Review

CHEMISTRY OF ORGANOPENTAFLUOROSILICATES *

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I. Introduction

The last decade has seen considerable progress in the application of organo-silicon compounds in organic synthesis: many new reactions have been discovered and many new techniques have been developed [1]. However, all these organosilicon compounds, with a few exceptions, have been restricted to ordinary tetracoordinate silicon derivatives. This review concerns 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.

Organopentafluorosilicates, $M_2[RSiF_5]$, have been known for some twenty years [2]. The first compounds of this class were prepared by Tansjoe in 1961 who treated phenyltriaminosilanes with water-free hydrogen fluoride in ether

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* Dedicated to Prof. R.C. Mehrotra on the occasion of his 60th birthday (February 16th, 1982).

solution:

$$PhSi(NHR)_3 + 6\ HF \xrightarrow{\text{ether}} (RNH_3)_2[PhSiF_5] + RNH_3F$$
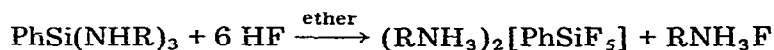
Since then several research groups have reported the synthesis, reactions, and structural studies based on spectroscopies, of organopentafluorosilicates [2b, 2s,2x,2y,3]. In particular, Mueller and collaborators had worked most extensively during the period of 1963—1970, and disclosed much chemistry [2c—2o]. Recently, the hexacoordination around the silicon atom in solution has been confirmed by ^{19}F NMR spectroscopy [2s,2y].
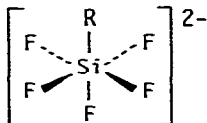
Because organopentafluorosilicates contain a doubly-negatively charged, coordinatively saturated, hexacoordinate silicon atom, their reactivities are expected to be quite different from those of neutral, coordinatively unsaturated, tetracoordinate normal organosilicon compounds. In fact, some noteworthy 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 [2i]. (2) Ammonium methylpentafluorosilicate reacts with $NH_4F \cdot HF$ to give the protonolysis product, methane [2i]. (3) Oxidation of ammonium or potassium methylpentafluorosilicate by $KMnO_4$ gives carbon dioxide together with a trace amount of methane [2i]. (4) Homo coupling products are obtained from vinyl- and perfluorovinyl-pentafluorosilicates (Na^+, K^+, or ammonium salts) by the action of $AgNO_3$ or $CuSO_4$ [2o]. (5) The organic group is transferred to other metals such as silver [2e,2i], mercury [2e,2g,2i], thallium [2v,2w], antimony [2k], and cobalt [2z] by treatment of the organosilicate with a salt of the corresponding metals.

In spite of these successful fundamental studies on the preparation and reactions of organopentafluorosilicates, little attention has 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 [4].

Since Mueller has already reviewed their pioneering work, we describe herein our own results, with particular emphasis on the transformation of olefins and acetylenes into various types of compound via organopentafluorosilicates.

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

## II. Preparation and properties of organopentafluorosilicates

Potassium organopentafluorosilicates are readily obtained as white precipitates by adding organotrichlorosilanes dropwise into a stirred aqueous or ethanolic solution of KF at 0°C. The precipitates are filtered, washed successively with a cold water/ethanol mixture, ethanol, and diethyl ether, and finally dried in a vacuum desiccator. The silicates are air-stable, white powders virtually insoluble

in organic solvents as well as in water. As intermediates in organic synthesis, those organopentafluorosilicates and hence organotrichlorosilanes which are accessible from alkenes and alkynes are of most considerable interest. For the purpose of preparing such organotrichlorosilanes, the well-established hydrosilylation of the unsaturated compounds with $HSiCl_3$ provides the most convenient route [5], which usually proceeds best in the presence of H_2PtCl_6 as catalyst ("Speier's catalyst") [5c], and also with high regio- and stereo-selectivity. In the case of linear alkenes, either terminal or internal, the terminal anti-Markownikoff adducts are produced almost exclusively. In the case of terminal alkynes, the addition of $HSiCl_3$ across the triple bond occurs in a *cis* fashion to give (*E*)-alkenyltrichlorosilanes, 2-silyl-1-alkenes being formed as a minor isomer in many cases.

$$RCH=CH_2 \;+\; HSiCl_3 \;\xrightarrow{H_2PtCl_6}\; RCH_2CH_2SiCl_3 \;\xrightarrow{KF}\; K_2[RCH_2CH_2SiF_5]$$
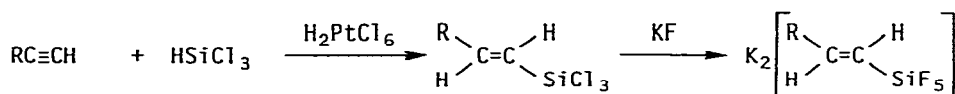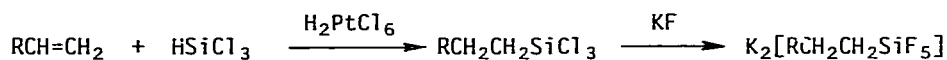
Furthermore, it should be noted that the hydrosilylation tolerates certain functional groups, such as halogen, ether, carbonyl, and alkoxycarbonyl.

Alternative routes to synthesis of the silicates involve the Diels-Alder reaction [6], the ene reaction [7], and the Friedel-Crafts reaction [8], exemplified below [4p,4q]. Most of the silicates prepared from these reactions are accessible only with great difficulty, if any, by the hydrosilylation method.


exo/endo 3/7

E/Z 83/17
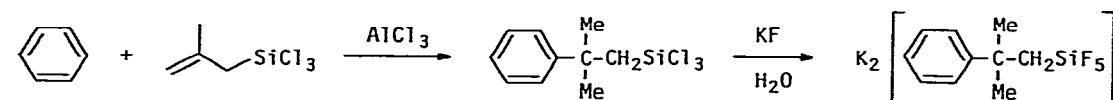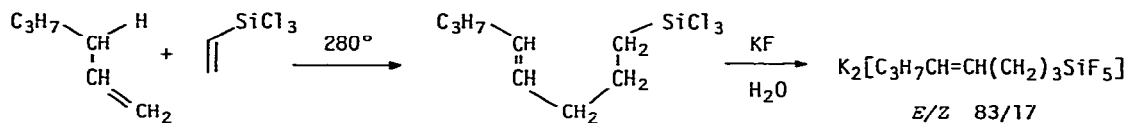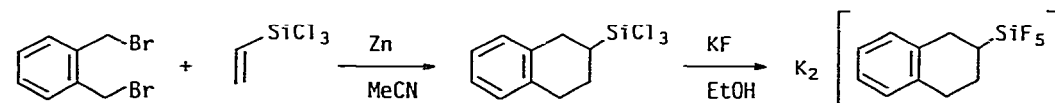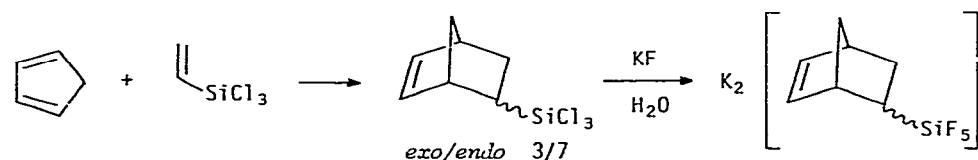
IR studies indicate that the force constant of the carbon—silicon bond in $[MeSiF_5]^{2-}$ is much smaller than that in tetracoordinate $MeSiF_3$ [2p]. CNDO/S

calculation implies that the ionization potential assignable to the silicon—carbon σ bond is much smaller (~ 8.3 eV) in the $Na_2[PhSiF_5]$ than in $PhSiMe_3$ (~ 11.5 eV) and in $PhSiF_3$ (~ 12.3 eV) [4m]. These unique bonding characters of organopentafluorosilicates may be responsible for their susceptibility towards various electrophilic or oxidizing agents.

