Alkali Metal Salts of Perfluorinated Complex Anions. Effective Reagents for Nucleophilic Fluorination

Omar Farooq* and George V. D. Tiers

Building 201-3N-04, Graphic Research & Science Research Laboratories, 3M Central Research, St. Paul, Minnesota 55144

Received November 5, 1993

Alkali metal salts of perfluorinated complex anions were used to effect halogen-exchange fluorination in organohalosilanes both in the presence and absence of solvent. By the use of salts of perfluorinated "non-nucleophilic" anions in a high-boiling multifunctional etheral solvent, organofluorosilanes have been conveniently prepared in high yields.

Introduction

Perfluorinated complex anions, e.g., BF_4^-, PF_6^-, SbF_6^-, AsF_6^-, and SiF_6^{2-}, have been regarded as non-nucleophilic and inert or "innocent" anions. When electrochemical experiments were conducted using fluoroborate salts as electrolytes for the anodic oxidation of organic compounds in aprotic solvents, it was assumed that these salts of BF_4^- anion were inert.[1] It was, however, clearly demonstrated from several controlled-potential oxidations that this anion is not truly inert and that high yields of fluorinated products result from the participation of this anion in the "followup" reactions of electrode intermediates. Thus, in the anodic oxidation of benzhydryl *p*-tolyl ketone with $Me_4N^+BF_4^-$ as the current carrier *p*-fluorotoluene was obtained as the major product.[1]

The tetrafluoroborate anion as its (expensive) silver salt has been used for halogen-exchange fluorination of certain halo carbonyl compounds, halo epoxides and *gem*-dihalides.[2] Neighboring group participation together with silver ion-assisted rapid elimination of halogen was held responsible for the respectable yields of the fluorinated compounds in these reactions.[2] The BF_4^-, PF_6^-, and SbF_6^- anions were also used, again, as their (expensive) silver salts, for halogen-exchange fluorination of chlorosilicon and chlorogermanium transition-metal complexes.[3] In these reactions, too, the role of silver ion is seemingly obvious in accounting for the reasonable yields of the fluorinated compounds.

Hexafluorosilicate anion as its sodium or ammonium salt has been used in effecting nucleophilic fluorination of organosilicon compounds. Although the high efficiency of these salts in the conversion of highly hindered chlorosilanes is of particular interest, the reactions are very sluggish, necessitating prolonged heating (days to weeks) in high-boiling solvents.[4] Further, the toxicity of these reagents limits their use in such chemical transformations.[4]

Nucleophilic fluorine transfer to aromatic compounds has been effected by heating an appropriate arenediazonium tetrafluoroborate normally prepared *in situ*; this is the classical "Balz–Schiemann" reaction,[5] which in recent years has undergone several modifications.[6]

Ionic fluorination of cage hydrocarbons and their bridgehead halogen derivatives has been effected in reasonable yield with (expensive) nitronium tetrafluoroborate in the presence of the not-easily-accessible pyridinium polyhydrogen fluoride.[7]

In the study of electrophilic nitration[8] of phenylhaloboranes with nitronium salts of BF_4^- anion, fluoride ion exchange with phenylhaloborane was observed, with phenylfluoroboranes formed as side products. We have recently reported[9] the use of perfluorinated complex anions as potential sources of fluoride ion for fluorodehalidation of arylhaloboranes in high conversion and yield. We now want to report a simple procedure of fluorodehalidation of various types of organohalosilanes using inexpensive and readily available alkali metal salts of perfluorinated complex anions.

Results and Discussion

When a mixture of triphenylchlorosilane and sodium tetrafluoroborate in a 1:1 molar ratio was heated to about 200 °C, evolution of boron trifluoride gas commenced and the corresponding fluorosilane was formed. The mixture was heated for 0.25–0.5 h, and the corresponding fluorosilane was distilled under reduced pressure in reasonable yield (Table 1). Formation of boron trifluoride indicates that the high affinity of silicon for fluorine induces polarization in the tetrafluoroborate anion which thermally dissociates with simultaneous formation of boron triflu-

* Abstract published in *Advance ACS Abstracts*, March 15, 1994.

