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SYNTHETIC ASPECTS OF THE USE OF ORGANOSILICON COMPOUNDS UNDER NUCLEOPHILIC CATALYSIS CONDITIONS

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1. INTRODUCTION

During the last decade there has been a tremendous growth in the chemistry of organosilicon compounds due to their role in organic synthesis.[1-4] Being the softest metal, silicon can generate electrophilic and nucleophilic agents from organic derivatives under relatively mild conditions and this has stimulated the creation of many new types of reaction. Trialkylsilylation of organic compounds was formerly used mainly for analytical purposes. The stabilizing effect of silyl groups on carbenium ions and anions, facile desilylation and their utility as protecting groups were the main reasons for the explosive growth in the preparative use of silylated compounds.[5] Selection of reagents and conditions generally permits high regio- and stereospecificity. Moreover, such processes are economic since the silicon-containing compounds may be recovered and recycled. Recently, the use of organosilicon compounds as reagents and as intermediates in organic synthesis has become a field of considerable importance. In particular, useful organosilicon reagents for carbon–carbon bond formation have been introduced into organic synthesis in the last decade. The variety of the reactions of organosilicon compounds makes this class of compounds one of the most synthetically promising. Some of these aspects are covered in monographs and reviews.[6-15] Moreover, this changes the strategy of organic synthesis by temporary transformation of the hydrocarbon frame by silylation and desilylation. This method is widely used for the isomerization of analogues of natural compounds. Of great importance is the creation of highly selective reagents. As shown by experience, introduction of organosilicon protecting groups on functional groups of varied chemical nature changes selectively the direction of the attack of nucleophilic and electrophilic reagents and increases their selectivity. This fulfils one of the most important tasks of organic synthesis. The use of organosilicon compounds in organic synthesis constantly grows and this stimulates the development of organic chemistry itself. It is quite impossible to cover all the data within one review. We shall therefore deal with only one aspect of this problem—the synthetic use of these reagents under nucleophilic catalysis conditions. We shall first consider catalysis by alkali metal fluorides, tetraalkylammonium fluoride and potassium cyanide.

These catalysts appeared in many respects to be preferable over those traditionally used for this purpose. The reactions proceed under milder conditions and in many cases are characterized by high selectivity and minimal amounts of by-products. The use of these compounds together with the latest achievements of phase transfer catalysis for promotion of processes and raising their selectivity is impressive.

The extremely high affinity of the fluoride anion toward the silicon atom parallels the high homolytic bond energy of the Si—F bond (142 kcal/mol, 561 kJ/mol).[16] The use of this property for protonolysis of Si—O has been known.[17] This property is the driving force for some reactions. The reaction of the fluoride ion with organosilicon compounds presumably starts from its initial attack on one of the vacant 3*d*-orbitals of silicon. This leads to formation of the anion containing the pentacoordinated silicon. Such pentacoordinate silicon intermediates have been isolated[18-21] and implicated as reactive intermediates in several cases.[22] Although a non-basic pentacoordinate organosilicon intermediate accounts for the remarkable selectivity demonstrated by various reactions, the actual nature of the nucleophilic species has not yet been determined. Further transformations of this intermediate depends on the properties of silicon-bonded groups and on the structure of the silicon atom. The atomic radius of silicon is 1.5 times greater than that of carbon, which makes the electron shell more easily polarizable.

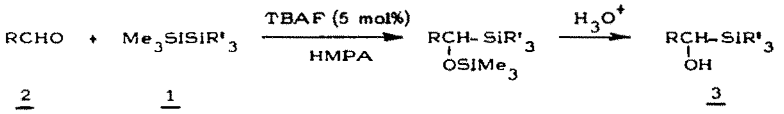
Currently there is a large variety of processes where the fluoride ion promotes transformations of organosilicon compounds. It should be noted that for the successful use of these reagents it is necessary to have simple methods of introducing organosilicon fragments into molecules and methods of removing protecting groups. Without these, no process, no matter how important and interesting it may be, can be performed in practice. The present review is concerned with the use of organosilicon reagents for the protection of organic functional groups in the presence of fluoride ion.

2. SILYLATION OF ORGANIC COMPOUNDS OF VARIOUS CLASSES UNDER NUCLEOPHILIC CATALYSIS CONDITIONS

There are many methods of introducing silyl groups into molecules. We shall consider the reagents introduced in the presence of the catalytic amounts of alkali metals, tetraalkylammonium fluoride, and potassium cyanide.

2.1. *Disilanes as silylating agents*

Substituted disilanes **1** react at 20°C in the presence of the catalytic amounts of tetra-n-butylammonium fluoride (TBAF) in hexamethyl phosphoric triamide (HMPA) with aliphatic aldehydes **2**, giving 1-trialkylsilyl-1-hydroxyalkanes **3** after hydrolysis.[15]



$$\underset{\mathbf{2}}{RCHO} + \underset{\mathbf{1}}{Me_3SiSiR'_3} \xrightarrow[\text{HMPA}]{\text{TBAF (5 mol\%)}} \underset{OSiMe_3}{RCH\text{-}SiR'_3} \xrightarrow{H_3O^+} \underset{\mathbf{3}}{\underset{OH}{RCH\text{-}SiR'_3}}$$

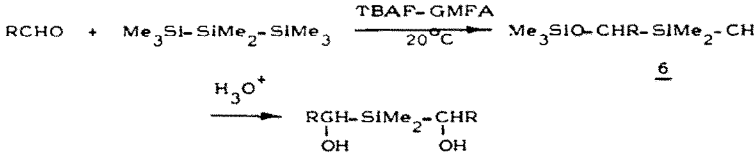
R	R'	Yield, %
H	Ph	38
$n\text{-}C_{10}H_{21}$	Me	67
$n\text{-}C_{10}H_{21}$	Me	64
$n\text{-}C_3H_7$	Ph	60
$i\text{-}C_3H_7$	Ph	61
$t\text{-}C_4H_9$	Me	30
$t\text{-}C_4H_9$	Ph	33

Aromatic aldehydes react with disilanes in the presence of TBAF in a different way, giving a mixture of *d,l*- and *meso*-1,2-diarylethanediols (~ 1 : 1). The reaction was applied to various disilanes **1** and 1,3-butadienes **4** to produce 1,4-disilyl-2-butenes **5**.

The *E*-isomers of **5** are produced with high selectivity. 1,2-Disilylation products were not formed to any measurable extent. Aprotic polar solvents such as HMPA or 1,3-dimethyl-2-imidazolidinone are particularly essential for the reaction. Dimethylformamide or THF are ineffective. The system disilane–TBAF is an efficient silylating agent to obtain the 1,4-dialkyl-2-butene derivatives.[23]

Oligomerization of 1,3-dienes in this process takes place only to a minor degree.[24–26] This method of silylation of 1,3-dienes is characterized by: (i) the absence of "mixing" of the SiR_3 and SiR'_3 groups upon treatment of 1,3-dienes by non-symmetric disilanes; (ii) high stereospecificity of the reaction (E:Z = 90:10) and (iii) high yields of end products (60–80%).

Aliphatic aldehydes and 1,3-dienes are silylated in the presence of TBAF by trisilane derivatives **6**.[27]

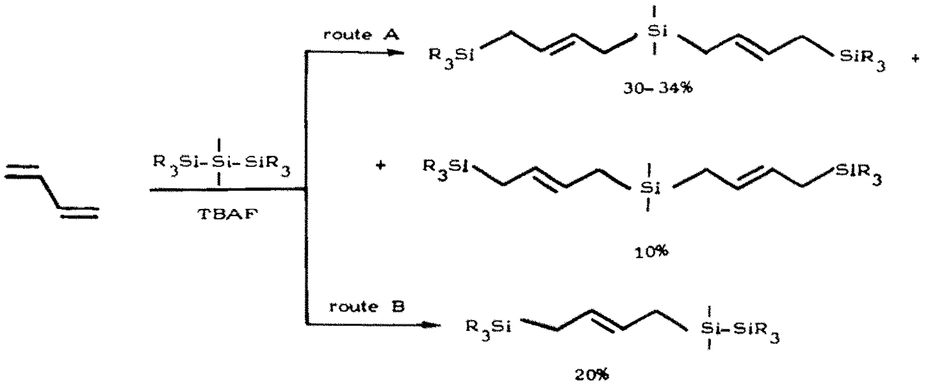


$$RCHO + Me_3Si\text{-}SiMe_2\text{-}SiMe_3 \xrightarrow[20\,^\circ C]{\text{TBAF-GMFA}} \underset{\mathbf{6}}{Me_3SiO\text{-}CHR\text{-}SiMe_2\text{-}CHR\text{-}OSiMe_3}$$

$$\xrightarrow{H_3O^+} \underset{OH}{RCH}\text{-}SiMe_2\text{-}\underset{OH}{CHR}$$

$R = C_5H_{11}, C_{10}H_{21}$ Yields 63–68%

The exclusive formation of these compounds indicates that the attack of the fluoride ion occurs on the terminal silicon atom of the trisilane, which appears to be more electrophilic than the internal one. The results also depend on the order of mixing of the reagents. Addition of the TBAF solution in tetrahydrofuran to the solution of 1,3-diene and the trisilane in HMPA leads to the intrusion of the *E*-2-butene fragment between two silicon atoms (route A). If, on the other hand, the trisilane is added to the solution of the diene and TBAF, then the major reaction product is the disilane (route B).



