Organofluorosilicates in Organic Synthesis. 12.[1] Preparation of Organopentafluorosilicates and Their Cleavage Reactions by Halogens and *N*-Bromosuccinimide. Synthetic and Mechanistic Aspects

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Received July 29, 1981

This report describes synthetic and mechanistic aspects of a new method for the regio- and stereoselective transformation of olefins and acetylenes to the corresponding alkyl and alkenyl halides, respectively, via halogen or NBS cleavage of the carbon–silicon bond in organopentafluorosilicates derived from hydrosilylation products. Potassium organopentafluorosilicates ($K_2[RSiF_5]$) have been prepared from the corresponding organotrichlorosilanes which are readily obtained by the well-established highly regio- and stereoselective hydrosilylation of olefins and acetylenes with trichlorosilane catalyzed by chloroplatinic acid. Treatment of the organotrichlorosilanes with potassium fluoride in water or ethanol at 0 °C affords the silicates as white, air-stable powder. The organosilicates containing other alkali-metal countercations (Na, Rb, and Cs) have also been prepared by the reaction of the corresponding organotrifluorosilanes with NaF, RbF, and CsF, respectively. The silicates have been found to react with Cl_2, Br_2, I_2, IBr, and NBS under mild conditions to give the corresponding organic halides. In both the halogen and NBS cleavage reactions a halogen atom is regioselectively introduced onto the carbon to which the silicon atom has been attached. The present procedure provides a new general method for anti-Markownikoff hydrohalogenation of olefins. The NBS cleavage tolerates some functional groups such as the alkoxycarbonyl, oxo, halo, and alkenyl groups. The reaction of (*E*)-alkenylsilicates with NBS affords (*E*)-alkenyl bromides with high stereoselectivity, while stereoselectivity of the bromine cleavage is relatively low. Stereochemistry at the aliphatic carbon in the cleavage reaction of alkylsilicates has also been investigated. Reactions of *exo*- and *endo*-2-norbornylpentafluorosilicates with Br_2 and NBS proceed stereospecifically with predominant inversion of configuration. Partial stereochemical scrambling has been observed, however, in the reaction of the exo silicate with Br_2 in nonpolar solvents. On the basis of these experimental results, a mechanism involving the initial one-electron transfer has been proposed for the bromine cleavage reaction of alkylsilicates. The reaction of alkylsilicates with IBr giving both alkyl iodide and bromide also supports the proposed mechanism. The NBS cleavage of alkylsilicates and all reactions of alkenyl- and arylsilicates, however, seem to proceed by an electrophilic mechanism.

The last decade has seen considerable progress in applications of organosilicon compounds in organic synthesis: many new reactions have been discovered and many new techniques have been developed.[2] However, all these organosilicon compounds, with a few exceptions, have been restricted to ordinary tetracoordinate silicon derivatives. This paper is concerned with one of the intriguing aspects of organosilicon chemistry—the chemistry of hexacoordinate organosilicon compounds, particularly, the preparation and applications in organic synthesis of potassium organopentafluorosilicates, together with some of the results of mechanistic studies.

It is known that silicon can expand its valence shell by use of vacant d orbitals[3] and that several types of penta- and hexacoordinate silicon compounds are obtained in the presence of electronegative ligands which cause contraction of d orbitals.[4–6] Organopentafluorosilicates, $M_2[RSiF_5]$, have been known for some 20 years.[4] The first compounds of this class were prepared by Tansjoe in 1961, who treated phenyltriaminosilanes with water-free hydrogen fluoride in ether solution.[4a]

$$PhSi(NHR)_3 + 6HF \xrightarrow{\text{ether}} (RNH_3)_2[PhSiF_5] + RNH_3F$$

Since then several research groups have reported the synthesis, reactions, and structural studies based on spectroscopies, of organopentafluorosilicates.[4p,s,x,y,5] Especially, Mueller and collaborators had worked most ex-

(1) For part 11, see ref 7l.

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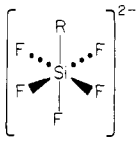
tensively during the period of 1963–1970 and disclosed much chemistry.[4c–o] Recently, the hexacoordination around the silicon atom in solution has been confirmed by ^{19}F NMR.[4s,y]



Because organopentafluorosilicates contain a doubly negatively charged, coordinatively saturated, hexacoordinate silicon atom, their reactivities are expected to be quite different from those of neutral, coordinatively unsaturated, tetracoordinate ordinary organosilicon compounds. IR studies also imply the higher reactivitiy of the silicates, where the force constant of the carbon–silicon bond in methylpentafluorosilicate $[CH_3SiF_5]^{2-}$ has been shown to be much smaller than that in tetracoordinate methyltrifluorosilane.[4p] In fact, some noteworthy examples of facile carbon–silicon bond cleavage reactions have been recorded in the literature. (1) A reaction of potassium methylpentafluorosilicate with bromine in water containing fluoride ions affords methyl bromide.[4i] (2) Ammonium methylpentafluorosilicate reacts with $NH_4F{\cdot}HF$ to give the protonolysis product methane.[4i] (3) Oxidation of ammonium or potassium methylpentafluorosilicate by $KMnO_4$ gives carbon dioxide together with a trace amount of methane.[4i] (4) Homo coupling products are obtained from vinyl- and perfluorovinylpentafluorosilicates (Na^+, K^+, or ammonium salts) by the action of $AgNO_3$ or $CuSO_4$.[4o] (5) The organic group is transferred to other metals such as silver,[4e,i] thallium,[4v,w] and antimony[4k] by treatment of the organosilicate with a salt of the corresponding metals.

In spite of these successful fundamental studies on preparation and reactions of organopentafluorosilicates, little attention had been paid to the synthetic applications of the organosilicates as useful and versatile intermediates until 1977 when we initiated systematic studies with this end in view.[7]

We were interested in the synthetically useful electrophilic cleavage reactions of the carbon–silicon, particularly the alkyl carbon–silicon, bond in organosilicon compounds. The addition of silicon hydrides to olefins and acetylenes has become one of the most important methods of forming silicon–carbon bonds.[8] However, the synthetic use of alkylsilanes thus obtained has been rather limited, while alkenylsilanes have recently been recognized as useful intermediates by many synthetic chemists.[2d] The major reason of this situation is that there has been virtually no method for transformation of the alkyl–silicon bonds into functional groups whereas the cleavage of the alkenyl–silicon bonds is quite easy. Tetraalkylsilanes are indeed cleaved by certain activated electrophiles such as H^+, RCO^+, R^+, or halonium ion, but there is no difference in selectivity between the alkyl group under consideration and other alkyl groups on silicon, being of little synthetic value.[9] Substitution of the alkyl groups by electronegative groups diminishes the reactivity of the remaining carbon–silicon bond toward electrophilic cleavage. For example, monoalkylsilicon compounds such as obtainable by hydrosilylation of olefins with trichlorosilane are inert to electrophilic reagents under usual conditions. We anticipated that an organopentafluorosilicate might solve this dilemma, because it contains only one organic group under consideration and an electron-rich alkyl group. Indeed, major part of our expectation has been realized, and several synthetically useful reactions have so far been developed.[7] We report herein the full details of the cleavage reactions of the carbon–silicon bond in organopentafluorosilicates by halogens and NBS providing a new synthetically useful route to organic halides from olefins and acetylenes.

$$\text{olefin or acetylene} \rightarrow RSiCl_3 \rightarrow K_2[RSiF_5] \rightarrow RX$$

Cleavage of the carbon–metal bonds in organometallics by halogens provides one of the unique and useful methods for preparation of organic halides.[10] Especially, the transformation involving hydrometalation of terminal olefins followed by halogenolysis leading to anti-Markownikoff alkyl halides has been successfully achieved by using organoboron,[11] organoaluminum,[12] and organozirconium compounds.[13] Our present development provides a useful alternative to the published procedures. The interest of the present reaction also stems from the expected unique feature of the reaction mechanisms due to the extracoordinate doubly negatively charged silicon atom. Investigation into this virgin field may contribute to the elucidation of the whole view of electrophilic cleavage of carbon–metal bonds.

(6) Other representative extracoordinate organosilicon compounds. $[RSi(-OC_6H_4O)_2]^-$: (a) Frye, C. L. *J. Am. Chem. Soc.* **1964**, *86*, 3170. (b) Boer, F. R.; Flynn, J. N.; Turley, J. W. *Ibid.* **1968**, *90*, 6973. $[RSi(-C_6H_4C(CF_3)_2O)_2]^-$: (c) Perozzi, E. F.; Martin, J. C. *Ibid.* **1979**, *101*, 1591. $[RSi(acac)_2]^+$: (d) Schott, F.; Golz, K. *Z. Anorg. Allg. Chem.* **1973**, *399*, 7. $[RSi(OCH_2CH_2)_3N]$: (e) For example, Vornokov, M. G. *Pure Appl. Chem.* **1966**, *13*, 35. (f) Voronkov, M. G. *Top. Curr. Chem.* **1979**, *84*, 77. $[RXSi(bpy)_2]^{2+}$: (g) Kummer, D.; Geisser, K. E.; Seshadri, T. *Chem. Ber.* **1977**, *110*, 1950. [PcSiRX] (Pc = phthalocyaninato): (h) Esposito, J. N.; Lloyd, J. E.; Kenney, M. E. *Inorg. Chem.* **1966**, *5*, 1979. (i) Pommier, J. C. *Rev. Silicon, Germanium, Tin, Lead Compd.* **1979**, *4*, 91. (j) Tamao, K.; Akita, M.; Kumada, M., unpublished results, 1979.

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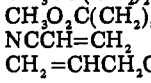
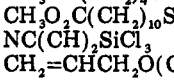
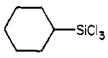
Table I. Preparation of Alkylpentafluorosilicates via Hydrosilylation of Olefins

olefin	hydrosilylation[a] conditns	product	yield, %	silicate formation[b] yield, %
n-$C_6H_{13}CH{=}CH_2$	rt,[c] 3 h	n-$C_8H_{17}SiCl_3$	86	98
n-C_8H_{16}[d]	140 °C, 9 h	n-$C_8H_{17}SiCl_3$[e]	82	98
t-$C_4H_9CH{=}CH_2$	rt,[c] 12 h	t-$C_4H_9CH_2CH_2SiCl_3$	71	64
n-$C_{10}H_{21}CH{=}CH_2$	60-70 °C, 6.5 h	n-$C_{12}H_{25}SiCl_3$	73	78
n-$C_{16}H_{33}CH{=}CH_2$	50-60 °C, 5 h	n-$C_{18}H_{37}SiCl_3$	90	91[f]
$PhCH{=}CH_2$	reflux, 3 h[g]	$PhCH_2CH_2SiCl_3$	92	96
	rt,[c] 22 h		88	73
$Br(CH_2)_9CH{=}CH_2$	50 °C, 11 h	$Br(CH_2)_{11}SiCl_3$	77	72
$CH_3CO(CH_2)_2CH{=}CH_2$	50-60 °C, 4 h	$CH_3CO(CH_2)_4SiCl_3$	85	87
$CH_3O_2C(CH_2)_8CH{=}CH_2$	60 °C, 7 h	$CH_3O_2C(CH_2)_{10}SiCl_3$	91	91
$NCCH{=}CH_2$	100 °C, 5 h[h]	$NC(CH)_2SiCl_3$	54	100
$CH_2{=}CHCH_2OCH_2CH{=}CH_2$	reflux, 2 h[i]	$CH_2{=}CHCH_2O(CH_2)_3SiCl_3$	28	81
	100 °C, 20 h[j]		78	76

[a] Hydrosilylation of olefins was carried out with excess (1.2-2.0 parts) trichlorosilane in the presence of chloroplatinic acid unless otherwise stated. [b] Alkyltrichlorosilane was added dropwise to excess (25 parts) aqueous KF at 0 °C. [c] rt = room temperature. An exothermic reaction took place when trichlorosilane was added to a mixture of the olefins and the catalyst. After it ceased, the reaction mixture was stirred at room temperature. [d] A mixture of terminal and internal olefins. [e] Only the terminal adduct was obtained. [f] The alkyltrichlorosilane was treated with KF in ethanol. [g] Hydrosilylation was carried out in THF. [h] Hydrosilylation was carried out in the presence of pyridine catalyst. [i] One equivalent of trichlorosilane was used. [j] The reaction was carried out in a sealed tube.

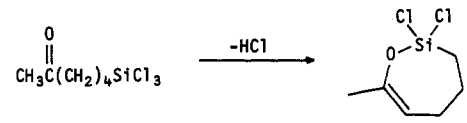
Results and Discussion

Preparation of Organopentafluorosilicates via Hydrosilylation of Olefins and Acetylenes. Various methods have been reported for the preparation of potassium organopentafluorosilicates from tetracoordinate organofluoro-, organochloro-, and organoalkoxysilanes.[4] Among these precursors organotrichlorosilanes may be the most practical from the synthetic viewpoint since a variety of organotrichlorosilanes can be directly prepared by hydrosilylation of olefins and acetylenes (Scheme I).

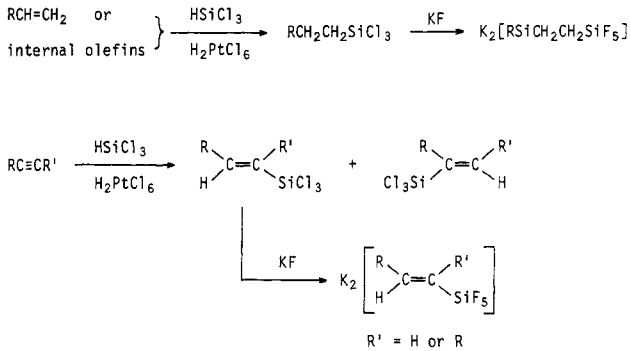
We will make a brief mention of the hydrosilylation relevant to our present study at first and then describe the preparation of organopentafluorosilicates. Hereafter, unless otherwise stated, the word "organopentafluorosilicates" refers to the "potassium" salts.