(1) (a) Koch, V. R.; Miller, L. L.; Clark, D. B.; Fleischmann, M.; Joslin, T.; Pletcher, D. *Electroanal. Chem. Interfac. Electrochem.* **1973**, *43*, 318. (b) Nikitin, E. V.; Kazakova, A. A.; Ignat'ev, Yu. A.; Parakin, O. V.; Kargin, Yu. M. *Zh. Obshch. Khim.* **1983**, *53*(1), 230.

(2) (a) Bloodworth, A. J.; Bowyer, K. J.; Mitchell, J. C. *Tetrahedron Lett.* **1987**, *28*(44), 5347. (b) Fry, A. J.; Migron, Y. *Tetrahedron Lett.* **1979**, 3357. (c) Griesbaum, K.; Keul, H.; Keibar, R.; Pfeffer, B.; Spraul, M. *Chem. Ber.* **1981**, *114* (5), 1858.

(3) (a) Marks, T. J.; Seyam, A. M. *J. Organomet. Chem.* **1971**, *31*, C62-C64. (b) Marks, T. J.; Seyam, A. M. *Inorg. Chem.* **1974**, *13*(7), 1624.

(4) Damraur, R., Simon, R. A. *Organometallics* **1988**, *7*, 1161.

(5) (a) Michael, R. C.; Gerstenberger and Alois, H. *Angew. Chem., Int. Ed. Engl.* **1981**, *20*, 647. (b) Newman, M. S.; Lijie, K. C. *J. Org. Chem.* **1979**, *44*, 1347. (c) Suster, D. C.; Botez, G.; Feyns, L. V.; Dobre, V.; Niculescu-Duvaz, I. *Rev. Roum. Chim.* **1977**, *22*, 257. (d) Mueller, A.; Roth, U.; Siegert, S.; Mietchen, R. *Z. Chem.* **1986**, *26*, 169.

(6) (a) Hartmann, G. D.; Biffer, S. E. *J. Org. Chem.* **1977**, *42*, 1468. (b) Sweeny, A. Jr.; Blair, R. D.; Chang, A.; Clark, L. *J. Fluorine Chem.* **1975**, *6*, 389. (c) Honore', T.; Hjeds, H. *Eur. J. Med. Chem.-Chim. Ther.* **1979**, *14*, 285. (d) Doyle, M. P.; Whitefleet, J. L.; Zaleta, M. A. *Tetrahedron Lett.* **1975**, 4201. (e) Reepmeyer, J. C.; Kirk, K. L.; Cohen, L. A. *Tetrahedron Lett.* **1975**, 4107. (f) Becker, H. G. O.; Israel, G. *J. Prakt. Chem.* **1979**, *321*, 579. (g) Fabra, F.; Vilarrasa, J.; Coll, J. *J. Heterocycl. Chem.* **1978**, *15*, 1447.

(7) (a) Olah, G. A.; Shih, J. G.; Singh, B. P.; Gupta, B. G. B. *J. Org. Chem.* **1983**, *48*(19), 3356. (b) Olah, G. A.; Shih, J. G.; Singh, B. P.; Gupta, B. G. B. *Synthesis* **1983**, 713. (c) Krishnamurthy, V. V.; Shih, J. G.; Singh, B. P.; Olah, G. A. *J. Org. Chem.* **1986**, *51*(8), 1354.

(8) Olah, G. A.; Piteau, M.; Laali, K.; Chandra, B. R.; Farooq, O. *J. Org. Chem.* **1990**, *55*(1), 46.

(9) Farooq, O. *J. Fluorine Chem.*, in press.