In the presence of catalytic amounts of TBAF, the silylation reactions of geminal dimethyltetrachlorosilane di- and trichlorides can be achieved.[28]

$$PhCCl_3 + MeSiCl_2\text{-}SiCl_2Me \xrightarrow{TBAF} \underset{71\%}{PhCCl_2SiCl_2Me}$$

2.2. *Reactions of dimethylsilylacetates with carbonyl compounds*

Ethyl(trimethylsilyl)acetate (ETSA) is widely used in organic synthesis as the deprotosilylating and carbalkoxymethylating agent.[29-38] It reacts with the derivatives of acetylene, primary, secondary and tertiary alcohols, phenols and thiols.[31,35] The method gives good yields and presents an advantage in the fact that no inorganic salt or amine hydrochloride is formed as in standard methods.[37b]

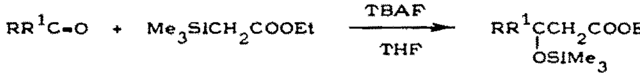
The reaction route of this silylation is explicable in terms of the deprotonation by the ester enolate and subsequent silylation by trimethylfuorosilane. The probable reaction route is represented by the following scheme.

$$Me_3SiCH_2COOEt + F^- \longrightarrow {}^-CH_2COOEt + Me_3SiF$$

$$^-CH_2COOEt + R\text{-}H \longrightarrow CH_3COOEt + R^-$$

$$R^- + Me_3SiF \longrightarrow RSiMe_3 + F^-$$

In the presence of a catalytic amount of TBAF, ETSA silylates ketones with excellent yields of products.[38]



$$RR^1C{=}O + Me_3SiCH_2COOEt \xrightarrow[THF]{TBAF} RR^1\underset{OSiMe_3}{\underset{|}{C}}CH_2COOEt$$

acetophenone	(98%)
cyclopentanone	(74%)
cyclohexanone	(98%)
cycloheptanone	(94%)
cyclooctanone	(86%)
cyclododecanone	(94%)
3-phenylpropanol	(92%)
diisopropylphenylcarbinol	(92%)

Silylation of non-symmetric ketones is characterized by relatively high regioselectivity. Investigation of the regioisomeric composition of the silyl ethers of enols obtained from these ketones shows that the reaction gives predominantly compound **8** (Table 1), the kinetic control product.

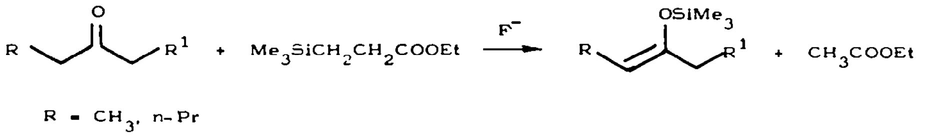
The reactions with aldehydes or non-enolizable ketones proceed under mild conditions (THF, -30°C, 2–4 h), in the presence of TBAF, giving the products of addition at the carbonyl group.[31,32] Aliphatic aldehydes in these conditions give lower yields of adducts as a result of the competing reaction of aldol condensation. Thus in the case of β-phenylpropional, only 24% of the adduct was obtained.

Table 1. Silylation of unsymmetric ketones by ETSA-TBAF[31]

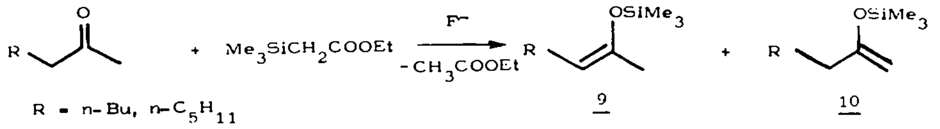
Ketones	Conditions (temperature, °C, time, h)	TBAF equiv.	% yield	Isomer ratio (%)	
				7[a]	**8**[b]
2-Methylcyclohexanone	−78 (5)	1/30	—	20	80
	0 (2)	1/100	98	30	70
	refluxing (1.5)	1/50	75	60	40
Methylisopropylketone	0 (2)	1/200	84	7	93
Methylisobutylketone	0 (2)	1/200	79	10	90
Benzylacetone	−30 (1.5)	1/100	88	38	62

[a] An isomer with the higher substituted olefin.
[b] The one with the less substituted olefin.

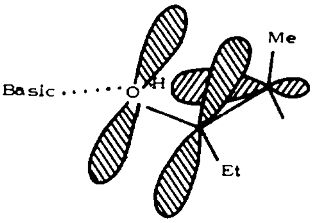
The stereoisomeric composition of silyl ethers of enols formed in the deprotosilylation reactions of a number of acylic ketones have been studied.[34]



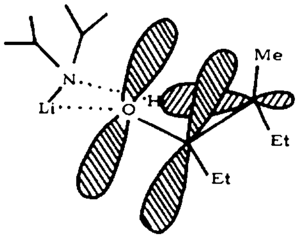
Thus treatment of 5-nonanone with ETSA at 0°C in the presence of 1 mol % of TBAF leads exclusively to the *Z*-silyl ether of the enol (91%). Silylation of 3-pentanone at −78°C also proceeds stereoselectively. This reaction gave *Z*-3-trimethylsiloxy-2-pentene of 99.5% isomeric purity (78%). In the reactions with non-symmetric ketones, high stereoselectivity is also observed.



Upon silylation of 2-heptanone (−78°C, 5 min; 20°C, 24 h), regioisomers **9** and **10** are formed, in 55 and 9% yields respectively. Similarly, the silylation of 2-octanone leads to an 86 : 14 mixture (91%) of regioisomers **9** and **10**. In both cases only the *Z*-isomer is formed. By contrast, treatment of the *Z*-isomer of 3-trimethylsiloxy-2-pentene with the 99.5% isomeric purity with TBAF (3 mol %) leads to a 13 : 87 mixture of *E* and *Z* isomers. The ratio of isomers *E* : *Z* = 28 : 72 was found after similar treatment of pure *Z* or a 49 : 51 mixture of *E*- and *Z*-isomers of the silyl ether of 5-nonanone enol. Thus easy isomerization of silyl ethers of enols indicates that the observed *Z*-stereoselectivity in the reactions with ETSA is the result of the kinetic control. The authors suggest that the stereochemical outcome of the reaction is determined by the steric repulsion between alkyl groups in the intermediate **11**.



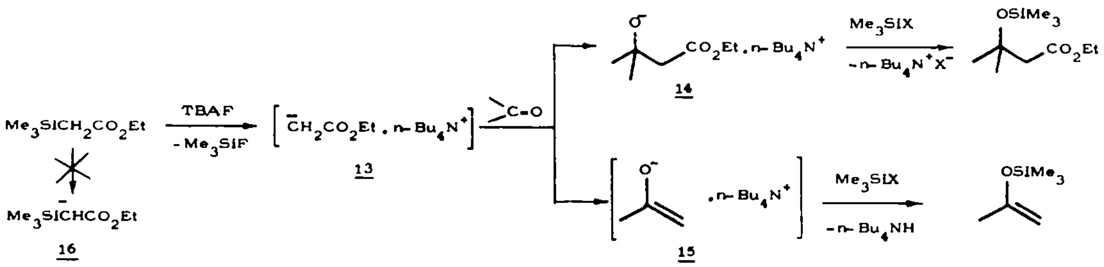
11



12

The use of (iso-Pr)$_2$NLi (THF, −78°C) as a deprotonating agent and subsequent silylation of the resulting enolate anion with trimethylchlorosilane yields the *E*-isomer-enriched silyl ethers of enols. The *E*-selectivity of the silyl ether of 3-pentanone enol obtained in this way may reach 78%.[34] In this case, the six-centre transition state **12** is postulated, and the stereoselectivity is determined by the 1,3-diaxial interaction (steric repulsion) between the iso-Pr and alkyl groups. Indeed, for lithium dialkylamides with more bulky substituents the *E*-stereoselectivity is higher. Thus, the use of lithium 2,2,6,6-tetramethylpiperidide in this reaction raises the content of the *E*-isomer up to 84%.[34]

Kuwajima[32] has suggested a mechanism for the catalytic reaction of ETSA with carbonyl compounds (Scheme 1).

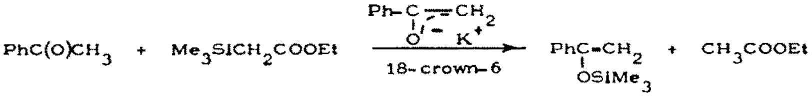


Scheme 1.

This mechanism involves the intermediate formation of the quaternary ammonium enolate **13**, which, depending on the structure of the carbonyl substrate, either deprotonates it or is added to it giving either the enolate **15** or the alkoxy anion **14**. Then follows the stage of silylation of these anions by trimethylfluorosilane (according to the catalytic mechanism). Some facts exclude the alternative of carbanion formation **16** under the given catalytic conditions.[15] (The carbanion formation has earlier been postulated by Birkofer[29,30] to explain the mechanism of the reaction of carbalkoxymethylation of aldehydes by ETSA in the presence of NaOH or $K[Al(OCH_3)_4]$.) First, ethyl α,α-dimethyl(trimethylsilyl)acetate (α-trimethylsilylisobutyrate), which has no α-protons, is added to aldehydes in the presence of TBAF at the same rate as ETSA.[32] Second, the reactions of the anion **16** with carbonyl compounds are known[39-41] to give readily a mixture of *E*- and *Z*-isomers of α,β-unsaturated ethers instead of the product of carbethoxymethylation.

$$>C{=}O + Me_3SiCH(Li)COOEt \longrightarrow >C{=}CHCOOEt + Me_3SiOLi$$

Recently Kuwajima *et al.* have obtained experimental data that suggested some amendments in the mechanism (Scheme 1). Treatment of a mixture of ETSA and acetophenone with the catalytic amount of $KCN \cdot$ 18-crown-6 or $KOCH_3 \cdot$ 18-crown-6 at 0°C leads to the quantitative formation of the silyl ether of acetophenone enol. These catalysts also initiate the reaction of deprotosilylation of 1-hexanethiol. Acetophenone is quantitatively silylated in 1 min at 0°C by treatment of a mixture of acetophenone and ETSA with a complex of the potassium enolate of acetophenone with crown-ether.



