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INTERACTION OF HEXAFLUOROACETONE AND HEXAFLUOROISOPROPYLIDENIMINE WITH SOME ORGANOSILICON- AND ORGANOTIN- AMINES, AZIDES AND PHOSPHINIMINES

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SUMMARY

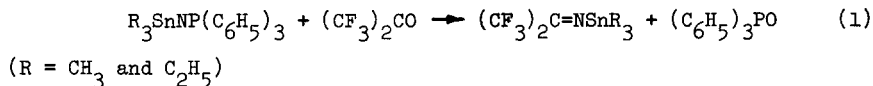
Metathetical and insertion reactions of perhalogenoketones and hexafluoroisopropylideneimine with organosilicon and organotin phosphinimines, dimethylaminotrimethyltin and trimethylsilyl azide are reported. Activation energies for nitrogen inversion in some of the organometallic ketimines produced have been determined.

INTRODUCTION

Perhalogeno ketones and imines have been shown to be versatile insertion reagents for both main group [1,2,3] and transition metal [4,5] compounds. We report some reactions of hexafluoroacetone and the analogous imine with organosilicon and organotin amines, azides and phosphinimines.

RESULTS AND DISCUSSION

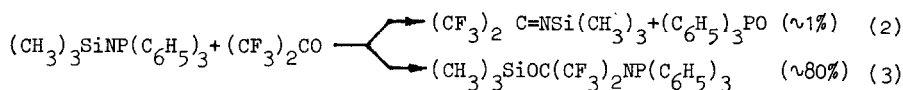
Both N-trimethyl- and N-triethyl-stannyltriphenylphosphinimine undergo reaction with hexafluoroacetone to eliminate triphenylphosphine oxide in a Wittig type of reaction.



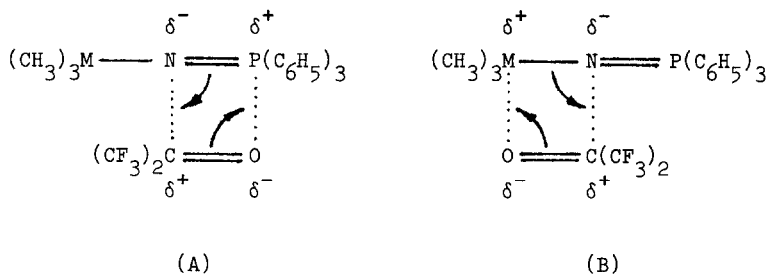
Yields of the hexafluoroisopropylideniminotrialkyltins were very good, and had the <sup>1</sup>H, <sup>19</sup>F n.m.r. and infrared spectra identical to those previously reported [6].

Extensions of reaction 1 with fluorochloroacetones gave analogous ketimines (Table 1), but it was found that with increasing chlorine content of the ketone, the product became slightly contaminated with trialkyltin chlorides; and the reaction with hexachloroacetone yielded only trialkyltin chlorides, no ketimine being isolated.

In contrast to reaction 1, the analogous reaction with the corresponding organosilicon phosphinimine produced only about 1% of the expected ketimine, (equation 2), the bulk of the reaction proceeding to produce a siloxane by the ketone insertion reaction (equation 3).



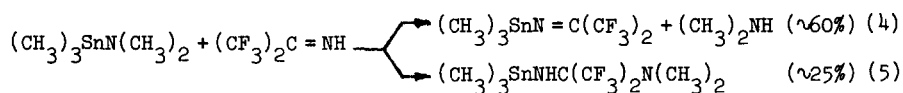
If the initial reaction involves attack of the ketone carbon atom by nitrogen, then two four-centre intermediates (A+B), for reactions 1-3 differ only in the subsequent orientation of the carbonyl bond.



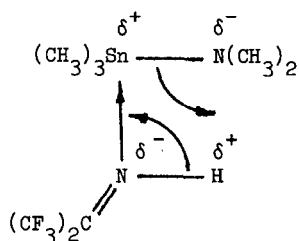
(M = Si and Sn)

In the silicon reaction (3) the formation of the very strong silicon-oxygen bond appears to favour the bulk of the reaction proceeding via intermediate step (B), with the formation of the P=O bond competing only to a very small extent. In the tin reaction, however, the formation of the phosphine oxide appears to be exclusively favoured (pathway A) and no insertion product involving stannoxane formation was detected.