0022-3263/94/1959-2122$04.50/0 © 1994 American Chemical Society

ED_005024_00000323-00001

Table 1. Fluorodechloridation of Triphenylchlorosilane with Sodium Tetrafluoroborate

BF_4^-:Ph_3SiCl (molar ratio)	solvent/vacuum	catalyst	Ph_3SiF % yield
1.1:1			63
1.1:1	vacuum		77
1.2:1		$BF_3{\cdot}Et_2O$	50
1.2:1		$AlCl_3$	41
1.1:1	tetraglyme		96

oride and fluorosilane. Organohalosilanes are known to form donor–acceptor types of complexes with Lewis acids.[10] To enhance the fluoride ion abstraction and thereby to increase the yield of fluorosilane, it was of interest to use a donor–acceptor complex of triphenylchlorosilane with a suitable Lewis acid. When, however, the reaction is carried out in presence of "catalytic" amounts of aluminum chloride or boron trifluoride–etherate the yield of fluorosilane actually is decreased (Table 1). This surprising apparent effect of an added Lewis acid suggested further study of this reaction.

When the above-mentioned reaction was carried out under vacuum, thereby continuously removing the boron trifluoride, the yield of fluorosilane was moderately increased (Table 1). This indicates that the *in-situ* generated boron trifluoride, when it is not continuously removed from the system, does exert an inhibitory action. If, therefore, the *in-situ* formed boron trifluoride could be more completely removed or trapped, the yield of fluorosilane should be increased. Indeed, when the reaction of triphenylchlorosilane with sodium tetrafluoroborate was carried out in a high-boiling etheral solvent (e.g., tetraethylene glycol dimethyl ether), a near-quantitative yield of fluorosilane was obtained (Table 1).

Following this procedure, salts of other perfluorinated counterions were used as a fluoride ion donor to obtain high yields of triphenylfluorosilane (Table 2). The procedure was further extended to fluorinate other halosilane precursors (Table 2). The near-quantitative yield was obtained almost in all cases, the balance being the mixed chlorofluorosilanes as determined by the ^{29}Si NMR spectra.

In all of these cases, the organofluorosilanes were distilled as a neat liquid either at atmospheric pressure or under reduced pressure. The products were characterized by their ^1H and ^{29}Si NMR spectra (Table 3) and elemental analysis.

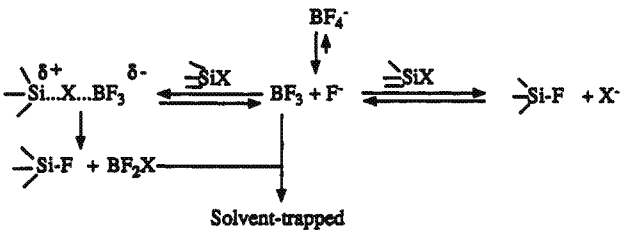
In all of these transformations, reaction with tetrafluoroborate salt was faster than those with hexafluorophosphate and hexafluoroantimonate salts. When the reactions were carried out with tetrafluoroborate and hexafluorophosphate salts in the absence of any solvent, boron trifluoride and phosphorous pentafluoride were the only gaseous byproducts and were trapped and recovered as their ether complexes. With hexafluoroantimonate salt the reaction mixture turned dark, perhaps owing to the formation of antimony pentafluoride and mixed antimony halides.

Table 2. Fluorodechloridation of Organosilicon Compounds

alkali metal salts	organosilicon precursor	organofluorosilane	% yield	bp/°C (Torr)
$NaPF_6$	Ph_3SiCl	Ph_3SiF[a]	92	165–169 (1)
$NaSbF_6$	Ph_3SiCl	Ph_3SiF[a]	87	165–169 (1)
$NaBF_4$	Ph_2SiCl_2	Ph_2SiF_2[b]	96	66–70 (0.5)
$NaPF_6$	Ph_2SiCl_2	Ph_2SiF_2[b]	93	66–70 (0.5)
$NaSbF_6$	Ph_2SiCl_2	Ph_2SiF_2[b]	95	66–70 (0.5)
$NaBF_4$	$PhMeSiCl_2$	$PhMeSiF_2$[c]	94	138–142
KBF_4	$PhMeSiCl_2$	$PhMeSiF_2$	92	138–142
$NaBF_4$	$Me(C_3H_5)SiCl_2$	$Me(C_3H_5)SiF_2$	92	85–90
$NaBF_4$	(*n*-octyl)$SiMe_2Cl$	(*n*-octyl)$SiMe_2F$[d]	97	175–180
$LiBF_4$	(*n*-octyl)$SiMe_2Cl$	(*n*-octyl)$SiMe_2F$[d]	96	175–180
$NaBF_4$	(*n*-octenyl)$SiMe_2Cl$	(*n*-octeneyl)$SiMe_2F$	93	174–180
KBF_4	(*n*-octenyl)$SiMe_2Cl$	(*n*-octeneyl)$SiMe_2F$	91	174–180
$NaPF_6$	(thexyl)Me_2SiCl	(thexyl)Me_2SiF	94	141–145
KBF_4	(thexyl)Me_2SiCl	(thexyl)Me_2SiF	97	141–145
$NaPF_6$	Ph_2-t-BuSiCl	Ph_2-t-BuSiF	67	135–140 (1)
		Ph-t-$BuSiF_2$	33	120–124 (1)