$$PhC(O)CH_3 + Me_3SiCH_2COOEt \xrightarrow[\text{18-crown-6}]{Ph-C(O^-K^+){=}CH_2} PhC(OSiMe_3){=}CH_2 + CH_3COOEt$$

An important factor that restricts the use of ETSA as a silylating agent is the acidity of the substrate relative to ethyl acetate (pK_a 24[42]). For example, phenylacetylene (pK_a 18.5[42]) is easily silylated (20°C, 26 h) by ETSA in the presence of the catalytic amount of TBAF.[31,35] However, triphenylmethane (pK_a 33[42]) which forms a stronger conjugated base (as compared to the acetate anion) is unreactive under similar conditions. Comparison of the reactivities of various electrophilic substrates shows that aliphatic ketones are silylated more readily than more acidic phenols and propionic acid reacts ~ 75 times more slowly than *p*-cresol. This may be a result of the different nucleophilicity (with respect to the silicon atom) of the conjugated bases of these substrates and is a good agreement with the autocatalytic mechanism. For the same reason the rate of the reaction with ETSA is lowered in the series $n\text{-}C_6H_{13}SH > PhCH_2SH \gg PhSH$. For 1-hexanethiol, the reaction rate is ~ 10 times higher than for benzylmercaptan: thiophenol does not react at all under these conditions.

The system ETSA–TBAF has a number of important advantages. In contrast with the Favorskii reaction, this system provides the carbalkoxymethylate anion of aldehydes and ketones having no α-protons. Many known methods for the preparation of enol silyl ethers are characterized by the formation of large amounts of inorganic salts or hydrohalogen salts of amines, which makes isolation of the required product difficult. The above system is free from these disadvantages and the only by-product in the deprotosilylation reaction is ethyl acetate.

2.3. *Reactions of hydrosilanes with carbonyl compounds*

One of the main distinctions of silicon chemistry from carbon chemistry is the higher and rather specific reactivity of the Si—H bond. This is a consequence of the fact that the Si—H bond is polarized in an opposite sense to that of the C—H bond. Silicon has a smaller electron affinity (0.6 eV) than hydrogen (0.76 eV), whereas carbon has a higher electron affinity than hydrogen (1.37 eV).[43] Due to this, the silicon-bonded hydrogen can be withdrawn as a hydride anion.

Silane hydrides silylate hydroxyl-containing organic compounds in the presence of the fluoride.[44-48] The conventionally used catalysts for these reactions were the transition element compounds. Alkali metal alkoxides, KF, CsF, TBAF in acetonitrile or DMF proved to be excellent catalysts for alcoholysis of silane hydrides and to have a number of advantages over these catalysts.[49] Primary, secondary and tertiary alkanols, unsaturated alcohols and phenols may be silylated in this way.

Substitution of hydrogen atoms in diorganosilane hydrides proceeds stepwise, depending on the temperature and the fluoride ion source.

Tertiary and secondary silanes are O-selective. With alcohols the corresponding silyl ethers are formed. CsF/imidazole (CsF/Im) is a better activating system than CsF alone.[50] Primary OH groups are silylated faster under CsF/Im activation than secondary OH groups and tertiary alcohols do not react. The primary OH groups are selectively protected also in the presence of the secondary OH groups by the silanes with bulky ligands such as triisopropylsilane $(\text{iso-Pr})_3SiH$. Secondary silanes form monosilyl ethers by amine activation; with CsF, the formation of disilyl ethers predominates. A specific synthetic route to compounds with $>Si(F)OR$ and $>Si(OR^1)R^2$ structures is reported (Table 2).

$$R^1R^2R^3SiH + R'OH \xrightarrow{CsF\,/\,Im} R^1R^2R^3SiOR' + H_2O$$

$R^1{=}R^2{=}R^3{=}Ph$ (17); $R^1{=}R^2{=}CH_3$, $R^3{=}Ph$ (18); $R^1{=}R^2{=}R^3{=}C_2H_5$ (19);
$R^1{=}R^2{=}R^3{=}\text{i-}C_3H_7$ (20); $R^1{=}R^2{=}Ph$, $R^3{=}CH_3$ (21); $R^1{=}R^2{=}Ph$, $R^3{=}H$ (22);
$R^1{=}Ph$, $R^2{=}$ 1-Naphthyl, $R^3{=}H$ (23); $R^1{=}CH_3$, $R^2{=}Ph$, $R^3{=}H$ (24);
$R^1{=}R^2{=}\text{i-}C_3H_7$, $R^3{=}H$ (25)

Andrianov *et al.* found that the route of alcoholysis of silane hydrides in the presence of fluoride ion depends on the nature of the substituent at silicon.[44-46] For example, O-silylation of methanol by methyldibenzylsilane proceeds mainly by the removel of benzyl groups. Upon substitution of methanol by some other alcohol, the relation between the Si—C and Si—H bond cleavages somewhat changes.[45]

The role of fluoride ion in the reactions of silane hydride with hydroxyl-containing compounds consists in ionization of the latter to give alkoxides.[47]

$$R'OH + F^- \longrightarrow R'O^- + HF$$

$$R'O^- + Me_3SiH + R'OH \longrightarrow R'OSiMe_3 + R'O^- + H_2O$$

The authors of Ref. 43 investigated the reactions of R_3SiH (R = Et, Pr, Bu) with alcohol in the presence of alkaline metal alkoxides. The mechanism of bimolecular nucleophilic substitution has been proposed.

$$R'O^- + R_3SiH \longrightarrow \underset{\underline{27}}{\left[R'O\,....\,SiR_3\,....\,H\right]^-} \xrightarrow[-H_2]{R'OH} R'OSiMe_3$$

This scheme suggests that the attack of the alkoxy anion on the silicon atom leads to the removal of the hydride ion, which is immediately bonded by alcohol with liberation of hydrogen. The last stage involves generation of the alkoxy anion. The authors admit that the activated complex **27**

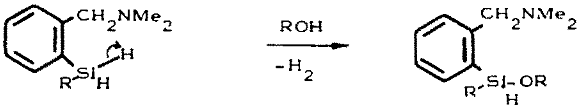
Table 2. The alcohols silylated in the presence of CsF/imidazole in DMF at 20°C

Silane	Alcohol	Yields (%)
17	$c\text{-}C_6H_{11}OH$	58
17	$HO(CH_2)_2N(CH_3)_2$	80
18	$c\text{-}C_6H_{11}OH$	70
18	$c\text{-}C_6H_{11}CH_2OH$	79
18	$HO(CH_2)_2N(CH_3)_2$	80
18	C_6H_5OH	75
19	$i\text{-}C_3H_7OH$	80
20	$c\text{-}C_6H_{11}OH$	71
20	$c\text{-}C_6H_{11}CH_2OH$	74
20	$n\text{-}C_4H_9OH$	70
21	$n\text{-}C_4H_9OH$	83
21	$c\text{-}C_6H_{11}OH$	77
22	$HO(CH_2)_2N(CH_3)_2$	75

may contain a molecule of alcohol as well as the alkoxy anion so that both stages could occur simultaneously.

A similar mechanism was suggested for the reactions of Et_3SiH with alcohols, initiated by fluoride ions (TBAF, CsF). In this case the alkoxy anions are formed by the reaction of alcohol with fluoride ions.[47] Corriu and his co-workers[48,49] suggest a different mechanism for the reactions of hydrosilanes with alcohols, initiated by alkali metal salts. According to this mechanism, the role of a salt is to activate the silane. As a result of coordination of the salt anion on the silicon atom, there occurs delocalization of the electron pair of the Si—H bond. This is followed by nucleophilic attack of alcohol on the atom of pentacoordinated silicon.

The role of the nucleophilic agent in the activation of the Si—H bond can also be played by neutral molecules capable of coordination with the silicon atom, for example, amines.[51]



In similar conditions $PhSi(R)H_2$ does not undergo alcoholysis.

Dene and Vol'pin showed in 1973[47,52] that Et_3SiH reduces aromatic aldehydes and ketones to the respective organylhydroxysilanes in the presence of CsF or TBAF. Thus, Et_3SiH reduces benzaldehyde to benzylhydroxytriethylsilane (30%) in 20 h (20°C, CH_3CN) in the presence of the equimolar amount of TBAF. In the presence of catalytic amounts of CsF, the same reaction proceeds to 96% in 10 h. The authors suggest two mechanisms for this reaction. The first one involves the initial activation of the carbonyl compounds.

$$PhCHO + F^- \rightleftharpoons PhCH(F)\text{-}O^-$$

$$PhCH(F)\text{-}O^- + R_3SiH + PhCHO \longrightarrow PhCH(F)\text{-}OSiMe_3 + PhCH_2O^-$$

$$PhCH_2O^- + R_3SiH + PhCHO \longrightarrow PhCH_2CH_2OSiR_3 + PhCH_2O^-$$

The second one was reported as proceeding by a hydride transfer process, this time catalysed by pentavalent silicon (Scheme 2). Presumably the pentavalent anion is an excellent hydride transfer agent. In a series of works,[51,53–57] Corriu and his co-workers have studied in detail the reactions of hydrosilanes with carbonyl compounds in the presence of alkali metal salts. For the reduction they used $NpSiH_3$,[53] H_2SiPh_2,[54] $MeSiH(OEt)_2$,[51,54,56] $HSi(OEt)_3$,[51,53–57] polymethylhydrosilane/$Me_3SiO(HSiMeO)_nSiMe_3$.[51,57] The activity of the silanes increases in the series $H_2SiPh_2 < MeSiH(OEt)_2 < HSi(OEt)_3$. Thus, to reduce ethyl valerate using diphenylsilane in the presence of CsF, heating to 140°C for 4 h is required; using $MeSiH(OEt)_2$ heating to 120°C for 3 h is required and using $HSi(OEt)_3$ a temperature of 25°C for 1 min is needed.[53] The reactivity of carbonyl compounds increases in the series: esthers < ketones < aldehydes. For example, triethoxysilane reduces benzaldehyde in the presence of CsF in 1 min at 0°C, acetophenone does likewise in 30 min at 0°C, and ethyl benzoate requires 30 min at 60°C.[51] Carbonic acid amides and chlorides are reduced extremely slowly in DMSO or DMF.[57] Benkesez and his co-workers successfully used Cl_3SiH to reduce tertiary aromatic amides in the presence of tertiary amines.[58]