Hydrosilylation of Olefins and Acetylenes. Many types of catalysts such as transition-metal compounds and radical initiators have been developed.[8] Of these catalysts, chloroplatinic acid (Speier's catalyst) is best established, is widely used, and is most convenient.[8d] The hydrosilylation of terminal olefins with trichlorosilane in the presence of H_2PtCl_6 proceeds regioselectively to give exclusively the terminal adducts. Internal olefins are less reactive than terminal ones, and hence selective monohydrosilylation can be achieved on polyenes which contain both terminal and internal double bonds, as exemplified by 4-vinylcyclohexene. Under rather drastic conditions internal olefins are also hydrosilylated with isomerization of the double bond to give terminal adducts. The hydrosilylation with trichlorosilane is compatible with various functional groups such as alkoxycarbonyl, oxo,[14] cyano, halo, ether, and alkenyl groups. Advantages also reside in that the hydrosilylation is usually conducted in the absence of solvent. Experimental results for these transformations are summarized in Table I.

(14) The hydrosilylation product of 1-hexen-5-one tends to undergo the thermal intramolecular condensation to form a cyclic enol silyl ether.



Scheme I



For hydrosilylation of acetylenes, regio- and stereoselectivity problems arise additionally. In the presence of H_2PtCl_6 as a catalyst a monoadduct is usually formed as a sole product. Although the stereochemistry is exclusively cis addition, two regioisomers are usually formed from terminal acetylenes. The terminal adducts are the major products, but a terminal/internal ratio depends upon the reaction conditions as well as the structure of the acetylenes. While *tert*-butylacetylene and phenylacetylene give only the terminal adducts, 1-hexyne, as a representative example of simple acetylenes, at the reflux temperature forms the two regioisomers in the ratio of ca. 82/18.[15]

Recently we have observed that the regioselectivity is remarkably improved up to 95/5 by using a preactivated catalyst which is prepared by refluxing a mixture of chloroplatinic acid as a catalyst precursor and small amounts of two reactants, 1-hexyne and trichlorosilane.[16] Fortunately the terminal adducts (*E*)-alkenyltrichlorosilanes are readily separated from their internal isomers by fractional distillation. Hydrosilylation of internal acetylenes proceeds without isomerization of the triple

(15) Cf., Miller, R.; McGarvey, G. *J. Org. Chem.* 1978, *43*, 4424.

(16) This procedure is based on the observation made by Dr. K. Nakagawa of our laboratories, who found that the distillation residue of the traditional H_2PtCl_6-catalyzed hydrosilylation was an effective catalyst for the highly regioselective hydrosilylation of terminal acetylenes.

(17) Mueller et al. have noted the formation of $(NH_4)_2[C_3H_7SiF_5]$ in an impure state from allyltrifluorosilane and aqueous NH_4F.[3i]

Table II. Preparation of Alkenylpentafluorosilicates via Hydrosilylation of Acetylenes

acetylene	hydrosilylation[a] conditns	product	terminal, %	yield, %	silicate formation[b] yield, %
n-$C_4H_9C{\equiv}CH$	2 °C or rt,[c] 15 h	n-C_4H_9 / $SiCl_3$	95[d]	75	94
t-$C_4H_9C{\equiv}CH$	rt,[e] 12 h	t-C_4H_9 / $SiCl_3$	100[f]	72	80
n-$C_6H_{13}C{\equiv}CH$	80 °C, 20 h	n-C_6H_{13} / $SiCl_3$	86[d]	92	90
n-$C_{16}H_{33}C{\equiv}CH$	rt,[e] 48 h	n-$C_{16}H_{33}$ / $SiCl_3$	100[f]	83	45[g]
$CH_3O_2C(CH_2)_8C{\equiv}CH$	rt,[e] 20 h	$CH_3O_2C(CH_2)_8$ / $SiCl_3$	87[d]	93	88
$CH_3OCH_2C{\equiv}CH$	55 °C, 8 h	CH_3OCH_2 / $SiCl_3$	78[d]	85	94
$NC(CH_2)_2OCH_2C{\equiv}CH$	rt,[e] 20 h	$NC(CH_2)_2OCH_2$ / $SiCl_3$	87[d]	93	73
$PhC{\equiv}CH$	rt, 20 h	Ph / $SiCl_3$	100[f]	88	100[g]
n-$C_4H_9C{\equiv}CC_4H_9$-n	100 °C, 24 h[h]	n-C_4H_9, C_4H_9-n, $SiCl_3$		90	93
n-$C_6H_{13}C{\equiv}CC_6H_{13}$-$n$	100 °C, 43 h	n-C_6H_{13}, C_6H_{13}-n, $SiCl_3$		89	55[i]

[a] Hydrosilylation of acetylenes was carried out with excess (1.2–2.0 parts) trichlorosilane in the presence of chloroplatinic acid. [b] The alkenyltrichlorosilane was added dropwise to excess (25 parts) aqueous KF at 0 °C unless otherwise stated. [c] rt = room temperature. A preactivated catalyst was used (see text). [d] Determined by GLC. [e] An exothermic reaction took place when trichlorosilane was added to a mixture of the acetylene and the catalyst. After it ceased, the reaction mixture was stirred at room temperature. [f] GLC analysis and ^1H NMR spectrum of the product showed that only the terminal adduct was formed. [g] The alkenyltrichlorosilane was treated with KF in ethanol. [h] In a sealed tube. [i] The alkenyltrichlorosilane was treated with KF in ethanol-water (1:1).

bond to give the internal (*E*)-alkenyltrichlorosilanes. Experimental results for these transformations are summarized in Table II.

Preparation of Organopentafluorosilicates. Although Mueller had described briefly the direct preparation of ammonium methylpentafluorosilicate from the corresponding methyltrichlorosilane,[4i] we examined the most convenient and reproducible procedure from the synthetic point of view. Most of potassium organopentafluorosilicates could be prepared by the simple dropwise addition of an organotrichlorosilane (1 mol) to a solution of potassium fluoride (25 mol) in water (1.5 times the weight of KF, almost a saturated solution) at 0 °C with vigorous stirring. The silicate which precipiated as white powder was separated by filtration.

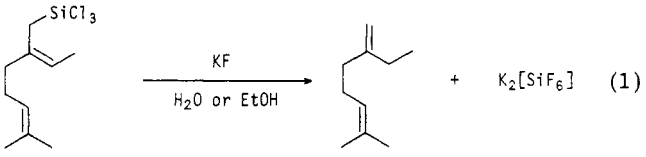
$$\underset{1:25}{RSiCl_3 + KF} \xrightarrow[\text{0 °C–room temp}]{H_2O} K_2[RSiF_5]$$

For styryltrichlorosilanes and long-chain alkyl- and alkenyltrichlorosilanes such as *n*-octadecyl-, 1-octadecenyl-, and 7-tetradecenyltrichlorosilanes, this procedure seemed to be less suitable, the silicates being contaminated with substantial amounts of siloxanes (by IR). Switching the reaction medium from water to ethanol afforded satisfactory results for these substrates. Yields of the silicates are given in Tables I and II.

Potassium organopentafluorosilicates thus obtained are all white, air-stable powder. While alkylsilicates can be stored almost indefinitely (longer than 2 years) in a closed polyethylene bottle at room temperature without any noticeable change (IR and reactivity), alkenylsilicates tend to decompose slowly at room temperature and can best be stored in a refrigerator. They exhibit intense IR absorptions in the 400–800-cm^{-1} region which are assigned to Si–F stretching.[4p]

Since they are practially insoluble in water and common organic solvents, purification of organopentafluorosilicates was quite difficult and some of them did not show satisfactory elemental analyses. They were used in further reactions directly as obtained.

Allylic trichlorosilanes gave no organosilicates under similar conditions but only the carbon–silicon bond cleavage product and hexafluorosilicate.[17] The cleavage reaction was accompanied by the allylic transposition, as exemplified by the conversion shown in eq 1.



(1)

Several types of organopentafluorosilicates containing other countercations have been known.[2] Since it was expected that their reactivity would depend upon the nature of the countercation, we prepared octylpentafluorosilicates containing other alkali-metal countercations by the reaction of octyltrifluorosilane with NaF, RbF, and CsF in acetonitrile. $Na_2[C_8H_{17}SiF_5]$ was obtained as white powder which was insoluble in water and common organic solvents (75% yield). Its elemental analysis was not satisfactory because of contamination of some impurities, the removal of which was quite difficult due to insolubility of the silicate. $Rb_2[C_8H_{17}SiF_5]$ (87% yield) and $Cs_2[C_8H_{17}SiF_5]$ (85% yield) were also obtained as white powder. Both of them were slightly souble in ethanol. They could be recrystallized from hot ethanol and satisfactory elemental analyses were obtained. These three octyl silicates showed similar characteristic IR absorptions at 400–800 cm^{-1} as their potassium analogues. Octylpentafluorosilicates containing lithium and alkali earth metals such as calcium and barium could not be prepared in a similar fashion.

UV Spectra of Organopentafluorosilicates. In order to get information about the bonding character of hexacoordinate organopentafluorosilicates, we have measured UV spectra of several representative compounds in a solid state (Nujol mull). The results are reproduced in Figure

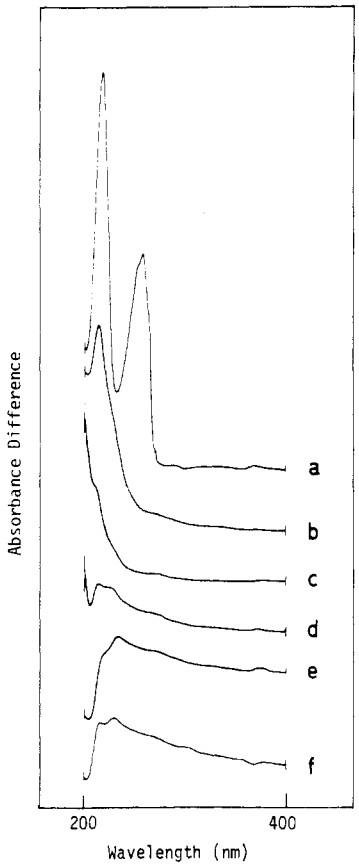


Figure 1. Ultraviolet spectra of (a) $K_2[PhSiF_5]$, (b) $K_2[C_4H_9C{-}H{=}CHSiF_5]$, (c) $K_2[cyclo{-}C_6H_{11}SiF_5]$, (d) $K_2[n{-}C_8H_{17}SiF_5]$, (e) $K_2[MeSiF_5]$, and (f) $K_2[SiF_6]$ in a solid state (Nujol mull).

Table III. UV Spectral Data of $K_2[RSiF_5]$, $RSiF_3$, and $RSiMe_3$

R	λ_{max}, nm (ϵ)		
	$K_2[RSiF_5]$[a]	$RSiF_3$[b]	$RSiMe_3$
Ph-	215[c]	208 (7.4×10^3)[d]	211 (1.03×10^4)[e]
	256	264 (8.3×10^2)	260 (3×10^2)
C_4H_9	211[c]	<200	<200[b]

[a] Solid state (Nujol mull). [b] In cyclohexane. [c] Intensities are not known. [d] Lit. data 210.0 and 263.5 nm: Veszpremi, T.; Reffy, J.; Nagy, J. *Kem. Kozl.* **1976**, *46*, 418; private communication from Professor T. Veszpremi. [e] In ethanol: Nagy, J.; Reffy, J.; Kuszmann-Borbely, A.; Becker, K. P. *J. Organomet. Chem.* **1967**, *7*, 393.

1. While the intensities of absorptions could not be determined, the absorption maxima are reliable. It seems to be interesting to compare the UV data of the phenyl- and hexenylsilicates with those of the corresponding trifulorosilyl and trimethylsilyl counterparts[18] (Table III). For the phenyl series the silicate exhibits an appreciable red shift of the primary band in comparison with the tetracoordinate compounds. A simple comparison of the benzenoid fine-structure band should be avoided owing to the difference of the state. It is also worth noting that hexenylsilicate has an absorption maximum at 211 nm, making a sharp contrast with the trifluorosilyl and trimethylsilyl derivatives which show no absorption maxima above 200 nm. Alkylsilicates and inorganic hexafluorosilicate show similar spectral behavior, but it seems questionable whether the observed rather peculiar absorptions are significant or not. The most significant feature of the UV data is that while there seems to be a tendency that substitution of the methyl groups on silicon by electronegative fluorine atoms ($RSiF_3$ vs. $RSiMe_3$) causes a shift to shorter wavelength,[19] introduction of further fluorine atoms ($RSiF_5^{2-}$) leads conversely to a red shift.

(18) Ramsey, B. G. "Electronic Transitions in Organometalloids"; Academic Press: New York, 1969; Chapter IV, p 65.

Table IV. CNDO/S Calculation Data on $PhSiMe_3$, $PhSiF_3$, and $Na_2[PhSiF_5]$[a]

	$PhSiMe_3$	$PhSiF_3$	$Na_2[PhSiF_5]$
first three IP's (eV)	9.746 (π_3)	10.094 (π_3)	7.707 (π_3)
	9.873 (π_2)	10.248 (π_2)	8.154 (π_2)
	11.469 (Si-C(ar))	12.298 (Si-C)	8.290 (Si-C)
UV absorptions above 200 nm (nm)	209	205	208
	259	255	257
bond order of the Si-C bond	1.039	1.042	0.914

[a] Carried out by Professor T. Veszpremi, private communication. The calculation includes d orbitals.

