

Nucleophilic cleavage of the Si–C bond in organotrifluorosilanes and diorganodifluorosilanes *

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Abstract

The Si–C bond in aryltrifluorosilanes, $4\text{-XC}_6\text{H}_4\text{SiF}_3$ ($X = \text{H}, \text{CH}_3, \text{Cl}, \text{Br}$ or NO_2), is readily cleaved by mercury(II) salts HgY_2 ($Y = \text{Cl}, \text{Br}, \text{I}, \text{CN}$ or OCOCH_3) or HgO to form organomercurials of the type $4\text{-XC}_6\text{H}_4\text{HgY}$ or $(4\text{-XC}_6\text{H}_4)_2\text{Hg}$, respectively. Electron-donating substituents X facilitate the reaction, whereas electron-withdrawing substituents make it more difficult. Mercury(II) salts and mercury(II) oxide also cleave the Si–C bond in chloromethyltrifluorosilanes, $\text{F}_3\text{Si}(\text{CH}_3\text{-}_n\text{Cl}_n)$ ($n = 1\text{--}3$) to produce the corresponding organic mercurials containing an $\text{Hg}(\text{CH}_3\text{-}_n\text{Cl}_n)$ group. The substitution of the fluorine atom in organotrifluorosilanes by an alkyl group hinders the bond cleavage between the silicon atom and the electronegative organic substituent. The reactions studied are believed to follow a nucleophilic mechanism involving asynchronous formation of a four-centered transition state with a pentacoordinate silicon atom.

Introduction

Investigations of the reaction of mercury salts with organosilicon compounds began long ago: as early as 1871, Ladenburg revealed that Et_3SiCl failed to react with mercury cyanide at even 270°C [1]. Kipping first showed the possibility of cleavage of the Si– C_6H_5 bond by mercury salts [2]; the reaction of dichlorodiphenylsilane with mercury(II) oxide, besides yielding oligocyclodiphenylsilanes, SiO_2 and HgCl_2 , gave phenylmercury chloride. He also found that heating hexaphenylcyclotrisiloxane with mercury(II) oxide at 200°C leads to diphenylmercury [2].

In the second half of this century, Eaborn described cleavage reactions of the Si– C_{Ar} bond in aryltrimethylsilanes in protic solvents [3,4]. The electrophilic mecha-

* Dedicated to Professor Colin Eaborn in recognition of his important contributions to organometallic chemistry on the occasion of his 65th birthday.

nism of these reactions is beyond any doubt, since the trimethylsilyl group exerts a considerable +I effect ($\sigma_f = -0.24$) on the aromatic ring.

Results and discussion

We have studied the effect of the nature of organic substituents at the silicon atom in organotrifluoro- and diorganodifluoro-silanes on cleavage of the Si-C bond by mercury(II) salts. We have found that the reaction of organotrifluorosilanes, RSiF_3 with mercury(II) salts in aprotic solvents (benzene or tetrahydrofuran (THF)) does not occur when the substituents are of an electron-donating character: the starting materials remain unchanged. This seems to be due to a decrease in the positive charge on the silicon atom, i.e. its electrophilicity.

Cleavage of the Si-C bond by mercury(II) salts in organotrifluorosilanes is observed only in the cases where R behaves as an electronegative group. Thus, the reaction of trifluorophenylsilane ($\sigma^*(\text{C}_6\text{H}_5) = 0.60$) with mercury(II) salts or mercury(II) oxide proceeds nearly quantitatively according to eq. 1 and 2. The reaction conditions and reagents are listed in Table 1.



The above reactions follow a nucleophilic mechanism, since the powerful electron-withdrawing effect of three fluorine atoms provides for a high effective positive charge on the silicon atom, and the SiF_3 group displays a significant electron-acceptor effect on the aromatic ring ($\sigma_f = 0.43$, $\sigma_R^o = 0.23$) [6].

When the aromatic ring is separated from the silicon atom by a methylenic or oxomethylenic group, in $\text{C}_6\text{H}_5\text{CH}_2\text{SiF}_3$ or $\text{C}_6\text{H}_5\text{OCH}_2\text{SiF}_3$, no cleavage of the Si-C bond by mercury(II) salts takes place.