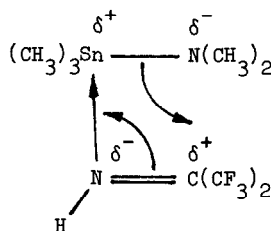
The interaction of dimethylaminotrimethyltin and hexafluoroisopropylideneimine further illustrates the dichotomy of some of these reactions as shown in equations 4 and 5.



The initial step is presumably the co-ordination of imino nitrogen to the tin atom, whereby both intermediates illustrated by (C) and (D) become possible.



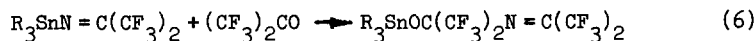
(C)



(D)

The two products of metathesis (via C) and insertion (via D) were separable by distillation and characterized.

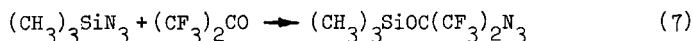
The hexafluoroisopropylideneiminotrialkyltins synthesised as in reaction (1) above from hexafluoroacetone, were themselves capable of taking up another molecule of the ketone by an insertion reaction according to equation (6).



(R = CH<sub>3</sub> and C<sub>2</sub>H<sub>5</sub>).

It is likely that this reaction proceeds initially by the organotin ketimine attacking the carbonyl carbon of the ketone. It is notable that the exactly analogous reaction with the organosilicon ketimine gave a recovery of the starting materials. Here it is likely that the nitrogen atom of the hexafluoroisopropylideneiminotrimethylsilane was insufficiently basic for the first step in the reaction, and therefore ketone insertion into the Si-N bond could not take place.

In the case of trimethylsilyl azide, however, insertion took place to give a virtually quantitative yield of the siloxane as in equation (7). The product is the trimethylsilyl derivative of the otherwise unknown alcohol azido hexafluoroisopropanol.



The compounds formed from metatheses and insertion reactions above were characterized by  $^1\text{H}$ ,  $^{19}\text{F}$  n.m.r. spectra, mass spectra and infrared spectra. A selection of more important data is given in Table 1.

Of particular interest was the  $^{19}\text{F}$  n.m.r. spectrum of certain of the products. Although organic fluorimines  $(\text{CF}_3)_2\text{C}=\text{NR}$  have shown [7] two  $^{19}\text{F}$  signals due to non equivalent  $\text{CF}_3$  groups, in the case of  $\text{R}_2\text{C}=\text{NGe}(\text{CH}_3)_3$  it was found [8] that rapid inversion about nitrogen, presumably aided by N-Ge  $p_\pi-d_\pi$  bonding, was only slowed down at temperatures below  $-110^\circ\text{C}$ . We, like others [6], find only one  $^{19}\text{F}$  signal in  $(\text{CF}_3)_2\text{C}=\text{NMR}_3$  compounds (M=Si and Sn) even below  $100^\circ\text{C}$ , and we presume that the effects of metalloid nitrogen interaction and the trifluoromethyl groups combine to produce a very low nitrogen inversion barrier in this class of compound.

