$$PO(OSO_2F)_3 + 12OH^- = PO_4^{3-} + 3SO_4^{2-} + 3F^- + 6H_2O$$

Anal. Calcd for $PO(OSO_2F)_3$: P, 9.06; S, 27.89; F, 16.56; moles of OH^- consumed, 12.0. Found: P, 8.97; S, 27.70; F, 16.70; moles of OH^- consumed, 12.4.

Melting Point.—While phosphoryl fluorosulfate had a tendency to form a glass on cooling, it could be made to form white crystals which melted at approximately −24°.

Infrared Spectrum.—The spectrum was studied using a Beckman IR-10 spectrometer with the sample contained in a 10-cm Pyrex glass cell fitted with silver chloride windows and a small trap. Phosphoryl fluorosulfate was distilled under vacuum into the trap. The infrared spectrum of the vapor in equilibrium with the liquid $PO(OSO_2F)_3$ in the trap was then recorded at 22 and ~45°. The spectra at the two temperatures were identical except for increased intensity at the higher temperature. Absorption bands and some probable assignments were as follows (cm^{-1}): 1493 s, S=O asymmetric stretch; 1396 s, P=O stretch; 1253 s, S=O symmetric stretch; 935 s (shoulder at 980), P—O stretch; 845 s, S—F stretch; 720 w; 540 m; 510 m (s, strong; m, medium; w, weak).

Nmr Spectrum.—Spectra were obtained by use of a Varian Model 4311B high-resolution nmr spectrometer with a 40-Mc oscillator. The ^{19}F nmr spectrum for $PO(OSO_2F)_3$ showed a single absorption in the fluorosulfate region at −130 ppm relative to CF_3COOH as an external reference. No spin–spin coupling was observed between phosphorus and the fluorine attached to sulfur.

Decomposition of $PO(OSO_2F)_3$.—During attempts to purify $PO(OSO_2F)_3$ by vacuum fractional distillation at temperatures above room temperature it was found that decomposition occurred slowly. Four major products were found: POF_3, SO_3, and two compounds tentatively identified as $POF(OSO_2F)_2$ and POF_2OSO_2F. While decomposition was slow even at 100°, significant decomposition probably occurred also at somewhat lower temperatures. The above two phosphoryl fluoride fluorosulfates were not isolated in pure form, but infrared spectra, nmr spectra, and vapor densities strongly supported their existence. The infrared spectrum of a mixture of the two showed the following major absorptions (cm^{-1}): 1495, S=O asymmetric stretch;[6] 1380–1400, P=O stretch;[7] 1255, S=O symmetric stretch;[6] 940–980, P=F and P—O stretches;[7,8] 850, S—F stretch;[6] 520.

The ^{19}F nuclear magnetic resonance spectrum of a sample produced by heating $PO(OSO_2F)_3$ for 2 hr at 100° showed in addition to the absorption for $PO(OSO_2F)_3$ others which could be assigned to POF_3, POF_2OSO_2F, and $POF(OSO_2F)_2$. There were two other absorptions in the fluorosulfate region which may have been caused by sulfur oxyfluorides such as sulfuryl fluoride and pyrosulfuryl fluoride. The nuclear magnetic resonance data are given in Table I. The J_{PF} value for POF_3 agrees well with that of Gutowsky, McCall, and Slichter, and the trend for J_{PF} from POF_3 to $POF(OSO_2F)_2$ agrees well with that observed for POF_3 to $POFCl_2$.[9]

Vapor densities were determined for ten successive fractions evaporated from a mixture of the substances considered to be $POF(OSO_2F)_2$ and POF_2OSO_2F. The first five fractions had densities close to 183 g/GMV (theoretical for POF_2OSO_2F, 184). Following that the vapor pressure of the remaining liquid became less as fractions were removed and the vapor density rose to about 260 (theoretical for $POF(OSO_2F)_2$, 264.1).

Acknowledgment.—This work was performed in part under contract with the Office of Naval Research. Nmr spectra were taken by Mr. Bernard J. Nist.

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[6] M. Lustig, *Inorg. Chem.*, **4**, 1828 (1965).

[7] M. L. Dewaulle and F. Francois, *Compt. Rend.*, **222**, 1193 (1946).

[8] K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York, N. Y., 1963, pp 112, 115.