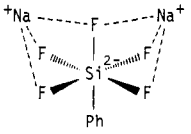
Recently, Veszpremi carried out the MO calculation (modified CNDO/S)[20] on phenylsilicon compounds including $PhSiMe_3$, $PhSiF_3$, and $Na_2[PhSiF_5]$.[21] Table IV lists the calculated first three ionization potentials, UV absorption maxima (>200 nm), and bond order of the silicon–C(ar) σ bond. Only the results on the calculation with d orbitals are listed, but the calculation without d orbitals shows quite similar results except for the silicate, the results for which will be briefly mentioned below. There are several remarkable features. (1) The ionization potentials decrease in the order $PhSiF_3 > PhSiMe_3 \gg Na_2[PhSiF_5]$. (2) The most striking feature is that in the phenylsilicate the ionization potential of the Si–C σ bond is comparable with those of the phenyl π electrons, while in $PhSiMe_3$ and $PhSiF_3$ the σ-bonding energy level lies much lower than the aromatic π levels. This correlation may be visualized in Figure 2. Interestingly, the calculation without d orbitals for the silicate shows that the ionization potential assignable to the Si–C σ bond (7.006 eV) is lower than π_3 (7.238 eV) and π_2 (7.791 eV). (3) The bond order of the Si–C σ bond in the silicate becomes considerably lower than those in the tetracoordinate silicon compounds. (4) The calculated UV absorption maxima agree with the experimental data shown in Table III.

It seems to be most informative to compare the data on $PhSiF_3$ and the corresponding silicate. Thus, the coordination of extra two fluoride ions to $PhSiF_3$ lowers the

(19) Cf. Petukhov, V. A.; Mironov, V. F.; Kravchenko, A. L. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1966**, 156.

(20) Bene, J. E.; Jaffe, H. H. *J. Chem. Phys.* **1968**, *48*, 1807.

(21) Veszpremi, T., unpublished results (private communication). The calculation assumes the following octahedral geometry for the silicate



The Si–F bond distance 1.676 Å is based on the published data on the crystal structures of hexafluorosilicates.[22] The Na–F distance of 2.36 Å is estimated to be the summation of the ionic radii of Na^+ and F^-. Since the calculated ionization potentials for $PhSiMe_3$ and $PhSiF_3$ are in good agreement with the experimental data, it is reasonable to suppose that the present calculation gives good estimation also for the phenylsilicate.

(22) Cu^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+} salts: (a) Ray, S.; Zalkin, A.; Templeton, D. H. *Acta Crystallogr., Sect. B* **1973**, B29, 2741, 2748. Ammonium salt: (b) Hanic, F. *Chem. Zvesti* **1966**, *20*, 738; *Chem. Abstr.* **1967**, *66*, 89253.

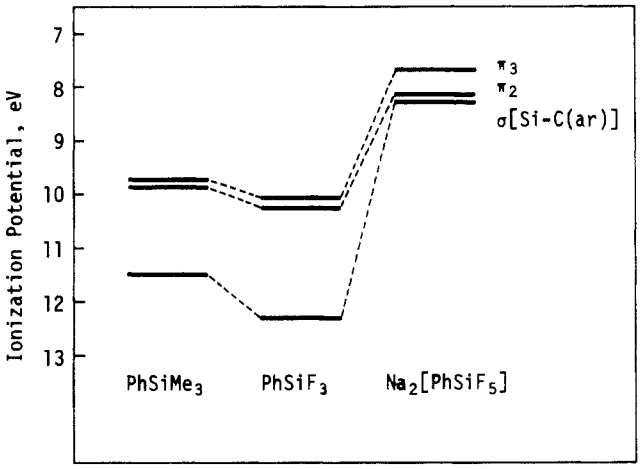


Figure 2. A schematic energy-level diagram for the calculated first three ionization potentials.

Si–C σ bond order and raises extremely the Si–C σ bond energy level up to the levels comparable to the aromatic π-bonding levels. These unique bonding characteristics of organopentafluorosilicates may be responsible for their susceptibility toward various electrophilic or oxidizing agents. It seems interesting to note here that the low ionization potential is comparable with 8.76 eV (by photoelectron spectroscopy)[23] of the silicon–silicon bond which has been well-known to be cleaved by various oxidizing agents including halogen and NBS.[24]

Reaction of Organopentafluorosilicates with Halogens and Interhalogen. Alkylpentafluorosilicates have been found to react exothermically with halogens such as chlorine, bromine, and iodine in carbon tetrachloride to give the corresponding alkyl halides in good yields.

$$K_2[RSiF_5] \xrightarrow{X_2} R\text{-}X \ (X = Cl, Br, I)$$

The results are summarized in Table V. While Mueller observed brominolysis of methylpentafluorosilicate in water containing extra fluoride ions,[4i] our findings revealed that extra fluorides are not requisite for the halogenolysis of organopentafluorosilicates.

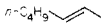
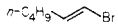
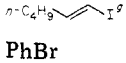
The reaction occurred heterogeneously, and the insoluble residue was easily separated by filtration. The IR spectrum of the residue showed only two intense absorptions at 735 and 475 cm^{-1} diagnostic of a hexafluorosilicate, SiF_6^{2-}, salt.[4p]

While the reaction of the primary alkylsilicates proceeded even at 0 °C, the reaction of the secondary alkylsilicates was rather slow and required higher temperatures, indicating that the present halogen-cleavage reaction is subject to the steric hindrance around the carbon. Iodine was less reactive than bromine and chlorine. For example, the reaction of cyclohexylpentafluorosilicate with iodine proceeded appreciably only around 50 °C.

The alkenyl- and arylpentafluorosilicates were also found to react with halogens to give the corresponding organic halides. The halogen atom was regioselectively introduced onto the carbon to which the silicon atom had been attached. Stereoselectivity of the reaction of alkenylsilicates with bromine was not satisfactory. For example, the reaction of (*E*)-1-hexenylpentafluorosilicate with bromine gave both (*E*)- and (*Z*)-1-hexenyl bromides in the ratio of 67/33, while the reaction with iodine gave (*E*)-1-hexenyl iodide almost exclusively.

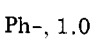
(23) Bock, H.; Ensslin, W. *Angew. Chem.* **1971**, *83*, 435.
(24) Kumada, M.; Tamao, K. *Adv. Organomet. Chem.* **1968**, *6*, 19.

Table V. Reaction of Organopentafluorosilicates with Halogens[a]

R in $K_2[RSiF_5]$	halogen	product	yield,[b] %
n-C_8H_{17}-	Cl_2	n-$C_8H_{17}Cl$	73
	Br_2	n-$C_8H_{17}Br$	69
	I_2	n-$C_8H_{17}I$	73
t-$C_4H_9CH_2CH_2$-	Br_2	t-$C_4H_9CH_2CH_2Br$	(74)[c]
	Cl_2		(47), (54)[d]
	Br_2		(67), (63)[d]
	I_2		(5),[d] (32)[e]
	Br_2	 (67% *E*)[f]	(61)
	I_2	 [g]	(48)
Ph-	Br_2	PhBr	(59)

[a] The reactions were carried out on a 5-mmol scale for isolation of the product and on a 1-mmol scale for GLC determination of yields. Halogen in CCl_4 was added dropwise to a mixture of a $K_2[RSiF_5]$ and CCl_4 at 0 °C. After the addition was completed, the mixture was stirred for 2 h at room temperature unless otherwise stated. [b] Isolated yields. Yields determined by GLC analysis are given in parentheses. [c] Stirred at room temperature for 9 h. [d] Carried out at 35 °C for 1 h. [e] Carried out at 50 °C for 1 h. [f] Determined by GLC. [g] (*Z*) isomer was not detected.

Table VI. Reaction of Organopentafluorosilicates with Iodine Monobromide

R in $K_2[RSiF_5]$, mmol	IBr, mmol	temp, °C	time, min	product yield,[b] % R-I	R-Br
n-C_8H_{17}-, 2.0	1.1	0	30	63	6
1.9	0.99[c]	0	10	68	7
1.0	1.0	20	120	17	27
 , 0.97	0.70	20	120	90	3
Ph-, 1.0	0.37	20	30	83	0

[a] Because iodine monobromide was contaminated by chlorine, a small amount of R-Cl was formed as a byproduct. [b] Yields were based on IBr and determined by GLC analysis. [c] I_2 (0.10 mmol) was added in order to remove free Br_2 in IBr.

Organopentafluorosilicates have been found to react with iodine monobromide (Table VI).

$$K_2[RSiF_5] + IBr \rightarrow RI + RBr$$

The distribution of the products may provide important information about the mechanism of the halogenolysis of organopentafluorosilicates (vide infra). The reaction of the octylsilicate with IBr in carbon tetrachloride gave both octyl iodide and octyl bromide in 63–68 and 6–7% yields, respectively. The cyclohexylsilicate gave cyclohexyl iodide and cyclohexyl bromide in comparable amounts, but the formation of organic bromides was greatly retarded with silicates containing an sp^2 carbon–silicon bond. The reaction of the 1-hexenylsilicate with IBr gave 1-hexenyl iodide almost exclusively, and only iodobenzene was obtained in the reaction of the phenylsilicate.

Reaction of organopentafluorosilicates with NBS. Organopentafluorosilicates were also found to undergo a rapid, usually exothermic reaction with *N*-bromosuccinimide (NBS) to give the corresponding organic bromides in high yields. The bromine atom was regioselectively

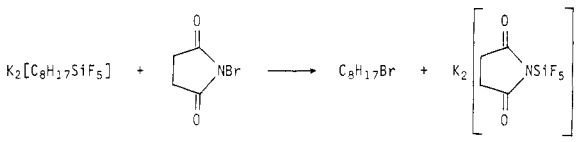
introduced onto the carbon to which the silicon atom had been attached. This reaction provides the frst case of the carbon–silicon bond cleavage reaction by NBS.

$$M_2[RSiF_5] + NBS \rightarrow RBr$$

Reactions of octylpentafluorosilicates containing four different alkali-metal countercations were examined. The results are summarized in Table VII. Although the reactions of $K_2[C_8H_{17}SiF_5]$, $Rb_2[C_8H_{17}SiF_5]$, and $Cs_2[C_8H_{17}SiF_5]$ with NBS proceeded smoothly to give octyl bromide in excellent yields, the reaction of $Na_2[C_8H_{17}SiF_5]$ was much slower and the yield was very low. The results, however, do not necessarily reflect the difference in reactivity of the carbon–silicon bond due to the countercation because there is a possibility that impurities in the sodium salt might have retarded the reaction.

The reactivities of the Rb and Cs derivatives were found to be comparable with the reactivity of $K_2[RSiF_5]$, but the use of the latter may be the most practical from the synthetic viewpoint, because they are most readily obtainable and KF is available at relatively low cost in comparison with RbF and CsF.

The stoichiometry of the NBS cleavage reaction may be written as shown in eq 2, based on the deuterium exper-



(2)

iments. Thus, the reaction between the octylsilicate and NBS in dry THF under nitrogen gave, together with octyl bromide, yellow insoluble precipitates which showed infrared absorptions at 1690 (C=O) and 800–670 cm^{-1} (fluorosilicates). The precipiates formed succinimide (IR 3150–3050, 1690 cm^{-1}) upon treatment with ethanol and *N*-deuteriosuccinimide (IR 2300, 1690 cm^{-1}) upon treatment with MeOD. The results are consistent with the formation of a succinimidyl–silicon species in the above reaction. Anyway, such a silicon moiety as well as the starting organosilicate is insoluble in the reaction medium, and hence the desired organic product can be readily separated by filtration. This provides one of the advantages of reactions of organopentafluorosilicates.

A wide-spread applicability of the present cleavage reaction is apparent from the data on various alkylsilicates and alkenylsilicates, summarized in Tables VIII and IX, respectively. The nature of the reaction medium did not significantly affect the yield, at least in the reaction of primary alkylsilicates, although aliphatic hydrocarbon and alcoholic solvents seemed to be less favorable. In contrast, methanol was the most suitable for the secondary alkylsilicates. The high yields of primary alkyl halides should particularly be noted, because this procedure provides a new convenient route to anti-Markownikoff hydrohalogenation of olefins under neutral conditions.[25] Rather low yields of alkyl bromides from (3,3-dimethylbutyl)silicate (t-$C_4H_9CH_2CH_2SiF_5^{2-}$), even at 60 °C for 8 h, and from the secondary alkylsilicates indicate that the reaction with NBS is also subject to the steric hindrance around the reacting carbon. Another significant feature the present reaction is that it is compatible with various functional groups such as alkoxycarbonyl, oxo, halo, and alkenyl groups. Therefore the transformation involving

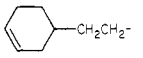
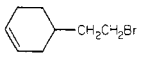
(25) Halogenolysis of organoboranes requires strongly basic conditions.[11] Procedures using other oganometallic compounds suffer from the rather limited functional group compatibility.

Table VII. Reaction of $M_2[C_8H_{17}SiF_5]$ with NBS[a]

M in $M_2[C_8H_{17}SiF_5]$	yield of $C_8H_{17}Br$,[b] %
Na[c]	31[d]
K	99
Rb	96
Cs	93

[a] $M_2[C_8H_{17}SiF_5]$ (1.0 mmol) was allowed to react with 1.1 mmol of NBS in 5.0 mL of benzene at room temperature for 2 h. [b] The yields were determined by GLC. [c] Purity of the silicate was not satisfactory. See the text for details. [d] The reaction was very slow, and after 160 h $C_8H_{17}Br$ was obtained in 66% yield.

