axes. The largest change is -0.005 for $\Delta g_z/\Delta x$, while $\Delta g_z/\Delta z$ is 0.000. Since g_z depends on the splitting between the MO's that are largely $3d(x^2 - y^2)$ and $3d(xy)$ AO's, respectively (see section on Spin–Orbit Coupling and g Values), a stress parallel to z has little effect, while a stress parallel to x raises the $^2B_{2g}$ excited state (see eq 6), having two electrons in the mostly-$3d(x^2 - y^2)$ MO, relative to the ground state, having only one, thus decreasing g_z. The experimental uncertainty[7,8] on g_z (or $g_{\|}$) is ± 0.01, so a change of -0.005 would not be detectable.

A similar analysis shows that if the tetragonally compressed structure for $CuCl_6^{4-}$ were lower in energy than the elongated structure (negative α barrier), then two minima would be raised in energy by stress, rather than one as is observed. In each case, stress primarily raises in energy the MO containing the Cu AO with its charge density concentrated along the axis parallel to the stress. The total states respond to the stress in accord with occupation numbers of 1 or 2 for the most strongly affected MO. Hence a compressed structure with its C_4 axis parallel to the stress is less affected than one with C_4 perpendicular to the stress, since the former has only one electron in the mostly-$3d(3z^2 - r^2)$ MO, while the latter has two in the mostly-$3d(z^2 - x^2$ or $z^2 - y^2)$ MO (the relative position of Y' relative to X' and Z' in Figure 7 holds even for negative barrier). Thus the stress-induced population changes provide an independent confirmation of the positive sign of the α barrier (eq 4) in $CuCl_6^{4-}$.

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The Reaction of Hexafluoroacetone with Silanes. II. Possible Ionic Intermediates[1]

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Received March 20, 1967

The mechanism of the reaction of hexafluoroacetone with trimethylsilane has been reconsidered in the light of results now available on other reactions involving nucleophilic attack on hexafluoroacetone; these include the reaction of the ketone with alkyl halides in the presence of sodium and the reaction of hexafluoroacetone with tertiary amines. It is now thought probable that the initial reaction of a silane with hexafluoroacetone is a hydride abstraction, giving a fluorinated alkoxide ion. Claims that hexafluoroacetone forms complexes with compounds of group IV elements are reexamined, and it is concluded that present evidence does not support such a suggestion.

The addition reactions of hexafluoroacetone across Si–H bonds have received attention recently. We have reported[2] the reaction of the ketone under free-radical conditions with methyl-, dimethyl-, trimethyl-, or trichlorosilane to give a variety of hexafluoroisopropoxysilanes containing the grouping $SiOCH(CF_3)_2$. Under ionic conditions (dark, liquid phase, 20° or below) only trimethylsilane reacted, the products being the 1:1 adduct, $(CH_3)_3SiOCH(CF_3)_2$, and a smaller yield of the 2:1 adduct, $(CH_3)_3SiOC(CF_3)_2OCH(CF_3)_2$.

In a paper appearing at the same time as ours, Cullen and Styan[3] described similar work on the reaction of hexafluoroacetone with trimethylsilane, -germane, and -stannane and with dimethylstannane. In each case, they reported ready formation of the hexafluoroisopropoxides. However, they did not find the 2:1 adduct of hexafluoroacetone with trimethylsilane mentioned above, but reported instead an unstable adduct, $(CH_3)_3SiOCH(CF_3)_2 \cdot (CF_3)_2CO$, dissociating readily at 20° to $(CH_3)_3SiOCH(CF_3)_2$ and hexafluoroacetone. They point out in a footnote that this would appear to be a different species from our 2:1 adduct, which is stable indefinitely at 20° and may be distilled repeatedly without dissociation at its normal boiling point of 135°. However, evidence from nuclear magnetic resonance spectra, discussed below, suggests that this point may be questioned.

