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SYNTHESIS AND REACTIONS OF SOME PERFLUOROALKYL ETHER SUBSTITUTED SILANES

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Summary

Perfluoroalkyl ether substituted silicon compounds of the type $(CH_3)_nSi(R_fOR_f)_{4-n}$ ($n = 1$–3) and $HSi(R_fOR_f)_3$ where $R_fOR_r = F(CF_3)_2COCF_2CF_2$ have been synthesized in good yields (64–81%) through the reaction between the organolithium reagent R_fOR_fLi and the corresponding silicon chloride. The stability of these compounds towards acid, base and aqueous media were studied and the ease of cleavage of the Si–R_fOR_f bond was found to be in the order $HSi(R_fOR_f)_3 > CH_3Si(R_fOR_f)_3 > (CH_3)_2Si(R_fOR_f)_2 > (CH_3)_3SiR_fOR_f$. The influence of the R_fOR_f group on some properties of these compounds is also described.

Introduction

The synthesis of $F(CF_3)_2COCF_2CF_2MgBr$ [1] and the organolithium reagent $F(CF_3)_2COCF_2CF_2Li$ [2] have been previously described. The reaction of these organometallic intermediates with a variety of substrates such as H_2O, and chlorosilanes (e.g. $(CH_3)_3SiCl$ and $HSi(CH_3)_2Cl$) have also been reported [1–3].

A number of perfluoro-aliphatic, olefinic, alkynyl and aromatic mono-substituted derivatives of silicon have been prepared in connection with studies on various perfluoroorganolithium and magnesium compounds [3–13]. As an example $F(CF_3)_2COCF_2CF_2Si(CH_3)_3$ has been prepared through the reaction between $F(CF_3)_2COCF_2CF_2MgBr$ and $(CH_3)_3SiCl$ in tetrahydrofuran solvent [3]. A number of reports describing the properties of perfluoroalkyl and arylsilicon compounds have also been published [8–15]. Very little however has been reported on the synthesis of poly(perfluoroalkyl)silanes [$(R_f)_nSiR_{4-n}$ where $n = 2, 3$ or 4; $R_f =$ perfluoroalkyl]. We now wish to report our studies on the synthesis of polysubstituted perfluoroalkyl ether (R_fOR_f) silanes, and the influence of the R_fOR_f group on their reactions and properties.

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TABLE 1

ANALYSES OF PERFLUOROALKYL ETHER SILICON COMPOUNDS

Compound[a]	B.p. (°C/mmHg)	Isolated yield(%)	^{1}H NMR[b] (ppm)	^{19}F NMR (ppm)	IR (cm^{-1})
$(CH_3)_3SiR_fOR_f$ (I)	109–111	71	0.28(s) (in $CDCl_3$)	−80.8(m) (6F,CF) −82.5(m) (2F,CF_2O) −127.0(s) (2F,CF_2Si) −145.8(t) (1F,CF; *J* 21.4 Hz) (in $CDCl_3$)	C–F: 1100–1350 C–H: 2975,2910w $SiCH_3$: 850,760
$(CH_3)_2Si(R_fOR_f)_2$ (II)	41/1.0	81	0.54(s) (in $CDCl_3$ + $CFCl_3$)	−81.0(s) (6F,CF) −82.2(m) (2F,CF_2O) −126.9(s) (2F, CF_2Si) −145.5(t) (1F, CF) (in $CDCl_3$ + $CFCl_3$)	C–F: 1100–1350 C–H: 2980–2920w $SiCH_3$: 790,845
$(CH_3)Si(R_fOR_f)_3$ (III)	98–99/4.6	73	0.83(bs) (in $CDCl_3$)	−81.2(bs) (6F,CF_3) −81.4(m) (2F,CF_2O) −121.6(s) (2F,CF_2Si) −145.4(t) (1F,CF) (in $CDCl_3$)	C–F: 1100–1350 C–H: 2930vw $SiCH_3$: 790
$HSi(R_fOR_f)_3$ (IV)	47–49/0.6	64	5.10(m) *J* 8.8 Hz (in C_6F_6)	−80.37(s) (6F,CF_3) −81.44(d) (2F,CF_2O) −81.59 −118.79(s) (2F,CF_2,Si) −143.91 −114.16(t) (1F,CF; −142.42 *J* 21.5 Hz) (in C_6F_6)	C–F: 1100–1350 SiH: 2230
$(CH_3)_2Si(OH)R_fOR_f$ (V)	58–59/15	86	0.36(s,6H) 3.15(bs,1H) (in $CDCl_3$)	–	C–F: 1100–1350 C–H: 2915w SiOH: 3260b
$(C_2H_5)Si(R_fOR_f)_2H$ (XIII)	–	–	4.4(m,1H) *J* 8.5 Hz 0.6–1.6(m,5H) (in benzene)	–	C–F: 1100–1350 Si–H: 2205 C–H: 2880–3000