[a–d] Refs 11–14, respectively.

Scheme 1



The role of multifunctional ether is rather important in the discussed halogen-exchange fluorination of halosilanes. Trapping of the *in-situ* thermally-formed Lewis acid from the non-nucleophilic anion by the multifunctional ether releases the "naked" or "nascent" fluoride ion as an active reagent which rapidly undergoes halogen-exchange fluorination with halosilane (Scheme 1). In the absence of trapping solvent the Lewis acid can form donor–acceptor types of complexes[10] which can also undergo thermally-assisted halogen-exchange fluorination leading to product. In the absence of trapping solvent, as the process continues under thermal conditions, a buildup of Lewis acid occurs which allows further complexation with either the reactant or the product. These complexation equilibria may be held responsible for the lower yield of the product fluorosilanes in the absence of trapping solvent. Although from a product formation point of view trapping of boron trifluoride with etheral solvent apparently is important, the formation of a donor–acceptor type of complex as a competing reaction with halosilanes cannot be ruled out even in the presence of such solvent.

When the reaction is performed under constant vacuum the continuous removal of gaseous Lewis acid shifts the equilibrium toward the fluoride ion and, hence, the product. It was observed that in the case where the byproduct Lewis acid cannot be removed by practical vacuum (e.g., in the case of SbF_6^- salt), the yield of fluorosilane is lower. The use of a high-boiling etheral solvent allows the *in-situ* formed Lewis acid to be strongly complexed with it immediately; this results in a near-quantitative yield of fluorosilane.

The well-recognized perfluorinated non-nucleophilic counterions are thermally labile as illustrated in this paper. The alkali metal salts of these counterions can conveniently be used for high yield preparation of organofluorosilanes.

(10) (a) Olah, G. A.; Field, L. D. *Organometallics* **1982**, *1*, 1485. (b) Olah, G. A.; Laali, K.; Farooq, O. *Organomet. Chem.* **1984**, *3*, 1337.

(11) Commercially available from Petrarch Systems, Inc.

(12) (a) Bp 157 °C: Marans, N. S.; Sommer, L. H.; Whitmore, F. C. *J. Am. Chem. Soc.* **1951**, *73*, 5127. (b) $\delta^{29}Si$ −49 [ref to $(MeO)_4Si$]: Hunter, B. K.; Reeves, L. W. *Can. J. Chem.* **1968**, *46*, 1399.

(13) (a) Bp 141 °C: see ref 12a. Bp 135–137 °C: Damrauer, R.; Danahey, S. E. *Organometallics* **1986**, *5*, 1490. (b) $\delta^{29}Si$ −12.4 in neat liquid: Schrami, J.; Nguyen-Duc-Chuy; Chvalovsky, V. *J. Organomet. Chem.* **1973**, *51*, C5–C7. (c) J_{Si-F} 287: Nguyen-Duc-Chuy; Chvalovsky, V.; Schrami, J.; Magi, M.; Lippmaa, E. *Coll. Czech. Chem. Commun.* **1975**, *40*, 875.