Corriu[53] used HCOOK, $o\text{-}C_6H_4(COOK)_2$, KF and CsF. The highest activity is shown by CsF. The activity of alkali metal fluorides increases in the series: $LiF \leqslant KF \leqslant CsF$, i.e. increase of the ionic character of the metal–fluorine bonds is observed.[51] The reduction of cinnamic aldehyde by triethoxysilane in the presence of KF at 25°C takes 24 h, in the presence of CsF it takes 1 h.

$$RCH{=}CR^1CHO + HSi{\equiv} \xrightarrow{F^-} RCH{=}CR^1CH_2OSi{\equiv}$$

$$R = Ph,\ R^1 = H;\ R,R^1 = \text{-}(CH{=}CHO)\text{-}$$

This reaction examplifies high regioselectivity of the reduction of α,β-unsaturated carbonyl compounds with hydrosilanes under nucleophilic catalysis conditions.[51,56,57] The reaction gives exclusively 1,2-adducts.

The NO_2 and Br groups and the C=C bond do not react with hydrosilanes under nucleophilic

$$R_3SiH + F^- \rightleftharpoons R_3SiH(F)^-$$

$$R_3SiH(F)^- + R_2C{=}O \longrightarrow R_3SiF + R_2CH{-}O^-$$

$$R_2CH{-}O^- + R_3SiF \longrightarrow R_2CH{-}OSi(F)R_3^- \longrightarrow R_2CH{-}OSiR_3 + F^-$$

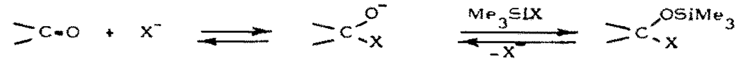
Scheme 2.

catalysis conditions. This allows selective reduction of carbonyl compounds containing these functional groups.

2.4. *Reactions of trimethylcyanosilane and trimethylsilylazide with carbonyl compounds*

Trimethylcyanosilane is widely used in organic synthesis.[59,60] One of its main uses is in addition reactions to heteroatom double bonds, such as C=O[61-74] and C≡N,[75-79] which lead to the formation of $NCCOSiMe_3$ and $NCCNSiMe_3$ fragments. These fragments serve as protecting groups or as sources of hydroxyamines and amino acids. In 1973 Evans first showed the efficiency of anionic (nucleophilic) catalysis during the addition of silicon pseudohalogenides, such as Me_3SiCN and Me_3SiN_3, to the carbonyl group of aldehydes and ketones.[61-63] The catalytic amount (0.1–0.2 equiv.) of cyanide ions quite suffices for cyanosilylation of carbonyl group.

As catalysts, KCN · 18-crown-6 and $n\text{-}Bu_4N^+CN^-$ complexes were used. The mechanism proposed by Evans[63] involves initial addition of the cyanide ion (X = CN) to the C=O group to form the alkoxy anion **28**. Subsequent silicon transfer to **28** leads to the formation of trimethylsiloxynitrile together with the X^- ion.



28

This catalytic model implies that cyanosilylation is initiated by the X^- ion which undergoes either addition to the C=O group or replacement of a ligand at the silicon atom. Complexes of 18-crown-6 with KN_3, KSCN and KOMe can activate the cyanosilylation reaction in the same way as the cyanide ion. Me_3SiSCN is known[80] to be inactive towards the carbonyl group both under acidic and basic catalysis conditions. This fact supports the view of ligand-by-silicon exchange as the first stage of initiation (at least in the case of the KSCN · 18-crown-6 complex).

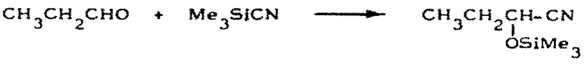
The use of Me_3SiCN under nucleophilic catalysis conditions considerably extends the applications of the cyanohydrin synthesis[81] which is usually restricted to aldehydes.[81,82] Even the sterically hindered systems (e.g., tert-butylphenylketone,[69] diarylketones,[83] camphor and tetralone),[64] which are not capable of forming cyanohydrins in the cyanohydrin synthesis, easily react with Me_3SiCN under catalytic conditions to yield quantitatively the corresponding silylated cyanohydrins.

The silylated cyanohydrins show higher thermal stability with respect to the non-silylated ones. This is apparently connected with the different ΔH values for the addition of a proton and Me_3Si group to the carbonyl.

X = H, $SiMe_3$

$\Delta H_{Si} - \Delta H_H = -39$ to -49 kcal/mol[64] Hence, the addition of Me_3SiCN to the carbonyl group is energetically more preferable than that of HCN.

The reaction of Me_3SiCN with aldehydes can occur without a catalyst, but only under rather severe conditions (e.g., in the case of propion aldehyde: τ = 10 h, t = 80°C).[84]



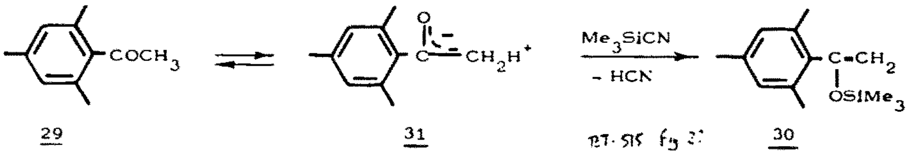
$$CH_3CH_2CHO + Me_3SiCN \longrightarrow CH_3CH_2CH(OSiMe_3){-}CN$$

(95%)

According to other authors,[62] milder conditions ($t \sim 20°C$) may also be applied.

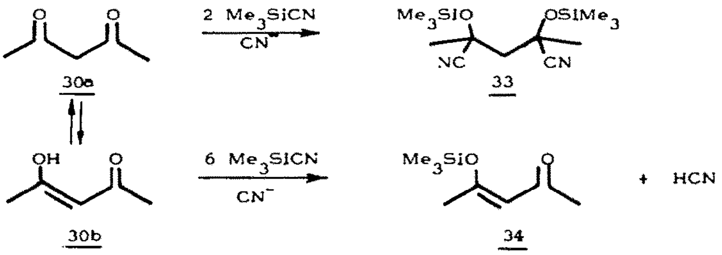
The addition of Me_3SiCN to ketones without a catalyst requires more severe conditions than for aldehydes. The reaction with cyclohexanone requires heating for 24 h at 115°C; with acetone or acetophenone temperatures of 90°C and 140°C during 18 and 25 h respectively.[84] Reaction of Me_3SiCN with α,β-unsaturated carbonyl compounds shows considerable regioselectivity.[62] 3-Methyl-3-penten-2-one[64] and 3,7-dimethyl-2,6-octadienal[85] form only the 1,2-addition products.

The reaction of methylmesitylketone (**29**) with trimethylcyanosilane in THF, initiated by the KCN · 18-crown-6 complex, leads to 1-mesityl-1-trimethylsiloxyethene **30**.[86] This probably involves the formation of an ambident anion **31** and silane heterolysis by Me_3SiCN.



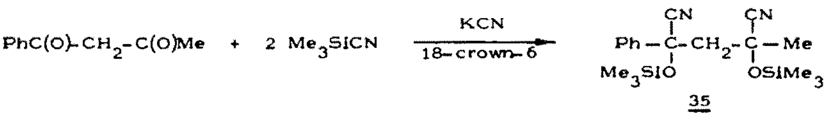
The reaction of Me_3SiCN with acetylacetone (**32**) occurs by a more complicated route.[87] The presence of catalytic amounts of KCN · 18-crown-6 in diethyl ether leads to 2,4-dicyano-2,4-bis(trimethylsiloxy)pentane (**33**, 100%). Without a catalyst only **34** is formed. This may be explained in terms of rapid tautomerism of the β-diketone. The formation of **33** involves the catalytic cyanosilylation of the keto form **30a** by Me_3SiCN.

Acetylacetone, being a rather strong acid, undergoes the enol-type reaction with Me_3SiCN involving protolysis of the Si—CN bond.



Hence, the reaction of Me_3SiCN with ketone **30** occurs regioselectively by the keto as well as the enol routes.