In the papers referred to above, both Cullen and Styan and ourselves suggested that the mechanism of the liquid-phase reactions of hexafluoroacetone with group IV hydrides involved as a first step the nucleophilic attack of the carbonyl oxygen on the central metal or metalloid atom, giving a five-coordinate intermediate. The hexafluoroisopropoxides were then formed by intermolecular hydride transfer.

Fresh evidence now available leads us to reject the above process in favor of an ionic mechanism in which the first step is the abstraction of a hydride ion by hexafluoroacetone, giving a hexafluoroisopropoxide ion, $HC(CF_3)_2O^-$.

Experimental Section

General techniques have been described previously,[2] as has the reaction of hexafluoroacetone with trimethylsilane. Nuclear magnetic resonance spectra were recorded on Varian Model A-60 and DP-60 instruments using 60 Mcps. Chemical shifts are relative to internal TMS, unless otherwise stated.

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[1] Presented in part at the 49th Conference of the Chemical Institute of Canada, Saskatoon, June 1966. Reference 2 is regarded as part I.

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

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

Reaction of Tertiary Amines with Hexafluoroacetone.—Hexafluoroacetone and various tertiary amines (trimethylamine, triethylamine, diethylmethylamine) were mixed in equimolar proportions in an nmr tube. The ^{1}H nmr spectrum in each case showed a septet near −3 ppm (J = 6 cps) partially overlapping with the expected pattern from the immonium ion. On increasing the relative amount of hexafluoroacetone in the tube, the septets decreased in intensity, being replaced by another septet at −4.8 ppm (J = 6.4 cps).

When trimethylchlorosilane was added to a 2:1 molar ratio mixture of hexafluoroacetone and trimethylamine, immediate reaction was apparent and fractionation gave the 2:1 adduct, $(CH_3)_3SiOC(CF_3)_2OCH(CF_3)_2$ in 55% yield. It was characterized by comparison with a known sample.[2]

Reaction of Methyl Iodide, Sodium, and Hexafluoroacetone.—Hexafluoroacetone (4.86 g, 29.2 mmoles), methyl iodide (3.74 g, 26.4 mmoles), and sodium (0.98 g, 42.6 g-atoms) with tetrahydrofuran (8 ml) in a sealed reaction tube (35 ml) were shaken at 25° for 20 hr, by which time the metal had dissolved and a white precipitate appeared. On adding trimethylchlorosilane (6.0 g, 55 mmoles) further solid precipitated immediately. After standing at 25° for 15 hr, the volatile products were removed *in vacuo* and distilled. The fraction boiling at 148–150° was further purified by vpc (silicone column at 120°) to give 2-(2-methylhexafluoroisopropoxy)hexafluoroisopropoxytrimethylsilane, $(CH_3)_3SiOC(CF_3)_2OC(CF_3)_2CH_3$, (3.35 g, 8.0 mmoles, 55% yield based on hexafluoroacetone). *Anal.* Calcd for $C_{10}H_{12}F_{12}O_2Si$: C, 28.6; H, 2.88; F, 54.3. Found: C, 28.8; H, 2.98; F, 53.1. The ^{1}H nmr spectrum (cyclohexane solution) showed a broad singlet (half-width 4.2 cps) at −0.39 ppm and a sharp singlet at +1.12 ppm (both relative to internal cyclohexane). The former peak is assigned to the protons of the $CH_3C(CF_3)_2$ grouping, the broadening being an unresolved septet from coupling with the six fluorine atoms, while the latter peak is due to the trimethylsilyl group. Integration showed the areas of the peaks to be in the ratio 3.08:9.00.

In another experiment hexafluoroacetone (7.62 g, 45.9 mmoles), sodium (2.16 g, 94.0 g-atoms), methyl iodide (6.53 g, 46.1 mmoles), and trimethylchlorosilane (5.06 g, 46.8 mmoles) in tetrahydrofuran (10 ml) were kept together at −26° for 8 hr in a sealed tube, then shaken at 25° for 4 hr. Fractionation as before gave the compound $(CH_3)_3SiOC(CF_3)_2OC(CF_3)_2CH_3$ in 51% yield (4.93 g).