[a] $R_fOR_f = F(CF_3)_2COCF_2CF_2$. [b] s = singlet, d = doublet, t = triplet, b = broad, m = multiplet, bs = broad singlet. all compounds had satisfactory elemental analyses.

Results and discussion

Synthesis of R_fOR_f–Si compounds

We have prepared the perfluoroalkyl ether (R_fOR_f) substituted silicon compounds by the following reactions:

$$(4-n)R_fOR_fLi + (CH_3)_nSiCl_{(4-n)} \xrightarrow[-78°C]{Et_2O} (4-n)LiCl + (CH_3)_nSi(R_fOR_f)_{4-n} \quad (1)$$

$$(R_fOR_f = F(CF_3)_2COCF_2CF_2) \quad \begin{array}{l} n = 3\ (I) \\ n = 2\ (II) \\ n = 1\ (III) \end{array}$$

$$3R_fOR_fLi + HSiCl_3 \xrightarrow[-78°C]{Et_2O} 3LiCl + \underset{(IV)}{HSi(R_fOR_f)_3} \quad (2)$$

With the exception of IV, all the other compounds (See Table 1) were readily prepared by the standard addition technique of adding a chlorosilane to the organolithium intermediate R_fOR_fLi.

An interesting side reaction was noted in the synthesis of $HSi(R_fOR_f)_3$ (IV) via the addition of $HSiCl_3$ to the R_fOR_fLi.

$$R_fOR_fI + CH_3Li \xrightarrow[-78°C]{Et_2O} CH_3I + R_fOR_fLi \quad (3)$$

$$3R_fOR_fLi + HSiCl_3 \xrightarrow[-78°C]{Et_2O} \underset{(III)}{CH_3Si(R_fOR_f)_3} + \underset{(IV)}{HSi(R_fOR_f)_3} \quad (4)$$

The standard addition procedure gave a 73% (GC area %) yield of the expected product IV, 10% (GC area %) of the unexpected product III and a number of smaller unidentified by-products. The unexpected compound III may possibly arise from the reaction of the R_fOR_fLi with product IV by the following sequence shown.

$$\underset{(IV)}{HSi(R_fOR_f)_3} + R_fOR_fLi \xrightarrow[-78°C]{Et_2O} R_fOR_fH + LiSi(R_fOR_f)_3 \quad (5)$$

$$LiSi(R_fOR_f)_3 + CH_3I \xrightarrow[-78°C]{Et_2O} LiI + \underset{(III)}{CH_3Si(R_fOR_f)_3} \quad (6)$$

As compound IV is being formed (eq. 4) it is in the presence of R_fOR_fLi (standard addition) and thus could react as shown in eqs. 5 and 6. When the reaction was repeated by adding the R_fOR_fLi to the $HSiCl_3$ (reverse addition) compound IV was formed in 91% (GC area %) and the formation of III was suppressed.