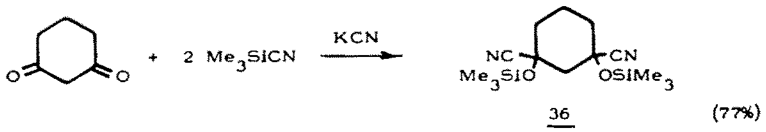
A similar reaction of Me_3SiCN with benzoyl acetone[88] leads to 1-phenyl-1,3-bis(trimethylsiloxy)-butane **35** (90%).



$$PhC(O)\text{-}CH_2\text{-}C(O)Me + 2\,Me_3SiCN \xrightarrow[\text{18-crown-6}]{\text{KCN}} Ph-\underset{Me_3SiO}{\overset{CN}{C}}-CH_2-\underset{OSiMe_3}{\overset{CN}{C}}-Me$$

35

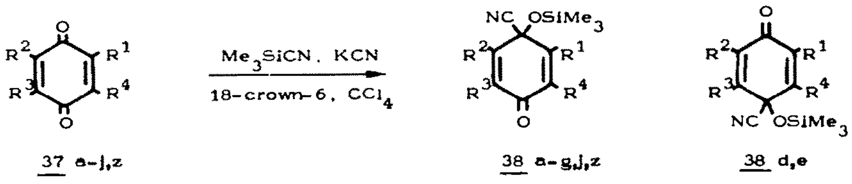
1,3-Cyclohexanedione reacts in the same way forming 1,3-dicyano-1,3-bis(trimethylsiloxy)cyclohexane (**36**, 77%).



Trimethylsilylcyanohydrins were used as protective groups for a variety of *p*-benzoquinones.[61] The regioselectivity of cyanosilylation for quinones **37a,g,j,z** was shown to be determined by the electrophilic character of the carbonyl group, the reaction giving the products of addition to the most electrophilic group **38a–g,j,z**. But in the case of **37d,e**, the steric factors become predominant and cyanosilylation occurs at the less crowded carbonyl group giving **38d,e**. In cases of considerable steric hindrance, such as in the quinone **37i**, the reaction was not observed.

Trimethylcyanosilane is very selective. It reacts with aldehydes and ketones but does not react with esters and anhydrides of carboxylic acids under catalytic conditions.[64]

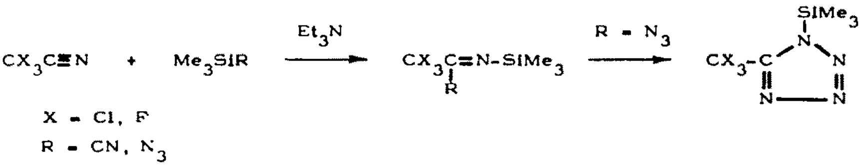
Evans[61] has shown that anion (nucleophilic) catalysis is also effective for promoting the addition of trimethylsilylazide to the carbonyl group. The reactions of both n-hexanal and iso-butyraldehyde with Me_3SiN_3 in the presence of catalytic amounts of the $KN_3 \cdot$ 18-crown-6 complex occur at room temperature yielding quantitatively the products of addition to the C=O group.



a, R^1=Me, R^2=R^3=R^4=H; b, R^1=OCH_3, R^2=R^3=R^4=H;
c, R^1=R^2=OCH_3, R^3=R^4=H; g, R^1=R^2=Me, R^3=R^4=H;
d, R^1=R^2=i-C_3H_7, R^3=R^4=H; e, R^1=R^2=t-Bu, R^3=R^4=H;
j, R^1=Me, R^2=R^3=C_4H_4, R^4=H; z, R^1=OCH_3, R^2=R^3=C_4H_4, R^4=H;
i, R^1=R^4=t-Bu, R^2=R^3=C_4H_4

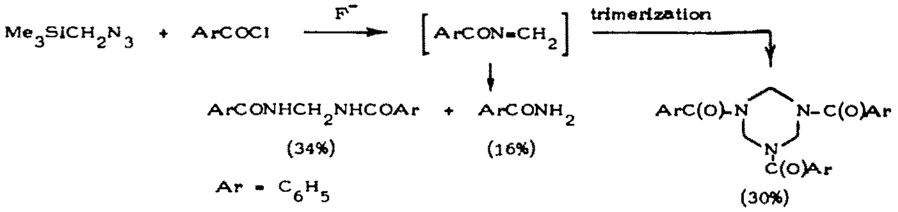
The reaction mechanism was supposed to be similar to the one mentioned above (see equation). The same aldehydes can also react in the presence of $ZnCl_2$, but in this case the reaction requires heating and the yields are lower than in the case of nucleophilic catalysis.[54]

Me_3SiCN and Me_3SiN_3 easily react with strongly electrophilic heteroatom double and triple bonds. Thus, Me_3SiN_3 reacts with hexafluoroacetone under mild conditions even without a catalyst.[90] Me_3SiCN and Me_3SiN_3 are easily added to the C≡N bond of trihaloacetonitriles in the presence of Et_3N as a catalyst.[91,92]



Acidic catalysts, such as Lewis acids, are ineffective in this reaction. Their use leads to polymerization of trihaloacetonitriles.

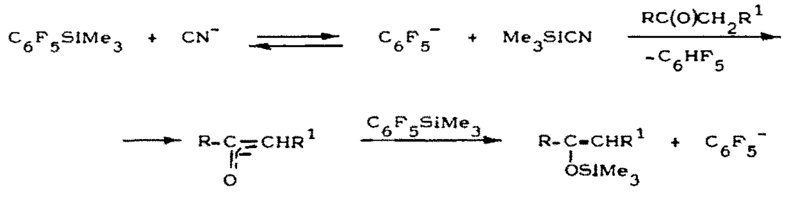
Trimethylsilylmethyl azide has various reaction sites and is used as a synthon for the amination of aromatic halides,[93] 1,3-dipolar cycloaddition[94] or heterocumulenes.[95] It has been shown that treatment of an aromatic acid halide with trimethylsilylmethyl azide in the presence of KF and crown ether gave triazide, methanediamine and benzamide derivatives.[96]



2.5. *The use of trimethylpentafluorophenylsilane as a trimethylsilylating agent*

Trimethylpentafluorophenylsilane was shown[97,98] to be an effective silylating agent in the presence of activated CN ions. Reaction with acetophenone, cyclohexanone and 2,2-dimethylbutanone-3 under the interphase catalysis conditions leads to 1-phenyl-1-trimethylsiloxyethylene (81%), 1-trimethylsiloxycyclohexene-1 (37%) and 3,3-dimethyl-2-trimethylsiloxybutene-1 (89%) respectively.

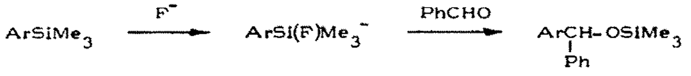
The reactions of $C_6F_5SiMe_3$ with ketones give trimethylsilyl ethers of the enols.[99] A possible mechanism of this reaction is given in the following scheme.



$$C_6F_5SiMe_3 + CN^- \rightleftharpoons C_6F_5^- + Me_3SiCN \xrightarrow[-C_6HF_5]{RC(O)CH_2R^1} R\text{-}\underset{O^-}{C}\text{=}CHR^1 \xrightarrow{C_6F_5SiMe_3} R\text{-}\underset{OSiMe_3}{C}\text{=}CHR^1 + C_6F_5^-$$

R = t-Bu, R^1= H; R=R^1= -$(CH_2)_4$- ; R= C_6H_5, R^1= H; R= CH_2=CH, R^1= Et

The reaction between (pentafluorophenyl)trimethylsilanes and benzaldehyde in the presence of KF gives the product **39**.[100] In this reaction the silicon complex coordinated with the fluoride ion was assumed to be a reaction intermediate.

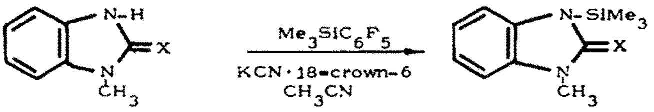


$$ArSiMe_3 \xrightarrow{F^-} ArSi(F)Me_3^- \xrightarrow{PhCHO} Ar\underset{Ph}{C}H\text{-}OSiMe_3$$

39

Ar = 3,5-Cl_2-2,4,6-F_3C_6 (68%), 3-Cl-2,4,5,6-F_4C_6 (60%)

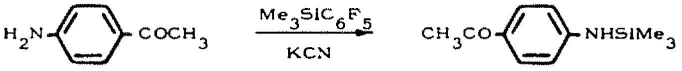
Protection of carbonyl groups is also possible in β-diketones.[101] The presence of KCN · 18-crown-6 leads to the possibility of protection of the methine group of acetylene.[101,102] *N*-Acetylacetamide can also be easily silylated stepwise.[103-105] $C_6F_5SiMe_3$ was used to protect the NH function in 1-methyl-2(3H)-benzimidazolinone (**40**) by the silyl group.[104]



40

X = O (64%), S (31%)

Anilines may also be silylated by $C_6F_5SiMe_3$, although only monosilylation occurs here.[105]



(85,5%)

3. DESILYLATION OF ORGANOSILICON COMPOUNDS AS A METHOD TO REMOVE THE PROTECTING GROUPS

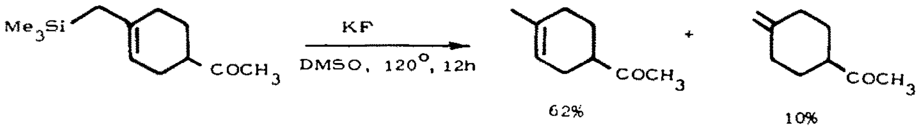
Until recently desilylation had been carried out mainly by acidic and basic hydrolysis. Recently the fluoride method has been developed. The advantages of this process consist in the mild reaction conditions, almost complete absence of side reactions, the simplicity of isolation and high yields of the required products.

3.1. *Desilylation of compounds containing* sp^3 *carbon atoms*

Desilylation of compounds containing a silicon substituent at an *sp*^{3} carbon atom occurs readily at room temperature. KF or CsF may be used as fluoride ion sources. These reagents easily remove the trimethylsilyl group at the tertiary carbon atom in **41**.[106-108]

41 (79%)

Desilylation of the trimethylsilyl group at the carbon atom in the benzyl position occurs easily,[109,110] whereas for the derivatives of allylsilane the reaction is complicated by an allylic rearrangement.[111] Thus, in the presence of KF the trimethylsilyl derivative of 4-acetylcyclohexene forms the methylenecyclohexane together with the expected methylcyclohexene.



