mmol) was added to **1** (0.70 g, 2.96 mmol) in 20 mL of CH_2Cl_2 with rapid stirring for 2 h. The solvent was then removed in vacuo, and the residues were chromatographed through a neutral alumina column using benzene as the eluting solvent. A red band was rapidly developed and collected. Removal of the solvent under reduced pressure gave a red oil, **8** (0.68 g, 1.71 mmol). Anal. Calcd for $C_{18}H_{18}FeO_6$: C, 56.05; H, 4.66. Found: C, 56.24; H, 4.73. IR (Nujol): ν(CO) 2030 (s), 1980 (s), 1770 (s) cm^{-1}, ν(C═C) 1605 cm^{-1} (s). ^1H NMR (400 MHz, C_6D_6): δ 3.40 (d, 2 H, H^1), 3.45 (s, 3 H, CH_3), 3.46 (s, 3 H, CH_3), 4.39 (s, 5 H, C_5H_5), 4.87 (dd, 1 H, H^6), 5.05 (dd, 1 H, H^5), 5.87 (m, 1 H, H^2), 6.19 (dd, 1 H, H^3), 6.28 (m, 1 H, H^4), J_{12} = 6.2 Hz, J_{23} = 13.3 Hz, J_{34} = 11.0 Hz, J_{45} = 15.6 Hz, J_{46} = 9.4 Hz, J_{56} = 1.2 Hz. $^{13}C\{H\}$ NMR (100 MHz, C_6D_6): δ 28.1 (CH_3), 30.2 (CH_3), 38.9 (CH^1), 86.8 (C_5H_5), 115.4 (CH^5H^6), 132.3, 133.0, 137.6 ($CH^2 + CH^3 + CH^4$), 139.3 (Fe*C*═), 153.4 (FeC═*C*), 170.0, 177.1 (–COOMe), 214.0 (CO).

(G) Synthesis of CpFe(CO)$_2$(–CF$_3$C═CCF$_3$CH$_2$CH═CHCH═CH$_2$) (9). Hexafluoro-2-butyne (0.44 g, 0.30 mmol) was condensed with **1** (0.56 g, 0.23 mmol) in 20 mL of CH_2Cl_2 at −195 °C. The solution was then warmed to 23 °C and left standing for 6 h. The solvent was then removed in vacuo, and the residues were chromatographed through a neutral alumina column using benzene as the eluting solvent. Removal of the solvent under reduced pressure gave a red oil, **9** (0.29 g, 7.2×10^{-2} mmol). Anal. Calcd for $C_{16}H_{12}FeF_6O_2$: C, 47.27; H, 2.96. Found: C, 47.54; H, 3.04. IR (Nujol): ν(CO) 2040 (s), 2000 (s), ν(C═C) 1600 (m) cm^{-1}. ^1H NMR (400 MHz, C_6D_6): δ 2.91 (m, 2 H, H^1), 4.2 (s, 5 H, C_5H_5), 4.90 (d, 1 H, H^6), 5.01 (d, 1 H, H^5), 5.58 (dt, 1 H, H^2), 6.06 (dd, 1 H, H^3), 6.14 (dt, 1 H, H^4), J_{12} = 7.2 Hz, J_{1-F} = 5.4 Hz, J_{23} = 15.0 Hz, J_{34} = 10.8 Hz, J_{46} = 10.8 Hz, J_{45} = 16.4 Hz. ^{13}C NMR (100 MHz, C_6D_6): δ 36.8 (CH^1), 86.2 (C_5H_5), 115.9 (CH^5H^6), 132.2, 133.1, 135.5 ($CH^2 + CH^3 + CH^4$), 139.0 (Fe*C*═C, q, J_{C-F} = 29 Hz), 141.2 (Fe–C═*C*, q, J_{C-F} = 29 Hz), 129.5, 133 ($2CF_3$, q, J_{CF} = 270 Hz), 213.6 (CO). ^{19}F NMR (93.6 MHz, C_6D_6): δ 56.6 (s), 62.4 (s).

(H) X-ray Diffraction Study of 2, 4, and 5. Intensity data were collected at room temperature on a CAD4 diffractometer, using graphite-monochromated Mo Kα radiation. All data reduction and structure refinement were performed by using the NRCC-SDP-VAX package on a VAX-785 computer. Crystal date, data collection, and structure analysis are summarized in Table VIII. The structure of three compounds were solved by the Patterson method. All non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were added at idealized positions and included in the structure factor calculations.

