Bis(trifluoromethyl)phosphinoxysilanes[1]

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Abstract: The new volatile compounds $(CF_3)_2POSiH_3$ (mp −116°; bp est 40°), $(CF_3)_2POSi(CH_3)_3$ (mp −69°; bp est 101°), $[(CF_3)_2PO]_3SiH$ (bp est 161°), and $[(CF_3)_2PO]_4Si$ (mp −54°; bp est 193°) have been made by relatively simple group-exchange methods. The P–O–Si bonding in these compounds apparently is quite stable against disproportionation to P–O–P and Si–O–Si bonds. Stability against the Arbuzov reaction and the analogous rearrangement also is noted. The infrared spectra show interesting intensity effects, qualitatively understood on the basis that vibrational distortion changes the polarity less when different polar bonds occur in the same molecule.

Compounds of the general type $(CF_3)_2POR$, where R = H,[2] alkyl,[2] $P(CF_3)_2$,[2] or acetates,[3] are so stable against either Arbuzov-like rearrangements or disproportionation into ROR and the diphosphoxane as to suggest the existence of many other such compounds, with a wider variety of R groups.

Accordingly, we now find that R can represent various groups containing silicon, still with no tendency toward conversion of the phosphinoxysilanes to phosphine oxides or for reversibility of their syntheses by any of the following processes (shown with quantitative stoichiometry in millimoles).

$$\underset{2.10}{(CF_3)_2P]_2O} + \underset{2.15}{(SiH_3)_2O} \longrightarrow \underset{0.808}{(CF_3)_2POSiH_3} + \underset{2.93}{(CF_3)_2PH} + \text{nonvolatiles} \tag{1}$$

$$\underset{1.54}{[(CF_3)_2P]_2O} + \underset{1.55}{[(CH_3)_3Si]_2O} \longrightarrow \underset{3.06}{2(CF_3)_2POSi(CH_3)_3} \tag{2}$$

$$\underset{3.08}{[(CF_3)_2P]_2O} + \underset{3.06}{(CH_3)_3SiCl} \longrightarrow \underset{3.05}{(CF_3)_2PCl} + \underset{3.04}{(CF_3)_2POSi(CH_3)_3} \tag{3}$$

$$\underset{1.02}{[(CH_3)_3Si]_2O} + \underset{1.05}{(CF_3)_2PCl} \longrightarrow \underset{1.01}{(CH_3)_3SiCl} + \underset{1.00}{(CF_3)_2POSi(CH_3)_3} \tag{4}$$

$$\underset{2.103}{3[(CF_3)_2P]_2O} + \underset{0.674}{HSiCl_3} \longrightarrow \underset{0.40}{[(CF_3)_2PO]_3SiH} + \text{nonvolatile liquid} + \underbrace{(CF_3)_2PCl + (CF_3)_2PH}_{2.3} \tag{5}$$

$$\underset{2.335}{4[(CF_3)_2P]_2O} + \underset{0.582}{SiCl_4} \longrightarrow \underset{2.30}{4(CF_3)_2PCl} + \underset{0.547}{[(CF_3)_2PO]_4Si} + \text{traces of nonvolatiles} \tag{6}$$

The failure of any such compounds to disproportionate in the manner of reversing process 2 suggests that a heterooxane gains stability through variety in its bonding of oxygen; for, if we define a group Q as a decidedly better π-electron acceptor than another group R, we can argue that QOQ + ROR going to 2QOR will increase the total π-bond energy because each Q gets a better share of the oxygen π electrons, while the decrease of O–R π-bond energy will be less important. Accordingly, the stability of $(CF_3)_2POSi(CH_3)_3$ should be obvious, but it is more surprising that $[(CF_3)_2PO]_4Si$ does not decompose to $[(CF_3)_2P]_2O$ and $[(CF_3)_2PO]_2SiO$ polymers or ultimately SiO_2.

These new P–O–Si compounds might be compared with some recently reported alkyl- and arylphosphinoxysilanes[4] in regard to resistance against rearrangement to phosphine oxides, but the major reasons for such stability may be different. For example, seven such compounds react with CH_3I to make R_3SiI and $CH_3R'_2PO$ (Arbuzov reaction),[4] whereas both $(CF_3)_2POSi(CH_3)_3$ and $[(CF_3)_2PO]_4Si$ seem inert to CH_3I (3 hr at 70°). It is apparent also that $(CH_3)_3Si-$ is very different from $(CH_3)_3C-$ in this regard, for $(CF_3)_2POC(CH_3)_3$ quickly converts to the phosphine oxide $(CH_3)_3C(CF_3)_2PO$ in the presence of CH_3I at 70°.[2] In general, our compounds lack the phosphine base strength to support such reactions. They also lack oxygen base strength, for $(CF_3)_2POSi(CH_3)_3$ proved to be inert to BF_3 either at 100° or at low temperatures.