Desilylation by fluoride ions was found to be a thermodynamically controlled process, whereas catalysis by a water–methanol solution of HCl is known to be kinetically controlled.

The replacement of the Me_3Si group at the C-3 atom by hydrogen was shown by the conversion of 3-trimethylsilyl-1,2,3-triphenylcyclopropene in the presence of TBAF in THF (65°C, 48 h). It is not clear whether the double bond is shifted in this reaction or not.[112]

3.2. *Desilylation of acetylene and ethylene derivatives*

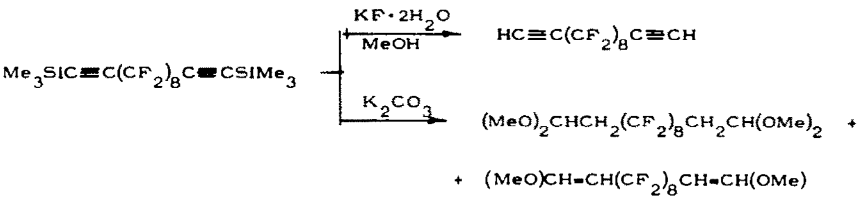
Desilylation of ethinylsilanes is catalysed by the fluoride ion. In most cases the reaction may be carried out by treating silylacetylene with the DMF or methanol solution of $KF\cdot H_2O$ for 20–30 min at 20°C. The yield is 80–95%.[113–115]

$$C_6H_{13}C{\equiv}C{-}C{\equiv}CSiMe_3 \xrightarrow{KF\cdot H_2O} C_6H_{13}C{\equiv}C{-}C{\equiv}CH \quad (79\%)$$

Desilylation of organyltrimethylsilanes by the fluoride ion occurs as a result of the formation of Me_3SiF and elimination of the organic group in the anionic form.[116]

$$PhC{\equiv}CSiMe_3 \xrightarrow{KF} PhC{\equiv}C^- + Me_3SiF \xrightarrow{EtOH} PhC{\equiv}CH$$

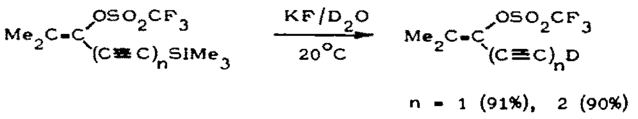
This procedure may be used to remove the protecting Me_3Si group in terminal acetylenes. For that purpose it is appropriate to use $KF\cdot H_2O$ in methanol[117] or TBAF in THF[114] or DMF.[118] The use of KF in methanol to split the $\equiv$C—Si bond in ethinylsilanes instead of the traditional K_2CO_3 helps to avoid many complications associated with the side-reactions of acetylenes with bases.[119]



$$Me_3SiC{\equiv}C(CF_2)_8C{\equiv}CSiMe_3 \xrightarrow[MeOH]{KF\cdot 2H_2O} HC{\equiv}C(CF_2)_8C{\equiv}CH$$

$$Me_3SiC{\equiv}C(CF_2)_8C{\equiv}CSiMe_3 \xrightarrow{K_2CO_3} (MeO)_2CHCH_2(CF_2)_8CH_2CH(OMe)_2 + (MeO)CH{=}CH(CF_2)_8CH{=}CH(OMe)$$

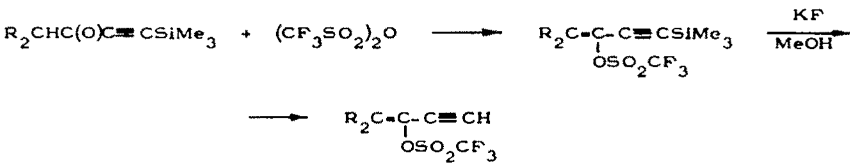
This method was successfully employed to obtain polyacetylenes containing a triflate group from the corresponding trimethylsilyl derivatives.[106,119] Deuterated acetylenes may be obtained when the reaction is carried out in the presence of D_2O or CH_3OD.[120]



$$Me_2C{=}C\begin{matrix}OSO_2CF_3\\(C{\equiv}C)_nSiMe_3\end{matrix} \xrightarrow[20^\circ C]{KF/D_2O} Me_2C{=}C\begin{matrix}OSO_2CF_3\\(C{\equiv}C)_nD\end{matrix}$$

n = 1 (91%), 2 (90%)

Protection of the triple bond permits[121] the reaction of trifluoromethane sulphonic anhydride with the carbonyl group yielding acetylenes **42**.

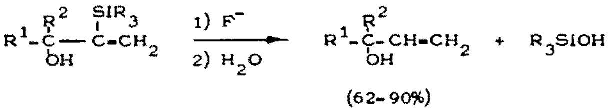


$$R_2CHC(O)C{\equiv}CSiMe_3 + (CF_3SO_2)_2O \longrightarrow R_2C{=}\underset{OSO_2CF_3}{C}{-}C{\equiv}CSiMe_3 \xrightarrow[MeOH]{KF} R_2C{=}\underset{OSO_2CF_3}{C}{-}C{\equiv}CH$$

42

Desilylation may also be carried out using a water–methanol solution of KOH.[122] The stability of the vinyl anion is known to be relatively low (pK_a 36[42]). This fact explains the inactivity of trimethylvinyl silane under nucleophilic catalysis conditions. $Me_3SiCH{=}CH_2$ is stable against KF in boiling ethanol[116] and $Me_3SiCH{=}CHCH_3$ does not react in hot aqueous alkali.[123] Removal of the silyl group by ionic fluorides is facilitated by the introduction of hydroxyl in the β-position to the silicon atom.[124] The OH group at the γ-position has no influence on the rate of desilylation.

Investigation of the synthetic applications of vinylsilanes[125] revealed unexpectedly that the Si—C bond in vinylsilanes containing the OH group at the β-sp^3 carbon atom undergoes cleavage under the action of fluoride ions (TBAF, KF, Me_4NF, CsF) in dipolar solvents (DMSO, DMF, CH_3CN).



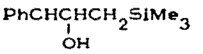
$$R^1\text{-}\overset{R^2}{\underset{OH}{C}}\text{—}\overset{SiR_3}{C}{=}CH_2 \xrightarrow[2)\ H_2O]{1)\ F^-} R^1\text{-}\overset{R^2}{\underset{OH}{C}}\text{-}CH{=}CH_2 + R_3SiOH$$

(62–90%)

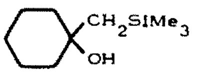
R = Me, R^1 = H, Ph, R^2 = H ; R^1 = Me, R^2 = $-(CH_2)_2CH{=}C(CH_3)_2$;

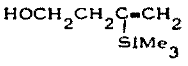
R^1,R^2 = $-(CH_2)_5-$, R = Ph, R^1 = Ph, R^2 = H , Ph ; R^1 = H , R^2 = n-$C_{10}H_{21}$

$Ph_3SiCH{=}CH_2$ and $Me_3SiCH{=}CH_2$ are not changed under similar or even more severe conditions. Moreover, this reaction is not typical for silanes, where the silicon atom is bonded with the sp^3 carbon atom or the OH group occupies the γ-position, e.g.



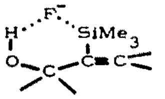
$$PhCH\underset{OH}{C}HCH_2SiMe_3$$





$$HOCH_2CH_2\underset{SiMe_3}{C}{=}CH_2$$

Splitting of the Si—C bond does not occur when the OH group is replaced by the AcO group. On the basis of these data the following cyclic transition state has been proposed.[125]



In this case the heterolysis of the Si—C bond may be explained by the simultaneous action of the following factors: (i) the presence of a strong hydrogen bond between the OH group and the fluoride ion; (ii) a favourable entropy factor of the six-membered ring; (iii) affinity of the fluoride ion towards the silicon atom; (iv) stability of the vinyl anion.

TBAF brings about the protodesilylation of vinylsilanes when the silicon contains one or more phenyl groups. The reaction is stereoselective.[126]

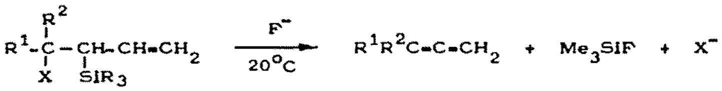
(60%)

Some more examples are given below.[127]

$$RCF{=}CClSiMe_3 \xrightarrow[DMSO]{KF\cdot H_2O} RCF{=}CHCl$$

R = n-C_5H_{11} (75%, E/Z = 98/2), Ph (85%, E/Z = 98/2)

Replacement of hydroxyl groups by a more active leaving group (e.g., the trifluoroacetate group or chlorine) facilitates β-elimination leading to the corresponding allenes.[124,125]



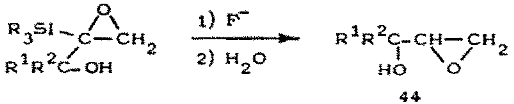
$$R^1\text{-}\overset{R^2}{\underset{X}{C}}\text{-}\underset{SiR_3}{C}H\text{-}CH{=}CH_2 \xrightarrow[20^\circ C]{F^-} R^1R^2C{=}C{=}CH_2 + Me_3SiF + X^-$$

X = Cl, $CF_3C(O)O$

The fluoride ion causes elimination of β-chlorovinylsilanes.[128]

(57–84%)

Hasan and Kishi have studied protodesilylation of some oxiranylsilanes by the fluoride ion (1.1 equivalents of $Et_4N^+F^-$) and CsF.[129] The reaction (DMSO or CH_3CN, 20°C, 2 h) occurs with quantitative formation of the corresponding oxirane without configuration changes at the carbon atom.