III. Cleavage of the carbon—silicon bond in organopentafluorosilicates

A. Cleavage with halogens and N-bromosuccinimide

The organopentafluorosilicates readily undergo cleavage by halogens (chlorine, bromine and iodine) and *N*-bromosuccinimide (NBS) in organic solvents to give the corresponding organic halides [4a,4m].
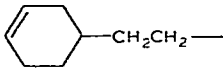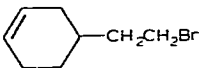
$$K_2[RSiF_5] + X_2 \rightarrow RX \ (X = Cl, Br, I)$$

$$K_2[RSiF_5] + NBS \rightarrow RBr$$
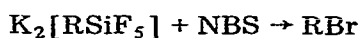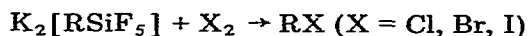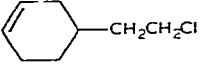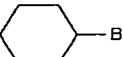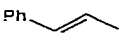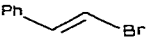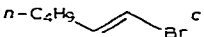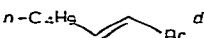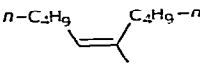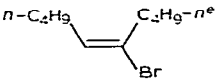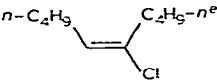
Some of the results obtained with common, sterically not hindered organo-pentafluorosilicates are given in Table 1, from which some significant features are noted: First, the yields of primary alkyl halides are very high, especially when NBS is used, this indicating that the procedures provide a new convenient route to anti-Markownikoff hydrohalogenation of alkenes under neutral conditions. Second, the reaction with NBS can tolerate certain functional groups, such as methoxycarbonyl, carbonyl, halo, and olefin. Third, the nature of the reaction medium does not significantly affect the yields, at least for primary alkylsilicates, while methanol seems to be most suitable for secondary alkyl-silicates.
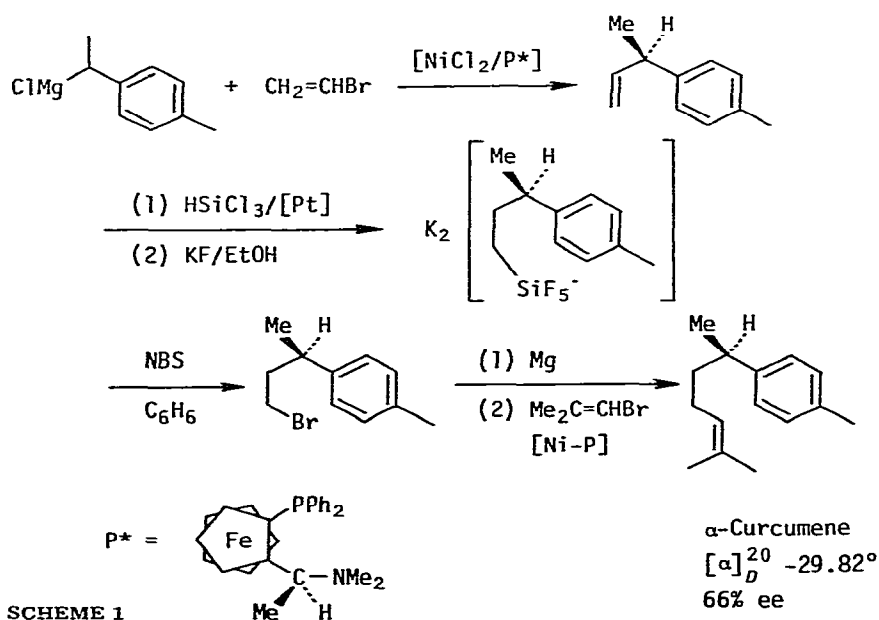
SCHEME 1

TABLE 1

REPRESENTATIVE RESULTS OF HALOGENATION OF ORGANOPENTAFLUOROSILICATES

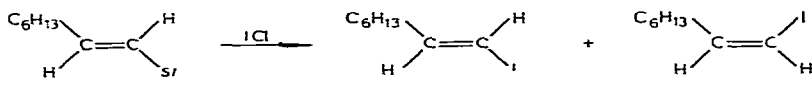| R in $K_2[RSiF_5]$	Reagent	Solvent	Time[a] (h)	Product	Yield[b] (%)
$n\text{-}C_8H_{17}\text{-}$	Cl_2	CCl_4	2	$n\text{-}C_8H_{17}Cl$	73
	Br_2	CCl_4	2	$n\text{-}C_8H_{17}Br$	69
	I_2	CCl_4	2	$n\text{-}C_8H_{17}I$	73
	NBS	C_6H_6	2	$n\text{-}C_8H_{17}Br$	77 (99)
	$CuCl_2$	Et_2O	2	$n\text{-}C_8H_{17}Cl$	(70)
	$CuBr_2$	THF	2	$n\text{-}C_8H_{17}Br$	(88)
(cyclohexenyl)$-CH_2CH_2-$	NBS	C_6H_6	2	(cyclohexenyl)$-CH_2CH_2Br$	54
	$CuCl_2$	Et_2O	20	(cyclohexenyl)$-CH_2CH_2Cl$	51 (73)
$CH_3O_2C(CH_2)_{10}\text{-}$	NBS	C_6H_6	2	$CH_3O_2C(CH_2)_{10}Br$	86
	$CuCl_2$	Et_2O	2	$CH_3O_2C(CH_2)_{10}Cl$	70
$Br(CH_2)_{11}\text{-}$	NBS	C_6H_6	2	$Br(CH_2)_{11}Br$	92
	$CuCl_2$	Et_2O	2	$Br(CH_2)_{11}Cl$	60
$CH_3CO(CH_2)_4\text{-}$	NBS	C_6H_6	28	$CH_3CO(CH_2)_4Br$	(73)
	$CuCl_2$	Et_2O	2	$CH_3CO(CH_2)_4Cl$	46 (66)
(cyclohexyl)$-$	NBS	MeOH	9	(cyclohexyl)$-Br$	(79)
	$CuCl_2$	Et_2O	54	(cyclohexyl)$-Cl$	(58)
Ph-	NBS	MeOH	10	PhBr	(79)
	$CuCl_2$	THF	14	PhCl	(75)
$Ph\diagdown\diagup$ (allyl)	NBS	MeOH	24	$Ph\diagdown\diagup Br$	(83)
	$CuCl_2$	THF	2	$Ph\diagdown\diagup Cl$	(46)
$n\text{-}C_4H_9\diagdown\diagup$	NBS	C_6H_6	4	$n\text{-}C_4H_9\diagdown\diagup Br$ [c]	(75)
	$CuBr_2$	MeOH	4	$n\text{-}C_4H_9\diagdown\diagup Br$ [d]	(63)
$n\text{-}C_4H_9\diagdown\diagup C_4H_9\text{-}n$	NBS	C_6H_6	2	$n\text{-}C_4H_9\diagdown\diagup C_4H_9\text{-}n$ [e], Br	(70)
	$CuCl_2$	MeOH	2	$n\text{-}C_4H_9\diagdown\diagup C_4H_9\text{-}n$ [e], Cl	(76)

[a] At room temperature. [b] Isolated yield. Yields determined by GLC are given in parentheses. [c] E 91%.
[d] E 97%. [e] E >99%.