Acknowledgment. We wish to thank the Chinese National Science Council for financial support of this work.

Registry No. **1**, 103225-91-8; **2**, 113404-08-3; **3**, 109638-07-5; **4**, 113404-09-4; **5**, 113404-10-7; **6** (isomer 1), 113404-11-8; **6** (isomer 2), 113472-63-2; **7** (isomer 1), 113404-12-9; **7** (isomer 2), 113472-64-3; **8**, 113404-13-0; **9**, 113404-14-1; TCNE, 670-54-2; maleic anhydride, 108-31-6; dimethyl acetylenedicarboxylate, 762-42-5; hexafluoro-2-butyne, 692-50-2.

Supplementary Material Available: Table IX, calculated atomic coordinates and estimated thermal parameters for the hydrogen atoms of molecule **2**, **4**, and **5** (1 page); listings of structure factors for **2**, **4**, and **5** (51 pages). Ordering information is given on any current masthead page.

Synthesis of Fluorosilanes from Chlorosilanes: The Use of Hexafluorosilicates

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The conversion of chlorosilanes to fluorosilanes has been studied by using sodium and ammonium hexafluorosilicate. Of particular interest has been their efficacy in the conversion of highly hindered chlorosilanes like dimesityldichlorosilane and di-*tert*-butyldichlorosilane. Ammonium hexafluorosilicate is found to be the superior reagent for these conversions, since its reactions are more easily worked up and give higher yields. In addition, ammonium hexafluorosilicate does not affect the Si–H, Si–Si, or Si–O–Si linkages as do many reagents which bring about chlorosilane to fluorosilane conversions.

The chemistry of organofluorosilanes has recently been revitalized by reports of their use in the preparation of pentacoordinate siliconates and highly hindered organosilanes.[1-3] Pentacoordinate siliconates are made in high yields by reacting organofluorosilanes such as diphenyldifluorosilane with fluoride ion solubilized in toluene by 18-crown-6 (eq 1).[2] Although hindered silanes have recently been prepared by reaction of either SiF_4 or a substituted trifluorosilane with hindered Grignard or organolithium reagents (eq 2–4),[3] the utility of fluorosilanes in such couplings was first recognized by Eaborn in 1952.[4] Indeed, many recent studies by Eaborn and co-workers have heightened interest in highly hindered silicon compounds as have studies where bulky substituents on silicon stabilize otherwise reactive silicon intermediates.[5,6]

$$(C_6H_5)_2SiF_2 \xrightarrow[\substack{\text{18-crown-6} \\ \text{toluene}}]{\text{KF}} (C_6H_5)_2\bar{S}iF_3 + K^+(\text{18-crown-6}) \tag{1}$$

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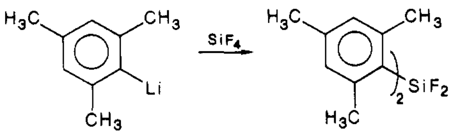
[1] Kanner, B. *Silicon Compounds, Register and Review, 1987*, Petrarch Systems Catalog, 40.

[2] (a) Damrauer, R.; Danahey, S. E. *Organometallics* **1986**, *5*, 1490. (b) A variation of this method has also been used recently by Corriu and co-workers to solubilize potassium methoxide, personal communication.

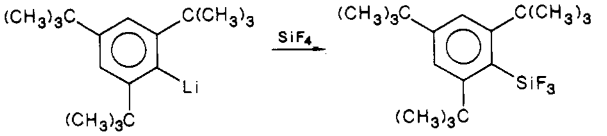
[3] (a) Nakadaira, Y.; Ohara, K.; Sakurai, H. *J. Organomet. Chem.* **1986**, *309*, 247. (b) Wiberg, N.; Neruda, B. *Chem. Ber.* **1966**, *99*, 740. (c) Weidenbruch, M.; Kramer, K. *J. Organomet. Chem.* **1985**, *291*, 159.

[4] Eaborn, C. *J. Chem. Soc.* **1952**, 2840.

