bis-pentafluorophenoxyethane (**IIIi**) which has been reported previously [30] was obtained as a colorless liquid boiling at 120 °C/1.5 mmHg. Spectral data obtained were as follows. ^{19}F NMR δ : -158.7 (m, 4F); -163.4 (m, 2F); -163.8 (m, 4F) ppm. 1H NMR δ : 4.5 (s) ppm.

Hexakis-phenoxybenzene (**IIj**) was obtained as a colorless solid and identified by comparison with data previously reported for this compound [15]. Spectral data obtained were as follows. 1H NMR δ : 6.6 (m); 6.9 (m); 7.1 (m) ppm. MS (CI) [*m/e* (species) intensity]: 630 (M^+) 28.

The compounds $C_6F_n(OC_6H_4F)_{6-n}$ ($n=0, 1, 2$) (**IIIk**) were obtained as a mixture of $C_6(OC_6H_4F)_6$, $C_6F(OC_6H_4F)_5$ and $C_6F_2(OC_6H_4F)_4$ when 25 mmol of $FC_6H_4OSi(CH_3)_3$ was reacted with 2.5 mmol of C_6F_6 at 120 °C for 24 h. Spectral data were as follows. MS (CI) [*m/e* (species) intensity]: 738 (M^+ for $n=0$) 4; 646 (M^+ for $n=1$) 50; 554 (M^+ for $n=2$) 100.

Preparation and properties of perfluoroethoxybenzene (**IIIb**)

Compound **IIa** (18.8 mmol) was placed in a 25 ml tubular quartz reactor. Chlorine was bubbled slowly into the liquid under direct illumination with a Hanovia model 30620 140 W desktop UV lamp while the temperature was maintained at 80–100 °C. After chlorination was complete (as determined by 1H NMR spectroscopy), 5.8 g (92% yield) of the product $C_6F_5OCCl_2CF_3$ (**IIIa**) was obtained by distillation as a light yellow liquid (b.p. 45–48 °C/1.5 mmHg). Spectral data obtained for **IIIa** were as follows. ^{19}F NMR δ : -82.3 (m, 3F); -146.7 (m, 2F); -154.2 (m, 1F); -161 (m, 2F) ppm. MS (CI) [*m/e* (species) intensity] (correct isotope ratios were observed): 334 (M^+) 17; 299 ($M^+ - Cl$) 30; 183 ($C_6F_5O^+$) 55; 167 ($C_6F_5^+$) 73; 151 ($CF_3CCl_2^+$) 100; 69 (CF_3^+) 52.

A mixture of **IIIa** (7.2 mmol) and SbF_3 (45 mmol) and $SbCl_5$ (1 g) was then stirred and heated at 150–160 °C for 4 h. The fluorinated product, $C_6F_5OCF_2CF_3$ (**IIIb**), was isolated by distillation and washed with a 20% aqueous hydrochloric acid solution. After drying over $CaCl_2$, the crude product was redistilled to give a 69% yield of a clear liquid (**IIIb**) boiling at 116–118 °C. Spectral data obtained for **IIIb** were as follows. ^{19}F NMR δ : -85.7 (m, 3F); -89.0 (m, 2F); -151.3 (m, 2F); -154.4 (m, 1F); -160.9 (m, 2F) ppm. MS (CI) [*m/e* (species) intensity]: 302 (M^+) 100; 283 ($M^+ - F$) 75; 233 ($M^+ - CF_3$) 9; 183 ($C_6F_5O^+$) 47; 167 ($C_6F_5^+$) 65; 119 ($C_2F_5^+$) 82; 69 (CF_3^+) 85. Analysis: Calc. for $C_8F_{10}O$: C, 31.79; F, 62.91%. Found: C, 31.20; F, 60.6%.

Acknowledgments

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