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USE OF SbF_5 INTERCALATED IN GRAPHITE AS FLUORINATING REAGENT IN ORGANO-SILICON AND -GERMANIUM CHEMISTRY

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Summary

The use of SbF_5 intercalated in graphite as fluorinating reagent of organo-silicon and -germanium derivatives is described. While Si—O and Si—Cl bonds are readily cleaved, Si—H and Si—S bonds are only reactive in bifunctional silanes. Ge—X bonds (X = Br, Cl, OR, H) are unreactive. Allyl—silicon and allyl—germanium bonds are broken under mild conditions and in high yields, leading to the corresponding fluorosilane or fluorogermane. With bifunctional silanes, it is always possible to obtain the difluorinated derivatives.

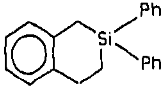
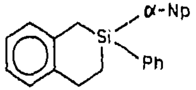
Introduction

Fluorinations of functional organosilanes $R_{4-n}SiX_n$ (X = H, OR, Cl, Br) with metal fluorides, hydrofluoric acid, boron trifluoride [1,2] or acyl fluorides [3] have been extensively used in syntheses. With BF_3 in Et_2O or pentane the reaction involves inversion of configuration. The formation of the Ge—F bond is not so well documented [5,6]. A few reports describe the fluorination of germanium—halide bonds (Cl, Br, I) with metal fluorides including PbF_2 [7], SbF_3 or HF [5,6]. Bis(triorganogermanium) oxides react with HF to give the corresponding organogermanium fluorides [6], and BF_3 reacts with bis(trimethylgermanium) oxide with quantitative formation of Me_3GeF [5].

Some intercalated derivatives in graphite (Br_2, $SbCl_5$) have been used for bromination or chlorination of organic substrates [8,9], and SbF_5 intercalated in graphite, which is easy to manipulate and to separate from the reaction mixture, is a mild reagent for exchange of halogens with organic chlorides [10]. In this paper, we describe a study of fluorination of various mono- or poly-functional organo-silicon and -germanium compounds with SbF_5 intercalated in graphite.

TABLE 1

REACTIONS WITH ORGANOSILANES OF SbF_5 INTERCALATED IN GRAPHITE

Run	Organosilane [a]	SbF_5/silane	Solvent [a]	Time/temp. (h/°C)	Product (%) [b]
1	Me_2PhSiH	0.22	Pentane	24/25	no reaction
2	Ph(α-Np)MeSiH	0.25	Pentane	50/25	no reaction
3	$Me_2PhSiOMe$	0.21	Pentane	20/25	Me_2PhSiF (81)
4	Ph(α-Np)MeSiOMe	0.30	Pentane (or Et_2O)	20/25	Ph(α-Np)MeSiF (79)
5	(p-MeO-C_6H_4)-α-NpViSiOme	0.50	Et_2O	1/25	(p-MeOPh)-α-NpMeSiF (75)
6	$Me_2PhSiCl$	0.25	Pentane	10/25	Me_2PhSiF (85)
7	Ph(α-Np)MeSiCl	0.23	Pentane (or Et_2O)	10/25	Ph(α-Np)MeSiF (80)
8	$Me_2PhSiSPh$	0.21	Pentane	100/55	no reaction
9	$Ph_3SiCH_2CH{=}CH_2$	0.50	Et_2O	10/25	Ph_3SiF (70)
10	Ph(α-Np)Me$SiCH_2CH{=}CH_2$	0.50	Et_2O	24/25	Ph(α-Np)MeSiF (80)
11	$Ph_2(OEt)SiCH_2CH{=}CH_2$	0.50	Et_2O	24/24	Ph_2SiF_2 (100)
12	Ph(α-Np)(OEt)$SiCH_2CH{=}CH_2$	0.50	Et_2O	24/25	Ph(α-Np)SiF_2 (100)
13		1	Pentane (or Et_2O)	96/25	no reaction
14		1	Et_2O	96/25	no reaction
15	Ph(α-Np)Si(H)Cl	0.39	Pentane	2/25	Ph-α-NpSi(H)F (52) Ph-α-NpSiF_2 (48)
16	Ph(α-Np)Si(H)OMe	0.47	Pentane	25/25	Ph-α-NpSi(H)F (50) Ph-α-NpSiF_2 (15) Ph-α-NpSi(F)OMe (35)
17	Ph(α-Np)Si(H)OMen	0.42	Pentane	24/25	Ph-α-NpSi(H)F (95) Ph-α-NpSiF_2 (5)
18	Ph(α-Np)Si(H)OEph	0.52	Pentane	72/25	Ph(α-Np)SiF_2 (100)
19	Ph(α-Np)$Si(OEt)_2$	0.30	Et_2O	0.5/25	Ph(α-Np)SiH(OPh) (38) Ph(α-Np)Si(H)F (45) Ph(α-Np)SiF_2 (17)
20	Ph(α-Np)$Si(OEt)_2$	0.30	Et_2O	17/25	α-NpPhSiF_2 (90)