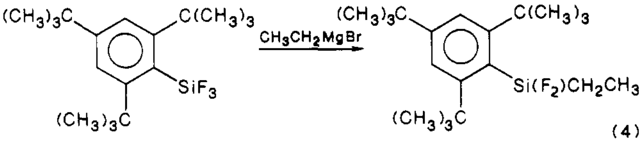
0276-7333/88/2307-1161$01.50/0



(2)



(3)



(4)

There are a number of methods which convert chlorosilanes to fluorosilanes. These have been reviewed in detail recently.[7] Many methods give high yields of fluorosilanes but suffer various disadvantages. Among these are reagent cost and toxicity as well as the stringent reaction conditions under which some of these conversion occur. Although we have used SbF_3 for fluorinations of chlorosilanes for quite some time, we have found it to be lacking in two respects. Not only is it toxic,[8] but also its reactions require high temperatures and prolonged reaction times for the conversion of hindered chlorosilanes. Other fluorination methods have similar drawbacks. Thus, we sought an alternative fluorinating agent and have found that hexafluorosilicate salts, which are inexpensive, presumably are less toxic,[8] and react more readily, are superior reagents. Both sodium and ammonium hexafluorosilicate effect the conversion of chloro- to fluorosilanes (eq 5) with the ammonium compound in 1,2-dimethoxyethane (DME) offering significant advantages. In this report we not only describe the use of these reagents but also briefly elaborate on their advantages in a variety of chloro- to fluorosilane conversions.

$$R_nSiCl_{4-n} \xrightarrow[(NH_4)_2SiF_6]{\substack{Na_2SiF_6 \\ \text{or}}} R_nSiF_{4-n} \qquad (5)$$

Experimental Section

General Remarks. The reactions studied were carried out under a blanket of argon by using handling conditions no more stringent than those required for handling organometallic compounds like simple Grignard or organolithium reagents. Except where noted reagent grade solvents have been used without further drying. A conscious attempt has been made to develop a procedure that could be simply carried out. NMR data were recorded on an IBM NR-80/B spectrometer. All ^1H and ^{13}C chemical shifts are reported relative to $(CH_3)_4Si$; ^{19}F shifts are reported relative to $CFCl_3$. Gas chromatographic (GC) analysis has been carried out by using a Perkin-Elmer 3020B or a Hewlett-Packard 5890A gas chromatograph, both with flame ionization detection. Estimates of yields using GC have been accomplished by using internal standards which are stable to the reaction conditions. However, we have only estimated yields (Table II) this way having, in most cases, sought to report yields of isolated, pure materials (Table I). GC analyses were done either on a $^1/_8$ in. × 6 ft 10% OV-1 silicone oil on Chromosorb WHP packed column or on a 25-meter cross-linked methylsilicone high performance capillary column. GC–MS analysis was carried out by using a Hewlett-Packard 5970B mass selective detector attached to a Hewlett-Packard 5890A gas chromatograph using a 25-m high performance capillary column of cross-linked methyl silicone. Elemental analyses were performed by Huffman Laboratories, Wheatridge, CO.

Table I. Fluorinations of Chlorosilanes Using $(NH_4)_2SiF_6$

product silane	solv	reactn time/temp	isolated yield, %	method
$(C_6H_5)SiF_3$	decalin	3 h/120 °C	65	A^a
Mes_2SiF_2	DME	24 h/reflux	33	B^b
Mes_2SiF_2	DME	20 h/reflux	80	C^c
$(t\text{-Bu})_2SiF_2$	DME	3 weeks/reflux	54	C
$(n\text{-}C_6H_{13})_3SiF$	DME	19 h/reflux	88	C
$(C_6H_5CH_2)SiMe_2F$	DME	1 h/22 °C	85	$C^{d,e}$
$(C_6H_5)_2(t\text{-Bu})SiF$	DME	120 h/reflux	75	C
$(C_6H_5)_2SiF_2$	DME	1 h/reflux	66	C
$(C_6H_5)_3SiF$	DME	3.6 h/reflux	68	C
$(C_6H_5)_2Si(H)F$	DME	0.5 h/reflux	96	$C^{d,f}$

[a] Na_2SiF_6/distillation from reaction. [b] Na_2SiF_6/aqueous workup. [c] $(NH_4)_2SiF_6$/aqueous workup. [d] Modified method C no aqueous workup. [e] Crude yield (95% pure by GC). [f] Crude yield (98+% pure by GC).