The halogenolysis with NBS, coupled with a chiral nickel-phosphine complex-catalyzed Grignard cross-coupling, has successfully been employed for the synthesis of $(R)\text{-}(-)\text{-}\alpha$-curcumene, shown in Scheme 1 [4k].

TABLE 2

STEREOCHEMISTRY IN CLEAVAGE REACTIONS OF ALKENYL-SILICON COMPOUNDS

si	Reaction conditions	Yield (%)	E/Z
SiF_5^{2-}	DMF/0°C—r.t./3 h	57	>99/1
	CCl$_4$/0°C—r.t./3 h	30 [a]	83/17
SiF_3	DMF/0°C—r.t./2 h	76	95/5
	(1) CCl$_4$/0°C/5 h, (2) DMF/0°C	64	<1/99
$SiMe_3$	(1) DMF/0°C/2 h, (2) Al$_2$O$_3$	68	<1/99
	(1) CCl$_4$/0°C—r.t./2 h, (2) Al$_2$O$_3$	45 [b]	6/94

[a] (Z)-Octenyl chloride, 5%. [b] Octenyl chloride (E/Z = 14/86), 9%.

The formation of (E)-alkenyl halides from (E)-alkenylsilicates with predominant retention of configuration makes a sharp contrast to the predominant inversion stereochemistry observed for the bromine cleavage of tetracoordinate alkenyltrimethylsilanes [1d]. In connection with this aspect, of particular interest is that an alkenyltrifluorosilane exhibits contrasting selectivity depending upon the nature of the solvent [9]. As shown by the most informative results summarized in Table 2, the reaction in DMF proceeds with retention of configuration, whereas the reaction in CCl$_4$ followed by addition of DMF results in inversion of configuration. The most plausible mechanisms are visualized in Scheme 2.

$$si = SiF_5^{2-} \quad or \quad SiF_3(DMF)_{1\ or\ 2}$$

SCHEME 2 $si = SiMe_3 \quad or \quad SiF_3$
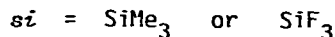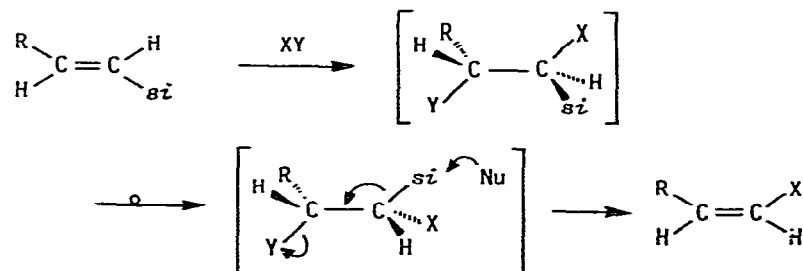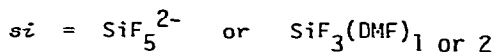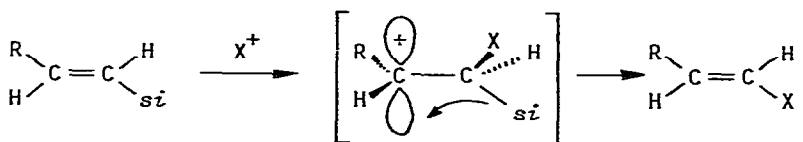
In order to learn the mechanism of the halogenolysis of the alkyl carbon—silicon bond, we have carried out stereochemical studies on the cleavage of *exo*- and *endo*-2-norbornylpentafluorosilicate by Br_2 and NBS in four organic solvents [4i,4m]. The results are summarized in Table 3.

NBS or Br_2
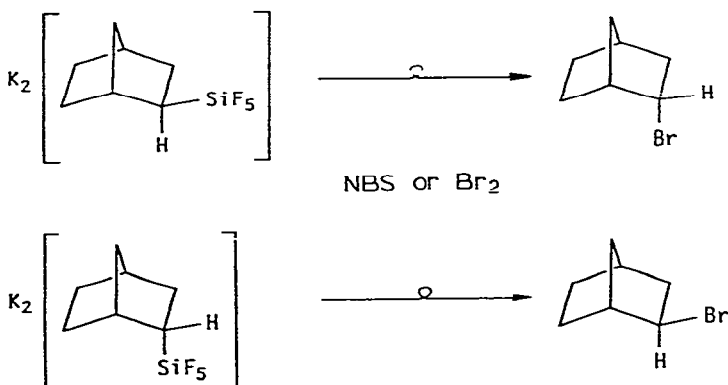
The Br_2-cleavage of both the isomers in polar solvents proceeded highly stereospecifically with inversion of configuration at carbon, whereas a significant decrease in selectivity was observed in the cleavage of the *exo* isomer in nonpolar solvents. These facts may be best explained in terms of the mechanism involving initial one-electron transfer from the silicate to bromine, followed by two different pathways, the major one being back-side attack of the bromide ion on the carbon atom bonded to silicon, and the minor one involving the free alkyl radical. In the case of the *exo* isomer, the bromide attack from the *endo* side must be unfavorable due to steric hindrance and hence the free radical pathway may become important, particularly in nonpolar solvents (Scheme 3).

$$RSiF_5{}^{2-} \ + \ Br_2 \ \longrightarrow \ [RSiF_5{}^{-\cdot} \ , \ Br\cdot, \ Br^-]$$
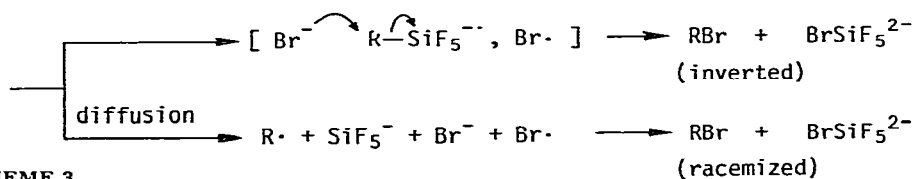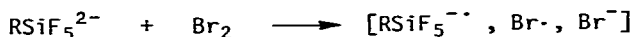
SCHEME 3

The cleaveage by NBS also proceeded highly stereospecifically with inversion of configuration at carbon irregardless of the nature of the solvent, but the yields of the products decreased remarkably in passing from polar to nonpolar solvents. One might argue for a mechanism involving an electrophilic back-side attack of the reagent on carbon rather than that involving the initial one-electron transfer, because the former is considered to be susceptible to the polarity of the solvent, viz., the transition state involves a charge-separated species as follows.
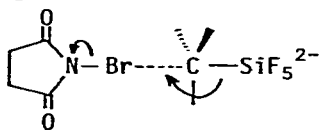
In the NBS cleavage of 5-norbornen-2-yl-silicate [4p], the *endo* isomer reacts much faster than the *exo* isomer, indicating that the more favorable process involves retention of configuration at aliphatic carbon center C^2. This result contrasts with the inversion stereochemistry observed in the saturated counterpart mentioned above.
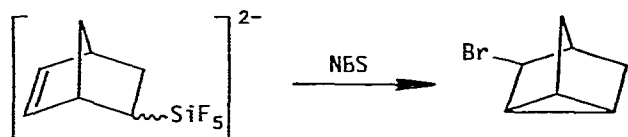
B. Cleavage with copper(II) salts [4n]