[9] H. S. Gutowsky, D. W. McCall, and C. P. Slichter, *J. Chem. Phys.*, **2**, 279 (1953). J_{PF} (cps): POF_3, 1055; POF_2Cl, 1120; $POFCl_2$, 1175.

CONTRIBUTION FROM THE FABRICS AND FINISHES DEPARTMENT,
EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS
AND COMPANY, WILMINGTON, DELAWARE

Addition of Hexafluoroacetone to Alkoxysilanes

BY R. A. BRAUN

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The reactions of hexafluoroacetone with compounds containing Si–H and Si–OH bonds have been reported recently. The addition of hexafluoroacetone across the Si–H bond of various methylsilanes and trichlorosilane occurred under the influence of ultraviolet irradiation to give alkoxysilanes.[1] The same reactions

$$\underset{}{R_3SiH + R^1{}_2CO \longrightarrow R_3SiOCHR^1{}_2} \qquad \text{I}$$

were observed without ultraviolet irradiation with hydrides of silicon, tin, and germanium.[2] Earlier, the reaction of dipropylsilane with hexafluorocyclobutanone to give dipropylbis(hexafluorocyclobutoxy)silane was observed.[3] The spontaneous reaction of trimethylsilanol with hexafluoroacetone was shown to give 2-trimethylsiloxyhexafluoroisopropyl alcohol (II). The

$$(CH_3)_3SiOH + (CF_3)_2CO \longrightarrow (CH_3)_3SiOC(CF_3)_2OH \qquad \text{II}$$

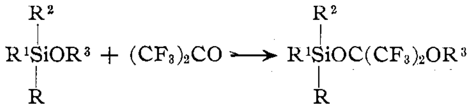
addition of aldehydes (*e.g.*, acetaldehyde, chloral, bromal, etc.) to tributyltin methoxide has been reported to give adducts (III) that are unstable above room temperature and could not be distilled.[4] While

$$(C_4H_9)_2SnOCHROCH_3 \qquad \text{III}$$

there is little known about the reaction of perhaloketones with alkoxysilanes, tributyltin methoxide and hexachloroacetone gives the adduct IV, which decomposes at 65°.[5]

$$(C_4H_9)_3SnOCH_3 + (CCl_3)_2CO \rightleftarrows (C_4H_9)_4SnOC(CCl_3)_2OCH_3 \longrightarrow (C_4H_9)_3SnCl_3 + CCl_3COOCH_3$$

We have found that the reaction of 1 mole or more of hexafluoroacetone with a wide variety of alkoxysilanes at 100–150° gives 1:1 adducts, V. The adducts are much more stable than the related tin adducts and can be distilled.[5]



$$R^1\overset{\overset{R^2}{|}}{\underset{\underset{R}{|}}{Si}}OR^3 + (CF_3)_2CO \longrightarrow R^1\overset{\overset{R^2}{|}}{\underset{\underset{R}{|}}{Si}}OC(CF_3)_2OR^3$$

V

Va, $R = R^1 = CH_3$; $R^2 = OC_2H_5$; $R^3 = C_2H_5$
Vb, $R = CH{=}CH_2$; $R^1 = R^2 = OC_2H_5$; $R^3 = C_2H_5$
Vc, $R = C_6H_5$; $R^1 = R^2 = OC_2H_5$; $R^3 = C_2H_5$
Vd, $R = R^1 = R^2 = OC_2H_5$; $R^3 = C_2H_5$
Ve, $R = R^1 = OC_2H_5$; $R^2 = (CH_2)_2COOC_2H_5$; $R^3 = C_2H_5$
Vf, $R = R^1 = OCH_3$; $R^2 = (CH_2)_3O\overset{\overset{O}{\|}}{C}C(CH_3){=}CH_2$; $R^3 = CH$
Vg, $R = H$, $R^1 = R^2 = OC_2H_5$; $R^3 = C_2H_5$

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[1] A. J. Janzen and C. J. Willis, *Can. J. Chem.*, **43**, 3063 (1965).

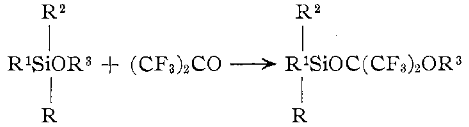
[2] W. R. Cullen and G. E. Styan, *Inorg. Chem.*, **4**, 1437 (1965).

[3] G. W. Parshall, *ibid.*, **4**, 52 (1965).