Table 1. Physical Data of Products of Metatheses and Insertion Reactions

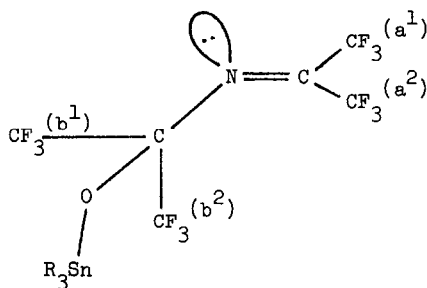
Compound	$\nu(\text{C}=\text{N})$ $\text{cm}^{-1}$ (a)	$\nu(\text{M}-\text{N})$ $\text{cm}^{-1}$ (a)	$^1\text{H}$ n.m.r. ( $\delta$ ) (f) (Integration)	$^{19}\text{F}$ n.m.r. (p.p.m. $\text{CFCl}_3$ ) (Integration)
$(\text{CH}_3)_3\text{SiN}=\text{C}(\text{CF}_3)_2$	1768	954	0.40 s. (g)	80.1 s.
$(\text{CH}_3)_3\text{SnN}=\text{C}(\text{CF}_3)_2$	1722	947	0.50 s.	76.2 s.
$(\text{C}_2\text{H}_5)_3\text{SnN}=\text{C}(\text{CF}_3)_2$	1721	945	1.25 m.	79.8 s.
$(\text{C}_6\text{H}_5)_3\text{SnN}=\text{C}(\text{CF}_3)_2$	1720 (b)	945 (b)	7.30 m.	78.6 s.
$(\text{C}_2\text{H}_5)_3\text{SnN}=\text{C}(\text{CF}_3)(\text{CF}_2\text{Cl})$	1720	958	1.30 m.	70.9 q.(2); 78.8 t.(3)
$(\text{C}_2\text{H}_5)_3\text{SnN}=\text{C}(\text{CF}_2\text{Cl})_2$	1717	959	1.32 m.	71.1
$(\text{C}_2\text{H}_5)_3\text{SnN}=\text{C}(\text{CF}_2\text{Cl})(\text{CFCl}_2)$	1709	955	1.26 m.	68.8 d.(2); 76.9 t.(1)
$(\text{CH}_3)_3\text{SnNHC}(\text{CF}_3)_2\text{N}(\text{CH}_3)_2$	3996 (c)	946	2.54 sp.(6); 0.28 s.(9) (g)	75.9 m.
$(\text{CH}_3)_3\text{SiOC}(\text{CF}_3)_2\text{N}=\text{P}(\text{C}_6\text{H}_5)_3$	1255 (b)(d)	948 (b)(e)	7.45 m.(15); 0.04 s.(9) (g)	83.4 s.
$(\text{CH}_3)_3\text{SnOC}(\text{CF}_3)_2\text{N}=\text{C}(\text{CF}_3)_2$	1717	978 (e)	0.26 s. (g)	63.3 s.(3); 75.4 s.(3); 83.5 s.(6)
$(\text{C}_2\text{H}_5)_3\text{SnOC}(\text{CF}_3)_2\text{N}=\text{CF}_3$	1709	976 (e)	1.30 m. (g)	66.9 s.(3); 78.0 s.(3); 86.5 s.(6)

(a) Thin film	(b) $\text{CCl}_4$ solution	(c) $\nu(\text{N}-\text{H})$	(d) $\nu(\text{P}=\text{N})$
(e) $\nu(\text{M}-\text{O})$	(f) T.M.S. reference	(g) Cyclohexane reference	

In contrast, the barrier to nitrogen inversion in  $R_3SnOC(CF_3)_2N=C(CF_3)_2$  is quite high. These compounds show three sharp  $^{19}F$  resonances at room temperature, which collapse to two resonances at  $\sim 100^\circ C$ . This is illustrated in Figure 1.

The four  $CF_3$  groups are labelled in (E), and assuming free rotation about the C-N single bond  $CF_3^{(b^1)}$  and  $CF_3^{(b^2)}$  are always magnetically equivalent. Due to the presence of the bent C-N=C bonding at nitrogen, however,  $CF_3^{(a^1)}$  and  $CF_3^{(a^2)}$  are non-equivalent.



(E)

The coalescence of  $CF_3^{(a^1)}$  and  $CF_3^{(a^2)}$  was studied over a range of temperatures for  $(CH_3)_3SnOC(CF_3)_2N=C(CF_3)_2$  and  $(C_2H_5)_3SnOC(CF_3)_2N=C(CF_3)_2$ , and calculations based upon the Eyring equation gave  $\Delta G_{350}^\ddagger$  for nitrogen inversion in these two compounds as  $94.1 \pm kJ mol^{-1}$  and  $102.5 \pm 2.1 kJ mol^{-1}$  respectively.