Table II. Gas Chromatographic Yields for Chloro- to Fluorosilane Transformations Using Method C

product silane	solv	reactn time/temp	convn[a] %	ref
$(C_6H_5)_3SiF$	DME	19 h/reflux	100	xylene
$(n\text{-}C_6H_{13})_3SiF$	DME	19 h/reflux	100	xylene
$Me_3SiSiMe_2F$	DME	2 h/reflux	97	$Me_3SiSiMe_3$
Mes_2SiF_2	DME	20 h/reflux	100	xylene
$(t\text{-Bu})_2SiF_2$	DME	2 weeks/reflux	100	mesitylene
$(C_6H_5)_2SiF_2$	DME	1 h/reflux	100	mesitylene
$(C_6H_5)_2Si(H)F$	DME	0.5 h/reflux	70	xylene

[a] GC yield, assuming $R_F(X) = 1$.

All compounds were obtained from either Aldrich Chemical Co. or Petrarch Systems. Purities have been checked by GC analysis; in general, compounds from these sources have had purities in excess of 97% and have been used without further purification. The fluorosilanes that are new have been suitably characterized by spectroscopic means and elemental analysis; all others have been characterized by spectroscopic means and by comparison with their reported properties.

General Procedure Using Sodium Hexafluorosilicate: Isolation by Distillation from High Boiling Hydrocarbon. Method A. Phenyltrichlorosilane (130.4 g, 0.6164 mol) was charged into a distillation apparatus. Decalin (150 mL) and Na_2SiF_6 (231.9 g, 1.233 mol) were added; when the temperature was raised to 120 °C, crude phenyltrifluorosilane (bp 60–116 °C) slowly distilled into a cooled collection flask. Redistillation through a 10-cm Vigreaux column (bp 96–99 °C) gave pure phenyltrifluorosilane (65% yield) identical with an authentic sample.[9]

General Procedure Using Sodium Hexafluorosilicate. Method B. Dimesityldichlorosilane (2.0 g, 5.9 mmol), Na_2SiF_6 (3.3 g, 18 mmol), and 1,2-dimethoxyethane (60 mL) were charged into a 100-mL three-necked flask equipped with a magnetic stirbar, condenser, and argon inlet tube. The heterogeneous reaction mixture was heated to reflux and monitored by GC and GC-MS. After 24 h, all of the starting silane had been consumed and only product dimesityldifluorosilane was detected by GC. The reaction mixture was filtered to remove the sodium salts, and the salts were washed with diethyl ether. Removal of solvent by rotary evaporation followed by sublimation yielded dimesityldifluoro-

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(5) Eaborn, C. *J. Organomet. Chem.* **1982**, *239*, 93.

(6) Raabe, G.; Michl, J. *Chem. Rev.* **1985**, *85*, 419.

(7) A number of fluorination methods are reviewed in: Pike, R. M.; Koziski, K. *J. Organomet. Chem. Libr.* **1980**, *9*, 41.

(8) Comparable toxicity data on SbF_3, Na_2SiF_6, and $(NH_4)_2SiF_6$ cannot be obtained. Aldrich Chemical, which sells each of these, supplied us with detailed toxicity data sheets. However, their data sheets allowed no quantitative comparisons. In summaries Aldrich called SbF_3 highly toxic and the other two only toxic. Suffice it to say that it is not clear about the relative toxicity of these compounds and that they should be handled with care.

(9) Kanner, B.; Bailey, D. L. U.S. Patent 3 128 297, 1964. Based on earlier work by: Bailey, D. L.; Pike, R. M. U.S. Patent 3 020 302, 1962.

Table III. ^{1}H, ^{13}C, and ^{19}F NMR Chemical Shifts of Fluorosilanes (δ)[a]