(14) Bp 80–100 °C/15 Torr; ^1H NMR 0.48–1.77 (m), 0.18 (d): Tamao, K.; Kakui, T.; Akita, M.; Iwahara, T.; Kanatani, R.; Yoshida, J.; Kumada, M. *Tetrahedron Lett.* **1983**, *24*(6), 983.

Table 3. ^{1}H and ^{29}Si NMR Spectra[a] of Organofluorosilanes

organofluorosilane	δ^1H, ppm	δ^{29}Si, ppm (J_{Si-F}, Hz)	ref
Ph_3SiF	7.63 (m), 7.43 (t), 7.37 (t)	−3.43 (280)	11
Ph_2SiF_2	7.90 (m), 7.35 (t), 7.21 (t)	−28.50 (290)	12
$PhMeSiF_2$	7.73 (m), 7.59 (t), 7.50 (t), 0.65 (t)	−10.94 (289)	13
$Me(C_3H_5)SiF_2$	5.65–5.75 (m), 5.00 (d), 1.40–1.50 (m), 0.37 (t)	−0.98 (310)	this work
n-$C_8H_{17}SiMe_2F$	1.21 (m), 0.82 (t), 0.61 (t), 0.14 (d)	33.54 (283)	14
(n-$CH_2{=}CHC_6H_{12}$)$SiMe_2F$	5.64–5.72 (m), 4.79–4.89 (m), 1.25 (m), 1.11 (t), 0.53 (m), 0.09 (d)	33.35 (279)	this work
$CHMe_2CMe_2SiMe_2F$	1.60 (m), 0.87 (d), 0.85 (d), 0.17 (d)	35.03 (290)	this work
Ph_2-t-BuSiF	7.81 (d), 7.75 (d), 7.47 (m), 1.19 (d)	4.40 (290)	this work
Ph-t-$BuSiF_2$	7.80 (m), 7.75 (d), 7.47 (m), 1.16 (t)	−17.55 (313)	this work

[a] TMS internal reference; chromium–acac was used to enhance silicon relaxation.

Experimental Section

Alkali metal salts of perfluorinated complex anions (Aldrich) and organohalosilanes (Petrarch) were of reagent grade and were used as received. Tetraglyme was dried over sodium under reflux. Boiling points are uncorrected. NMR spectra were recorded on a 400-MHz Varian superconducting NMR spectrometer using TMS as internal standard.

General Procedure of Fluorination. To 3 g (12 mmol) diphenyldichlorosilane in a 50-mL round-bottom flask equipped with a condenser were added 26 mmol of sodium tetrafluoroborate and 5 g of tetraglyme, and the mixture was refluxed for 0.5–0.75 h. Distillation under vacuum afforded the diphenyldifluorosilane in near-quantitative yield. Fluorodechloridations of other silicon precursors with sodium tetrafluoroborate and other alkali metal salts were similarly carried out. The products were distilled either at atmospheric pressure or under reduced pressure as needed and characterized by ^{1}H and ^{29}Si NMR spectra and elemental analysis. Ph_3SiF, Ph_2SiF_2, and $PhMeSiF_2$ are known compounds.[11–13] Elemental analyses of other organofluorosilanes are as follows:

$Me(C_3H_5)SiF_2$. Anal. Calcd: C, 39.32; H, 6.60. Found: C, 38.56; H, 6.2.

(*n*-Octyl)$SiMe_2F$. Anal. Calcd: C, 63.09; H, 12.18. Found: C, 62.99; H, 12.11.

(*n*-Octenyl)$SiMe_2F$. Anal. Calcd: C, 63.76; H, 11.24. Found: C, 63.12; H, 11.30.

(Thexyl)Me_2SiF. Anal. Calcd: C, 59.19; H, 11.79. Found: C, 59.01; H, 11.50.

Ph_2-t-BuSiF: Anal. Calcd: C, 74.36; H, 7.41. Found: C, 73.92; H, 7.20.

Ph-t-$BuSiF_2$: Anal. Calcd: C, 59.96; H, 7.04. Found: C, 60.10; H, 6.92.