Copper(II) chloride and bromide cleave the carbon—silicon bond in organo-pentafluorosilicates to produce the corresponding organic halides in good yields [4c,4n]. Representative results are summarized in Table 1. The copper(II) salt is reduced to copper(I) with no formation of the metal, and it has been established that the reaction strictly obeys a stoichiometry shown in the following equation:

$$K_2[RSiF_5] + 2\,CuX_2 \rightarrow RX + 2\,CuX + K_2[XSiF_5]$$
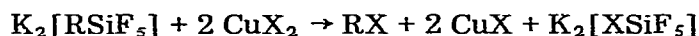
This type of reaction is the first case of the copper(II) cleavage of silicon—carbon bonds involving a ligand transfer from copper to the organic group.

The following observations support a two-step mechanism involving initial

TABLE 3

STEREOCHEMISTRY AT ALIPHATIC CARBON IN BROMINATION REACTIONS
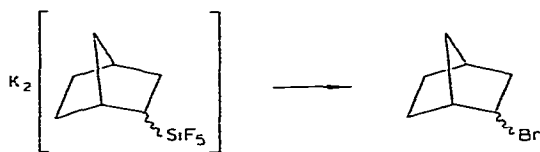
Reagent	Solvent	*exo/endo* ratio [a] and yield (%) of bromide	
		from *exo*	from *endo*
NBS [b]	MeOH	2/98 (71)	98/2 (70)
	THF	10/90 (33)	96/4 [c] (42)
	Benzene	7/93 (8)	94/6 (3)
	CCl$_4$	2/98 (6)	98/2 (3)
Br$_2$ [d]	MeOH	5/95 (57)	96/4 (56)
	THF	5/95 (31)	96/4 (43)
	Benzene	42/58 (67)	98/2 (58)
	CCl$_4$	27/73 (63)	97/3 (57)
CuBr$_2$ [b]	MeOH	71/29 (39)	78/22 (20)
	THF	73/27 (51)	76/24 (48)
	Benzene	70/30 (46)	84/16 (38)
	CCl$_4$	80/20 (35)	87/13 (18)

[a] By ^{1}H NMR ($\leqslant\pm3\%$). [b] 50°C, 4 h. [c] Slightly impure. [d] 0°C ~ r.t., 4 h.

formation of an organic radical and subsequent ligand transfer from another equivalent of the copper(II) halide.

$$RSiF_5^{2-} + CuX_2 \rightarrow R\cdot + CuX + \text{``}XSiF_5^{2-}\text{''}$$

$$R\cdot + CuX_2 \rightarrow RX + CuX$$
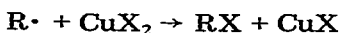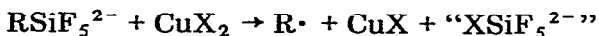
First, when the reaction was performed in methanol under an oxygen atmosphere, the chloride transfer was suppressed considerably and the oxygenation became the major course of the reaction to form octanal in 30% yield.

$$K_2[C_8H_{17}SiF_5] + CuCl_2 + O_2 \xrightarrow[\text{r.t.}]{\text{MeOH}} C_7H_{15}CHO + C_8H_{17}Cl$$
$$\qquad\qquad\qquad\qquad\qquad 30\% \qquad\quad \text{trace}$$
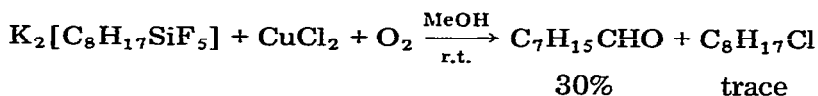
Second, in the CuBr$_2$-cleavage of *exo*- and *endo*-2-norbornylpentafluorosilicate, complete loss of the stereochemistry was observed [4i]. The *exo*- to *endo*-bromide ratio was approximately 7:3 regardless of starting with either isomer of the silicate, as shown in Table 3.

Third, a n-alkyl radical adduct of a nitroso compound could be observed by ESR:

$$K_2[n\text{-}C_8H_{17}SiF_5] \quad + \quad CuCl_2 \quad +$$

D$_3$C, CD$_3$
——NO
D$_3$C, CD$_3$

$$\xrightarrow{Et_2O}$$

D$_3$C, CD$_3$
——N——CH$_2$R
|
O$\cdot$
D$_3$C, CD$_3$

ESR Parameters

$g = 2.006_1$
$a_N = 13.4_4$ G
$a_H = 10.5_1$ G
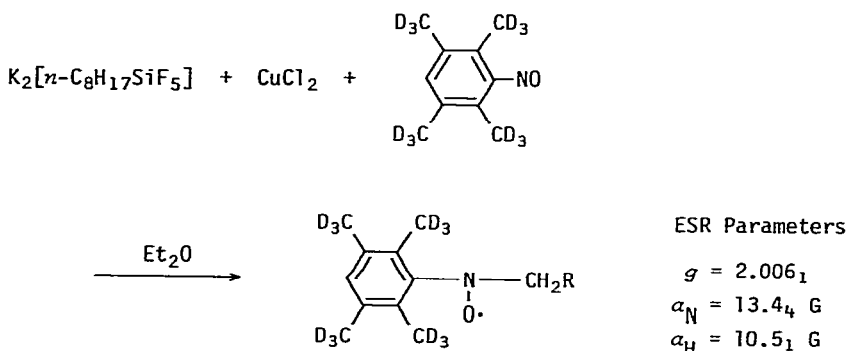
Under forced conditions alkylsilicates have been found to be cleaved by copper(II) acetate, conjugate addition products being formed with α,β-unsaturated ketones. For example:

$$K_2[C_8H_{17}SiF_5] + CH_2{=}CHCOCH_3 \xrightarrow[135°C]{Cu(OAc)_2} C_{10}H_{21}COCH_3$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad 70\%$$

In contrast to the inertness of alkylsilicates, alkenylsilicates react with copper(II) thiocyanate to give the corresponding alkenyl thiocyanates [4h].

$$K_2[R{\diagup}SiF_5] \quad + \quad 2\,Cu(NCS)_2 \xrightarrow{\;DMF\;}$$

$$R{\diagup}SCN \quad + \quad 2\,Cu(NCS) \quad + \quad K_2[(SCN)SiF_5]\ (?)$$
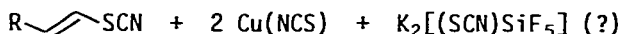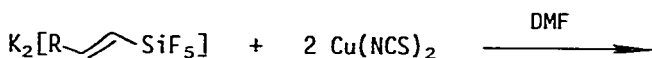
Alkenylsilicates also undergo solvolytic cleavage in the presence of copper(II) acetate to give the corresponding enol ethers [41]. The reaction proceeds catalytically with respect to copper(II) acetate under an oxygen atmosphere:

$$K_2[R\diagdown\!\!\diagup\!\!\diagdown SiF_5] \quad + \quad R'OH \xrightarrow[\text{r.t.}]{\text{cat. Cu(OAc)}_2/O_2} \quad R\diagdown\!\!\diagup\!\!\diagdown OR'$$