fluorosilane	^{1}H	^{13}C	^{19}F
$C_6H_5SiF_3$	7.638 (m), 7.766 (m)	129.96, 134.85, 135.70	−141.06 (J_{SiF} = 266.49 Hz)
Mes_2SiF_2	2.266 (s, 6 H), 2.356 (t, $^5J_{HF}$ = 3.66 Hz, 12 H), 6.910 (s, 4 H)	21.22, 23.04 (t, $^4J_{CF}$ = 5.49 Hz), 130.33, 142.77, 145.53	−122.96 (J_{SiF} = 295.72 Hz, J_{CF} = 106.60 Hz)
$(C_6H_5)_2SiF_2$	7.550 (m), 7.690 (m)	129.50, 133.27, 135.27	−141.46 (J_{SiF} = 292.3 Hz, J_{CF} = 108.32 Hz)
(*t*-Bu)$_2$SiF$_2$	1.086 (t, $^4J_{HF}$ = 1.95 Hz)	19.58 (t, $^3J_{CF}$ = 3 Hz), 26.22	−156.38 (d, J_{HF} = 2.58 Hz, J_{SiF} = 324.95 Hz, J_{CF} = 109.18 Hz)
(*n*-C$_6$H$_{13}$)$_3$SiF	0.890 (m, 5 H), 1.336 (s, br, 8 H)	14.29 (d, $^3J_{CF}$ = 1.22 Hz), 14.93, 23.22, 32.23, 33.69	−170.08 (m, J_{HF} = 5.91 Hz, J_{SiF} = 291.40 Hz, J_{CF} = 106.32 Hz)
(C$_6$H$_5$)$_2$(*t*-Bu)SiF	1.077 (d, $^4J_{HF}$ = 1.22 Hz, 9 H), 7.440 (m, 6 H), 7.733 (m, 4 H)	19.36 ($^2J_{CF}$ = 3.3 Hz), 26.25, 128.84, 131.24, 133.38 ($^2J_{CF}$ = 3.3 Hz), 135.09	−141.86 (J_{SiF} = 289.70 Hz, J_{CF} = 106.60)
$(C_6H_5)_2Si(H)F$	5.487 (d, $^2J_{HF}$ = 54.3 Hz, 1 H), 7.508 (m, 14 H)[b]	129.32, 132.27, 135.15	−173.97 (d, $^2J_{HF}$ = 55.13 Hz, J_{SiF} = 338.65 Hz, J_{CF} = 232.32 Hz)
$(C_6H_5)CH_2SiMe_2F$	0.175 (d, $^3J_{HF}$ = 7.32 Hz, 6 H), 2.279 (d, $^3J_{HF}$ = 6.22 Hz, 2 H), 7.131 (m, 5 H)		−160.12 (m, $^2J_{HF}$ = 5.91 Hz, J_{SiF} = 275.64 Hz, J_{CF} = 86.62 Hz)

[a] $Si(CH_3)_4$ reference for ^{1}H and ^{13}C NMR; $CFCl_3$ reference for ^{19}F NMR; acetone-d_6 as solvent for all samples and all spectra run on an IBM NR80/B spectrometer. [b] Integration values incorrect due to disiloxane impurity.

silane (0.6 g, 33% yield, mp 139–141 °C) identical with authentic material.[3b]

General Procedure Using Ammonium Hexafluorosilicate: Aqueous Workup. Method C. Dimesityldichlorosilane (2.0 g, 5.9 mmol), $(NH_4)_2SiF_6$ (2.1 g, 12 mmol), and 1,2-dimethoxyethane (60 ml) were charged into a 100-mL three-necked flask equipped with a magnetic stirbar, condenser, and argon inlet tube. The heterogeneous reaction mixture was heated to reflux and monitored by GC and GC–MS analysis. After 20 h all the starting silane had been consumed and only product dimesityldifluorosilane was detected by GC. The reaction mixture was poured into a saturated solution of ammonium chloride; the organic layer of the resulting mixture was separated, and the aqueous layer was easily extracted with several portions of diethyl ether. The ether layer was separated and dried over anhydrous $MgSO_4$. Removal of solvent by rotary evaporation and sublimation (or recrystallization from acetone) yielded dimesityldifluorosilane (1.4 g, 80% yield; mp 143–144 °C) identical with authentic material.[3b]

Conversion of Diphenylchlorosilane to Diphenylfluorosilane Using Ammonium Hexafluorosilicate. This reaction was carried out on a 3.0-g scale by using a modification of Method C where no aqueous workup was carried out. We have found that unless the DME has been carefully dried (by benzophenone ketyl followed by $LiAlH_4$ distillation), only disiloxane products were obtained. When dried DME is used, high yields of diphenylfluorosilane are obtained after filtration and DME removal (2.6 g, 96% crude yield of material of 98% purity identical with an authentic sample).[10]