Experimental Part

Syntheses and Formulas. High-vacuum methods were used for quantitative monitoring of the synthetic processes, with mercury float-valves employed to avoid the effects of grease, with fractional condensation as the usual technique for isolating the products, and with infrared identification when possible. The only difficult separation was the removal of spectroscopic traces of $[(CH_3)_3Si]_2O$ (trapped at −30°) from $(CF_3)_2POSi(CH_3)_3$ (trapped at −45°); hence process 3 was preferred over 2 or 4.

The quantitative processes 2, 3, 4, and 6 all were completed during 5–6 days at 100°, with the reaction mixtures in sealed tubes. Process 1 ran for 3 days at 100°, with the yield seriously diminished by the action of Si–H bonds upon P–O bonds to form P–H and Si–O bonds. Similar side reactions also spoiled the yield in process 5, which ran for 5 days at 100°. Since neither process 1 nor 5 was a single quantitative reaction (equivalent to elementary analysis), their products required analysis, which was done by basic hydrolysis. Thus 0.386 mmole of $(CF_3)_2POSiH_3$ (by weight) yielded 0.76 mmole of HCF_3 and 1.14 mmoles of H_2 (calcd, 0.77 and 1.16); and 0.116 mmole of $[(CF_3)_2PO]_3SiH$ gave 0.68 mmole of HCF_3 (calcd, 0.70), while 0.250 mmole of it gave 0.247 mmole of H_2.

The formulas of the four new compounds were confirmed by vapor-phase molecular weight determinations: for $(CF_3)_2POSiH_3$, 222 *vs.* calcd 216; for $(CF_3)_2POSi(CH_3)_3$, 254 *vs.* calcd 258; for $[(CF_3)_2PO]_3SiH$, 592 *vs.* calcd 584; and for $[(CF_3)_2PO]_4Si$, 768, as calculated. Their purity was indicated by the conformity of their vapor-tension curves to normal principles (Tables I–IV), by the

Table I. Volatility of $(CF_3)_2POSiH_3$
($\log P = 5.618 + 1.75 \log T - 0.005T - 1733/T$)
(t_{760} = 39.6°; Trouton constant = 21.8 eu; mp −116°)

Temp, °C	−52.0	−46.0	−30.0	−21.7	−15.0	−7.0	0.00
P_{obsd}, mm	6.0	9.5	28.0	46.7	68.3	104.6	148.5
P_{calcd}, mm	6.0	9.5	28.2	46.7	68.4	104.7	148.5

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[2] J. E. Griffiths and A. B. Burg, *J. Am. Chem. Soc.*, 84, 3442 (1962).

[3] L. K. Peterson and A. B. Burg, *ibid.*, 86, 2587 (1964).

[4] K. Issleib and B. Walther, *Angew. Chem.*, 79, 59 (1967); *Angew. Chem. Intern. Ed. Engl.*, 6, 88 (1967).

Table II. Volatility of $(CF_3)_2POSi(CH_3)_3$
($\text{Log } P = 6.037 + 1.75 \log T - 0.005T - 2168/T$)
($t_{760} = 101°$; Trouton constant = 21.4 eu; mp −69.3°)

Temp, °C	−23.0	−20.3	−11.8	0.00	8.6	19.45
P_{obsd}, mm	2.10	2.60	4.60	9.90	16.5	30.3
P_{calcd}, mm	2.07	2.53	4.62	9.95	16.6	30.2

Table III. Volatility of $[(CF_3)_2PO]_3SiH$
($\text{Log } P = 7.7390 + 1.75 \log T - 0.006T - 2983/T$)
($t_{760} = 161.1°$; Trouton constant = 23.7 eu)

Temp, °C	42.0	51.0	60.0	70.0	80.0	90.4
P_{obsd}, mm	5.62	9.69	16.1	26.7	43.0	68.1
P_{calcd}, mm	5.67	9.67	15.9	26.6	43.0	68.1

Table IV. Volatility of $[(CF_3)_2PO]_4Si$
($\text{Log } P = 7.2132 + 1.75 \log T - 0.005T - 3110/T$)
($t_{760} = 193.1°$; Trouton constant = 21.5 eu; mp −53.8°)

Temp, °C	52.0	60.1	75.5	82.6	93.0	98.0
P_{obsd}, mm	2.53	4.32	9.93	14.39	23.69	29.84
P_{calcd}, mm	2.62	4.26	9.98	14.35	23.72	29.84

Table V. Infrared Spectra of Phosphinoxysilanes (10-Cm Cell)