Reaction of Ethyl Bromide, Sodium, and Hexafluoroacetone.—Hexafluoroacetone (5.94 g, 35.8 mmoles), ethyl bromide (3.94 g, 36.2 mmoles), sodium (1.25 g, 54.4 g-atoms), and tetrahydrofuran (15 ml) in a sealed tube (60 ml) were kept at −26° for 31 hr, followed by 3 hr at 25°, by which time the sodium had reacted and a white solid appeared. Immediate reaction was apparent when trimethylchlorosilane (4.08 g, 37.7 mmoles) was added, and further solid precipitated. Fractionation of the more volatile components showed the presence of ethylene (identified spectroscopically, not quantitatively estimated). Less volatile materials were shown by vpc to contain at least five components. The major product was the compound $(CH_3)_3SiOC(CF_3)_2OCH(CF_3)_2$ (0.71 g, 1.8 mmoles). A second component had infrared and nmr spectra consistent with the structure $(CH_3)_3SiOC(CF_3)_2OC(CF_3)_2CH_2CH_3$ showing a quartet (J = 7.5 cps) at −2.35 ppm, a triplet at −1.08 ppm, and a singlet at −0.18 ppm. Integrated peak areas support the assignment of these to the $-CH_2-$, $-CH_3$, and $(CH_3)_3Si$ protons, respectively, in the above structure.

Proton Nmr Spectra of $(CH_3)_3SiOC(CF_3)_2OCH(CF_3)_2$.—In view of conflicting previous reports, this spectrum was reinvestigated. A mixture of redistilled samples of $(CH_3)_3SiOCH(CF_3)_2$ and $(CH_3)_3SiOC(CF_3)_2OCH(CF_3)_2$ in a 1:4 molar ratio was prepared and its ^{1}H nmr spectrum recorded (undiluted). Hexafluoroacetone was then added in twofold, threefold, and eightfold excess, using sealed nmr tubes. No change in the appearance of the spectra was observed; the integrated areas of the peaks corresponding to the two compounds remained in a 1:4 ratio.

Results and Discussion

We feel that an ionic mechanism is now the only one which will give a complete explanation of the experimental results reported here and previously.[2,3] The hexafluoroacetone molecule is known to be a very electrophilic species,[4,5] and it is quite reasonable to suggest that it may abstract a hydride ion from trimethylsilane, the resulting trimethylsilyl cation being solvated with further hexafluoroacetone. The 2:1 adduct observed by us would then arise from the reaction of that ion with a further hexafluoroacetone molecule

$$(CH_3)_3SiH + (CF_3)_2CO \longrightarrow (CH_3)_3Si^+ + HC(CF_3)_2O^-$$

$$HC(CF_3)_2O^- + (CF_3)_2CO \longrightarrow HC(CF_3)_2OC(CF_3)_2O^-$$

Combination of these anions with a trimethylsilyl cation would then give the observed products. We previously observed that, of the silane compounds investigated by us, only trimethylsilane reacted in the liquid phase and gave the 2:1 adduct. With dimethylsilane, methylsilane, or trichlorosilane, reaction occurred on irradiation, giving only the hexafluoroisopropoxides. This may be ascribed to the more ready formation of the trimethylsilyl cation as compared with the cations which would be formed by hydride abstraction from the other silanes.

Support for such a mechanism is given by the manner in which hexafluoroacetone reacts with certain tertiary amines. Gambaryan and Knunyants[5] have recently reported that hexafluoroacetone abstracts a hydride ion from diphenylmethylamine and similar compounds to give 1:1 adducts which they formulate as immonium salts, *e.g.*, $[(C_6H_5)_2\overset{+}{N}{=}CH_2]HC(CF_3)_2O^-$. On hydrolysis, these give hexafluoroisopropyl alcohol.