Reaction of R_fOR_f–Si compounds

The hydrolytic stability of compounds I–IV towards water, acid and base were examined (see Table 2). The relative ease of cleaving the Si–R_fOR_f bond by hydrolysis appears to be in the order $HSi(R_fOR_f)_3 > CH_3Si(R_fOR_f)_3 > (CH_3)_2Si(R_fOR_f)_2 > (CH_3)_3SiR_fOR_f$. These results are consistent with a nucleophilic attack at the positive silicon center. As the silicon becomes more substituted by the R_fOR_f groups it becomes more electrophilic in nature. Molecular

TABLE 2

HYDROLYSIS OF R_fOR_f-Si [a] COMPOUNDS (in %)

Conditions (at room temperature)	$(CH_3)_3SiR_fOR_f$	$(CH_3)_2Si(R_fOR_f)_2$	$CH_3Si(R_fOR_f)_3$	$HSi(R_fOR_f)_3$
H_2O Et_2O				
5 min	0	40	100	100
30 min	0	92	–	–
2 h	0	100	–	–
2 *N* HCl Et_2O				
2 h	0	–	–	–
2 *N* HCl Et_2O				
4 d	0	–	–	–
2 *N* KOH Et_2O				
5 min	67			
30 min	91			
1 h	100			

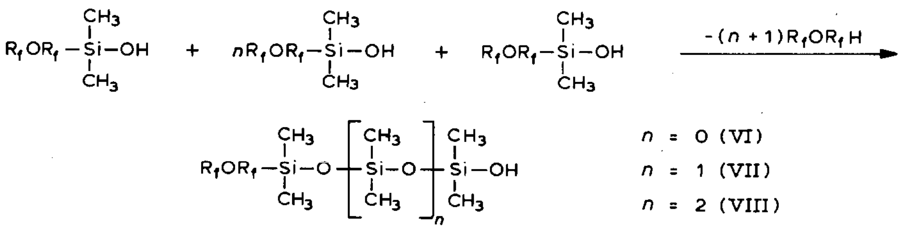
[a] $R_fOR_f = F(CF_3)_2COCF_2CF_2$.

models of the various compounds did not indicate steric hindrance to be a main factor in hydrolysis of the Si–R_fOR_f bond. In general all the compounds were cleaved under basic conditions. Compound I, containing the fewest R_fOR_f substituents, was stable in water and 2*N* HCl at room temperature. Compound II, on hydrolysis in a diethyl ether/water mixture at ambient temperature, was only partially cleaved.

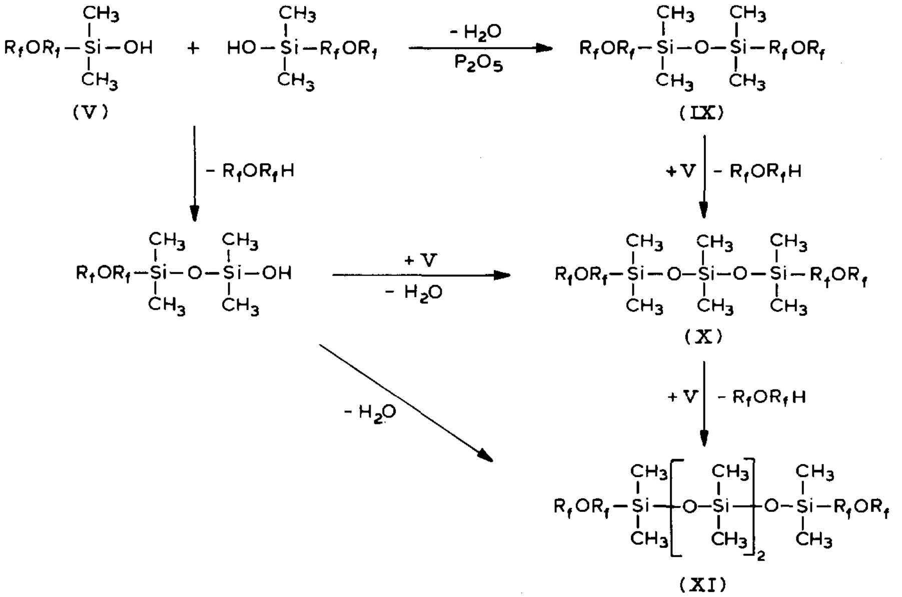
$$\underset{\text{(III)}}{(CH_3)_2Si(R_fOR_f)_2} + H_2O \xrightarrow[\text{RT}]{Et_2O} R_fOR_fH + \underset{\text{(V)}}{(CH_3)_2Si(R_fOR_f)OH} \tag{7}$$