Results and Discussion

The most widely used methods for the preparation of fluorosilanes have involved cleavage of either Si–Cl or Si–O bonds (eq 6 and 7). Thus, chlorosilanes have been con-

$$R_nSiCl_{4-n} \xrightarrow[\text{CuF}_2\text{ XeF}_2\text{, or etc.}]{\text{SbF}_3\text{, ZnF}_2\text{,}} R_nSiF_{4-n} \qquad (6)$$

$$[(CH_3)_3Si]_2O \xrightarrow[\text{or etc.}]{\text{HF, NH}_4\text{F, BF}_3\text{,}} (CH_3)_3SiF \qquad (7)$$

verted to fluorosilanes with a wide variety of inorganic fluorides, particularly metal fluorides like SbF_3, CaF_2, ZnF_2, XeF_2, CuF_2, etc., and disiloxanes and alkoxysilanes have been fluorinated with a variety of reagents including HF, NH_4F, and BF_3.[7] Although these methods have had wide use, they sometimes require costly reagents, ones which are toxic and/or ones which are difficult to handle. There is also quite a lot of lore about their use leading to a situation where little experimental description or systematic study has been published for methods that are fairly widely used.

Because we have had to prepare a number of fluorosilanes in recent years,[2,11] we became directly aware of some of the problems of their synthesis. Though we have used Sharpe's SbF_3 procedure with success for quite some time,[12] the reported[8] high toxicity of SbF_3 worried us. In addition, we found it unsuitable for certain chloro- to fluorosilane conversions, particularly when bulky groups were present and when silicon chlorohydrides were to be converted to fluorohydrides. For example, using SbF_3 in Sharpe's typical experimental regime, di-*tert*-butyldichlorosilane does not react to give the corresponding difluoride although it has been reported to react in good yield at elevated temperature.[13] Similarly, when we reacted diphenylchlorosilane and SbF_3, we did not obtain diphenylfluorosilane. In fact, we were unable to identify any tractable products using this procedure. Therefore, in seeking other reagents which could convert chloro-to fluorosilanes, we desired a reagent which was (1) inexpensive, (2) relatively safe to handle, and (3) easy to handle. The reagent also had to convert both bulky chlorosilanes and silicon chlorohydrides to their respective fluoro derivatives and to tolerate other functionalities like the disiloxane and disilane moieties. Earlier work by one of us with sodium hexafluorosilicate in hydrocarbon medium suggested that this reagent might suitably fit our requirements.[9,14] Though sodium hexafluorosilicate works well for a variety of applications, we have found that ammonium hexafluorosilicate in DME is a generally superior system for these conversions.

Even though sodium hexafluorosilicate has disadvantages for the preparation of certain fluorosilanes, it can be used in hydrocarbon medium to effect many such conversions (eq 5) in high yield. Thus, when the desired fluorosilane is relatively low boiling and unhindered, it can

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(10) Horner, L.; Mathias, J. *J. Organomet. Chem.* **1985**, *282*, 155.

(11) DePuy, C. H.; Damrauer, R.; Bowie, J.; Shelton, J. *Acc. Chem. Res.* **1987**, *20*, 127.

(12) Sharpe, K., personal communication. Also see ref 2 for experimental details of this procedure which to our knowledge has never been published by Sharpe.

(13) Weidenbruch, M.; Pesel, H.; Peter, W.; Steichen, R. *J. Organomet. Chem.* **1977**, *141*, 9.

(14) One other brief report of the use of sodium hexafluorosilicate has appeared: Kuroda, K.; Ishikawa, N. *Nippon. Kagaku Zasshi* **1969**, *90*, 322.

be prepared and distilled from a reaction mixture of chlorosilane, sodium hexafluorosilicate, and high boiling hydrocarbon (method A). Phenyltrifluorosilane has been prepared in 65% yield by using this method (Table I). Less successful have been reactions where the fluorosilane products have a higher boiling point than the hydrocarbon solvent. For example, only modest yields (32%) of di-*p*-tolyldifluorosilane are obtained by using a filtration procedure followed by fractional distillation after reaction in decalin. This method is inconvenient in another respect: reaction rates are quite slow with chlorosilanes having bulky substituents. Having discovered that DME accelerates this conversion and preferring to isolate the fluorosilane products using a simple aqueous workup and extraction procedure, we investigated the use of sodium hexafluorosilicate in DME (method B) and ammonium hexafluorosilicate in DME (method C). We have not carried out a detailed study of various ether solvents. Brief work in refluxing diethyl ether demonstrated reaction, but at rates much slower than those obtained in refluxing DME. This is probably a temperature effect and, since DME worked so well for the systems we studied, was not investigated further.