Table VIII. Reaction of Alkylpentafluorosilicates with NBS[a]

R in $K_2[RSiF_5]$	solvent	time, h	product	yield,[b] %
n-C_8H_{17}-	C_6H_6	2	n-$C_8H_{17}Br$	77 (99)
	CCl_4	2		(99)
	THF	2		(98)
	Et_2O	2		(91)
	n-hexane	2		(78)
	MeOH	2		(72)
n-$C_{12}H_{25}$-	C_6H_6	2	n-$C_{12}H_{25}Br$	75
	C_6H_6	2		54
t-$C_4H_9CH_2CH_2$-	CCl_4	8[c]	t-$C_4H_4CH_2CH_2Br$	(46)
$PhCH_2CH_2$-	C_6H_6	2	$PhCH_2CH_2Br$	(60)
$MeO_2C(CH_2)_{10}$-	C_6H_6	2	$MeO_2C(CH_2)_{10}Br$	86
$Br(CH_2)_{11}$-	C_6H_6	2	$Br(CH_2)_{11}Br$	92
$CH_3CO(CH_2)_4$-	C_6H_6	28	$CH_3CO(CH_2)_4Br$	(73)
	THF	2		37
	MeOH	9		(79)

[a] The reactions were carried out on a 5-mmol scale for isolation of the product and on a 1-mmol scale for GLC determination of the yields using 1.1 equiv of NBS at room temperature. [b] Isolated yield based on the alkylsilicates. Yields determined by GLC analysis are given in parentheses. [c] Carried out at 60 °C. No reaction was observed at room temperature.

the present reaction can be applied to various types of compounds containing these functional groups.

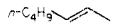
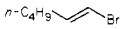
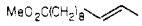
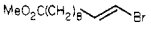
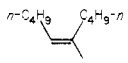
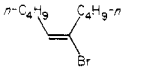
Stereoselectivity of the reaction of alkenylsilicates with NBS was higher than that with bromine. For example, the reaction of (*E*)-1-hexenylsilicate with NBS gave 1-hexenyl bromide in the ratio of E/Z = 79–91/21–9, depending upon the nature of the reaction medium. In the reaction of the (*E*)-5-decenylsilicate, an example of the internal alkenylsilicate, (*E*)-5-bromo-5-decene was obtained with high stereoselectivity (>99% *E*). The predominant to complete retention of configuration of the double bond in the present transformation seems to be interesting because inversion has been the main stereochemical course of the so far developed preparation of alkenyl bromides from alkenyltrimethylsilanes by bromine cleavage.[15,26]

Synthetic Utility. Although there have been reported several synthetic procedures for the transformation to organic halides by means of hydrometalation of olefins[10–12] or acetylenes[27] such as hydroboration, hydroalumination,

(26) (a) Chan, T. H.; Lau, P. W. K.; Mychajlowskij, W. *Tetrahedron Lett.* **1977**, 3317. (b) Jarvie, A. W. P.; Holt, A.; Thompson, J. *J. Chem. Soc. B* **1969**, 852.

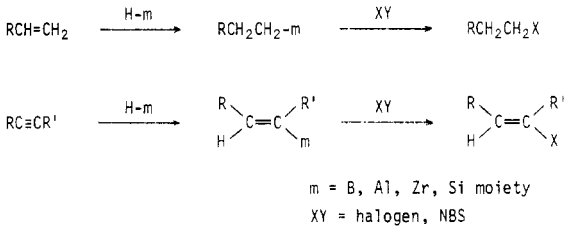
(27) Hydroboration: (a) Brown, H. C.; Hamaoka, T.; Ravindran, N. *J. Am. Chem. Soc.* **1973**, *95*, 5786. (b) Brown, H. C.; Hamaoka, T.; Ravindran, N. *Ibid.* **1973**, *95*, 6456. Hydroalumination: (c) Zweifel, G.; Whitney, C. C. *Ibid.* **1967**, *89*, 2753. (d) Zweifel, G.; Steele, R. B. *Ibid.* **1967**, *89*, 5085. Hydrozirconation: (e) Hart, D. W.; Blackburn, T. F.; Schwartz, J. *Ibid.* **1975**, *97*, 679.

Table IX. Reaction of Alkenyl- and Arylpentafluorosilicates with NBS[a]

R in $K_2[RSiF_5]$	solvent	time, h	product	E/Z[b]	yield,[c] %
	C_6H_6	4		91/9	(75)
	THF	4		79/21	(80)
	MeOH	4		83/17	(73)
	MeOH	24		100/0	(83)
	C_6H_6	2		>95/<5[d]	68
	C_6H_6	2		>99/<1	(70)
Ph-	MeOH	10	PhBr		(74)

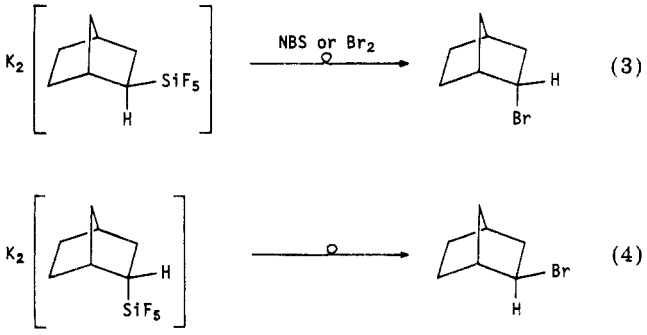
[a] The reactions were carried out on a 5-mmol scale for isolation of the product and on a 1-mmol scale for determination of the yields using 1.1 equiv of NBS at room temperature. [b] Determined by GLC analysis. [c] Isolated yield based on the organosilicate. Yields determined by GLC analysis are given in parentheses. [d] The Z isomer was not detected by ^1H NMR.

and hydrozirconation, the following features and advantages may prove that the transformation via organopentafluorosilicates is an attractive alternative to these published procedures. (1) Regio and stereoselectivity of

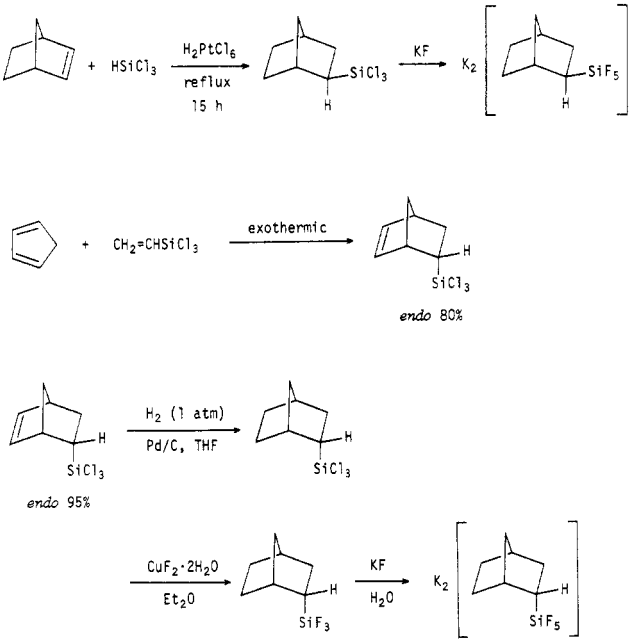


the hydrosilylation have been well established. (2) Various kinds of catalysts exhibiting different selectivities for the hydrosilylation have been discovered.[28] (3) A ready accessibility of less expensive, air-stable trichlorosilane allows a large scale preparation, in comparison with similar conversions using organoboron, -aluminum or -zirconium compounds. (4) In contrast to air-sensitive organoboron or -aluminum analogues, organopentafluorosilicates are air-stable and hence no special precaution in handling is necessary. (5) Reactions with organopentafluorosilicates proceed under mild neutral conditions and give high yields of products with wide functional group compatibility and high regio- and stereoselectivity. (6) Fluorosilicates, either the starting material or the reaction byproduct, mostly hexafluorosilicate, are almost insoluble in common organic solvents. Therefore, the desired organic product can be separated by simple filtration only.

Stereochemistry at Aliphatic Carbon in the Cleavage of the Carbon–Silicon Bond by Bromine and NBS. Not only to elucidate mechanism but also to get the basis for new methods of controlling stereochemistry in organic synthesis using organosilicates, we have examined the stereochemistry at carbon in the reactions of *exo*- and *endo*-2-norbornylpentafluorosilicates with bromine and NBS. Both reactions (eq 3 and 4) were found to



Scheme II



proceed stereospecifically with predominant inversion of configuration. This is the first stereochemical aspect at carbon in electrophilic intermolecular cleavage of aliphatic carbon–silicon bonds.[29]

exo- and *endo*-2-norbornylpentafluorosilicates were prepared as shown in Scheme II. *exo*-2-Norbornyltrichlorosilane was prepared by the stereoselective hydrosilylation of norbornene with trichlorosilane catalyzed by chloroplatinic acid.[30] The silicate formation could be achieved in the usual manner by treatment with aqueous KF. *endo*-2-Norbornyltrichlorosilane (endo 95%) was prepared by the palladium-charcoal-catalyzed hydrogenation (1 atm) of *endo*-norborn-5-en-2-yltrichlorosilane which was obtained by careful fractional distillation of the Diels–Alder adducts[30,31] between vinyltrichlorosilane and

(28) For new catalysts for hydrosilylation, see: Yamamoto, K.; Hayashi, T.; Zembayashi, M.; Kumada, M. *J. Organomet. Chem.* **1976**, *118*, 161 and references cited therein.

(29) It has been shown that the base-catalyzed intramolecular rearrangement of α-silylbenzyl alcohols to silyl ethers proceeds with inversion at carbon: (a) Biernbaum, M. S.; Mosher, H. S. *J. Am. Chem. Soc.* **1971**, *93*, 6221. (b) Brook, A. G.; Pascoe, J. D. *Ibid.* **1971**, *93*, 6224. Brominolysis of the aryl–silicon bond has been found to proceed with inversion of configuration at silicon: (c) Eaborn, C.; Steward, O. W. *J. Chem. Soc.* **1965**, 521.

(30) (a) Petrov, A. D.; Plate, A. F.; Chernyshev, E. A.; Dolgaya, M. E.; Belikova, N. A.; Krasnova, T. L.; Leites, L. A.; Pryanishnikova, M. A.; Taits, G. S.; Kozyrkin, B. I. *Zh. Obsh. Khim.* **1961**, *31*, 1199. (b) Kuivila, H. G.; Warner, C. R. *J. Org. Chem.* **1964**, *29*, 2845. (c) Green, M.; Spencer, J. L.; Stone, F. G. A.; Tsipis, C. A. *J. Chem. Soc., Dalton Trans.* **1977**, 1159.

(31) (a) Wagner, G. H.; Bailey, D. L.; Pines, A. N.; Dunham, M. L.; McIntire, D. B. *Ind. Eng. Chem.* **1953**, *45*, 367. (b) Cunico, R. F. *J. Org. Chem.* **1971**, *36*, 929.

Table X. Cleavage Reactions of *exo*- and *endo*-Norbornylsilicate with Bromine and NBS To Form 2-Norbornyl Bromide

reagent	solvent	exo/endo ratio[a] (yield of bromide,[b] %) from exo	from endo[c]
Br_2[d]	MeOH	5/95 (57)	96/4 (56)
	THF	5/95 (31)	96/4 (43)
	benzene	42/58 (67)	98/2 (58)
	CCl_4	27/73 (63)	97/3 (57)
NBS[e]	MeOH	2/98 (71)	98/2 (70)
	THF	10/90[f] (33)	96/4[f] (42)
	benzene	7/93 (8)	94/6 (3)
	CCl_4	2/98 (6)	98/2 (3)

[a] Determined by ^{1}H NMR ($\leq\pm5\%$). [b] Determined by GLC. [c] endo 95%. Ratios are corrected, based on this purity. [d] At 0 °C–room temperature for 4 h. [e] At 50 °C for 4 h. [f] The bromide was contaminated with unknown impurities.

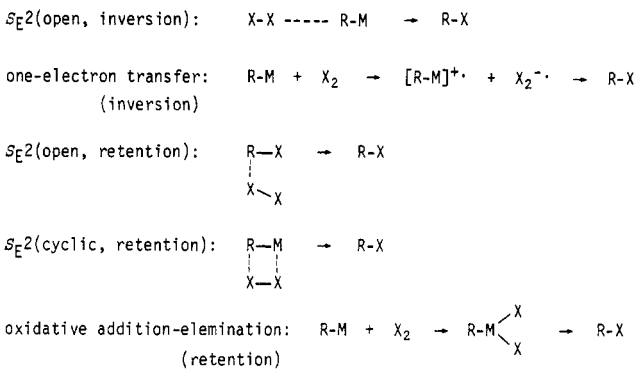
cyclopentadiene. The trichlorosilyl derivative was converted into the trifluorosilyl derivative by treatment with copper(II) fluoride dihydrate in ether and then reacted with aqueous KF to give the *endo*-silicate. During the silicate formation no stereochemical scrambling occurred, as confirmed by comparison of the isomeric purity of 2-norbornyltrimethylsilane[31] obtained by methylation (MeMgBr in ether) of the silicates with that obtained from the trichlorosilyl precursors.