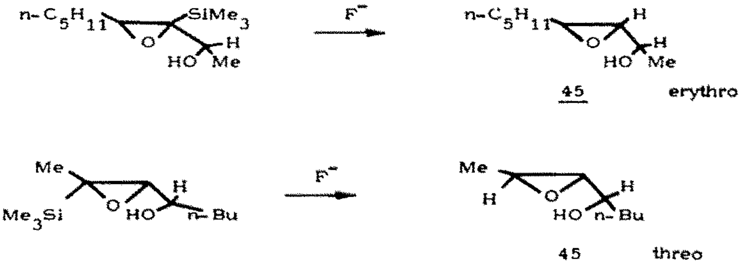
44

R = Ph, R^1 = H, R^2 = Me, Ph;

R = Me, R^1 = Ph, R^2 = H;

R^1R^2 = $-(CH_2)_5-$

Caesium fluoride was found to be as effective as tetrabutylammonium fluoride for the elimination of Me_3Si group from α,β-epoxysilanes. Thus, treatment of α,β-epoxysilane with CsF in DMSO at 25°C for 2 h leads to the epoxyalcohol **45** (90%).[130]



45 erythro

45 threo

Chan[131-134] has carried out detailed investigations of the heterolysis of the Si—C bond in oxiranylsilanes initiated by the fluoride ion.

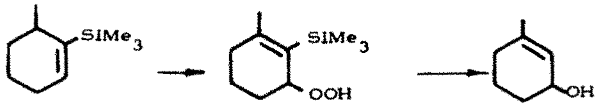
R^1 = H, R = Ph, R^2 = H, D;

R^1 = Ph, R = CH_3, R^2 = H, D

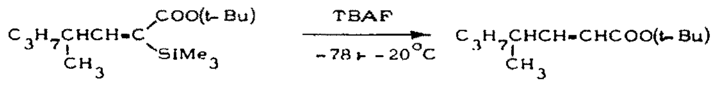
Triphenyl oxirane reacts with KF in EtOH–DMSO to form Ph_3SiF and ethylene oxide. Similarly, *trans*-1-phenyl-trimethylsilyl oxirane, after stepwise treatment by TBAF in DMSO and H_2O, forms styrene oxide in quantitative yield. The same reaction carried out using D_2O (DMSO-d_6, 20°C, 1 min) gave solely the *trans*-isomer of styrene oxide (R^2 = D). Hence, the rate of inversion of oxiranyl anion supposed by the authors is much smaller than that of the proton transfer from the electrophilic substrate (NuR^2) to the carbanion centre.

By comparison of the reaction rates the authors found that splitting of the Si—C bond by the fluoride ion occurs more easily in oxiranylsilanes than in vinylsilanes of corresponding structure.[125] α-Trimethylsilyl epoxides are converted in TBAF to non-substituted derivatives.[129,135] The existence of the β-hydroxy effect upon the cleavage of the Si—C bond by the fluoride ion has been demonstrated in numerous observations.[131,136]

The protecting group may also be removed by the reduction of the peroxide.[136,137]

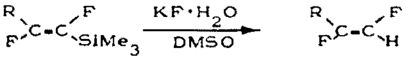


Desilylation of silylolefins is facilitated by the presence of electron-withdrawing substituents at the carbon atom bonded to the silicon atom. For example, formation of the tert-butyl ester of 3-methylhexene-2-carboxylic acid (91%) from a trimethylsilyl derivative in the presence of TBAF in wet THF was observed even at low temperatures.[138]



$$\mathrm{C_3H_7\underset{CH_3}{CH}CH{=}C(COO(t\text{-}Bu))(SiMe_3) \xrightarrow[-78\text{ to }-20^{\circ}C]{TBAF} C_3H_7\underset{CH_3}{CH}CH{=}CHCOO(t\text{-}Bu)}$$

Desilylation of *E*-difluoroalkenyltrimethylsilanes in the presence of KF occurs easily and shows a high regioselectivity[139] which is not observed in the absence of fluoride.[140]



R = Bu (85%), Me (86%), t-Bu (86%), Ph (76%), Iso-Bu (90%)

The reaction of *trans*-α,β-difluorovinylsilanes with water initiated by the fluoride ion (KF, DMSO, 20°C, 3–5 h) leads exclusively to products of protodesilylation.[139]

The reactions of *E*-2-trimethylsilylalk-2-enenitriles with electrophilic substrates occur via the intermediate formation of carbanions.[140,141] Protodesilylation of these silanes by fluoride ion (TBAF) or OH$^-$ ions (NaOH/MeOH) occurs extremely easily (0°C, 1 h) yielding *Z*-alk-2-enenitriles (up to 91% yield[140]).

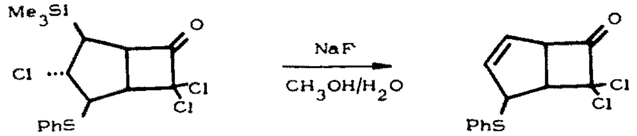
R = n-Bu, n-C$_5$H$_{11}$, C$_6$H$_{13}$, Et(n-Bu)CH, PhCH$_2$CH$_2$, Ph, p-MeOC$_6$H$_4$

3.3. *Desilylation of silicon-aromatic compounds and the removal of protecting groups from oxygen and nitrogen*

Stereoselectivity of these reactions can reach 96–100%. This favourably distinguishes it from the other known methods of synthesis of alk-2-enenitriles (e.g., from aldehydes[142–147] with predominant formation of *E*-isomers). Potassium alkylpentafluorosilicates K$_2$[RCH$_2$CH$_2$SiF$_5$] may be desilylated in high yields, but the reaction products contain terminal olefin.[143] Desilylation of the derivatives of 1-trimethylsilyl-1-methoxy-1,2-propadiene by TBAF in the THF/methanol mixture and subsequent hydrolysis of the reaction mixture leads to the formation of *trans*-α,β-unsaturated aldehydes. The reaction occurs under mild conditions with a high regioselectivity and reasonably high yields (92%).[148]

$$\mathrm{BuCH{=}C{=}C(OCH_3)SiMe_3 \xrightarrow{TBAF} BuCH{=}CH{-}C(O)CH_3}$$

α-Trimethylsilyl triflates give rise to free electrophilic vinyl carbenes.[149] The presence of halogen in the β-position leads to the elimination of Me$_3$SiCl and the formation of a double bond.[150,151]



The course of the desilylation of vinylacetylenes containing two trimethylsilyl groups bonded to two multiple bonds depends on the catalyst employed. Thus, in the presence of TBAF both silyl groups are removed whereas in the case of KOH the elimination takes place only at the triple bond.[152]

In the series of aryl and heteroaryl silanes under the influence of fluoride ions, desilylation reactions occur readily. Treatment of silylated indolizines with a 1 M solution of TBAF in THF leads to the quantitative removal of their trimethylsilyl groups.[153] The reaction of 2-trimethylsilyl-3-(trimethylsilylethynyl)furan occurs similarly.[154] 3-Trimethylsilyl-4-phenylpyrazole is converted in the presence of fluoride ion to 4-phenylpyrazole (75%).[155] Carbinol **46** gives the carbinol **47**.[156]

46 → 47

R = Ph (82%), PhCH=CH (57%), n-C_6H_{13} (27%)

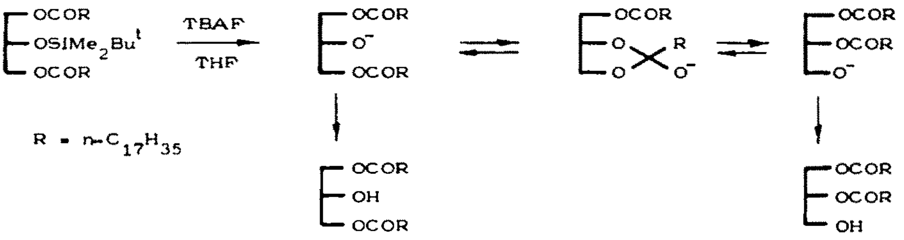
Arylsilanes are more stable against fluoride ions than alkyl-, alkinyl- and alkenyl-silanes. The introduction of donor substituents on the benzene ring leads to a further decrease of the desilylation rate.[157]

Cleavage of the aryl–Si bond in 2-methyl-5-methoxy-6-trimethylsilyl-*N*,*N*-diethylbenzamide requires prolonged boiling with CsF in aqueous DMF.[110] It is interesting to note that treatment of acylsilanes with KF·2H_2O in DMF or with TBAF in wet THF leads to aldehydes, the products of desilylation.[158]

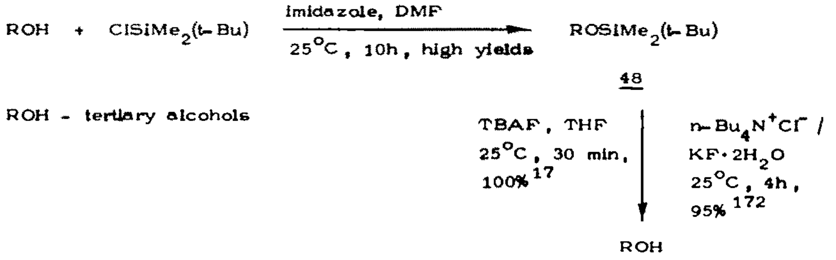
$$C_6H_5C(O)SiMe_3 \xrightarrow[\text{DMSO, 20°C, 1h}]{KF\cdot 2H_2O} C_6H_5CHO$$

The use of TBAF for cleavage of silyl ethers was reported in 1972.[159] The reaction is usually carried out in tetrahydrofuran at 25°C. The use of KF with a crown ether for deprotection of t-butyldimethylsilyl ethers is also known. Alternatively, tetra-n-butylammonium chloride with potassium fluoride dihydrate in acetonitrile at 25°C may be used.