$(CF_3)_2POSiH_3$ (P = 5 mm)	$(CF_3)_2P$-$OSi(CH_3)_3$ (P = 5 mm)	$[(CF_3)_2PO]_3SiH$ (P = 3.6 mm)	$[(CF_3)_2PO]_4Si$ (P = 0.73 mm)
...	2970 (1.4)	...	...
2214 (4.5)	...	2310 2275 (0.25)	...
...	1367 (0.4) 1267 (2.8)	1396 1421 (0.25)	1365 (3?)
		(combinations?)	
1224 (14)	1225 (7)	1230 (15)	1231 (95)
1183 (25)	1174 (20)	1184 (30)	1183 (165)
1145 (9)	1153 (5)	1152 (10)	1148 (80)
1124 (14)	1109 (8)	1127 (16)	1129 (103)
1067 (1.9)	1058 1049 (0.7)	1025 (9)	1035 (53)
1036 (2.3)			
...	999 (5)	...	...
956 (28)	858 (9)	864 (8)	883 (7)
727 (1.9)	760 (0.8)	(Not seen)	748 727 (2)
572 (0.6)	...	...	...
458 (5)	...	...	457 (53)

sharp melting points of three of them, and by the absence of any obvious impurity bands in their infrared spectra. The proton nmr spectrum (Varian A-60) of $(CF_3)_2POSi(CH_3)_3$ showed a single sharp peak, 7.38 ppm downfield from external $Si(CH_3)_4$.

Infrared Spectra. The Beckman IR7 instrument was used for obtaining the gas-phase infrared spectra of these compounds in the NaCl region, and the Perkin-Elmer 337 instrument for the 650–400-cm^{-1} region. The latter range is not very distinctive for CF_3–P compounds, showing only a CF_3 deformation in the 550–570-cm^{-1} range (often very weak) and a strong P–CF_3 stretching mode at 420–460 cm^{-1}.

The results, shown in Table V as frequencies of band peaks with parenthetical relative intensities roughly on the same scale, illustrate the principle that a highly polar bond in one part of a molecule works against high intensity for modes not strongly involving the same polar bond. For example, the C–F, P–O, and Si–O bonds tend toward mutual limitation of intensities of stretching modes, while Si–H stretching and some C–H modes may be very difficult to detect.

The assignments for the CH_3 group are obvious—rocking at 999, deformations at 1267 and 1367, and asymmetric stretching at 2970 cm^{-1}—but symmetric stretching was not observed. Si–H stretching would be found in the 2200–2300-cm^{-1} region, where C–F stretching overtones also might record. The 1100–1250-cm^{-1} region usually includes all C–F stretching modes, with each compound showing a characteristic and unique frequency–intensity pattern, suitable for identification. The 1000–1100-cm^{-1} range would belong to Si–O stretching (with Si–H bending not necessarily absent); the high intensity of this mode for the fourth compound might be due to the vibrational disturbance of the highly symmetrical SiO_4 pattern. This symmetry also would account for the failure of the Si–O bonds to suppress the high intensity of C–F stretching. The 850–960-cm^{-1} region is attributed to P–O stretching, with wide variations possibly due to differences of coupling with Si–O bonds. The 720–760-cm^{-1} range normally belongs to CF_3-symmetric deformation, and often is weak.

Donor Properties of Hexamethylcyclotrisilazane

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Abstract: The donor properties of the heterocycle hexamethylcyclotrisilazane, $[(CH_3)_2SiNH]_3$ (abbreviated HMT), have been investigated from reactions with various reference acid systems. Although the trimeric (Si–N) ring is a potential pseudo-aromatic system, attempts to isolate half-sandwich complexes of the type $(\pi\text{-HMT})M(CO)_3$, where M = Cr and Mo, proved abortive, and no indication of six π-donor capacity was evident. Instead reaction with the typical class A acids titanium trichloride and vanadium trichloride provided neutral stable adducts of the type $MCl_3 \cdot HMT$. Evidence that the ligand acts as a terdentate nitrogen donor to give monomeric hexacoordinate titanium(III) and vanadium(III) species has been obtained and discussed from spectral, magnetic, conductivity, infrared (4000–200 cm^{-1}), and nmr measurements of these complexes.

The colorless liquid hexamethylcyclotrisilazane, $[(CH_3)_2SiNH]_3$ (I), has a slightly puckered ring structure containing alternate electron-acceptor (Si) and electron-donor (N) sites.[2] Two extreme mechanisms can be proposed involving the distribution of the nitrogen lone-pair electrons.

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[2] The recent reviews by (a) W. Fink, *Angew. Chem. Intern. Ed Engl.*, **5**, 760 (1966), and (b) K. A. Andrianov and L. M. Khananashvili *Organometal. Chem. Rev.*, **2**, 142 (1967), adequately summarize the properties and reactions of such silazane systems.