Table X summarizes the stereochemistry of the cleavage of *exo*- and *endo*-2-norbornylpentafluorosilicates with bromine and NBS in methanol, THF, benzene, and carbon tetrachloride. The exo/endo ratios of 2-norbornyl bromide were determined by ^{1}H NMR analysis (2-methine proton ratio) of a crude product after usual workup.[32] The bromine cleavage in polar solvents proceeded in a highly stereospecific fashion with greater than 95% inversion of configuration at carbon. In nonpolar solvents, a low order of stereoselectivity was observed for the cleavage of the exo isomer, while the cleavage of the endo isomer proceeded with higher than 97% inversion. Predominant inversion ($\geq$93%) has also been observed in the NBS cleavage. The reaction was very sluggish in nonpolar solvents such as benzene and carbon tetrachloride, but stereospecificity was little dependent upon the nature of the solvent.

The present stereospecific cleavage, particularly with NBS in methanol, provides the most efficient and convenient method for the stereoselective preparation of *endo*-2-norbornyl bromide (endo 98%). On the basis of the high stereospecificity, we have recently demonstrated that optically active organic halides can be synthesized from olefins via the chiral phosphine palladium complex catalyzed asymmetric hydrosilylation.[33]

Reaction Mechanism of the Cleavage of Carbon–Silicon Bonds in Organopentafluorosilicates by Halogens and NBS. Since kinetic data are not available owing to the insolubility of organosilicates, the reaction mechanism will be discussed, mainly based on the stereochemical aspects. Much attention has been paid to the stereochemistry of electrophilic cleavage of carbon–metal bonds,[34] and both retention and inversion of configuration

Scheme III



at carbon have been observed.[35,36] Attempts have recently been made to analyze the stereochemistry in terms of initial attack on a HOMO of a metal alkyl.[36j,k,w] Thus, for d^0 and d^{10} systems the HOMO would be a carbon–metal σ-bonding orbital, while for d^1–d^9 systems it would be either a nonbonding orbital of essentially d character or a carbon–metal σ-bonding orbital. Inversion may result from either an S_E2 (inversion) mechanism (attack on carbon) or one-electron transfer (attack on metal) followed by a backside attack by a nucleophile. Retention of configuration may result from either an S_E2 (retention) mechanism (attack on carbon) or an oxidative addition–reductive elimination sequence (attack on metal) (see Scheme III). Evidence for the electron-transfer mechanism has been obtained for halogenolysis of organoiron and -cobalt complexes.[37] For main-group organometallics, data as yet do not seem to be sufficient to rationalize the stereochemical courses. It should be noted that stereochemical observations relevant to our present results have recently been reported by Gielen and his co-workers.[36i] They

(32) We call attention to the ready epimerization of 2-norbornyl bromide on analytical and preparative GLC. In the early stage of this work, we have encountered this trouble, despite the fact that the literature has described the analysis and purification by GLC of this compound.[36a,c]

(33) Hayashi, T.; Tamao, K.; Katsuro, Y.; Nakae, I.; Kumada, M. *Tetrahedron Lett.* **1980**, *21*, 1871.

(34) For example: (a) Matteson, D. S. "Organometallic Reaction Mechanism"; Academic Press: New York, 1974. (b) Kochi, J. K. "Organometallic Mechanism and Catalysis"; Academic Press: New York, 1978; Chapter 18. (c) Johnson, M. D. *Acc. Chem. Res.* **1978**, *11*, 57. (d) Reutov, O. A. *Tetrahedron* **1978**, *34*, 2827.

(35) Jemmis, E. D.; Chendrasekhar, J.; Schleyer, P. V. R. *J. Am. Chem. Soc.* **1979**, *101*, 527.

(36) The halogen-cleavage reaction has been most extensively studied. Inversion of configuration has been shown for *lithium*: (a) Applequist, D. E.; Chmury, G. N. *J. Am. Chem. Soc.* **1967**, *89*, 875. (b) Glaze, W. H.; Selman, C. M.; Ball, A. L.; Bray, L. E. *J. Org. Chem.* **1969**, *34*, 641. *Boron*: (c) Brown, H. C.; Lane, C. F. *J. Chem. Soc. D* **1971**, 521. (d) Brown, H. C.; De Lue, N. R.; Kabalka, G. W.; Hedgecock, H. C., Jr. *J. Am. Chem. Soc.* **1976**, *98*, 1290. (e) Bergbreiter, D. E.; Rainville, D. P. *J. Organomet. Chem.* **1976**, *121*, 19. *Tin*: (f) Jensen, J. R.; Davis, D. D. *J. Am. Chem. Soc.* **1971**, *93*, 4048. (g) Rahm, A.; Pereyre, M. *Ibid.* **1977**, *99*, 1672. (h) McGahey, L. F.; Jensen, F. R. *Ibid.* **1979**, *101*, 4397. (i) Gielen, M.; Fosty, R. *J. Chem. Res., Synop.* **1977**, 214; *J. Chem. Res., Miniprint* **1977**, 2379. *Manganese*: (j) Dong, D.; Hunter, B. K.; Baird, M. C. *J. Chem. Soc., Chem. Commun.* **1978**, 11. (k) Dong, D.; Baird, M. C. *J. Organomet. Chem.* **1979**, *172*, 467. *Iron*: (l) Bock, P. L.; Boschetto, D. J.; Rasmussen, J. R.; Demers, J. P.; Whitesides, G. M. *J. Am. Chem. Soc.* **1974**, *96*, 2814. (m) Flood, T. C.; Miles, D. L. *J. Organomet. Chem.* **1977**, *127*, 33. *Cobalt*: (n) Jensen, F. R.; Madan, V.; Buchanan, D. H. *J. Am. Chem. Soc.* **1971**, *93*, 5283. (o) Anderson, S. N.; Ballard, D. H.; Chrzastowski, J. Z.; Dodd, D.; Johnson, M. D. *J. Chem. Soc., Chem. Commun.* **1972**, 685. (p) Magnuson, H.; Halpern, J.; Levitin, I. Y.; Vol'pin, M. E. *Ibid.* **1978**, 44. (q) Kitchin, J. P.; Widdowson, D. A. *J. Chem. Soc., Perkin Trans. 1* **1979**, 1384. Retention of configuration has been observed for *lithium*: (r) Applequist, D. E.; Peterson, A. H. *J. Am. Chem. Soc.* **1961**, *83*, 862. (s) Walborsky, H. W.; Impastato, F. J.; Young, A. E. *Ibid.* **1964**, *86*, 3283. *Tin*: ref 21 g. (t) Baeckelmans, P.; Gielen, M.; Nasielski, J. *Tetrahedron Lett.* **1967**, 1149. (u) Sisido, K.; Miyanishi, T.; Isida, T.; Kozima, S. *J. Organomet. Chem.* **1970**, *23*, 117. *Manganese*: ref 36j. (v) Johnson, R. W.; Pearson, R. G. *J. Chem. Soc. D* **1970**, 986. *Iron*: (w) Slack, D. A.; Baird, M. C. *J. Am. Chem. Soc.* **1976**, *98*, 5539. *Zirconium*: (x) Labinger, J. A.; Hant, D. W.; Seibert, W. E., III; Schwartz, J. *Ibid.* **1975**, *97*, 3851. *Palladium*: (y) Coulson, D. R. *Ibid.* **1969**, *91*, 200. *Mercury*: (z) Jensen, F. R; Whipple, L. D.; Wedegaertner, D. K.; Landgrebe, J. A. *Ibid.* **1960**, *82*, 2466. (z′) Sayre, L. M.; Jensen, F. R. *Ibid.* **1979**, *101*, 1900.

(37) (a) Flood, T. C.; DiSanti, F. J. *J. Chem. Soc., Chem. Commun.* **1975**, 18. (b) Attig, T. G.; Teller, R. G.; Wu, S.-M.; Bau, R.; Wojcicki, A. *J. Am. Chem. Soc.* **1979**, *101*, 619.

have observed that stereochemistry at carbon in brominolysis of a tetraorganostannane dramatically changes from retention to inversion by the addition of a catalytic amount of the fluoride ion which coordinates to the tin atom to prevent the interaction with a nucleophilic part of the reagent.

Inversion stereochemistry observed in the bromine and NBS cleavage reactions of *exo*- and *endo*-2-norbornylpentafluorosilicates may result either from an S_E2 (open, inversion) process involving backside attack on carbon by a bromine or NBS molecule (A) or a one-electron-transfer mechanism leading to backside nucleophilic attack on carbon by a bromide ion (B).

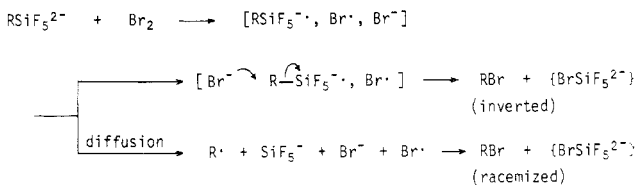
(A) (B)

The MO calculation mentioned above suggests that in alkylsilicates which have no π electrons the Si–C σ bond should be the HOMO having remarkably low ionization potential around 8.3 eV. An electrophilic agent may attack this silicon–carbon bond at first, suggesting the S_E2 (open, inversion) mechanism as a plausible process. We have recently show, however, that the facile reaction of the alkylsilicates with TCNE (tetracyanoethylene) proceeds through an initial one-electron transfer from the alkylsilicates to TCNE.[7j] The electron-transfer process may be favorable also in the present halogenation reactions.

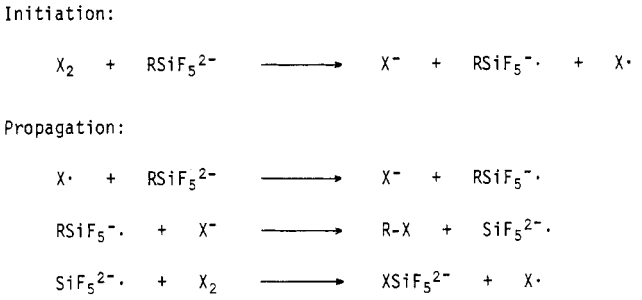
Although no clear distinction between S_E2 and one-electron transfer mechanisms is possible at present, we suggest here the possibility of a one-electron-transfer mechanism for the inversion stereochemistry in bromine cleavage, based on the following arguments (cf. Scheme IV).

(1) The cleavage reaction occurred smoothly irrespective of the nature of the solvent. (2) The stereochemical scrambling observed with *exo*-2-norbornylsilicate in nonpolar solvents suggests the presence of a competing path which proceeds through the formation of an alkyl radical[38] or, if less likely, a carbonium ion.[39] Nucleophilic attack on the exo isomer from the more crowded endo side may be less favorable than that on the endo isomer from the exo side, particularly in nonpolar solvents. Partial diffusion of a norbornyl radical might occur from the "cage" arising from the exo silicate, giving rise to the formation of a mixture of exo and endo bromide. (3) The reaction of the alkylsilicates with IBr gave both the alkyl iodides and bromides. Generally the reaction with interhalogens such as IBr and ICl may provide a useful probe for distinguishing a one-electron-transfer mechanism from electrophilic cleavage.[34b,40] If both halogen atoms of IBr or ICl are transferred to the organic group, a one-electron-transfer mechanism may be operative, while if only the iodine atom is introduced, electrophilic cleavage is considered to be favorable. The present results for the alkylsilicates indicate that both fragments of the IBr might be an active attacking species on the carbon and are consistent with the one-electron-transfer mechanism.

Scheme IV

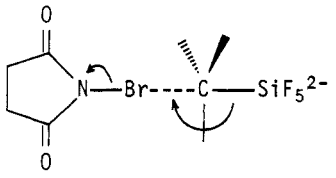


Scheme V



In addition to the nonchain mechanism shown in the above equation, a radical chain mechanism may also be possible, since one-electron transfer from the alkylsilicate to halogen can initiate the following radical chain processes (Scheme V). During the propagation steps the stereochemically inverted alkyl bromide is produced by nucleophilic backside attack of the halide ion on $RSiF_5^-\cdot$. Under some conditions $RSiF_5^-\cdot$ may decompose to R· and SiF_5^- resulting in racemization (cf. Scheme IV).

The NBS cleavage of the alkylsilicates seems to be mechanistically different from their bromine cleavage. The reaction of primary alkyl-silicates was too fast to observe the solvent effect, but retardation of the reaction of the 2-norbornylsilicates with NBS in nonpolar solvents implies that the transition state might involve a charge-separated species. Thus an S_E2 (inversion) mechanism would be plausible. The fact that the stereochemical scrambling did not occur in nonpolar solvents also supports the electrophilic mechanism.



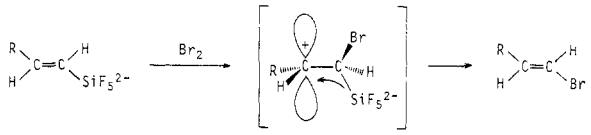
The reactions of aryl- and alkenylpentafluorosilicates with halogens seem to proceed by a different mechanism. Almost exclusive formation of organic iodides in the reactions with IBr inidicates that only potentially positive iodine attacked the carbon and the electrophilic cleavage would be plausible. Predominant formation of the (*E*)-alkenyl halides in the reaction of the (*E*)-alkenylsilicates with halogens and NBS may also support the electrophilic mechanism. It has already been reported that carbon–silicon bonds in the tetracoordinate alkenylsilanes, mostly alkenyltrimethylsilanes, were readily cleaved by bromine with predominant inversion of configuration with respect to the olefinic double bond.[15,16] A mechanism involving trans addition of bromine followed by the base-induced trans elimination of $BrSiMe_3$ has been proposed. Exceptionally, the reaction of styrylsilane with bromine has been observed to proceed with retention of configuration and a mechanism involving the attack of a bromonium ion producing the benzylic carbocation stabilized by the car-

(38) Bartlett, P. D.; Fickes, G. N.; Haupt, F. C.; Helgeson, R. *Acc. Chem. Res.* **1970**, *3*, 177 and reference cited therein.