The above two reactions characteristic of alkenylsilicates proceed also with retention of configuration at the (*E*)-alkenyl group. In contrast to the alkyl-silicates, no free alkenyl radical can be involved, but an alkenylcopper species might play an important role in the reactions of alkenylsilicates, as shown in Scheme 4.

$$R\diagdown\!\!\diagup\!\!\diagdown SiF_5{}^{2-} \quad + \quad 2\,CuX_2 \quad \longrightarrow \quad \left[\begin{array}{c} R\diagdown\!\!\diagup\!\!\diagdown SiF_5{}^{-\cdot}/CuX_2{}^{-\cdot} \\ \vdots \\ CuX_2 \end{array} \right]$$

$$[R\diagdown\!\!\diagup\!\!\diagdown CuX_2] \quad + \quad XSiF_5{}^{2-} \quad + \quad CuX$$

$$R\diagdown\!\!\diagup\!\!\diagdown X \quad + \quad CuX$$

(X = halogen, pseudohalogen)

R'OH

$$R\diagdown\!\!\diagup\!\!\diagdown OR' \quad + \quad CuX \quad + \quad XH$$

(X = OAc)
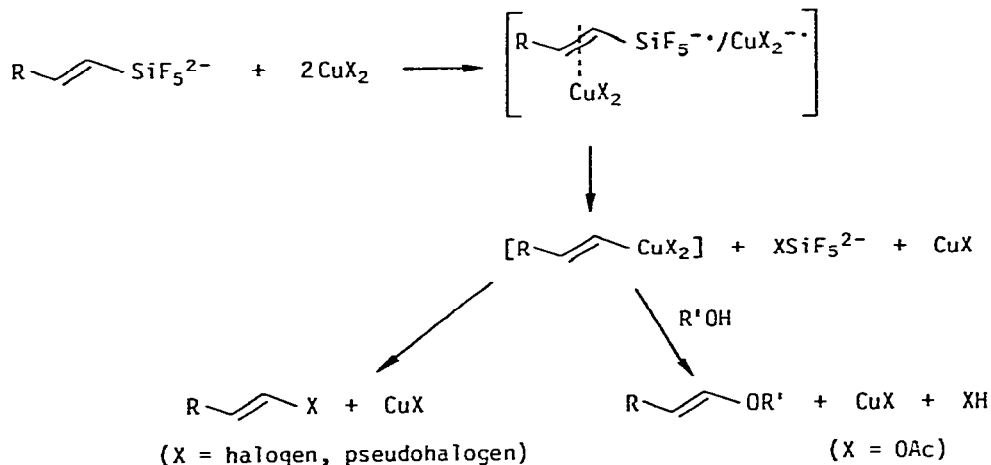
SCHEME 4

C. Reaction with tetracyanoethylene [4j]

In order to confirm the possibility of the electron-transfer mechanism being operative in some of the carbon—silicon cleavage reactions of $K_2[RSiF_5]$, we have investigated the reaction of alkylpentafluorosilicates with tetracyano-ethylene (TCNE), which is well known as a typical one-electron acceptor.

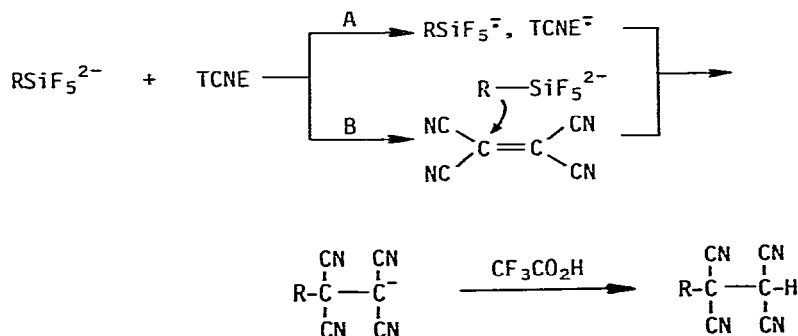The addition of TCNE to a suspension of n-octylpentafluorosilicate in CH_3CN at $-10°C$ under a nitrogen atmosphere resulted in formation of a deep blue mixture. Upon warming up to $3°C$ it turned to greyish green and gradually became dark brown after 30 min. Treatment of the reaction mixture with CF_3COOH gave 1,1,2,2-tetracyanodecane, the alkylation product, in 64% isolated yield.

$$RSiF_5{}^{2-} \quad + \quad TCNE \longrightarrow$$

A $\longrightarrow RSiF_5{}^{\overline{\cdot}}$, $TCNE^{\overline{\cdot}}$

B $\longrightarrow$ $R\!-\!SiF_5{}^{2-}$, $\begin{array}{c} NC \\ NC \end{array}\!\!>\!\!C\!=\!C\!<\!\!\begin{array}{c} CN \\ CN \end{array}$

$$\begin{array}{cc} CN & CN \\ | & | \\ R\!-\!C\!-\!C^- \\ | & | \\ CN & CN \end{array} \xrightarrow{CF_3CO_2H} \begin{array}{cc} CN & CN \\ | & | \\ R\!-\!C\!-\!C\!-\!H \\ | & | \\ CN & CN \end{array}$$

SCHEME 5

Electron spin resonance studies have proved the formation of the TCNE anion radical ($a_N = 0.1571$, $g = 2.00277$). This fact suggests that the present reaction proceeds by initial one-electron transfer from silicate to TCNE (route A) rather than direct electrophilic alkyl transfer (route B) (Scheme 5).

The relative reactivities of alkylpentafluorosilicates, n-C_8H_{17} > cyclohexyl > C_2H_5 ≃ 2-norbornyl ≫ CH_3 (inert), provide further support for the electron-transfer mechanism. In the reaction of *exo*-2-norbornylpentafluorosilicate with TCNE, a 1:1 mixture of *exo*- and *endo*-(2-norbornyl)-1,1,2,2-tetracyano-ethylene was formed, whereas from the *endo*-silicate only the *exo* isomer of the alkylation product was obtained. This stereochemical result suggests a partial diffusion of the norbornyl radical from a cage arising from the *exo*-silicate. In the main reaction course, there must be some interaction between the carbon and silicon atoms during the transfer of an alkyl group to the TCNE anion radical or TCNE molecule.