[a] Ph = phenyl, α-Np = α-naphthyl, Vi = vinyl, OEph = ephedrinoxy, DME = dimethoxyethane. [b] In runs 3—7, and 20 the yields are calculated after distillation of the product. In runs 11, 12, 15—19 the yields are derived from GLC analysis of the reaction mixture. In runs 9 and 10 the yields are based on the crystalline product isolated.

II. Results and discussion

A. Fluorination of organosilanes

The experimental results are summarized in Table 1.

The features of the results are as follows: (i) SbF_5 intercalated in graphite (referred to subsequently as SbF_5/C) reacts with a large variety of organosilicon compounds. Reactions of $\equiv Si—Cl$ or $\equiv Si—OCH_3$ bonds give quantitative formation of the corresponding fluorosilanes (runs 3—7), which are recovered in high yields by distillation or crystallization. No reaction takes place in the case of $\equiv Si—H$ and $\equiv Si—SPh$ bonds (runs 1, 2 and 8).

(ii) Generally Si—C bonds do not react; for example alkyl (CH_3), aryl (Ph or α-Np), benzyl and vinyl groups are not cleaved from silicon. However, the silicon—allyl bond is easily cleaved under mild conditions to give high yields of the corresponding fluorosilanes (runs 9—12).

(iii) With bifunctional organosilanes, α-NpPhSi(H)X (runs 15—20), the fluorination reaction is not selective. Cleavage of the $\equiv Si—X$ bond (X = Cl, OR or SPh) first occurs, leading to α-NpPhSi(H)F, but when the reaction is continued until complete disappearance of the substrate, α-NpPhSiF$_2$ is always formed.

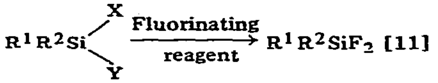
The easy elimination of SbF_5/C from the reaction mixture by filtration provides access to difluorosilanes of high purity. Using a slight excess of this reagent (Table 2) gives pure $(m\text{-}CF_3C_6H_4)_2SiF_2$, the only route we have found to a pure sample of this material.

We examined the stereochemistry of this new fluorination reaction with optically active α-NpPhMeSiX compounds (X = Cl, OMe), and the results are summarized in Table 3. They show that SbF_5/C is not of value for preparing optically active fluorosilanes, the stereoselectivities being around 60%. Better stereoselectivities have been reported for reactions with BF_3, Et_2O [4], ZnF_2 [13] or cyclohexylammonium fluoride [14].

B. Fluorination of organogermanes R_3GeX

SbF_5/C does not react with monofunctional organogermanes R_3GeX (X = H, OMe, Cl, or Br), and it does not cleave alkyl— or aryl—germanium bonds (alkyl = CH_3, aryl = phenyl or α-naphthyl). However, allyl—germanium bond

TABLE 2



$$R^1R^2Si(X)(Y) \xrightarrow[\text{reagent}]{\text{Fluorinating}} R^1R^2SiF_2\ [11]$$

Silane	Fluorinating reagent	Yield after distillation (%)	Purity
α-NpPhSi(OMe)$_2$	SbF_5/C	73	pure
$Ph_2Si(H)OMe$	SbF_5/C	75	pure
$PhCH_2(PhCH_2CH_2)Si(OMe)_2$	SbF_5/C	80	pure
PhMeSi(H)Cl	SbF_5/C	75	pure
	NH_4PF_6	no complete reaction	mixture
$(m\text{-}CF_3C_6H_4)_2Si(OMe)_2$	BF_3, Et_2O	65	a small amount of borates
	SbF_5/C	80	pure

TABLE 3

Ph(α-Np)MeSiX + SbF_5/C → Ph(α-Np)MeSiF

X	SbF_5/silane	Solvent	Time/temp. (h/°C)	$[\alpha]_D$	Stereochemistry [a]
Cl	0.28	Pentane	15/15	—10°	Inv. 61%
OCH_3	0.45	Pentane	15/25	+3°	Inv. 53%
OCH_3	0.5	Et_2O	3/25	+9.3°	Inv. 58%
$CH_2CH{=}CH_2$	0.31	Et_2O	24/25	0°	Rac.