Compound V was isolated in 86% yield. Under these experimental conditions the second group appears to be stable towards cleavage similar to the $(CH_3)_3SiR_fOR_f$. Compound V however on standing at room temperature for a period of time slowly reacts intermolecularly to form a series of compounds. After standing for 24 h at room temperature, approximately 40% of V changed to VI, VII and VIII in a 30/6/1 (GC area) ratio respectively. These compounds were partially characterized by GC/MS analysis and their formation is consistent with the following suggested reaction shown in Scheme 1.

Compound V also rapidly reacted with P_2O_5 to form another series of com-



SCHEME 1



SCHEME 2

pounds, identified by GC/MS, as IX, X, and XI in a 4.3/1.4/1 (GC area) ratio respectively. The products are consistent with the following reactions shown in Scheme 2.

Compound IV, besides being hydrolytically unstable, also reacts slowly with oxygen. A sample exposed in air for a period of 10 d reacted completely with oxygen. Infrared analysis of the exposed material indicated the absence of the Si–H band and the appearance of the Si–OH band at 3610 cm^{-1}. Proton NMR also confirmed the absence of any Si–H bond and the appearance of a broad band at 4.85 ppm suggestive of an Si–OH. Attempts to isolate the suspected $(R_fOR_f)_3SiOH$ for further characterization were unsuccessful in view of the possible intermolecular reaction as shown in Scheme 1.

The reaction between $(R_fOR_f)_3SiH$ and a Grignard reagent (or an organolithium reagent, see eq. 5) was of interest since two possible reaction sites are available on IV: (a) nucleophilic reaction at the $Si{-}R_fOR_f$ bond would result in the elimination of an R_fOR_f group; (b) an acid base reaction (metalation) at the Si–H bond would result in the formation of a Si–MgBr intermediate. The reaction between IV with an equal molar quantity of C_2H_5MgBr, in the presence of an excess of CH_3I (trapping agent), at −75°C in a diethyl ether/THF solution was studied. Two principal products were indicated by GC analysis. The major product was isolated by GC and characterized as $(R_fOR_f)_2Si(C_2H_5)H$ (XIII) while the minor product was characterized only by GC/MS analysis as $(R_fOR_f)_3SiCH_3$ (III) showing that the cleavage reaction of the $Si{-}R_fOR_f$ bond, (eq. 8) occurred preferentially to the metalation of the Si–H bond (eq. 9).

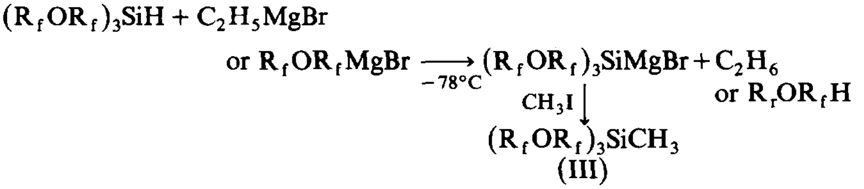
$$(R_fOR_f)_3SiH + C_2H_5MgBr \xrightarrow[-78^\circ C]{} \underset{(XIII)}{(R_fOR_f)_2Si(C_2H_5)H} + R_fOR_fMgBr \qquad (8)$$

TABLE 3

IR AND ^1H NMR DATA FOR Si–H

	IR (cm^{-1})	^1H NMR (ppm)
$(CH_3)_3SiH$ [a]	2118	3.85
$[F(CF_3)_2CO(CF_2)_4]Si(CH_3)_2H$ [b]	2170	4.25
$(R_fOR_f)_2Si(C_2H_5)H$	2205	4.40
$(R_fOR_f)_3SiH$	2230	5.10

[a] From refs. 16 and 17. [b] From ref. 3.