Monitoring method B by GC, we found high conversions to fluorosilanes; however, the aqueous workup proved troublesome since large excesses of Na_2SiF_6 were generally used to increase the reacton rate and the limited aqueous solubility of the excess Na_2SiF_6 gave difficult to manage precipitates which affected yields (Table I). However, ammonium hexafluorosilicate reaction with dimesityldichlorosilane gave an 80% yield when dimesityldifluorosilane could be prepared in only 33% yield in DME by using the sodium salt. In the ammonium cases, the aqueous workup (method C) gives easily separable phases and, consequently, much higher isolated yields. Even in cases where Na_2SiF_6 was used in exact stoichiometric proportion (2 equiv of F delivered/equiv of Na_2SiF_6), the aqueous workup could not be smoothly carried out. As indicated in Table I, we have applied method C to other cases. Diphenyldifluorosilane, di-*tert*-butyldifluorosilane, trihexylfluorosilane, *tert*-butyldiphenylfluorosilane, and triphenylfluorosilane have been isolated in 66, 54, 88, 75%, and 68 yields, respectively (Table I). Even benzyldimethylfluorosilane can be obtained from its chloro precursor in 85% isolated yield although without an aqueous workup. Another practical advantage of ammonium over the sodium hexafluorosilicate is that its reactions are more rapid. We have carried out several comparison studies and in each case find ammonium hexafluorosilicate to affect faster reaction.

We have also demonstrated that method C can be used without affecting certain substituents commonly found in silanes. As already mentioned, benzylsilanes can be smoothly reacted. Diphenylchlorosilane can be converted to diphenylfluorosilane in 96% yield (eq 8), but only when extreme care is taken in drying the DME. Disiloxane linkages are not cleaved by ammonium hexafluorosilicate even though some fluorosilanes are prepared by disiloxane cleavage (e.g. NH_4F, HF, BF_3).[7] For example, dimethylphenylsiloxane is stable to the reaction conditions of method C. Finally, 1-chloropentamethyldisilane reacts by method C to give high yields of the corresponding fluorodisilane with no destruction of the Si–Si linkage.

$$(C_6H_5)_2Si(H)Cl \xrightarrow[\text{dry DME}]{(NH_4)_2SiF_6} (C_6H_5)_2Si(H)F \qquad (8)$$

We have examined several other reactions of sodium and ammonium hexafluorosilicate by GC (Table II). With the exception of bis(dimethylamino)methylchlorosilane, which reacts but gives no identifiable products, all the other silanes listed give very high conversions to the corresponding fluorosilanes. In general, GC studies demonstrate that sodium hexafluorosiliconate brings about high conversions to fluorosilanes; however, because of aqueous workup difficulties, ammonium hexafluorosiliconate gives far superior isolated yields. We recommend its use for such conversions and believe these studies demonstrate its wide applicability and ease of use. It is an excellent method for chloro- to fluorosilane conversions with hindered silanes and ones where a benzyl, disiloxane, disilane, and/or Si-H functionality must survive the conversion.

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Registry No. $(C_6H_5)SiF_3$, 368-47-8; MeS_2SiF_2, 5599-30-4; $Me_3SiSiMe_2F$, 812-20-4; $(t\text{-}Bu)_2SiF_2$, 558-63-4; $(n\text{-}C_6H_{13})_3SiF$, 113352-64-0; $(C_6H_5CH_2)SiMe_2F$, 1842-25-7; $(C_6H_5)_2(t\text{-}Bu)SiF$, 113352-65-1; $(C_6H_5)_2SiF_2$, 312-40-3; $(C_6H_5)_3SiF$, 379-50-0; $(C_6H_5)_2Si(H)F$, 1013-91-8; $(C_6H_5)SiCl_3$, 98-13-5; Mes_2SiCl_2, 5599-27-9; $Me_3SiSiMe_2Cl$, 1560-28-7; $(t\text{-}Bu)_2SiCl_2$, 18395-90-9; $(n\text{-}C_6H_{13})_3SiCl$, 3634-67-1; $(C_6H_5CH_2)SiMe_2Cl$, 1833-31-4; $(C_6H_5)_2(t\text{-}Bu)SiCl$, 58479-61-1; $(C_6H_5)_2SiCl_2$, 80-10-4; $(C_6H_5)_3SiCl$, 76-86-8; $(C_6H_5)_2Si(H)Cl$, 1631-83-0; Na_2SiF_6, 16893-85-9; $(NH_4)_2SiF_6$, 16919-19-0.