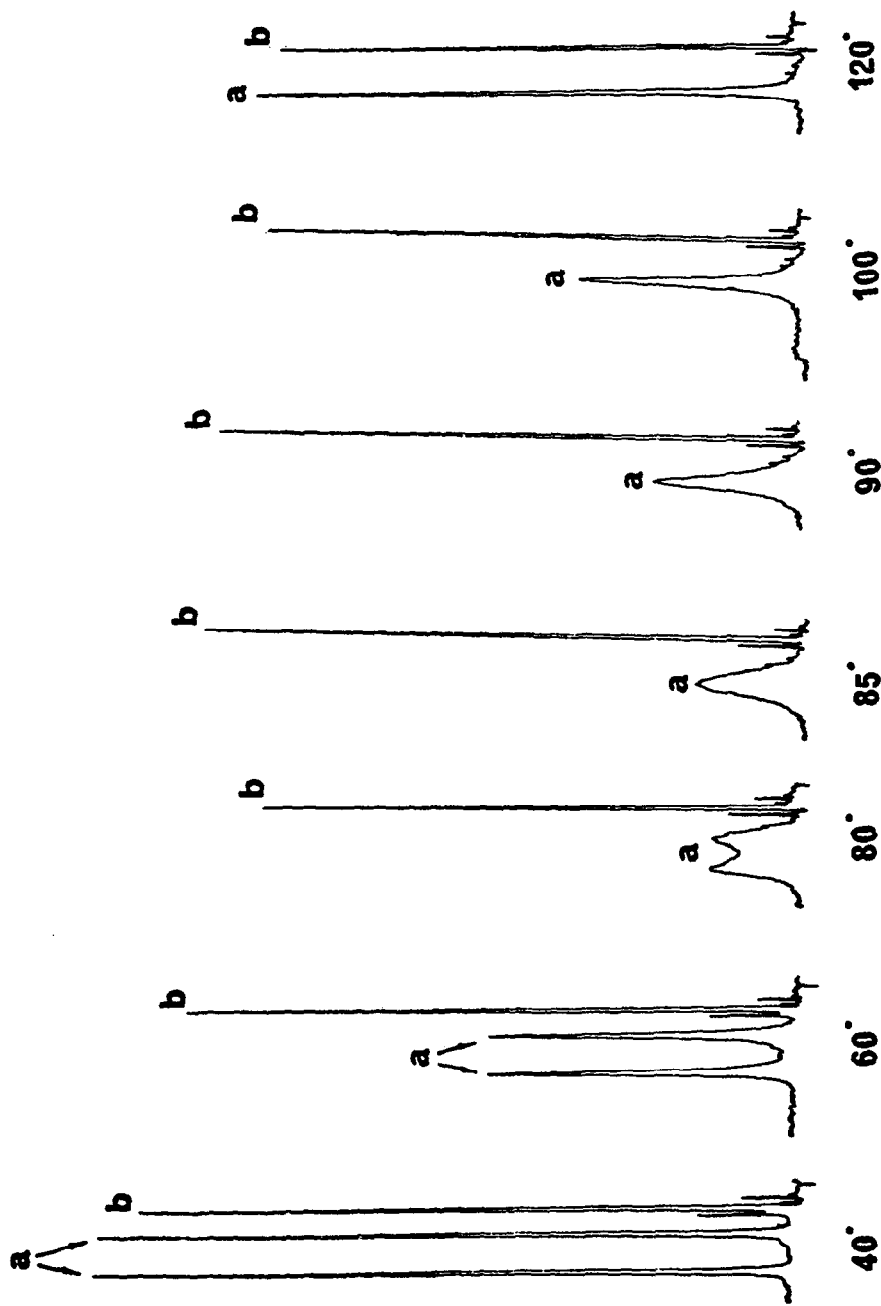


Figure 1. The Variable Temperature  $^{19}\text{F}$  nmr Spectrum of  $(\text{C}_2\text{H}_5)_3\text{SnOC}(\text{CF}_3)_2\text{N}=\text{C}(\text{CF}_3)_2$ .

## EXPERIMENTAL

The usual precautions were taken for the handling of moisture sensitive compounds.  $^{19}\text{F}$  spectra were recorded at 94.1 MHz on a Varian HA100 spectrometer and mass spectra were obtained on the AEI MS9 instrument.

Interaction of hexafluoroacetone with N-triethylstannyltriphenylphosphinimine

The ketone (10.4 g., 63 mmol), the phosphinimine (30.1 g., 62 mmol) and benzene (40 ml) were sealed in a Carius tube and placed in an oven at 60 °C for 30 h. Removal of the benzene by distillation at atmospheric pressure, and subsequent distillation of the residue under reduced pressure gave hexafluoroisopropylideniminotriethyltin (14.6 g., 65%) as a yellow liquid, b.p. 66-67 °C/8 mm. Analysis: Found: C, 29.4; H, 4.24; F, 30.5; N, 3.98; Sn, 32.8%.  $\text{C}_9\text{H}_{15}\text{F}_6\text{NSn}$  requires C, 29.3; H, 4.10; F, 30.8; N, 3.79; Sn, 32.1%, and a final residue of triphenylphosphine oxide (m.p. 160 °C after recrystallization from ethanol).

In an exactly analogous reaction with the corresponding trimethyltin compound, there was produced hexafluoroisopropylideniminotrimethyltin in 80% yield, b.p. 50-52 °C/10 mm. Analysis: Found: C, 21.6; H, 2.83; N, 4.18%.  $\text{C}_6\text{H}_9\text{F}_6\text{NSn}$  requires C, 21.9; H, 2.74; N, 4.26%.