$$\begin{array}{l} (R_fOR_f)_3SiH + C_2H_5MgBr \\ \qquad \text{or } R_fOR_fMgBr \xrightarrow[-78^\circ C]{} (R_fOR_f)_3SiMgBr + C_2H_6 \\ \qquad\qquad\qquad\qquad\qquad {\scriptstyle CH_3I}\Big\downarrow \qquad\qquad \text{or } R_fOR_fH \\ \qquad\qquad\qquad\qquad (R_fOR_f)_3SiCH_3 \\ \qquad\qquad\qquad\qquad\qquad (III) \end{array} \tag{9}$$

The inductive effect of the R_fOR_f group on the Si–H bond can be seen in Table 3. The infrared data show that the Si–H band increases to longer wavelengths with increasing R_fOR_f substitution. Similarly the chemical shift of the proton of the Si–H bond occurs further downfield as the R_fOR_f substitution increases on the silicon atom. The nature of the Si bond character changes from $Si^+–H^-$ in a nonfluorinated compound as $(CH_3)_3SiH$ to a $Si^-–H^+$ in the highly substituted R_fOR_f compounds. The change in the nature of the Si–H bond would account for the acid–base (metalation) reaction (eqs. 5 and 9) noted.

Several attempts were made to synthesize the tetrasubstituted silane, $(R_fOR_f)_4Si$ and were unsuccessful under our experimental conditions. Since the relative hydrolytic and thermal stability of these compounds is a function of R_fOR_f substitution, a tetrasubstituted compound may prove to be unstable at room temperature. It should be noted however that $(R_f)_4Si$ compounds where $R_f = (CF_2{=}CF)$, [18] and C_6F_5 [8] have been prepared previously and are stable. This difference could be rationalized on the basis of stabilization by π bond interaction between the Si and the vinyl or phenyl groups.

Experimental

All reactions were carried out in an atmosphere of dry nitrogen with the usual precautions for vigorous exclusion of moisture and air. Tetrahydrofuran was dried over sodium and distilled from lithium aluminium hydride. Infrared spectra were taken as thin films with a Perkin–Elmer Model 600 spectrophotometer under anhydrous and oxygen free conditions to avoid hydrolytic cleavage of the $Si–R_fOR_f$ bond and oxidation of the Si–H bond. All the temperatures reported are uncorrected. ^1H NMR were recorded on a Varian CFT-20 or A-56/60A spectrometer. ^{19}F NMR were obtained with an XL-100 or NT-300 spectrometer. Chemical shifts are expressed in ppm relative to tetramethylsilane (TMS) as an internal standard for ^1H and fluorotrichloromethane ($CFCl_3$) as internal standards for ^{19}F NMR spectra. GC analyses were performed on a Perkin–Elmer Sigma I or IIB instrument with 10% SE-30 on 80–100 mesh Supelcoport packed 6 ft columns. The GC/MS analyses were performed on a Finnigan 4021 mass spectrometer using chemical ionization mode. Analytical data for all isolated compounds are given in Table 1. Mass spectral analyses were performed on all compounds and will be reported in detail later in an appropriate journal.

Synthesis of $(CH_3)_3SiCF_2CF_2OCF(CF_3)_2$ *(I)*

To a diethyl ether (140 ml) solution of $(CF_3)_2CFOCF_2CF_2I$ (10.1 g, 24.5 mmol) was added CH_3Li (13.6 ml of 1.80 *M* in diethyl ether solution, 24.5 mmol) dropwise over 15 min period at −78°C. After stirring at −78°C for 20 min, $(CH_3)_3SiCl$ (2.58 g in 20 ml diethyl ether, 23.8 mmol) was added. The progress of the reaction was monitored by withdrawing small aliquots for GC analyses. After stirring for 1 h, the reaction mixture was hydrolyzed at −78°C with conc. HCl (10 ml). The mixture was then poured into 2 *M* HCl (100 ml), phase separated, dried over $MgSO_4$ and concentrated by distillation. The crude product was analyzed by GC using an internal standard (n-C_9H_{20}). Analysis indicated a 90% yield of I. Distillation of the crude product on a micro spinning band column gave I (see Table 1).