[a] The absolute configuration and $[\alpha]_D$ of the starting materials and of the fluorosilane are known [4,12].

breaking occurs under mild conditions (24 h at 25°C in ether) and in high yields (80—85%), leading to the corresponding fluorogermane.

$$R_3GeCH_2CH{=}CH_2 \xrightarrow{SbF_5/C} R_3GeF$$

The fluorination reaction with the optically active α-naphthylphenylmethylallylgermane leads to racemic fluorogermane α-NpPhMeGeF.

III. Conclusion

SbF_5/C appears to be a mild fluorinating reagent in organosilicon chemistry, leading to fluorosilanes in high yields. Chloro-, bromo-, alkoxy- and also allyl—silicon bonds are easily cleaved; in the case of bifunctional organosilanes, the lack of selectivity limits the synthetic interest of SbF_5/C to the preparation of difluorosilanes of high purity with good yields.

Another interesting aspect of this study is the allyl—germanium bond cleavage; this offers a good synthetic route to fluorogermanes, compared to the more drastic methods using, for instance, aqueous hydrofluoric acid [5,6] which are normally used.

Experimental

Materials

Antimony(V) fluoride in graphite was obtained from Alfa Division. The organo-silanes and -germanes were prepared by published methods, viz. Me_2Ph-SiX (X = H, OMe, Cl, SPh) [15]; α-NpPhMeSiX (X = H, OMe, Cl, $CH_2CH{=}CH_2$) [16]; $Ph_3SiCH_2CH{=}CH_2$ [17]; $Ph_2(EtO)SiCH_2CH{=}CH_2$ [18]; α-NpPh(EtO)Si-$CH_2CH{=}CH_2$ [18]; 1,3,4-trihydro-2-silanaphthalene derivatives [19,20]; Ph-(α-Np)Si(H)X (X = Cl, OMe, SPh, OMen, OEph) [21,22]; Ph(α-Np)Si$(OEt)_2$ [21].

The preparations of the optically active products have also been described previously; α-NpPhMeSiX (X = Cl, OMe, alkyl) [16]; α-NpPhMeGe (CH_2-$CH{=}CH_2$) [23].

Reactions

General procedure. The reactions were carried out under nitrogen. A solution of the silicon or germanium compound in anhydrous ether or pentane was added to a suspension of SbF_5/C in the same solvent. The reaction was monitored by thin layer chromatography (benzene/chloroform, 50/50) and carried to completion. SbF_5/C was filtered off, and the solvent removed under vacuum. The silane or germane was purified either by crystallization from pentane or by distillation.

In a typical procedure 5.00 g (30 mmol) of $PhMe_2SiOMe$ in pentane (5 ml) were added dropwise to 2.95 g (6.39 mmol) of SbF_5/C in anhydrous pentane (10 ml). The mixture was stirred at room temperature for 20 h under N_2. SbF_5/C was filtered off, and the solvent removed under vacuum. The fluorosilane $PhMe_2SiF$ was purified by distillation (B.p. 162°C/760 mmHg, yield 81%).

Product analysis

The products were identified by their NMR and IR spectra and by elemental analysis: (a) Dimethylphenylfluorosilane [15]. B.p. 162°C/760 mmHg, NMR (δ, ppm); 7.2—7.6 (5H, m); 0.41 (6H, d).

(b) α-Naphthylphenylmethylfluorosilane [16]. B.p. 150°C/0.15 mmHg, NMR (δ, ppm); 7.3—7.7 (12H, m); 0.83 3H, d).

(c) α-Naphthyl-*p*-methoxyphenylvinylfluorosilane. NMR (δ, ppm); 6.6—8.2 (11H, m); 5.7—6.5 (3H, m); 3.65 (3H, s). (Anal. Found: C, 75.82; H, 3.51; F, 6.38. $SiC_{19}H_{10}FO$ calcd.: C, 75.74; H, 3.32; F, 6.31; O, 5.31; Si, 9.30%).

(d) Triphenylfluorosilane, diphenyldifluorosilane, α-naphthylphenylfluorosilane, α-naphthylphenyldifluorosilane and α-naphthylphenylfluoromethoxysilane were identified by comparison of their NMR and IR spectra with authentic samples prepared independently [22,24].

(e) α-Naphthylphenylmethylfluorogermane. NMR (δ, ppm); 7.1—8.2 (12H, m); 1.1 (3H, d). (Anal. Found: C, 65.19; H, 4.89; F, 6.06. $GeC_{17}H_{15}F$ calcd.: C, 65.68; H, 4.83; F, 6.12; Ge, 23.37%.)

(f) Triphenylfluorogermane was identified by comparison of its NMR and IR spectra with an authentic sample prepared independently [5] (Melting point: 72°C).

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