D. Oxidative cleavage by m-chloroperoxybenzoic acid [4b]

The carbon—silicon bond in organopentafluorosilicates is readily cleaved by the action of *m*-chloroperoxybenzoic acid (MCPBA) to afford the corresponding alcohols in high yields. This reaction provides a simple and practical procedure for the conversion of alkenes into primary alcohols.
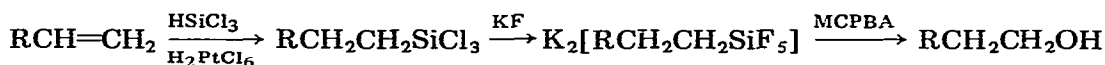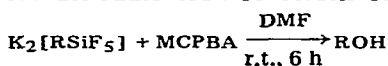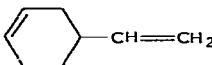
$$RCH{=}CH_2 \xrightarrow[\text{H}_2\text{PtCl}_6]{\text{HSiCl}_3} RCH_2CH_2SiCl_3 \xrightarrow{\text{KF}} K_2[RCH_2CH_2SiF_5] \xrightarrow{\text{MCPBA}} RCH_2CH_2OH$$
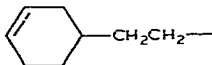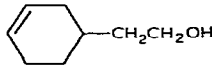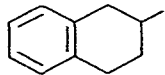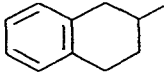
Table 4 summarizes representative results obtained in DMF as solvent. The following particular points deserve comments. First, the MCPBA cleavage of, at least, a primary alkyl—silicon bond in silicates proceeds much faster than the epoxidation of carbon—carbon double bonds, as indicated by the selective preparation of 4-(2-hydroxyethyl)cyclohexene from 4-vinylcyclohexene. This

TABLE 4

MCPBA CLEAVAGE OF ORGANOPENTAFLUOROSILICATES

$$K_2[RSiF_5] + MCPBA \xrightarrow[\text{r.t., 6 h}]{\text{DMF}} ROH$$

Olefin	R in $K_2[RSiF_5]$	Product	Yield (%)
n-$C_6H_{13}CH{=}CH_2$	n-C_8H_{17}-	n-$C_8H_{17}OH$	82
n-C_8H_{16} [a]	n-C_8H_{17}-	n-$C_8H_{17}OH$	68
n-$C_{10}H_{21}CH{=}CH_2$	n-$C_{12}H_{25}$-	n-$C_{12}H_{25}OH$	75
$MeO_2C(CH_2)_8CH{=}CH_2$	$MeO_2C(CH_2)_{10}$-	$MeO_2C(CH_2)_{10}OH$	77
			54
—			65
—	Ph-	PhOH	(64)

[a] An olefin mixture.

may open up a new route to unsaturated primary alcohols from various polyenes. Second, because the platinum-catalyzed hydrosilylation of internal alkenes forms primary alkylsilicon compounds almost exclusively, the present procedure provides a novel route to primary alcohols from a mixture of positional isomers of alkenes. This is exemplified by the result given for a mixture of n-octene isomers.

Stereochemical studies of the MCPBA-oxidation of *exo-* and *endo-*2-norbornylsilicate revealed that, unlike the halogenolysis by bromine and NBS, the reaction proceeds highly stereospecifically with almost complete retention of configuration at carbon [10], indicating that the reaction mechanism is quite different from that for the halogenolysis. In view of the fact that the oxidation is retarded by added KF, it seems likely that the mechanism involves initial dissociation of a fluoride ligand(s) from the silicon center, followed by attack of MCPBA on the coordinatively unsaturated silicon center.

$$K_2 \left[\text{norbornyl}-SiF_5 \right] \xrightarrow[\text{DMF, 50°C}]{\text{MCPBA}} \text{norbornyl}-OH$$

exo 100%   *exo* 100%

$$K_2 \left[\text{norbornyl}-SiF_5 \right] \xrightarrow[\text{DMF, 50°C}]{\text{MCPBA}} \text{norbornyl}-OH$$

endo 95%   *endo* 90-95%
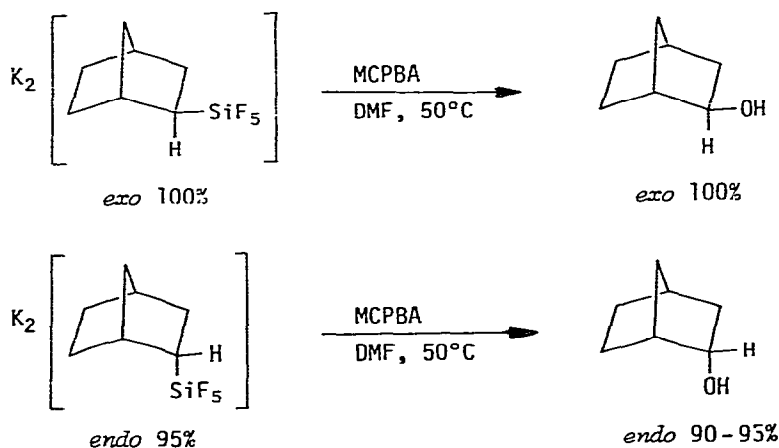
In addition to silicates, organofluorosilanes are also cleaved by MCPBA to form alcohols; all of the organic groups being transformed into alcohols. The reaction of organotrifluorosilanes occurs exothermically in donor solvents such as DMF, *N*-methylpyrrolidone and HMPA, diorganodifluorosilanes require a catalytic amount of fluoride ion, and excess amounts of fluoride ion are necessary for the cleavage of triorganofluorosilanes. Alkenyltrifluorosilanes are readily converted into the corresponding carbonyl compounds even at −50°C. Representative results are summarized in Table 5.

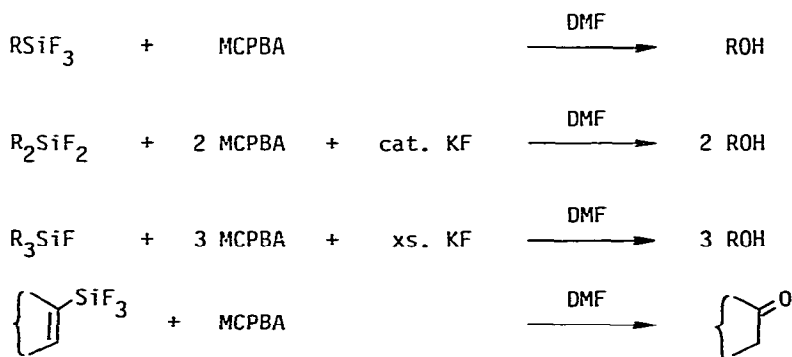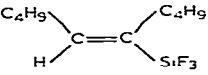$$RSiF_3 + MCPBA \xrightarrow{DMF} ROH$$

$$R_2SiF_2 + 2\ MCPBA + cat.\ KF \xrightarrow{DMF} 2\ ROH$$

$$R_3SiF + 3\ MCPBA + xs.\ KF \xrightarrow{DMF} 3\ ROH$$

$$\text{cyclopentyl-}SiF_3 + MCPBA \xrightarrow{DMF} \text{cyclopentanone}$$
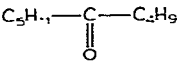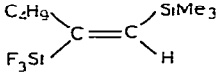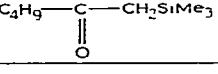
TABLE V