Synthesis of $(CH_3)_2Si[CF_2CF_2OCF(CF_3)_2]_2$ *(II)*

The lithium reagent, prepared from $(CF_3)_2CFOCF_2CF_2I$ (80.0 g, 194 mmol) and CH_3Li (125.3 ml of 1.55 *M* in diethyl ether solution, 194 mmol) in diethyl ether (1000 ml) at −78°C, was treated with $(CH_3)_2SiCl_2$ (11.3 g, 87.6 mmol) and stirred at −78 to −62°C for 20 h. The reaction mixture was hydrolyzed at −75°C with conc. HCl (40 ml) and stirred for 20 min. The upper diethyl ether solution was decanted at low temperature (−60°C). The lower layer (solids and ice mixture) was added to diethyl ether (300 ml) and saturated NH_4Cl solution (300 ml). The diethyl ether layer was separated as quickly as possible. The diethyl ether solutions were combined and dried over $MgSO_4$. The solvent was removed under vacuum and the crude residue was distilled to give II, 44.7 g (81%) (see Table 1).

Synthesis of $CH_3Si[CF_2CF_2OCF(CF_3)_2]_3$ *(III)*

To the lithium reagent, prepared from $(CF_3)_2CFOCF_2CF_2I$ (80.0 g, 194 mmol) and CH_3Li (125.3 ml of 1.55 *M* in diethyl ether solution, 194 mmol) in diethyl ether (1000 ml) at −78°C was added CH_3SiCl_3 (8.10 g, in 10 ml diethyl ether, 54.2 mmol) dropwise over 2 min period. After the reaction mixture was stirred for 2 h at −70°C, it was allowed to warm slowly to room temperature. An aliquot sample was removed and analyzed by GC. Analysis indicated one major product, III (93 area%) and three undetermined minor products (7 area%). The reaction mixture was separated by fractional distillation at reduced pressure. The crude product (41.6 g, 93.3 GC area%) was collected at 40–90°C/2.0–0.6 mmHg. The crude product was redistilled to give III (see Table 1).

Synthesis of $HSi[CF_2CF_2OCF(CF_3)_2]_3$ *(IV)*

Method 1. Addition of the R_fOR_fLi to $HSiCl_3$ (reverse addition technique). The lithium reagent, prepared from $(CF_3)_2CFOCF_2CF_2I$ (153.4 g, 372 mmol) and CH_3Li (240 ml of 1.55 *M* in diethyl ether, 372 mmol) in diethyl ether (1400 ml) at −78°C, was poured under nitrogen into $HSiCl_3$ solution (15.9 g in 700 ml diethyl ether, 117 mmol) over a 2–3 min period at −78°C. The temperature rose to −73°C after completion of addition. The mixture was stirred at −78 to −71°C for approximately 18 h and then warmed to room temperature. A high boiling fluid,

$CH_3Si(n\text{-}C_9H_{19})_3$ (18.7 g), was added to facilitate distillation of product. The solvent was distilled at reduced pressure and the crude product (76.5 g) was collected at 30–75°C/0.3–0.5 mmHg. GC analysis indicated 91 area % of (IV). The crude was redistilled to give IV (see Table 1).

Method 2. Addition of $HSiCl_3$ to the lithium reagent (standard addition technique). To the lithium reagent, prepared from $(CF_3)_2CFOCF_2CF_2I$ (75.0 g, 182 mmol) and CH_3Li (117.4 ml of 1.55 *M* in diethyl ether, 182 mmol) in diethyl ether (1000 ml) at −78°C, was added $HSiCl_3$ (8.10 g in 10 ml diethyl ether) rapidly. The solution was stirred at −70°C for 1 h and then warmed to room temperature. The solvent was distilled at reduced pressure and the crude product (33.8 g) was collected at 25–75°C/0.8 mmHg. GC analysis indicated two products, the expected product IV (73 area%) and un unexpected product III (10 area%) and some minor products (17 area%). Distillation of the mixture on a spinning band column under dry nitrogen yielded IV (15.6 g, 96 GC area% pure) and III (2.3 g, 97 GC area% pure).