[4] A. G. Davies and W. R. Symes, *Chem. Commun.* (London), **25**, 1965.

[5] A. G. Davies and W. R. Symes, *J. Organometal. Chem.*, **5**, 394 (1966).

TABLE I[a]



$$\begin{array}{ccc} \mathrm{R^2} & & \mathrm{R^2} \\ | & & | \\ \mathrm{R^1SiOR^3} + (\mathrm{CF_3})_2\mathrm{CO} & \longrightarrow & \mathrm{R^1SiOC(CF_3)_2OR^3} \\ | & & | \\ \mathrm{R} & & \mathrm{R} \end{array}$$

Compd					Yield, %	Bp, °C (mm)	n^{25}_D	Formula	Calcd, %				Found, %			
	R	R^1	R^2	R^3					C	H	F	Si	C	H	F	Si
Va	CH_3	CH_3	OC_2H_5	C_2H_5	54.7	42 (0.35)	1.3483	$C_9H_{16}F_6O_3Si$	34.4	5.1	36.3	8.9	34.5	5.2	36.8	8.6
Vb	$CH{=}CH_2$	OC_2H_5	OC_2H_5	C_2H_5	57.9	100 (46.0)	1.3622	$C_{11}H_{18}F_6O_4Si$	37.1	5.1	32.0	7.9	37.3	5.2	32.0	7.8
Vc	C_6H_5	OC_2H_5	OC_2H_5	C_2H_5	88.3	92–93 (1.4)	1.4029	$C_{15}H_{20}F_6O_4Si$	44.3	5.0	28.1	6.9	44.3	5.1	28.1	7.2
Vd	OC_2H_5	OC_2H_5	OC_2H_5	C_2H_5	81.8	60 (2.0)	1.3520	$C_{11}H_{20}F_6O_5Si$	35.3	5.4	30.5	7.5	35.3	5.4	30.5	7.7
Ve	OC_2H_5	OC_2H_5	$(CH_2)_2COOC_2H_5$	C_2H_5	83.0	82–83 (0.35)	1.3872	$C_{14}H_{24}F_6O_6Si$			26.5	6.5			26.2	6.5
Vf	OCH_3	OCH_3	$(CH_2)_3OC({=}O)C(CH_3){=}CH_2$	CH_3	65.5	110–112 (1.5)	1.3933	$C_{13}H_{20}F_6O_6Si$			27.5	6.8			27.4	6.8
Vg	H	OC_2H_5	OC_2H_5	C_2H_5	73.2	27–28 (0.08)	1.3343	$C_9H_{16}F_6O_4Si$	32.7	4.9		8.5	33.0	5.1		8.5

[a] All products are colorless liquids. The infrared and proton nmr spectra of all compounds are in agreement with the proposed structures.

Compounds Va, Vb, and Ve are stable up to 170°, where the reaction is reversed and hexafluoroacetone is liberated. The new adducts are water insoluble and much less susceptible to hydrolysis than the parent alkoxysilanes.

The reaction of excess hexafluoroacetone with a monoalkoxysilane results in the insertion of only one molecular equivalent of hexafluoroacetone into the Si–O bond. This is different from the observed repeated insertion of many moles of chloral in the Sn–O bond of tributyltin methoxide.[5] As expected, hexafluoroacetone reacts with triethylsilane at 150° to give 1,1,1,3,3,3-hexafluoropropoxytriethylsilane (VI). With compounds such as triethoxysilane or methyl diethoxysilane, containing both an Si–H and $SiOC_2H_5$ group, we have found that the reaction occurs exclusively at the $SiOC_2H_5$ group, even when the second mole of hexafluoroacetone is introduced.

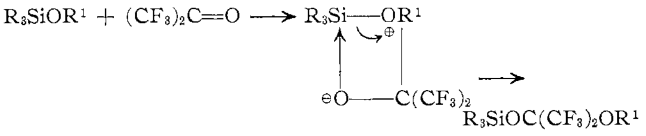
$$(\mathrm{C_2H_5})_3\mathrm{SiH} + (\mathrm{CF_3})_2\mathrm{C{=}O} \longrightarrow \underset{\mathrm{VI}}{(\mathrm{C_2H_5})_3\mathrm{SiOC(CF_3)_2H}}$$

$$(\mathrm{C_2H_5O})_3\mathrm{SiH} + (\mathrm{CF_3})_2\mathrm{C{=}O} \longrightarrow \underset{\mathrm{Vg}}{(\mathrm{C_2H_5O})_2\mathrm{SiHOC(CF_3)_2OC_2H_5}} \not\longrightarrow (\mathrm{C_2H_5O})_3\mathrm{SiOC(CF_3)_2H}$$

$$2(\mathrm{CF_3})_2\mathrm{C{=}O} \longrightarrow \underset{\mathrm{VII}}{\mathrm{C_2H_5OSiH(OC(CF_3)_2OC_2H_5)_2}}$$