We have repeated this reaction, using trimethylamine and other tertiary amines, and studied the resulting products by proton and fluorine nmr. When the ketone and amine are mixed in a 1:1 molar ratio, as was done by Gambaryan and Knunyants, the spectra are in accord with their formulation. However, on increasing the ratio of hexafluoroacetone to amine above 1:1, a low-field septet (J = 6.4 cps) appeared at −4.84 ppm associated with the ion $HC(CF_3)_2OC(CF_3)_2O^-$. On reaction of trimethylchlorosilane with such a mixture (ketone to amine ratio 2:1) the 2:1 adduct, $(CH_3)_3SiOC(CF_3)_2OCH(CF_3)_2$, was produced in high yield.

When the ketone to amine ratio was considerably increased, up to 7:1, there was no change in the nmr spectrum, indicating that species of the type $H[C(CF_3)_2O]_nC(CF_3)_2O^-$, where $n \geq 2$, were not formed. Furthermore, we have at no time isolated analogous silicon derivatives containing more than two hexafluoroacetone molecules, *i.e.*, $(CH_3)_3Si[OC(CF_3)_2]_3H$, etc. These observations indicate that only two anionic species are present in the ketone–amine or ketone–silane mixtures, the ions $HC(CF_3)_2O^-$ and $HC(CF_3)_2OC(CF_3)_2O^-$, and that these are in equilibrium

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(4) A. F. Janzen, P. F. Rodesiler, and C. J. Willis, *Chem. Commun.*, 672 (1966).

(5) N. P. Gambaryan and I. L. Knunyants, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **4**, 722 (1965).

$$\underset{\text{I}}{HC(CF_3)_2O^-} + (CF_3)_2CO \rightleftharpoons \underset{\text{II}}{HC(CF_3)_2OC(CF_3)_2O^-}$$

It is not surprising that further condensation with hexafluoroacetone does not occur. The ease of attack of an anion on hexafluoroacetone will be influenced by the nucleophilicity of the anion. Anion I, in which the oxygen atom carrying the negative charge is linked to a carbon atom attached to two trifluoromethyl groups and a hydrogen atom, will clearly have a greater degree of nucleophilicity than anion II, where the corresponding carbon atom is linked to two trifluoromethyl groups and an oxygen atom. Hence anion II shows no tendency to react with further hexafluoroacetone.

On the above argument, the substitution of an electron-releasing group, such as methyl, for the hydrogen atom in anion I should increase its nucleophilicity and displace the equilibrium to the right, and we find this readily confirmed by experiment. The methyl derivative of hexafluoroacetone, *i.e.*, the hexafluoro-*t*-butyl anion, $CH_3(CF_3)_2CO^-$, was readily prepared by allowing methyl iodide to react with sodium in the presence of hexafluoroacetone in tetrahydrofuran

$$CH_3I + (CF_3)_2CO + 2Na \xrightarrow{\text{THF}} [CH_3(CF_3)_2CO^-]Na^+ + NaI$$

The intermediate in this reaction is presumably sodium methyl, $NaCH_3$. Although we have shown elsewhere[4] that sodium will react with hexafluoroacetone in donor solvent, we do not favor such a process here, since the reaction was much more rapid than that occurring in the absence of methyl iodide and the products were entirely different from the perfluoropinacol derivatives obtained in the latter case. When the above reaction was performed using equimolar amounts of methyl iodide and hexafluoroacetone, the resulting solution reacted immediately with trimethylchlorosilane. However, the expected product, $(CH_3)_3SiOC(CF_3)_2CH_3$, was not found, but instead the adduct containing two hexafluoroacetone units was formed in good yield. This indicated that, even in the absence of excess hexafluoroacetone, the equilibrium position of the reaction

$$CH_3C(CF_3)_2O^- + (CF_3)_2CO \rightleftharpoons CH_3C(CF_3)_2OC(CF_3)_2O^-$$

lies to the right, consistent with the increased nucleophilicity of the ion $CH_3C(CF_3)_2O^-$. However, the two reaction systems are not strictly comparable, and the preponderance of the 2:1 adduct in the methyl iodide reaction may be to some extent a kinetic effect. In the silane–hexafluoroacetone reaction a reactive siliconium ion is postulated, whereas in the methyl iodide reaction only a sodium cation is present and the final product is probably formed by S_N2-type attack of the anion on trimethylchlorosilane. When methyl iodide, sodium, hexafluoroacetone, and trimethylchlorosilane were simultaneously mixed in tetrahydrofuran, the products were the same as those found when the reaction was carried out in two stages.