(39) Interestingly, similar stereochemical phenomena have been observed for the conversion of 2-norbornanol to 2-norbornyl bromide by triphenylphosphine dibromide: Schaefer, J. P.; Weinberg, D. S. *J. Org. Chem.* **1965**, *30*, 2635, 2639.

(40) (a) Stock, L. M.; Spector, A. R. *J. Org. Chem.* **1963**, *28*, 3272. (b) Bhattacharya, S. N.; Raj, P.; Srivastava, R. C. *J. Organomet. Chem.* **1976**, *105*, 45. (c) Dreos, R.; Tauzher, G.; Marsich, N.; Costa, G. *Ibid.* **1976**, *108*, 235. (d) Espenson, J. H.; Samuels, G. J. *Ibid.* **1976**, *113*, 143. (e) Dreos, R.; Tauzher, G.; Marsich, N.; Costa, G. *Ibid.* **1975**, *92*, 227.

bon–silicon σ bond was suggested.[41] The reaction of hexacoordinate alkenylpentafluorosilicates with halogens and NBS is considered to proceed by a mechanism similar to that proposed for the styrylsilane. As shown in eq 5, the carbocation may be stabilized by the electron-rich silicon moiety which is coordinatively saturated and ready for the elimination.



(5)

Formation of the (*Z*)-alkenyl bromide as the minor product in the reaction of the (*E*)-alkenylsilicates with bromine may be ascribed to either the partial radical nature of the reaction or the competing addition–elmination pathway. Further mechanistic studies, currently in progress in our laboratories,[42] on the electrophilic cleavages of alkenylsilicon compounds will hopefully delineate the mechanism in detail.

Summarizing Remarks

We have developed a new methodology for the transformation of olefins and acetylenes to the corresponding alkyl and alkenyl halides, respectively, via a sequence of hydrosilylation, silicate formation, and halogen or NBS cleavage of the silicon–carbon bond. In light of the novel properties of the organosilicates such as air stability and facile reactivity, mildness of reaction conditions, high regio- and stereoselectivity of the cleavage reactions, and high yields of products, the present method may prove to be synthetically useful as an alternative to hitherto developed hydrometalation reactions. The present method is based on the unique reactivity of doubly-negatively charged hexacoordinate organosilicates which may have remarkably low ionization potential assignable to the silicon–carbon σ bond, as suggested by the MO calculation. Further work should be directed to accumulate the experimental data on the bonding character and to establish the structure–reactivity correlation.

Experimental Section

General Remarks. Infrared spectra were recorded on a Hitachi EPI-G3 grating infrared spectrometer. ^{1}H NMR spectra were determined with a JEOL JNM-MH-100 (100-MHz) spectrometer in carbon tetrachloride. Chemical shifts (δ) are recorded in parts per million downfield from Me_4Si. Mass spectra were measured on a JEOL JMS-D300 mass spectrometer connected with a JEOL LGC-20K gas chromatograph, equipped with a 1-m glass column packed with OV-17 (1%) on Chromosorb B, and a JMA-2000 data processing system. Ionization voltage was 24 eV for all compounds. UV spectra of organosilicates in the solid state were recorded on a Shimadzu UV-300 spectrophotometer and other UV spectra on a Hitachi 340 recording spectrophotometer. GLC analyses and preparative purification were performed on a Shimadzu GC-4B gas chromatograph, equipped with a 3-m column packed with 30% Silicone DC550 on Chromosorb B or Celite 545. GC peak integrals were recorded by using a Shimadzu Chromatopac C-E1B integrator. All the elemental analyses were performed at the Microanalysis Center of Department of Pharmacy, Kyoto University, except the analysis of chlorine in organotrichlorosilanes.

Materials. 11-Bromoundecene,[43] 1-hexyne,[44] *tert*-butylacetylene,[45] 5-decyne,[46] 7-tetradecyne,[46] methyl propargyl ether,[47] 2-cyanoethyl propargyl ether,[48] methyl 10-undecynoate,[43] and authentic samples of *exo*-[49] and *endo*-2-norbornyl bromide[36c] were prepared according to the literature procedures. Ethyltrichlorosilane was prepared by the reaction of ethylmagnesium chloride with silicon tetrachloride in ether. Trichlorosilane, methyltrichlorosilane, phenyltrichlorosilane, vinyltrichlorosilane, and a *m*-xylene dispersion of sodium acetylide for the preparation of 1-hexyne[44b] were provided by Shin-etsu Chemical Co., Ltd. An isomeric mixture of octenes was provided by Lion Co., Ltd. Other chemicals including KF, NaF, RbF, CsF, $H_2PtCl_6 \cdot 6H_2O$, $CuF_2 \cdot 2H_2O$, halogens, IBr, NBS, 1-octyne, methyl 10-undenenoate, 4-vinylcyclohexene, 5-hexen-2-one, dially ether, phenylacetylene, 3,3-dimethylbut-1-ene, myrcene, and norbornene were used as obtained commercially. Organic solvents were dried in the usual manner and distilled before use.

Hydrosilylation of Olefins and Acetylenes. Hydrosilylation of olefins and acetylenes catalyzed by chloroplatinic acid was carried out according to the published procedures[8] with minor modifications. Almost all reactions were carried out by the following general procedure. To a mixture of an olefin or an acetylene (1.0 part) and a 0.1 M solution of chloroplatinic acid in 2-propanol (10^{-2}–10^{-3} mol %) was added an excess amount (1.2–2.0 parts) of trichlorosilane. The mixture was allowed to react under the prescribed conditions (Tables I and II). After the reaction was completed (monitored by GLC), the organotrichlorosilane was isolated by distillation.

Hydrosilylation of octene, consisting of terminal and internal olfeins, was carried out under reflux condition, the bath temperature being maintained at 140 °C.[50] Hydrosilylation of cyclohexene (6.0 g, 73 mmol) with trichlorosilane (9.0 mL, 87 mmol) catalyzed by H_2PtCl_6 (2×10^{-3} mol %) was carried out in a sealed glass tube at 100 °C for 20 h. For the selective terminal hydrosilylation of styrene THF was used as a solvent.[51] The amine-catalyzed reaction (Nozakura's method) was employed for the addition of trichlorosilane to acrylonitrile.[52]

Two regioisomers arising from the hydrosilylation of $C_4H_9C{:}CH$, $C_6H_{13}C{:}CH$, $CH_3OCH_2C{:}CH$, and $NC(CH_2)_2OCH_2C{:}CH$ were separated by fractional distillation through a column (ca. 25 cm) packed with glass helices. Since the minor internally silylated products had lower boiling points, the desired (*E*)-alkenyltrichlorosilanes were readily obtained pure by fractional distillation. For example, $CH_3OCH_2(Cl_3Si)C{=}CH_2$ boiled at 70–71 °C (27mmHg), while (*E*)-$CH_3OCH_2CH{=}CHSiCl_3$ at 79.5–80 °C (27mmHg).

For the purpose of improving the regioselectivity of the hydrosilylation of 1-alkynes, a mixture of 1-hexyne (6.5 g, 80 mmol), trichlorosilane (8.0 mL), and a 0.1 M solution of H_2PtCl_6 in 2-propanol (5 drops) was kept at 2 °C in a refrigerator for 15 h. The hydrosilylation was completed and the ratio $C_4H_9(Cl_3Si)C{=}CH_2/C_4H_9CH{=}CHSiCl_3$ was 5/95. With different lots of trichlorosilane the hydrosilylation did not always proceed at such low temperatures and in some cases a vigorous reaction occurred suddenly after a few hours' induction period.[8d] In order to overcome such problems, we have developed a preactivated-catalyst method. For a 0.1-mol scale preparation, the catalyst solution (several drops) was mixed with several millimoles of 1-alkyne and trichlorosilane and the mixture was refluxed for ca. 1 h. To the cooled mixture was added the remaining alkyne and trichlorosilane at room temperature. The mixture was kept at room temperature or in a refrigerator for 15–20 h. The regioisomer ratio was improved to 7/93–5/95 and the total yield was higher than 90%. Alternatively, the distillation residue of the hydrosilylation mixture was also effective for the highly regioselective hydrosilylation, giving essentially the same result as above. Reaction conditions and yields of the organotrichlorosilanes obtained here are sum-

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marized in Tables I and II. Boiling points (°C (mmHg)) and consistent ^{1}H NMR spectral data are given below. n-$C_8H_{17}SiCl_3$: 86–90 (3); δ 0.90 (t, J = 6 Hz, 3 H), 1.1–1.8 (m, 14 H). n-$C_{12}H_{25}SiCl_3$: 124 (3); δ 0.8–1.9 (m, 3 H), 1.1–1.7 (m, 22 H). n-$C_{18}H_{37}SiCl_3$: 182–187 (5); 0.8–1.0 (m, 3 H), 1.0–1.8 (m, 34 H). t-$C_4H_9CH_2CH_2SiCl_3$: 71–73 (22); δ 0.95 (s, 9 H), 1.2–1.6 (m, 4 H). $PhCH_2CH_2SiCl_3$: 85 (6); δ 1.6–1.8 (m, 2 H), 2.7–3.0 (m, 2 H), 6.9–7.3 (m, 5 H). Cyclo-$C_6H_9CH_2CH_2SiCl_3$: 102–103 (8); δ 1.4–1.8 (m, 7 H), 1.9–2.4 (m, 4 H), 5.63 (m, 2 H). $CH_3CO(CH_2)_4SiCl_3$: 99–126 (10); δ 1.2–1.9 (m, 6 H), 2.08 (s, 3 H), 2.44 (t, J = 6 Hz, 2 H). $Br(CH_2)_{11}SiCl_3$: 134–158 (1); δ 1.0–2.1 (m, 20 H), 3.35 (t, J = 7 Hz, 2 H). $CH_3O_2C(CH_2)_{10}SiCl_3$: 151 (1); δ 1.1–1.9 (m, 18 H), 2.36 (t, J = 8 Hz, 2 H), 3.72 (s, 3 H). $NC(CH_2)_2SiCl_3$: 111–114 (35); δ 1.7–2.0 (m, 2 H), 2.5–2.8 (m, 2 H). $CH_2{=}CHCH_2O$-$(CH_2)_3SiCl_3$: 103–109 (18); δ 1.3–1.7 (m, 2 H), 1.7–2.1 (m, 2 H), 3.43 (t, J = 6 Hz, 2 H), 3.8–4.0 (m, 2 H), 5.0–5.4 (m, 2 H), 5.6–6.1 (m, 1 H). Cyclo-$C_6H_{11}SiCl_3$: 92 (23); δ 1.1–1.6 (m, 6 H), 1.6–2.2 (m, 5 H). (E)-n-$C_4H_9CH{=}CHSiCl_3$: 84 (30); δ 1.07 (t, J = 6 Hz, 3 H), 1.2–1.7 (m, 4 H), 2.15–2.45 (m, 2 H), 5.79 (d, J = 19 Hz, 1 H), 6.68 (dt, J = 19 (d) and 6 (t) Hz, 1 H). (E)-t-$C_4H_9CH{=}CHSiCl_3$: 72 (22); δ 1.11 (s, 9 H), 5.67 (d, J = 19 Hz, 1 H), 6.64 (d, J = 19 Hz, 1 H). (E)-n-$C_6H_{13}CH{=}CHSiCl_3$: 130–145 (45); δ 0.90 (t, J = 6 Hz, 3 H), 1.2–1.6 (m, 8 H), 2.15–2.45 (m, 2 H), 5.76 (d, J = 18 Hz, 1 H), 6.66 (dt, J = 18 (d) and 6 (t) Hz, 1 H). (E)-$CH_3O_2C(CH_2)_8CH{=}CHSiCl_3$: 161–163 (5); δ 1.1–1.8 (m, 12 H), 2.15–2.45 (m, 4 H), 3.60 (s, 3 H), 5.76 (d, J = 19 Hz, 1 H), 6.65 (dt, J = 19 (d) and 6 (t) Hz, 1 H). (E)-$CH_3OCH_2CH{=}CHSiCl_3$: 79.5–80 (27); δ 3.30 (s, 3 H), 3.84–4.05 (m, 2 H), 5.95 (dt, J = 18 (d) and 1 (t) Hz, 1 H), 6.50 (dt, J = 18 (d) and 2 (t) Hz, 1 H). (E)-$NC(CH_2)_2OCH_2CH{=}CHSiCl_3$: 150–155 (12); δ 2.57 (t, J = 6 Hz, 2 H), 3.69 (t, J = 6 Hz, 2 H), 4.12 (q, J = 2 Hz, 2 H), 6.12 (dt, J = 19 (d) and 2 (t) Hz, 1 H), 6.64 (dt, J = 19 (d) and 3.5 (t) Hz, 1 H). (E)-$PhCH{=}CHSiCl_3$: 156–159 (45); δ 6.38 (d, J = 19.5 Hz, 1 H), 7.34 (d, J = 19.5 Hz, 1 H), 7.3–7.6 (m, 5 H). (E)-n-$C_4H_9CH{=}C(C_4H_9$-$n)SiCl_3$: 130 (25); δ 0.94 (t, J = 6 Hz, 6 H), 1.1–1.7 (m, 8 H), 2.05–2.5 (m, 4 H), 6.40 (t, J = 7 Hz, 1 H). (E)-n-$C_6H_{13}CH{=}C(C_6H_{13}$-$n)SiCl_3$: 122–125 (2); δ 0.90 (t, J = 6 Hz, 6 H), 1.1–1.9 (m, 16 H), 2.05–2.5 (m, 4 H), 6.40 (t, J = 7 Hz, 1 H).