Interaction of hexafluoroacetone with N-trimethylsilyltriphenylphosphinimine

The ketone (5.1 g., 31 mmol), the phosphinimine (10.6 g., 30 mmol) and diethylether (20 ml.) were sealed in a Carius tube and placed in an oven at 60 °C for 48 h. On cooling to 25 °C triphenylphosphine oxide m.p. 161-161.5 °C crystallized from the solution and was removed by filtration. Removal of volatile materials (25 °C/0.01 mm) and condensation at -196 °C, gave a pale yellow solution, which on removal of the ether (25 °C/15 mm) gave a yellow liquid residue of hexafluoroisopropylideniminotrimethylsilane ( $^1\text{H}$ ,  $^{19}\text{F}$  and infrared spectrum identical to literature report [6]).



Recrystallization of the residue from hexane gave

N-(trimethylsiloxyhexafluoroisopropyl)triphenylphosphinimine (12.1 g., 78%) as a pale yellow solid m.p. 89-90 °C. Analysis: Found: C, 56.7; H, 4.83; F, 21.0; N, 2.71; P, 6.26%.  $C_{24}H_{24}F_6NOPSi$  requires C, 55.8; H, 4.65; F, 22.1; N, 2.71; P, 6.21%.

Interaction of hexafluoroisopropylideneimine and dimethylaminotrimethyltin

The isopropylideneimine (11.8 g., 71 mmol) was condensed into a flask containing the aminotin (14.1 g., 68 mmol) and diethylether (50 ml) at -78 °C. The mixture was allowed to warm slowly to 0 °C, and the contents stirred for 5 h. at this temperature and then for 2 h. at 25 °C.

Removal of the ether (25 °C/15 mm) and subsequent careful fractional distillation of the residue yielded hexafluoroisopropylideneimino-trimethyltin (13.5 g., 61%), b.p. 56-58 °C/40 mm. (identical in  $^1H$ ,  $^{19}F$  n.m.r. and infrared spectrum to sample prepared and characterized above) and (dimethylaminohexafluoropropyl)aminotrimethyltin (6.0 g., 24%), b.p. 96-97 °C/40 mm. Analysis: Found: C, 26.7; H, 4.12; N, 7.61%.  $C_8H_{16}F_6N_2Sn$  requires C, 25.6; H, 4.28; N, 7.49%.

Interaction of hexafluoroacetone and hexafluoroisopropylideneiminotrimethyltin

The ketone (0.70 g., 4.2 mmol), the organotin (1.32 g., 4 mmol) and benzene (5 ml) were sealed in a Carius tube and placed in an oven at 60 ° for 24 h. Removal of solvent (25 °C/15 mm) and distillation of the residue gave N-(trimethylstannoxyhexafluoroisopropyl)hexafluoroisopropylideneimine (1.2 g., 63%) as a colourless liquid b.p. 58-60 °C/3.0 mm. Analysis: Found: C, 22.1; H, 1.71; N, 3.11%.  $C_9H_9F_6NOSn$  requires C, 21.8; H, 1.82; N, 2.83%.

In an exactly analogous experiment there was produced N-(triethylstannoxyhexafluoroisopropyl)hexafluoroisopropylideneimine

(59%) as a colourless liquid b.p. 67-68 °C/3 mm. Analysis: Found: C, 26.9; H, 2.66; N, 3.21%.  $C_{12}H_{15}F_6NOSn$  requires C, 26.8; H, 2.79; N, 2.65%).

Interaction of hexafluoroacetone and hexafluoroisopropylidenimino-trimethylsilane

The ketone (0.9 g., 5.42 mmol) and the silane (1.27 g., 5.36 mmol) were sealed in a Carius tube which was placed in an oven at 80 °C for 5 days. Distillation of the reaction mixture after this time yielded unchanged hexafluoroisopropylideniminotrimethylsilane (1.1 g., 86% recovery) b.p. 84-85 °C, characterised by  $^1H$ ,  $^{19}F$  n.m.r. spectra and infrared spectroscopy.

Interaction of hexafluoroacetone and trimethylsilyl azide

The ketone (5.0 g., 3.0 mmol) and the azide (3.3 g., 2.9 mmol) were sealed in a Carius tube and left at 25 °C for 5 days. Distillation yielded azidohexafluoroisopropoxytrimethylsilane (6.8 g., 82%) b.p. 116-118 °C. Analysis: Found: C, 25.6; H, 3.30; F, 41.1; N, 15.8%.  $C_6H_9F_6N_3OSi$  requires C, 25.6; H, 3.21; F, 40.6; N, 14.9%.

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