Reaction between $(F(CF_3)_2COCF_2CF_2)_3SiH$ (IV), C_2H_5MgBr and CH_3I

A diethyl ether (70 ml) and tetrahydrofuran (30 ml) solution of IV (5.54 g, 6.27 mmol) and CH_3I (1.40 g, 9.86 mmol) was cooled to −75°C. To this solution was added C_2H_5MgBr (5.5 ml of a 1.14 *M* in THF solution, 6.27 mmol) and stirred at −75 to −67°C for approximately 18 h. The reaction was slowly allowed to warm to room temperature during 2 h. After removing the solvent under vacuum the residue was distilled. The fraction, 3.58 g, boiling between 15 to 40°C/0.3 mmHg was collected. A GC analysis indicated a residual amount of solvents, $F(CF_3)_2COCF_2CF_2H$, $[F(CF_3)_2COCF_2CF_2]_3SiH$ in addition to two reaction products. The major reaction product was isolated by preparative GC and characterized as $[F(CF_3)_2COCF_2CF_2]_2Si(C_2H_5)H$ (XIII) (see Table 1). The minor product was characterized by GC/MS only as $[F(CF_3)_2COCF_2CF_2]_3$ $SiCH_3$ (III). The GC area ratio of XIII to III was 3/1.

Hydrolysis of $[F(CF_3)_2COCF_2CF_2]_2Si(CH_3)_2$ (II)

A sample of II (15.0 g) was dissolved in diethyl ether (150 ml) to which was added H_2O (30 ml). After stirring for 2.5 h at room temperature, a GC analysis indicated the absence of any starting compound II and the presence of two major peaks, $F(CF_3)_2COCF_2CF_2H$ and the product V. The mixture was phase separated, the diethyl ether layer dried ($MgSO_4$) and concentrated by distillation. The crude residue was distilled under vacuum to give the compound $[F(CF_3)_2COCF_2$ $CF_2Si(CH_3)_2OH$(V)], 7.41 g, b.p. 58–59°C/15 mmHg in 86% yield. By GC analysis, V on standing at room temperature for 24 h, was shown to be converted to $F(CF_3)_2OCF_2CF_2H$ and a series of products VI, VII and VIII (30/6/1 GC area ratio). These compounds were characterized by GC/MS analysis and are consistent with the structures: $[F(CF_3)_2COCF_2CF_2]Si(CH_3)_2OSi(CH_3)_2OH$ (VI), $[F(CF_3)_2COCF_2CF_2]Si(CH_3)_2[OSi(CH_3)_2]_2OH$ (VII), and $[F(CF_3)_2COCF_2CF_2]$ $Si(CH_3)_2[OSi(CH_3)_2]_3OH$ (VIII).

Reaction between $[F(CF_3)_2COCF_2CF_2]Si(CH_3)_2OH$ (V) and P_2O_5

A sample of V (0.5 g) was treated with an excess of P_2O_5 at room temperature. The reaction was very exothermic. After stirring for 0.5 h, a GC analysis showed trace amounts of starting material V and 4 new components which were identified by GC/MS as $F(CF_3)_2COCF_2CF_2H$, $[F(CF_3)_2COCF_2CF_2Si(CH_3)_2]_2O$ (IX), $[F(CF_3)_2COCF_2CF_2Si(CH_3)_2O\}_2Si(CH_3)_2$ (X) and $F(CF_3)_2COCF_2CF_2$-$Si(CH_3)_2O[Si(CH_3)_2O\}_2Si(CH_3)_2CF_2CF_2OC(CF_3)_2F$ (XI).

Hydrolysis studies

A 0.46 g sample of each compound was individually dissolved in diethyl ether (5.0 ml) and then treated with 2 ml of either H_2O, 2*N* HCl or 2*N* KOH. The diethyl ether solutions, at room temperature, were periodically analyzed by GC. The stability of the silicon compound was inferred by the amount of unreacted starting material present and the amount of hydrolysis product, R_fOR_fH formed (see Table 2).

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