Preparation of Potassium Organopentafluorosilicates. We have adopted the following two procedures for the preparation of potassium organopentafluorosilicates from organotrichlorosilanes depending upon the nature of the organic group.

Method A. Almost all of the organotrichlorosilanes could be transformed into the silicates by this method. An organotrichlorosilane (0.10 mol) was added *dropwise* to a solution of KF (145 g, 2.50 mol) in 220 mL of water at 0 °C with *vigorous stirring*. The reaction was exothermic, and it was essential to maintain the reaction temperature at 0 °C. The organopentafluorosilicate began to precipitate immediately as white solid matters. After the addition was completed, the mixture was stirred at room temperature for 2 h to overnight. The silicate formed was separated by filtration with suction using two sheets of filter paper (No. 131, Toyo Roshi, Co., Ltd.) followed by washing successively with cold water (300 mL), ethanol (or THF) (100 mL), and ether (100 mL) and then dried over P_2O_5 in a vacuum desiccator. In some cases, the silicate so obtained was contaminated by some siloxanes (IR a broad absorption in 1000–1100 cm^{-1} region) and purified by trituration with THF followed by filtration, washing with THF and ether, and drying in vacuo.

Method B. Styryl-, n-octadecyl-, 1-octadecenyl-, and 7-tetradecenylsilicates were most satisfactorily prepared by the following method. An organotrichlorosilane (0.10 mol) was added dropwise to a suspension of KF (145 g, 2.50 mol) in 300 mL of ethanol at 0 °C. After the addition was completed the mixture was stirred at room temperature for 20 h. After the mixture was coded to 0 °C, 500 mL of water was added in order to dissolve the excess KF and the resulting KCl. The silicate was then separated by filtration followed by washing with water, ethanol and ether and was dried under vacuum, as above.

Yield of the organopentafluorosilicates are given in Tables I and II.

Preparation of Octylpentafluorosilicates Containing Na, Rb, and Cs Countercations. Octyltrifluorosilane was prepared as follows. To a suspension of $CuF_2{\cdot}2H_2O$ (5.15 g, 37.4 mmol) in 15 mL of ether was added dropwise octyltrichlorosilane (5.14 g, 20.8 mmol) at 0 °C. After being stirred at room temperature for 20 h the mixture was diluted with pentane (15 mL) and filtered. The solid matters were washed with pentane. The combined filtrate was dried over Na_2SO_4 and distilled (78–85 °C (120mmHg)) to give 2.61 g of octyltrifluorosilane (63% yield): ^{1}H NMR δ 0.65–1.1 (m, 2 H), 0.88 (t, J = 6 Hz, 3 H), 1.1–1.7 (m, 12 H).

To a suspension of MF (M = Na, Rb, or Cs) (10 mmol) in 5.0 mL of acetonitrile was added octyltrifluorosilane (995 mg, 5.01 mmol) dropwise at room temperature. After the mixture was stirred at room temperature overnight, 10 mL of dry ether was added. The silicate that precipitated as white powder was separated by filtration, washed with ether, and then dried under vacuum. Analytical samples of $Rb_2[C_8H_{17}SiF_5]$ and $Cs_2[C_8H_{17}SiF_5]$ were purified by recrystallization from hot ethanol. $Na_2[C_8H_{17}SiF_5]$ was not purified in a similar manner, and satisfactory elemental analysis was not obtained.

$Na_2[C_8H_{17}SiF_5]$: 75% yield; IR (KBr) 2955 (w), 2915 (m), 2845 (w), 1608 (m, br), 1469 (m), 1380 (w), 1215 (m), 765 (s), 710 (w), 650 (vs), 540 (m), 454 (m) cm^{-1}.

$Rb_2[C_8H_{17}SiF_5]$: 87% yield; IR (KBr) 2955 (w), 2920 (m), 2850 (w), 2800 (w), 1520 (w), 1465 (w), 1376 (w), 1256 (w), 1176 (w), 740 (s), 640 (vs), 532 (m), 445 (m) cm^{-1}. Anal. Calcd for $C_8H_{17}F_5Rb_2Si$: C, 23.60; H, 4.21; F, 23.33. Found: C, 23.55; H, 4.45; F, 23.25.

$Cs_2[C_8H_{17}SiF_5]$: 85% yield; IR (KBr) 2950 (w), 2915 (m), 2845 (w), 2800 (w), 1470 (w), 1380 (w), 740 (s), 643 (vs), 535 (w), 520 (w), 483 (w), 448 (w) cm^{-1}. Anal. Calcd for $C_8H_{17}F_5SiCs_2$: C, 19.14; H, 3.12; F, 18.92. Found: C, 19.33; H, 3.40; F, 19.14.

Potassium Fluoride Treatment of 2-Methyl-6-(trichlorosilylmethyl)-2,6-Octadiene. To a solution of KF (1.7 g) in water (3 mL) was added dropwise the titled chlorosilane[53] (0.363 g, 1.33 mmol) at 0 °C with stirring. Immediately white precipitate deposited. The mixture was filtered, and the solid was washed with ethanol and ether. The white solid was identified as $K_2[SiF_6]$ by IR. The filtrate was extracted with ether. GLC analysis of the ether layer showed that 2-methyl-6-methylene-2-octene, $Me_2C{=}CHCH_2CH_2C(C_2H_5){=}CH_2$, was formed in 55% yield. The product was isolated by flash distillation and preparative GLC: n^{20}_D 1.4471; ^{1}H NMR δ 1.05 (t, J = 5 Hz, 3 H), 1.60 (s, 3 H), 1.68 (s, 3 H), 1.85–2.2 (m, 6 H), 4.65 (s, 2 H), 4.95–5.15 (m, 1 H); mass spectrum, m/e (%) 138 (M^+, 4), 54 (100). Similar results were obtained by the reaction in ethanol.

UV Spectra of Organopentafluorosilicates. The spectra reproduced in Figure 1 were observed on 0.3–0.5 M Nujol mulls of silicates, except the phenylsilicate for which the data were obtained with a 0.05 M Nujol mull. The Nujol mull was spread on a small piece of filter paper and a piece of filter paper applied by Nujol only was used as the reference.

Reaction of Organopentafluorosilicates with Halogens and IBr. General Procedure. To a mixture of an organopentafluorosilicate (5.0 mmol) in 10 mL of a solvent was added a halogen in CCl_4 dropwise at 0 °C until a slight color of the halogen remained. The mixture was stirred at room temperature for 2 h. The reaction of cyclohexylsilicate with halogens, especially with iodine, was rather slow and hence, after the addition of 1 equiv of halogen, the still colored mixture was heated at 35 or 50 °C for 1 h. After the reaction aqueous $Na_2S_2O_3$ was added and the mixture was filtered. The organic layer of the filtrate was separated, washed with water, dried over Na_2SO_4, and concentrated by evaporation. The residue was distilled (bulb-to-bulb distillation) to give the corresponding organic halide. Yields of some organic halides, especially the products arising from the reaction with IBr, were determined by GLC analysis of the reaction mixture. The halides obtained were identified by comparison of their retention time on GLC and spectral data with those of commercially available authentic materials, excepting two alkenyl halides. For characterization of (E)-1-hexenyl bromide, see the section of the NBS clevage (vide infra). Because (E)-1-hexenyl iodide was thermally less stable, it was isolated by column chromatography on silica gel (pentane): n^{20}_D 1.5069 (lit.[27c] 1.5072); IR (liquid film) 3055, 2965, 2930, 2875, 2860, 1609, 1464, 1433, 1378, 1282, 1250, 1218, 1180, 950, 920, 658 cm^{-1}; ^{1}H NMR δ 0.7–1.1 (m, 3 H), 1.1–1.6 (m, 4 H), 1.9–2.1 (m, 2 H), 5.95 (dt, J = 1.5 (t) and 15 (d) Hz, 1 H), 6.45 (dt, J = 7 (t) and 15 (d) Hz,

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1 H); mass spectrum, m/e (%) 211 (M^+ + 1, 7), 210 (M^+, 100), 83 (M^+ − I, 21).

Reaction of Organopentafluorosilicates with NBS. General Procedure. An organopentafluorosilicate (1.0 mmol), NBS (1.1 mmol), and a solvent (5.0 mL) were combined. An exothermic reaction started almost immediately. After the mixture was stirred for 2 h at room temperature, hexane was added. The mixture was filtered, and the insoluble white precipitate was washed with hexane. The combined filtrate was washed with water, dried over Na_2SO_4, and concentrated by evaporation. The product was isolated by distillation, column chromatography, or preparative GLC. The yields of some organic halides were determined by GLC analysis of the reaction mixture.

Preparation of *exo*-2-Norbornylpentafluorosilicate. *exo*-2-Norbornyltrichlorosilane.[30] A mixture of norbornene (45.1 g, 0.479 mol), trichlorosilane (97 mL, 0.958 mol), and 50 μL of 0.1 M solution of chloroplatinic acid in 2-propanol was refluxed at 1100–1300mmHg for 40 h. Distillation of the mixture (97–105 °C (17mmHg)) gave 86.3 g (79% yield) of *exo*-2-norbornyltrichlorosilane. GLC analysis and ^1H NMR of the product showed that the exo isomer was formed exclusively.

***exo*-2-Norbornylpentafluorosilicate.** To a solution of KF (66.8 g, 1.15 mol) in 100 mL of deionized water was added *exo*-2-norbornyltrichlorosilane (10.312 g, 44.9 mmol) dropwise at 0 °C. The mixture was stirred at room temperature overnight. White solid formed was separated by filtration followed by washing with water, acetone, and ether and was dried under vacuum at room temperature (10.714 g, 80% yield); IR (KBr) 2950 (s), 2860 (m), 1450 (w), 1260 (w), 975 (w), 910 (w), 875 (w), 840 (w), 780 (w), 690 (sh), 645 (s), 615 (m), 525 (m), 450 (w) cm^{-1}. Anal. Calcd for $C_7H_{11}F_5K_2Si$: C, 28.36; H, 3.74; F, 32.04. Found: C, 28.55; H, 3.96; F, 31.78.

In order to confirm the stereochemistry, the exo silicate thus obtained was methylated. To the exo-2-norbornylsilicate (889 mg, 3.0 mmol) was added 10 mL of a 2.9 M solution of methylmagnesium bromide in ether at 0 °C. After the mixture was refluxed for 2 h, the usual workup and bulb-to-bulb distillation gave *exo*-2-norbornyltrimethylsilane (372 mg, 74% yield). The exo stereochemistry was confirmed by comparison of its ^1H NMR spectrum with that reported for an authentic sample.[30b]

Preparation of *endo*-2-Norbornylpentafluorosilicate. *endo*-Norborn-5-en-2-yltrichlorosilane.[30,31] To 64.0 g (0.396 mol) of vinyltrichlorosilane was added freshly distilled cyclopentadiene (26.5 g, 0.401 mol) dropwise with stirring. During the addition an exothermic reaction began to take place. The addition was continued with gentle reflux. After the addition the reaction mixture was allowed to stand overnight at room temperature. GLC analysis of the mixture showed that endo and exo adducts were formed in a ratio of 75/25. A careful fractional distillation (105 °C (53mmHg)) of the reaction mixture through a short column (25 cm) packed with glass helices gave *endo*-norborn-5-en-2-yltrichlorosilane (95% endo) (14.4 g, 16% yield).

***endo*-2-Norbornyltrichlorosilane.** A mixture of *endo*-norborn-5-en-2-yltrichlorosilane (95% endo) (24.989 g, 0.110 mol), dry THF (50 mL), and palladium on charcoal (10%, 500 mg) was placed in a 200-mL bottle. The bottle was alternately evacuated and filled with hydrogen, and the mixture was stirred under the hydrogen atmosphere (1 atm). After 7 h additional palladium on charcoal (500 mg) was added. In 15 h 0.12 mol of hydrogen was taken up and the absorption ceased. The reaction mixture was filtered under a stream of nitrogen. The filtrate was concentrated and distilled (98 °C (16mmHg)) to give 19.191 g (76% yield) of *endo*-2-norbornyltrichlorosilane: ^1H NMR δ 1.1–2.1 (m, 9 H), 2.42 (br s, 1 H), 2.62 (br s, 1 H). Anal. Calcd for $C_7H_{11}Cl_3Si$: Cl, 46.32. Found: Cl, 46.19. The stereochemical purity was unable to be determined by GLC or ^1H NMR.

***endo*-2-Norbornyltrifluorosilane.** To a suspension of 18.40 g (134 mmol) of $CuF_2{\cdot}2H_2O$ in 50 mL of ether was added dropwise 18.807 g (82.1 mmol) of *endo*-2-norbornyltrichlorosilane at 0 °C with stirring. The color changes from light blue to brown. After being stirred at room temperature overnight, the mixture was diluted with pentane (50 mL) and filtered and the yellow-green solid matters were washed with pentane several times. The combined filtrate was concentrated and distilled (69–70 °C (117mmHg)) to give 10.627 g (72% yield) of *endo*-2-norbornyltrifluorosilane: ^1H NMR δ 1.0–1.75 (m, 9 H), 1.95–2.25 (m, 2 H).