MCPBA CLEAVAGE OF ORGANOFLUOROSILANES IN DMF

Organofluorosilane	Conditions		Product	Yield (%) [a]
$C_8H_{17}SiF_3$	r.t.,	5 h	$C_8H_{17}OH$	(95)
$PhCH_2CH_2SiF_3$	r.t.,	4 h	$PhCH_2CH_2OH$	81
$PhMe_2CCH_2SiF_3$	r.t.,	3 h	$PhMe_2CCH_2OH$	67
(norbornyl)—SiF₃	r.t.,	5 h	(norbornyl)—OH	(80)
$PhSiF_3$	r.t.,	5 h	PhOH	(77)
$(C_8H_{17})_2SiF_2$ [b]	r.t.,	5 h	$C_8H_{17}OH$	(95)
$(C_8H_{17})Me_2SiF$ [c]	r.t.,	5 h	$C_8H_{17}OH$	(76)
$(C_8H_{17})_3SiF$ [c]	50°C,	5 h	$3 C_8H_{17}OH$	(72)
$Ph(C_8H_{17})_2SiF$	r.t.,	5 h	$\begin{cases} 2 C_8H_{17}OH \\ PhOH \end{cases}$	79 (100)
(E)-$C_6H_{13}CH{=}CHSiF_3$	−50°C,	1 h	$C_7H_{15}CHO$	82 (95)
(E)-$PhCH{=}CHSiF_3$	−50°C,	1 h	$PhCH_2CHO$	(75)
$\underset{H}{\overset{C_4H_9}{>}}C{=}C\underset{SiF_3}{\overset{C_4H_9}{<}}$	−50°C,	1 h	$C_5H_{11}{-}\underset{O}{\overset{\|}{C}}{-}C_4H_9$	76
(norbornenyl)—SiF₃	−50°C,	1 h	(norbornenyl)=O	(56)
$\underset{F_3Si}{\overset{C_4H_9}{>}}C{=}C\underset{H}{\overset{SiMe_3}{<}}$	−50°C,	1 h	$C_4H_9{-}\underset{O}{\overset{\|}{C}}{-}CH_2SiMe_3$	56

[a] GLC yields are given in parentheses. [b] Two equiv. of MCPBA and 1 mol% of KF. [c] Three equiv. of MCPBA and two equiv. of KF.

These MCPBA cleavage reactions may involve migration of an organic group from silicon to oxygen in an extracoordinate intermediate, as shown in Scheme 6.

$$R{-}L_nSi{-}\cdots{-}O \cdots \longrightarrow L_nSi{-}OH \rightleftharpoons L_nSi{-}O \longrightarrow ROH$$
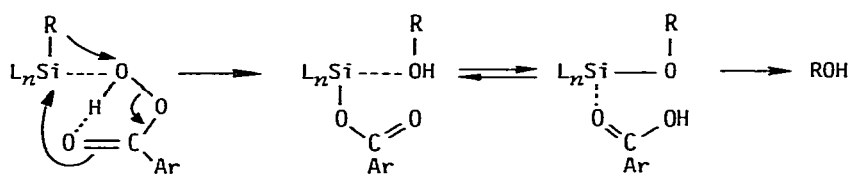
SCHEME 6   L = F, R, and/or donor solvent: n = 3 or 4

E. Asymmetric synthesis of optically active alkyl halides and alcohols [11]

The high stereospecificity of NBS and MCPBA cleavage reactions of alkylsilicates has opened up a new method for asymmetric synthesis of optically active organic halides and alcohols from olefins in combination with catalytic asymmetric hydrosilylation. As shown in Scheme 7, optically active 2-nor-

bornyl bromide, 2-norbornanol and 1-phenylethyl alcohol have been obtained in about 50% ee via asymmetric hydrosilylation of norbornene and styrene catalyzed by a palladium complex coordinated by (R)-(S)-PPFA.
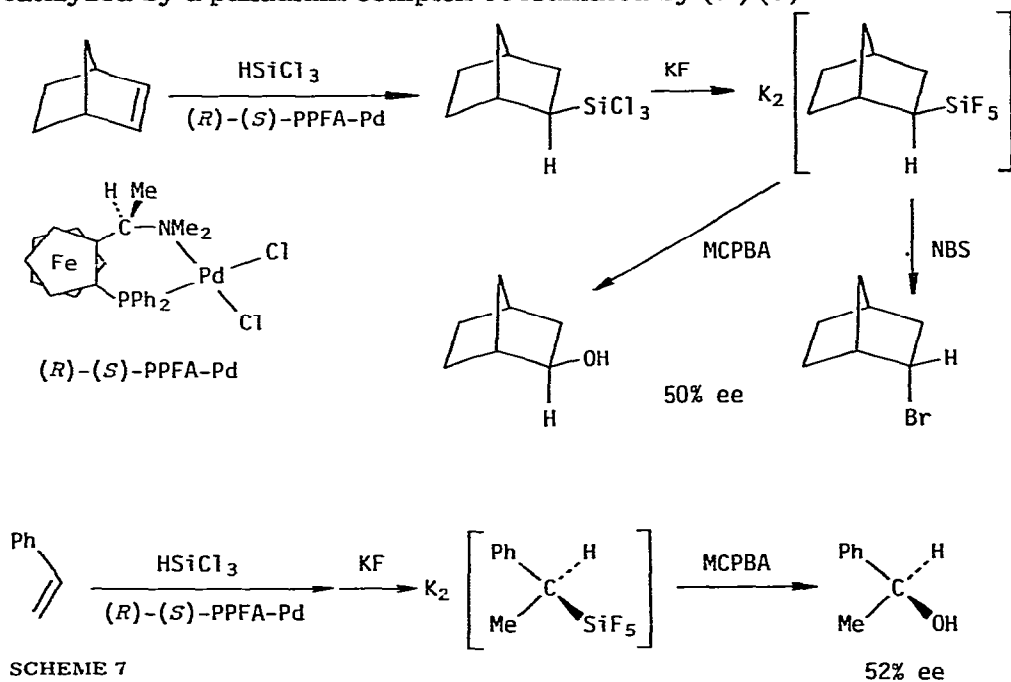
SCHEME 7

F. Homo coupling of alkenylsilicates promoted by silver(I) salts

As mentioned by Mueller as the color test for organopentafluorosilicates, a characteristic color appears upon mixing the silicate with a silver(I) salt [2c]. Mueller and his coworkers have also reported homo coupling of vinyl- and perfluorovinyl-silicate induced by silver nitrate to give the corresponding 1,3-dienes [2o]. We have found that symmetrical (E,E)-1,3-dienes can be prepared stereoselectively in high yields from (E)-alkenylsilicates either by treating them with silver fluoride in acetonitrile or by stirring with silver nitrate in water/ether [4f]. Representative results are given in the following equations.
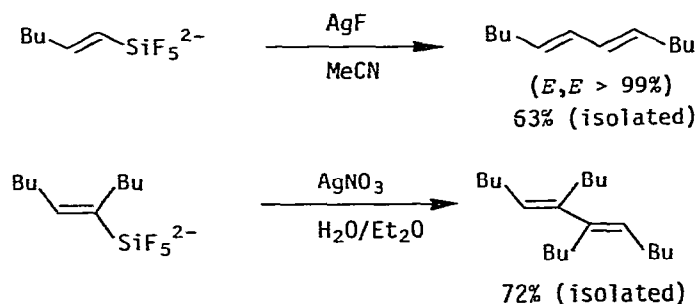
G. Carbon—carbon-bond-forming reactions of alkenylsilicates in the presence of palladium salts