When ethyl bromide was used instead of methyl iodide in the reaction, the product $(CH_3)_3SiOC(CF_3)_2OC(CF_3)_2C_2H_5$, analogous to that given by methyl iodide, was tentatively identified as a minor product. However, the known compound $(CH_3)_3SiOC(CF_3)_2OCH(CF_3)_2$ was produced in larger amount, with ethylene also being detected in the volatile products. This result is entirely consistent with ionic processes of the type described above, and may be explained through hydride abstraction by hexafluoroacetone from an intermediate ethyl anion

$$C_2H_5Br + 2Na \longrightarrow [C_2H_5^-]Na^+ + NaBr$$

$$C_2H_5^- + (CF_3)_2CO \longrightarrow C_2H_5(CF_3)_2CO^- \text{ etc.}$$

or

$$C_2H_5^- + (CF_3)_2CO \longrightarrow HC(CF_3)_2O^- + C_2H_4$$

As a final argument supporting our suggestion of an ionic equilibrium system, we may note the difference in behavior between the hexafluoroisopropoxytrimethylsilane and the corresponding tin compound. Whereas our results show that the silicon compound does not undergo further reaction with hexafluoroacetone, the tin compound, as reported by Cullen and Styan, readily undergoes addition and the 2:1 adduct produced will react with trimethylstannane to regenerate the 1:1 adduct

$$(CH_3)_3SnOCH(CF_3)_2 + (CF_3)_2CO \longrightarrow (CH_3)_3SnOC(CF_3)_2OCH(CF_3)_2$$

$$(CH_3)_3SnOC(CF_3)_2OCH(CF_3)_2 + (CH_3)_3SnH \longrightarrow 2(CH_3)_3SnOCH(CF_3)_2$$

This difference in behavior between the two elements is readily explained by the known difference between the trimethyltin and triethylsilyl groups. The former much more readily forms a cation, as a result not only of the difference in electronegativity between tin and silicon, but also of the stronger π bonding to oxygen shown by the latter, strengthening the covalent structure. The formation of the trimethyltin hexafluoroisopropoxide from its ions is therefore reversible; that of the hexafluoroisopropoxytrimethylsilane is not. The observation by Cullen and Styan that trimethyltin chloride does not react with hexafluoroacetone, despite its ready ionization, may be readily explained on the nucleophilicity argument advanced previously. With the chloride ion in solution in hexafluoroacetone, the equilibrium

$$Cl^- + (CF_3)_2CO \rightleftharpoons Cl(CF_3)_2CO^-$$

will be displaced to the left by the relatively low nucleophilicity of the chloride ion.

We have referred above to the difference in stability in the 2:1 adducts of hexafluoroacetone with trimethylsilane as reported by us and by Cullen and Styan. An obvious conclusion would be that these are differently constituted compounds, but a consideration of their ^1H nmr spectra shows that they are in fact identical. Each compound contains two types of proton, the chemical shifts being those shown in Table I.

The constant difference, Δ_1, between the chemical shifts observed by Cullen and Styan and ourselves is due to the choice of reference used. Whereas their standard was external TMS, ours was internal TMS. It will be noted that this difference found in the 1:1

TABLE I

	Ppm		
	This work	Cullen and Styan	Δ_1
(a) 1:1 Adduct, $(CH_3)_3SiOCH(CF_3)_2$			
$CH(CF_3)_2$	-4.24	-3.90	-0.34
$(CH_3)_3Si$	-0.21	$+0.16$	-0.37
Δ_2	-4.03	-4.06	
(b) 2:1 Adduct, $(CH_3)_3SiOC(CF_3)_2OCH(CF_3)_2$			
$CH(CF_3)_2$	-4.77	-4.45	-0.32
$(CH_3)_3Si$	-0.30	$+0.08$	-0.38
Δ_2	-4.47	-4.53	

adduct (where there is no dispute on the identity of the compound) is, within experimental error, the same as that found for the 2:1 adduct. On the difference in chemical shift between the two types of proton in the same compound, Δ_2, the agreement between the measurements on both compounds is very good. We are forced to conclude, therefore, that the 2:1 adducts reported by ourselves and Cullen and Styan are in fact the same compound, and we suggest that the claim of the latter workers that their adduct dissociated at 20° is in error.