In the reaction of mercury(II) ethanoate with 4-substituted phenyltrifluorosilanes, $4\text{-XC}_6\text{H}_4\text{SiF}_3$, in benzene at 80°C , the rate of cleavage of the Si-C bond (monitored by liberation of gaseous $\text{SiF}_3(\text{O}_2\text{CMe})$) decreases with increasing the σ_p constant of the substituent X (Table 2). This is due to the fact that the electron-

Table 1
Reactions of trifluorophenylsilane with a variety of mercury(II) reagents

Reagent	Reaction conditions			Reaction product	Yield (%)	M.p. ($^\circ\text{C}$) ^a
	Solvent	Temperature ($^\circ\text{C}$)	Time (h)			
$\text{Hg}(\text{OCOCH}_3)_2$	C_6H_6	25	2	PhHgOCOCH_3	99	150(149) ^a
PhHgOCOCH_3	C_6H_6	60	3	Ph_2Hg	83	125(125)
HgCl_2	THF	65	0.5	PhHgCl	98	251(251)
HgBr_2	THF	65	1	PhHgBr	94	275(275)
HgI_2	THF	65	1	PhHgI	60	270(270)
$\text{Hg}(\text{CN})_2$	C_6H_6	25	2	PhHgCN	97	205
HgO	C_6H_6	25	2	Ph_2Hg	99	126(125)

^a Figures in parentheses are taken from the literature data [5].

Table 2

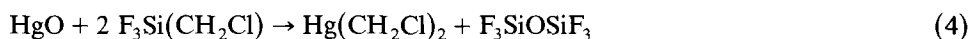
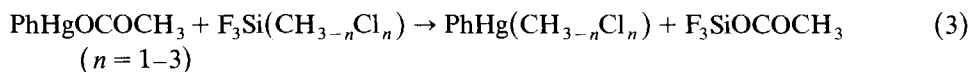
Reactions of 4-substituted phenyltrifluorosilanes, 4- $\text{XC}_6\text{H}_4\text{SiF}_3$, with mercury(II) ethanoate in benzene at 80 °C

X	σ_p	Reaction time (min)	Reaction product, $\text{RHg}(\text{O}_2\text{CMe})$	Yield (%)	M.p. (°C)
			R =		
CH_3	-0.170	5	4- $\text{CH}_3\text{C}_6\text{H}_4$	100	155
H	0	10-15	C_6H_5	100	150
Cl	+0.227	70	4- ClC_6H_4	82	122
Br	+0.232	90	4- BrC_6H_4	80	179-183
NO_2	+0.778	240	4- $\text{NO}_2\text{C}_6\text{H}_4$	65	176-177

donating substituents in position 4 of the aromatic ring enhance the electronic density on the carbon atom attached to silicon, i.e., enhance its nucleophilicity, whereas the electron-withdrawing substituents, on the contrary, decrease this value.

It should be noted that the reaction of substituted phenyltrifluorosilanes with mercury(II) salts allows the synthesis of previously unknown or difficultly accessible organomercury compounds, such as $\text{XC}_6\text{H}_4\text{HgY}$.

Mercury(II) salts react with organotrifluorosilanes, RSiF_3 with $\text{R} = \text{CH}_2\text{Cl}$, CHCl_2 or CCl_3 ($\sigma^* = 1.05$, 1.94 or 2.65, respectively) in benzene at room temperature to form the corresponding organomercury derivatives in yields up to 20%, according to eq. 3 and 4. At elevated temperatures, the product $\text{C}_6\text{H}_5\text{Hg}(\text{CH}_{3-n}\text{Cl}_n)$ decomposes



to give PhHgCl , whereas at lower temperatures this reaction does not occur (Table 3).

In contrast, (3-chloropropyl)trifluorosilane ($\sigma^*(\text{CH}_2)_3\text{Cl} = 0.13$) is not cleaved by mercury(II) salts.

The stability of diorganodifluorosilanes, $\text{RR}'\text{SiF}_2$ to the action of mercury(II) salts is determined by the combined electronic effect of substituents R and R'. The presence of an electron-donating substituent R' along with an electron-withdrawing substituent R sharply diminishes the positive charge at the silicon atom and,

Table 3

The reaction of RSiF_3 with mercury(II) compounds

R	Reagent	Reaction conditions			Product	Yield (%)	M.p. (°C)
		Solvent	T (°C)	Time (h)			
CH_2Cl	PhHgOCOCH_3	Me_3COH	100	1	PhHgCl	86	258
CH_2Cl	PhHgOCOCH_3	C_6H_6	20	1	$\text{PhHg}(\text{CH}_2\text{Cl})$	15	43
CH_2Cl	HgO	$\text{C}_6\text{H}_6/\text{Me}_3\text{COH}^a$	30	3	$\text{Hg}(\text{CH}_2\text{Cl})_2$	18	85
CHCl_2	PhHgOCOCH_3	Me_3COH	50	0.3	$\text{PhHg}(\text{CHCl}_2)$	23	71-72
CCl_3	PhHgOCOCH_3	C_6H_6	20	1	$\text{PhHg}(\text{CCl}_3)$	20	115-116

^a Ratio 1/1.