The properties of these compounds are summarized in Table I and their structures have been established by their infrared, nmr, and mass spectra, which were completely consistent with the proposed structures.

In view of the known electrophilic nature of the carbonyl carbon atom of hexafluoroacetone, the most likely reaction sequence for the reaction between an alkoxysilane and hexafluoroacetone is



$$\mathrm{R_3SiOR^1} + (\mathrm{CF_3})_2\mathrm{C{=}O} \longrightarrow \begin{array}{ccc} \mathrm{R_3Si} & \text{—} & \overset{\oplus}{\mathrm{O}}\mathrm{R^1} \\ \uparrow & & | \\ \ominus\mathrm{O} & \text{—} & \mathrm{C(CF_3)_2} \end{array} \longrightarrow \mathrm{R_3SiOC(CF_3)_2OR^1}$$

Experimental Section[6]

Diethoxy 2-Ethoxy-1,1,1,3,3,3-hexafluoropropoxysilane (Vg) and Ethoxybis(2-ethoxy-1,1,1,3,3,3-hexafluoropropyl)silane (VII).—Triethoxysilane (65.5 g, 0.4 mole) and hexafluoroacetone (133.0 g, 0.8 mole) were heated in a stainless steel bomb at 150° for 6 hr at autogenous pressure. The crude product (173.0 g) fractionated to give 76.8 g (58.7%) of IIIg (see Table I) and 65.0 g (32.7%) of IV; bp 45° (0.5 mm), n^{25}_D 1.3418. The infrared spectra of both compounds contained a strong Si–H band at 2221 cm^{-1} and no OH peaks.

Anal. Calcd for $C_{12}H_{16}F_{12}O_5Si$: C, 29.0; H, 3.3; F, 45.9; Si, 5.7. Found: C, 29.4; H, 3.6; F, 45.7; Si, 5.7.

The mass spectrum was consistent with the proposed structure for IIIg and contained $m/e = 450$ and 427 (parent ion minus $C_2H_5^+$ and CF_3^+, respectively).

In another reaction, triethoxysilane (24.9 g, 0.15 mole) and hexafluoroacetone (100.0 g, 0.6 mole) were heated at 175° for 6 hr in a bomb. The only product isolated was VII, 58.8 g (73.2%). Both Vb and VII have a singlet in their nmr spectra at τ 5.55 which is attributed to the silane hydrogen atom.

Related reactions were conducted under similar conditions and are summarized in Table I.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF SOUTH DAKOTA, VERMILLION, SOUTH DAKOTA

Thermal Properties of Dimethylaminomethylborane Cyclic Dimer

BY N. E. MILLER, M. D. MURPHY, AND D. L. REZNICEK

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Two isomeric derivatives of the heterocyclic ring[1] system I (aminomethylborane dimer) have been reported recently.[2,3] Compound II, in which the nitrogen atoms are methylated (dimethylaminomethylborane dimer), apparently exists only as a dimer,[2] whereas compound III, in which the boron atoms are methylated (aminomethyldimethylborane) exists as an equilibrium mixture of monomer and polymers.[3] This difference in properties of the methylated derivatives is not unexpected and is readily explained by simple Lewis acid–base interactions. It is well-established that increasing methyl substitution increases base strength of amines (in the absence of steric hindrance) and conversely decreases acid strength of

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[6] Boiling points are uncorrected. The silanes were obtained from Peninsular Chemical Research, Inc.

[1] The ring system could be named 1,4-bisazonia-2,5-bisborylacyclohexane.

[2] N. E. Miller and E. L. Muetterties, *Inorg. Chem.*, **3**, 1196 (1964).

[3] R. Schaeffer and L. J. Todd, *J. Am. Chem. Soc.*, **87**, 488 (1965).