We must also take issue with the claim of Cullen and Styan that the nmr spectrum of the 2:1 adduct may be seen when the 1:1 adduct is dissolved in excess hexafluoroacetone. We have carefully reexamined the relevant spectra and find no evidence to support this. As an explanation of the observations of Cullen and Styan, we suggest that their sample of hexafluoroisopropoxytrimethylsilane contained unreacted trimethylsilane, which, by reaction with the hexafluoroacetone added in their nmr studies, would have produced detectable quantities of the 2:1 adduct.

In conclusion, therefore, we suggest that the liquid-phase reaction of hexafluoroacetone with trimethylsilane and similar compounds of group IV elements proceeds by an ionic mechanism in which hydride ion abstraction is the first step and the products are exclusively simple four-covalent derivatives incorporating one or two hexafluoroacetone residues. We do not find it necessary to postulate the existence of any product involving higher coordination and we suggest that it is misleading to represent any reactions of this type as examples of the ability of fluorinated ketones to form complexes.

Acknowledgments.—This work was supported in part by the Defense Research Board of Canada through Grant 7583-05. The authors also gratefully acknowledge the award of an Ontario Graduate Fellowship (to A. F. J.).

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Synthesis of Amino Derivatives of Sulfur Tetrafluoride and Phosphorus Pentafluoride by Silicon–Nitrogen Bond Cleavage Reactions[1]

BY GREGORY C. DEMITRAS, F.S.C., AND ALAN G. MACDIARMID

Received October 25, 1966

The compounds N-dimethylaminosulfur trifluoride, $(CH_3)_2NSF_3$, N-dimethylaminotetrafluorophosphorane, $(CH_3)_2NPF_4$, and 1,3,2,4-diazadiphosphetidine, $(CH_3NPF_3)_2$, have been synthesized by the reaction of N-methyl-N-trimethylsilylamines with SF_4 or PF_5, respectively. The structures of these compounds were studied by means of their infrared, mass, and nuclear magnetic resonance spectra.

Although it has been known for several years that the silicon–nitrogen bond may be cleaved by a variety of covalent or semicovalent halides,[2] little attention has been given to exploiting such reactions for the specific purpose of preparing volatile derivatives of the nonmetal fluorides. The synthesis of methylamino derivatives of PF_5 and SF_4 by the reaction of these parent fluorides with appropriate silicon amines was therefore attempted and the present communication describes in greater detail the previously reported[3] preliminary results of this investigation.

It has been found that PF_5 rapidly cleaves the Si–N bond in $(CH_3)_2NSi(CH_3)_3$ at, or below, room temperature to give high yields of $(CH_3)_2NPF_4$, *viz.*

$$PF_5 + (CH_3)_2NSi(CH_3)_3 \longrightarrow (CH_3)_2NPF_4 + (CH_3)_3SiF \tag{1}$$

The reaction proceeds *via* the adduct, $(CH_3)_2NSi(CH_3)_3 \cdot PF_5$, which is stable at $-78°$ and which decomposes to give the products on warming to room temperature. The compound $(C_2H_5)_2NPF_4$ has also been prepared by a similar method[4] and $(CH_3)_2NPF_4$

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[1] This report is based on portions of a thesis submitted by Gregory C. Demitras, F.S.C., to the Graduate School of the University of Pennsylvania in partial fulfillment of the requirements for the degree of Doctor of Philosophy. It was supported in part by the Advanced Research Projects Agency, Office of the Secretary of Defense.

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