Several types of palladium-promoted carbon—carbon-bond-forming reac-
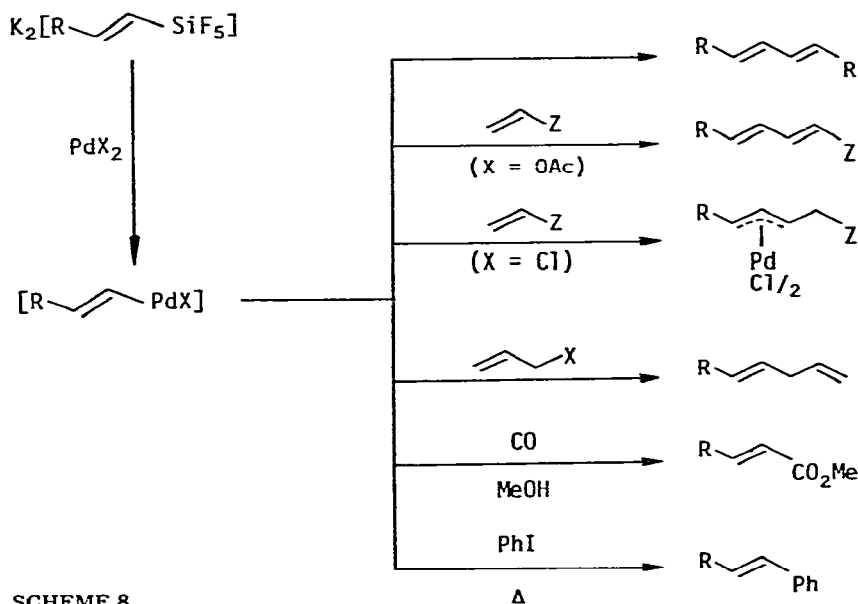
SCHEME 8

tions have been achieved with alkenylsilicates as summarized in Scheme 8 [4o]. Brief mention will be made for a few representative reactions only. 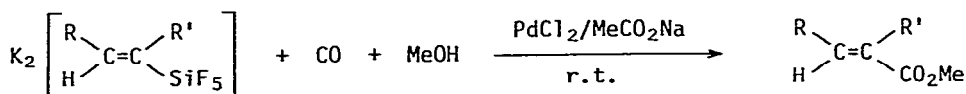These reactions are all characteristic of alkenylpalladium intermediates [12] arising from transfer of the alkenyl group from silicon to palladium. Direct evidence for the alkenyl transfer has been provided by isolation of a π-allylpalladium complex. Thus, the reaction of (*E*)-1-hexenylpentafluorosilicate with ethyl acrylate in the presence of palladium chloride at 0°C gave di-μ-chlorodi(1-ethoxycarbonyl-oct-2-enyl)palladium(II) [4o].
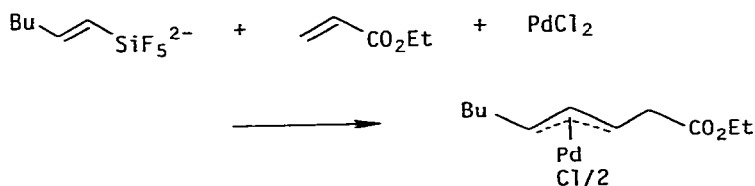
(*E*)-Alkenylsilicates have been found to react with carbon monoxide (atmospheric pressure) at room temperature in the presence of a palladium salt and sodium acetate as an essential additive in methanol to give (*E*)-α,β-unsaturated carboxylic esters in excellent yields [4e]. This reaction is not catalytic with respect to the palladium. The most remarkable feature is the high stereoselectivity of the carbonylation step.

R	R'	Yield (%)
n-C_6H_{13}	H	91
t-C_4H_9	H	90
Ph	H	76
$MeO_2C(CH_2)_8$	H	72
n-C_4H_9	n-C_4H_9	88

(E)-1,4-dienes are formed from the reaction of (E)-alkenylpentafluorosilicates with allylic chlorides in the presence of a catalytic amount (10 mol%) of palladium acetate [4d]. Allyl chloride, methallyl chloride, and 3-chloro-1-butene are effective as allylic substrates. In the reaction with the latter compound the carbon—carbon-bond formation occurred at the γ position exclusively. The reaction maintains the (E)-configuration of the alkenylsilicate and tolerates some functional groups such as the alkoxycarbonyl group. As an application of the present coupling reaction based on these unique features, we have developed a new route to methyl (±)-11-hydroxy-(8E)-dodecenoate, a precursor of recifeiolide, the naturally occurring macrolide (Scheme 9).
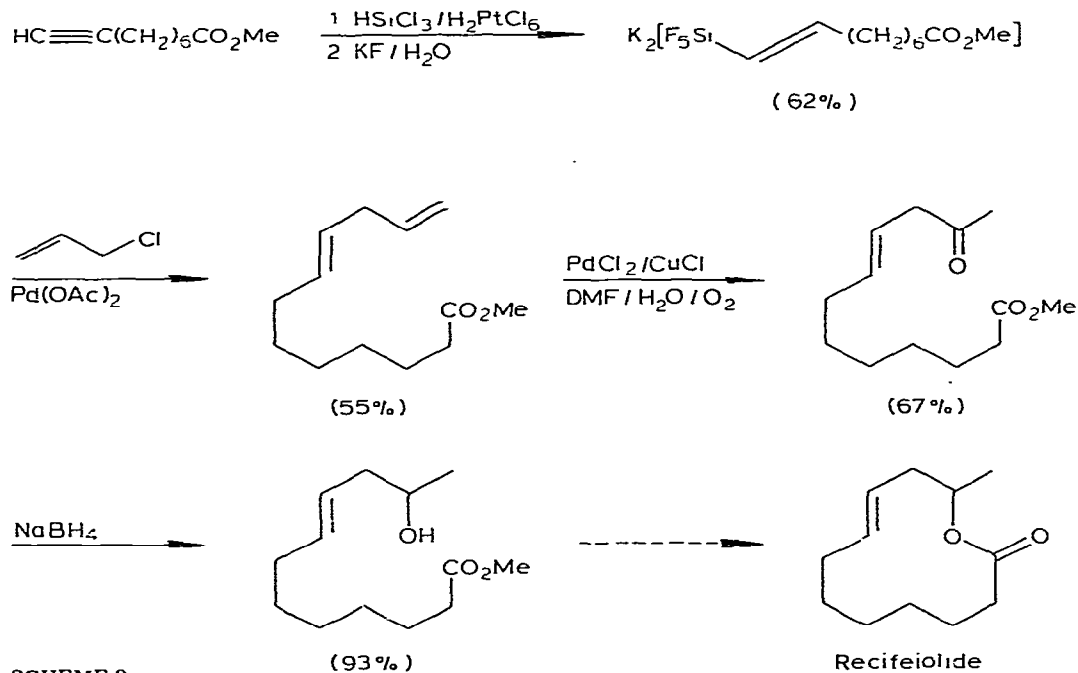
SCHEME 9

IV. Conclusions

We have presented the chemistry of hexacoordinate organosilicon compounds, particularly the preparation and application in organic synthesis of potassium organopentafluorosilicates. The carbon—silicon bonds in organopentafluorosilicates are cleaved by various electrophiles and many types of functional group are introduced onto the carbon to which the silicon atom is attached. The alkenyl- and aryl-silicates undergo several types of carbon—carbon-bond-forming reaction under the influence of metal salts. Potassium organopentafluorosilicates can be readily prepared as air-stable easy-to-handle powders directly from organotrichlorosilanes, which are obtainable mostly from the hydrosilylation of olefins and acetylenes with trichlorosilane. In view of the ready accessibility of organosilicates and their unique reactivities, the present methodology may prove to be a useful alternative to the transformations using organo-boron

[13], -aluminum [14], or -zirconium [15] compounds.

The novel reactivities of organosilicates seem to be interesting also from a mechanistic point of view. Some of the results of mechanistic studies suggest that a one-electron-transfer process may play an important role as well as an electrophilic process. We anticipate that the present results may contribute to the elucidation of the whole area of electrophilic cleavage of carbon—metal bonds.

Acknowledgments

V. References

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