***endo*-2-Norbornylpentafluorosilicate.** To a solution of KF (50 g, 860 mmol) in 75 mL of deionized water was added *endo*-2-norbornyltrifluorosilane (10.554 g, 58.6 mmol) dropwise at 0 °C. After the addition was completed, the mixture was stirred at room temperature for 3 h. White solid matters thus obtained were separated by filtration, washed with water, ethanol, and ether, and then dried under vacuum (8.811 g, 51% yield): IR (KBr) 2990 (w), 2945 (m), 2910 (w), 2860 (m), 1475 (w), 1450 (w), 1263 (w), 1253 (w), 1195 (w), 1163 (w), 1040 (w), 1000 (w), 980 (w), 915 (w), 870 (w), 835 (w), 775 (w), 695 (s), 645 (w), 620 (s), 552 (m), 543 (m), 465 (w), 455 (w), 445 (w) cm^{-1}. Anal. Calcd for $C_7H_{11}F_5K_2Si$: C, 28.36; H, 3.74; F, 32.04. Found: C, 27.67; H, 3.78; F, 32.09. 3 h. White solid matters thus obtained were separated by filtration, washed with water, ethanol, and ether, and then dried under vacuum (8.811 g, 51% yield): IR (KBr) 2990 (w), 2945 (m), 2910 (w), 2860 (m), 1475 (w), 1450 (w), 1263 (w), 1253 (w), 1195 (w), 1163 (w), 1040 (w), 1000 (w), 980 (w), 915 (w), 870 (w), 835 (w), 775 (w), 695 (s), 645 (w), 620 (s), 552 (m), 543 (m), 465 (w), 455 (w), 445 (w) cm^{-1}. Anal. Calcd for $C_7H_{11}F_5K_2Si$: C, 28.36; H, 3.74; F, 32.04. Found: C, 27.67; H, 3.78; F, 32.09.

In order to confirm the stereochemical purity, the *endo*-2-norbornylsilicate was methylated. Thus a 3.0 M solution of methylmagnesium bromide in ether (7.0 mL) was added to the silicate (593 mg, 2.0 mmol) at 0 °C. The mixture was stirred at room temperature for 5 h. Usual workup followed by distillation gave *endo*-2-norbornyltrimethylsilane in 78% yield. ^1H NMR analysis of the product showed that its stereochemical purity was higher than 95%.[30b]

Reaction of *exo*- and *endo*-2-Norbornylpentafluorosilicates with Br_2. To a mixture of either the *exo*- or *endo*-2-norbornylsilicate (296 mg, 1.0 mmol) and a solvent (5.0 mL) was added dropwise excess bromine (ca. 2 mmol) at 0 °C. After the addition was completed, the mixture was stirred at room temperature for 4 h. Aqueous Na_2SO_3 was added in order to reduce the excess of bromine, and the product was extracted with pentane. The pentane layer was dried over Na_2SO_4 and concentrated by evaporation. The residue, crude 2-norbornyl bromide, was submitted to ^1H NMR analysis. The exo/endo ratio of the product was determined by relative intensities of 2-methine protons. The results are summarized in Table X. An analytical sample of the product was purified by preparative GLC (partial exo–endo isomerization took place) and identified by comparison of its spectral data with those of an authentic material.

Reaction of *exo*- and *endo*-2-Norbornylpentafluorosilicates with NBS. A mixture of either *exo*- or *endo*-2-norbornylpentafluorosilicate (296 mg, 1.0 mmol), NBS (196 mg, 1.1 mmol), and a solvent (5.0 mL) was stirred at 50 °C for 4 h. Pentane (20 mL) was added, and the insoluble matters were removed by filtration. The filtrate was washed with water, dried over Na_2SO_4, and evaporated. The residue, crude 2-norbornyl bromide, was submitted to ^1H NMR analysis. The exo/endo ratio of the product was determined by relative intensities of 2-methine protons. The results are summarized in Table X.

Acknowledgment. We thank the Ministry of Education for the Grant-in-Aid for Scientific Research (Grants 143022, 203518, 265253, 303523), The Yamada Science Foundation, Shin-etsu Chemical Co., Ltd., and the Kurata Foundation (K.T.) for support of this work. We also acknowledge Dr. M. Wada and Dr. H. Kurosawa of Department of Petroleum Chemistry, Osaka University, for valuable suggestions for measuring UV spectra of solid samples, Professor O. Hayaishi and Dr. K. Takai of Department of Medical Chemistry, Kyoto University, for the use of their spectrophotometer which was used for recording UV spectra of organosilicates in solid states, and Professor T. Veszpremi, Technical University of Budapest, Hungary, for helpful discussion on the UV spectral data during his stay in Japan and generous permission of citing the MO calculation data prior to publication.

Registry No. n-$C_6H_{13}CH{=}CH_2$, 111-66-0; t-$C_4H_9CH{=}CH_2$, 592-41-6; n-$C_{10}H_{21}CH{=}CH_2$, 112-41-4; n-$C_{16}H_{33}CH{=}CH_2$, 112-88-9; $PhCH{=}CH_2$, 100-42-5; $Br(CH_2)_9CH{=}CH_2$, 7766-50-9; $CH_3CO(C$-

$H_2)_2CH{=}CH_2$, 109-49-9; $CH_3O_2C(CH_2)_8CH{=}CH_2$, 111-81-9; NCCH=$CH_2$, 107-13-1; $CH_2{=}CH\text{-}CH_2OCH_2CH{=}CH_2$, 557-40-4; *n*-$C_8H_{17}SiCl_3$, 5283-66-9; *t*-$C_4H_9CH_2CH_2SiCl_3$, 928-65-4; *n*-$C_{12}H_{25}SiCl_3$, 4484-72-4; *n*-$C_{18}H_{37}SiCl_3$, 112-04-9; $PhCH_2CH_2SiCl_3$, 940-41-0; $Br(CH_2)_{11}SiCl_3$, 79769-48-5; $CH_3CO(CH_2)_4SiCl_3$, 4848-05-9; $CH_3O_2C(CH_2)_{10}SiCl_3$, 4211-29-4; $NC(CH_2)_2SiCl_3$, 1071-22-3; $CH_2{=}CHCH_2O(CH_2)_3SiCl_3$, 79745-60-1; (*E*)-*n*-$C_4H_9CH{=}CHSiCl_3$, 13095-00-6; (*E*)-*n*-$C_6H_{13}CH{=}CHSiCl_3$, 79745-61-2; (*E*)-*n*-$C_{16}H_{33}CH{=}CHSiCl_3$, 79745-62-3; (*E*)-$CH_3O_2C(CH_2)_8CH{=}CHSiCl_3$, 79745-63-4; (*E*)-$CH_3OCH_2CH{=}CHSiCl_3$, 79769-49-6; (*E*)-$NC(CH_2)_2OCH_2CH{=}CHSiCl_3$, 79745-64-5; (*E*)-$PhCH{=}CHSiCl_3$, 3412-59-7; (*E*)-*n*-$C_4H_9CH{=}C(C_4H_9\text{-}n)SiCl_3$, 79745-65-6; (*E*)-*n*-$C_6H_{13}CH{=}C(C_6H_{13}\text{-}n)SiCl_3$, 79745-66-7; $K_2[(E)\text{-}n\text{-}C_4H_9CH{=}CHSiF_5]$, 68732-24-1; $K_2[(E)\text{-}n\text{-}C_6H_{13}CH{=}CHSiF_5]$, 70995-82-3; $K_2[(E)\text{-}n\text{-}C_{16}H_{33}CH{=}CHSiF_5]$, 71686-43-6; $K_2[(E)\text{-}CH_3O_2C(CH_2)_8CH{=}CHSiF_5]$, 70995-86-7; $K_2[(E)\text{-}CH_3OCH_2CH{=}CHSiF_5]$, 70995-85-6; $K_2[(E)\text{-}NC(CH_2)_2OCH_2CH{=}CHSiF_5]$, 74463-90-4; $K_2[(E)\text{-}PhCH{=}SiF_5]$, 68901-41-7; $K_2[(E)\text{-}n\text{-}C_4H_9CH{=}C(C_4H_9\text{-}n)SiF_5]$, 70995-87-8; $K_2[(E)\text{-}n\text{-}C_6H_{13}CH{=}C(C_6H_{13}\text{-}m)SiF_5]$, 71686-45-8; $K_2[PhSiF_5]$, 5507-59-5; KF, 7789-23-3; $K_2[n\text{-}C_8H_{17}SiF_5]$, 65599-39-5; $K_2[t\text{-}C_4H_9CH_2CH_2SiF_5]$, 79746-13-7; $K_2[n\text{-}C_{12}H_{25}SiF_5]$, 65599-40-8; $K_2[n\text{-}C_{18}H_{37}SiF_5]$, 71686-42-5; $K_2[PhCH_2CH_2SiF_5]$, 79746-14-8; $K_2[Br(CH_2)_{11}SiF_5]$, 79618-87-4; $K_2[CH_3CO(CH_2)_4SiF_5]$, 79618-86-3; $K_2[CH_3O_2C(CH_2)_{10}SiF_5]$, 65599-43-1; $K_2[NC(CH_2)_2SiF_5]$, 79746-15-9; $K_2[CH_2{=}CHCH_2O(CH_2)_3SiF_5)$, 79618-88-5; $C_6H_{11}SiCl_3$, 98-12-4; $K_2[cyclo\text{-}C_6H_{11}SiF_5]$, 65599-42-0; *n*-$C_4H_9C{\equiv}CH$, 693-02-7; *n*-$C_6H_{13}C{\equiv}CH$, 629-05-0; *n*-$C_{16}H_{33}C{\equiv}CH$, 629-89-0; $CH_3O_2C(CH_2)_6C{\equiv}CH$, 2777-66-4; $CH_3OCH_2C{\equiv}CH$, 627-41-8; $NC(CH_2)_2OCH_2C{\equiv}CH$, 1904-22-9; $PhC{\equiv}CH$, 536-74-3; *n*-$C_4H_9C{\equiv}CC_4H_9$, 1942-46-7; *n*-$C_6H_{13}C{\equiv}CC_6H_{13}\text{-}n$, 35216-11-6; NaF, 7681-49-4; RbF, 13446-74-7; CsF, 13400-13-0; $Na_2[PhSiF_5]$, 16924-58-6; Cl_2, 7782-50-5; Br_2, 7726-95-6; I_2, 7553-56-2; *n*-$C_8H_{17}Cl$, 111-85-3; *n*-$C_8H_{17}Br$, 111-83-1; *n*-$C_8H_{17}I$, 629-27-6; *t*-$C_4H_9CH_2CH_2Br$, 1647-23-0; *c*-$C_6H_{11}Cl$, 542-18-7; *c*-$C_6H_{11}Br$, 108-85-0; *c*-$C_6H_{11}I$, 626-62-0; (*E*)-*n*-$C_4H_9CH{=}CHBr$, 13154-13-7; (*Z*)-*n*-$C_4H_9CH{=}CHBr$, 13154-12-6; (*E*)-*n*-$C_4H_9CH{=}CHI$, 16644-98-7; PhBr, 108-86-1; IBr, 7789-33-5; Ph-I, 591-50-4; $Na_2[C_8H_{17}SiF_5]$, 79746-11-5; $Rb_2[C_8H_{17}SiF_5]$, 79746-10-4; $Cs_2[C_8H_{17}SiF_5]$, 79746-12-6; NBS, 128-08-5; *n*-$C_{12}H_{25}Br$, 143-15-7; $PhCH_2CH_2Br$, 103-63-9; $MeO_2C(CH_2)_{10}Br$, 6287-90-7; $Br(CH_2)_{11}Br$, 16696-65-4; $CH_3CO(CH_2)_4Br$, 10226-29-6; (*E*)-$PhCH{=}CHBr$, 588-72-7; (*E*)-$MeO_2C(CH_2)_8CH{=}CHBr$, 79745-67-8; (*E*)-*n*-$C_4H_9CH{=}C(C_4H_9\text{-}n)Br$, 72612-74-9; $K_2[SiF_6]$, 16871-90-2; $K_2[CH_3SiF_5]$, 17979-70-3; $K_2[C_2H_5SiF_5]$, 17193-21-4; 4-(2-bromoethyl)cyclohexene, 63540-01-2; 5-decyne, 1942-46-7; (*Z*)-5-bromo-5-decene, 72612-75-0; potassium (2-(cyclohexen-4-yl)ethyl)pentafluorosilicate, 65599-41-9; 4-ethenylcyclohexene, 100-40-3; cyclohexene, 110-83-8; 4-[2-(trichlorosilyl)ethyl]cyclohexene, 18290-60-3; norborene, 498-66-8; trichlorosilane, 10025-78-2; *exo*-2-norbornyltrichlorosilane, 65118-93-6; *exo*-2-norbornyltrimethylsilane, 79745-68-9; *endo*-norborn-5-en-2-yltrichlorosilane, 27544-82-7; vinyltrichlorosilane, 75-95-5; cyclopentadiene, 542-92-7; *endo*-2-norbornyltrichlorosilane, 79812-96-7; *endo*-2-norbornyltrifluorosilane, 79745-69-0; potassium *endo*-2-norbornylpentafluorsilicate, 74410-83-6; *endo*-2-norbornyltrimethylsilane, 79745-70-3; potassium *exo*-2-norbornylpentafluorosilicate, 74380-89-5; *exo*-2-norbornyl bromide, 2534-77-2; *endo*-2-norbornyl bromide, 13237-87-1; 2-methyl-6-methylene-2-octene, 10054-09-8; 2-methyl-6-(trichlorosilylmethyl)-2,6-octadiene, 68898-14-6; *t*-$C_4H_9C{\equiv}CH$, 917-92-0; *t*-$C_4H_9CH{=}CHSiCl_3$, 79745-71-4; $K_2[t\text{-}C_4H_9CH{=}CHSiF_5]$, 70995-83-4; octyltrifluorosilane, 58589-72-3.

Supplementary Material Available: A listing of IR spectral data and/or elemental analyses for the alkali-metal organopentafluorosilicates in Tables I and II and of IR and mass spectral data, refractive indexes, ^1H NMR spectra, and analyses of the organic bromides prepared in this work (6 pages). Ordering information is given on any current masthead page.