Table 4

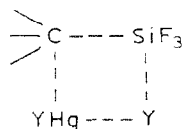
The reaction of diorganodifluorosilanes, $RR'SiF_2$ with mercury(II) ethanoate and mercury(II) oxide

R	R'	Reagent	Reaction conditions			Product	Yield (%)	M.p. (°C)
			Solvent	T (°C)	Time (h)			
Ph	Et	Hg(OCOCH ₃) ₂	CH ₂ Cl ₂	20	10	PhHgOCOCH ₃	10	149
Ph	Et	Hg(OCOCH ₃) ₂	C ₆ H ₆	80	10	PhHgOCOCH ₃	15	149
Ph	Et	HgO	CH ₂ Cl ₂	20	10	HgPh ₂	9	125
Ph	Me	Hg(OCOCH ₃) ₂	C ₆ H ₆	80	10	PhHgOCOCH ₃	20	149
CH ₂ Cl	Me	HgO	C ₆ H ₆ /Me ₃ COH ^a	80	3	Hg(CH ₂ Cl) ₂	28	85
CH ₂ Cl	Me	PhHgOCOCH ₃	C ₆ H ₆	80	3	PhHgCH ₂ Cl	31	43

^a Ratio 1/1.

consequently, the ability of the Si–C bond to undergo cleavage by mercury(II) salts. It should be noted that only the electron-withdrawing substituent R is lost (Table 4).

The Si–C bond cleavage in organotrifluorosilanes and diorganodifluorosilanes seems to proceed by a nucleophilic mechanism. The first reaction step would be nucleophilic attack at the silicon atom by the mercury salt anion, which would lead to a pentacoordinate silicon atom. Transmission of the electronic density from pentacoordinate silicon onto the aromatic ring or another electron-withdrawing substituent would result in a strong polarization of the Si–C bond (cf. data from ref. 7 and 8). An increase of the positive charge at the silicon atom would favour the electrophilic attack by the mercury unit at the nucleophilic carbon atom of the Si–C bond, thus forming a cyclic four-centered transition state:



Experimental

Aryltrifluorosilanes and diorganodifluorosilanes were obtained by reaction of the corresponding chloro or alkoxy derivatives with 40% HF [9]; compounds of the series $Cl_3Si(CH_{3-n}Cl_n)$ are converted to the corresponding $F_3Si(CH_{3-n}Cl_n)$ by reaction with SbF_3 in 1,4-dimethylbenzene at -10 to $0^\circ C$ [10].

Reaction of trifluorophenylsilane with mercury(II) ethanoate. To a suspension of mercury(II) ethanoate (3.18 g, 0.01 mol) in dry benzene (30 ml), trifluorophenylsilane (1.62 g, 0.01 mol) was added. After heating under reflux for 10–15 min. all the mercury(II) ethanoate has dissolved. On cooling, crystalline $PhHgO_2CMe$ (3.34 g, 100%; m.p. 149 – $150^\circ C$) was obtained.

Reaction of trifluoro-4-nitrophenylsilane with mercury(II) ethanoate. A suspension of mercury(II) ethanoate (1.59 g, 0.005 mol) trifluoro-4-nitrophenylsilane (1.04 g, 0.005 mol) in dry benzene (50 ml) was heated for 4 h. The reaction course was monitored by the volume of F_3CSiO_2CMe evolved. After cooling, 4- $NO_2C_6H_4HgO_2CMe$ (1.33 g, 70%; m.p. $177^\circ C$) was collected by filtration.

The reactions of mercury(II) ethanoate with other 4-substituted phenylfluorosilanes were carried out in an analogous manner (see Table 2).

Reaction of PhHgO₂CMe with (trichloromethyl)trifluorosilane. To a solution of PhHgO₂CMe (1.68 g, 0.005 mol) in dry benzene (40 ml), (trichloromethyl)trifluorosilane (1.8 g, 0.009 mol) was added. A vigorous reaction with gas liberation and the formation of a white precipitate took place. (Trichloromethyl)phenylmercury (0.18 g, 20%); m.p. 115–116° C) was isolated by filtration.

(Dichloromethyl)phenylmercury and (chloromethyl)phenylmercury were obtained in a similar manner.

Reaction of ethyldifluorophenylsilane with mercury(II) ethanoate. To mercury(II) ethanoate (6.37 g, 0.02 mol) in dry benzene (40 ml), ethyldifluorophenylsilane (3.45 g, 0.02 mol) was added. The reaction mixture was heated under reflux for 10 h, and the unreacted mercury(II) ethanoate was removed by filtration of the hot solution. After cooling the filtrate, crystalline PhHgO₂CMe (1.0 g, 15%; m.p. 149° C) precipitated.

The reactions of mercury(II) ethanoate and mercury(II) oxide with diorganodifluorosilanes were carried out in an analogous manner.

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