Many investigators have used the trimethoxysilyl group to protect hydroxyl groups. However, such a protection is very sensitive to solvolysis in a protic medium. The isopropyldimethoxysilyl group was shown to undergo solvolysis 100–1000 times more slowly than Me_3SiO. But this group is unstable towards Grignard reagents and oxidation by chromic anhydride, and is labile under Wittig reaction conditions. The tert-butyldimethoxysilyl group is 1000 times more stable to solvolysis than Me_3SiO. Therefore, this group is preferable for use in multistage syntheses.[160] All the above protecting groups may be easily and virtually quantitatively removed by 30 min treatment with TBAF in THF at 20°C. Examples of the quantitative removal of the protecting tert-butyldimethylsilyl and triisopropylsilyl groups from hydroxyls may be found in oligoribonucleotide syntheses.[161-164] The removal of tert-butyldimethylsilyl protection by TBAF in THF is accompanied in the above reactions by migration of the acyl group.[165]



Later it was shown that the hydroxyl group may be protected by dialkyldisiloxane groups. In this case the desilylation reaction occurs as easily as with trialkylsiloxy groups.[166,167] Examples of migration were also reported for other substrates (e.g., carbohydrates,[168] prostaglandins[169] and nucleosides[170,171]). Hence, the t-butyldimethylsilyl group should not be used for hydroxyl protection when acyl migration is possible.



$$ROH + ClSiMe_2(t\text{-}Bu) \xrightarrow[\text{25°C, 10h, high yields}]{\text{imidazole, DMF}} ROSiMe_2(t\text{-}Bu)$$

48

ROH – tertiary alcohols

TBAF, THF, 25°C, 30 min, 100%[17] ↓ $n\text{-}Bu_4N^+Cl^-$ / KF·2H_2O, 25°C, 4h, 95%[172]

ROH

t-Butyldiphenylsilyl ether **48** was used to protect the primary hydroxyl group in the synthesis of thromboxane B_2 from D-glucose.[173-175]

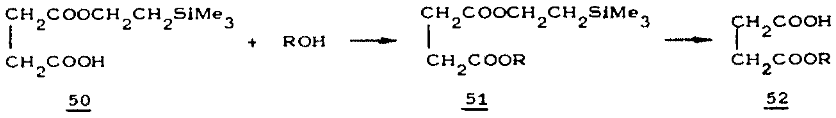
$$\mathrm{ROSiPh_2(t\text{-}Bu)} \longrightarrow \mathrm{ROH}$$

A new protecting group for alcohols has been described recently. Tert-butylmethoxyphenylsilyl ethers are stable to hydrolytic conditions but are extremely sensitive to fluoride treatment. This permits their selective removal in the presence of t-butyldimethylsilyl or t-butyldiphenylsilyl ethers. Selective protection of primary hydroxyl groups or, by varying the solvent, of secondary and tertiary hydroxyl groups and enols is possible.

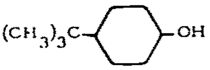
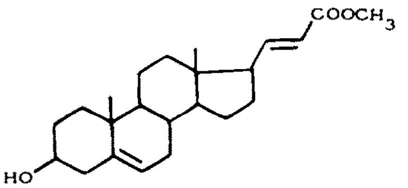
t-Butyldiphenylchlorosilane may also be used to protect the phenolic hydroxyl groups.

$$\underset{\underline{49}}{\mathrm{ArOH}} \xrightarrow[25^{\circ}\mathrm{C},\ 3\mathrm{h},\ 96\%]{\mathrm{(t\text{-}Bu)Me_2SiCl,\ DMF}} \mathrm{ArOSiMe_2(t\text{-}Bu)} \xrightarrow[\mathrm{THF},\ 25^{\circ}\mathrm{C},\ 2\ days]{0{,}1\mathrm{M\ HK},\ 0{,}1\mathrm{M\ NaF}} \underline{49}$$

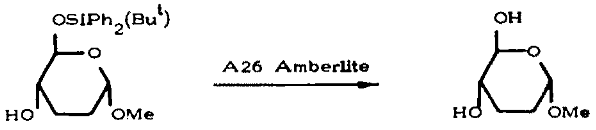
The 2-(trimethylsilyl)ethyl group[176] seemed especially favourable for protection of one carbonyl group in a mixed succinate, because it can be removed with TBAF under non-hydrolytic, neutral conditions.[176,177] Condensation of primary and secondary alcohols by the hemisuccinate **50** gave the corresponding mixed succinate **51** in excellent yield. The deprotection step has also been included in the preparation of the hemisuccinates **52** in good yield.[178] The method is unsuitable for the preparation of estrone hemisuccinate because the ester group may be attacked by TBAF. Estrone hemisuccinate and acetate decomposed to estrone when treated with TBAF under standard conditions.



$$\underset{\underline{50}}{\begin{matrix}\mathrm{CH_2COOCH_2CH_2SiMe_3}\\|\\\mathrm{CH_2COOH}\end{matrix}} + \mathrm{ROH} \longrightarrow \underset{\underline{51}}{\begin{matrix}\mathrm{CH_2COOCH_2CH_2SiMe_3}\\|\\\mathrm{CH_2COOR}\end{matrix}} \longrightarrow \underset{\underline{52}}{\begin{matrix}\mathrm{CH_2COOH}\\|\\\mathrm{CH_2COOR}\end{matrix}}$$

ROH	Yield ,%	51	52
$CH_3(CH_2)_{16}CH_2OH$		93	74
	cis	91	76
	trans	84	76
Cholesterol		85	81
Estrone		92	-
		83	70

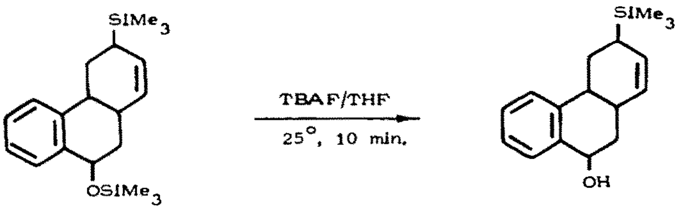
The efficiency of different desilylating agents in the series of nucleotides and nucleosides has been considered.[179] Other sources of fluoride ion have also been suggested, e.g. the A26 Amberlite ion-exchange resin in the F^- form.[180]



(94%)

However, they do not possess any distinct advantages over the readily available alkali metal fluorides.

The removal of protecting groups bonded with oxygen by the ionic fluorides in protic solvents occurs easily in comparison with carbon-bonded groups. This makes possible the selective elimination of silyl groups.[181]

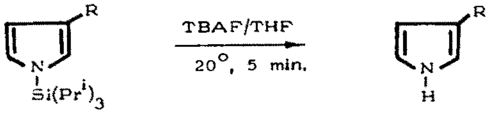


Triorganylsilyl esters of alcohols, enols and phenols may also be desilylated.[182-184]

$$Me_3SiO\text{-}\underset{R^5}{\overset{R^4}{C}}\text{-}\underset{R^2}{\overset{R^1}{C}}\text{-}COOR^3 \xrightarrow{TBAF} HO\text{-}\underset{R^5}{\overset{R^4}{C}}\text{-}\underset{R^2}{\overset{R^1}{C}}\text{-}COOR^3$$

The peculiarity of the fluoride desilylation of compounds containing the O-bonded trimethylsilyl group is evident in the high chemoselectivity of the reaction. Even in the case of complex polyfunctional molecules it allows splitting of only the bonds, while other potential reaction centres remain unchanged.[185,186] Desilylation of tert-butyldimethylsilyl ethers of allyl alcohols by TBAF in THF or by KF · 18-crown-6 in DMSO was shown to proceed in quantitative yield without isomerization or rearrangement.[187] Dramatic examples of the high selectivity of desilylation processes have been found.[188] The optical purity of the substances remains unchanged.[188]

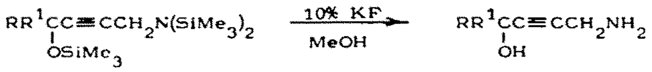
Some examples of desilylation of compounds containing the protective silyl group bonded with hydrogen by the fluoride ion have been reported, e.g. the formation of 3-substituted pyrrols from *N*-triisopropylsilyl derivatives.[189]



R = Br (65%), NO$_2$ (100%), COOEt (100%)

Substituted thiazole is also quantitatively desilylized by TBAF in THF.[184]

Removal of the protecting group from the amino nitrogen atom should be mentioned.[190]



$$RR^1\underset{OSiMe_3}{C}C\equiv CCH_2N(SiMe_3)_2 \xrightarrow[MeOH]{10\%\ KF} RR^1\underset{OH}{C}C\equiv CCH_2NH_2$$

R = H, R^1 = Ph (78%); r = H, R^1 = EtCH=C(Me) (90%)

4. DESILYLATION AS A METHOD TO GENERATE ACTIVE NUCLEOPHILES

It should be noted that the easy formation of nucleophilic species in desilylation reactions by fluoride ion promotes reactions with electrophiles. Here are some examples.

4.1. *Alkylation and arylation of carbonyl compounds*

The easy F$^-$-catalysed desilylation of organosilicon compounds containing a C—SiR$_3$ bond has been developed into a general method for the transfer of acyl,[191] alkinyl,[192,193] benzyl,[194,195] allyl[196] and oxiranyl[131] carbanions to electrophilic centres. However, in spite of the large number of papers in this field, this synthetic methodology has been applied with very few exceptions only to aldehydes and ketones as the electrophiles. The ability of organosilanes to be cleaved by the fluoride ion with formation of carbanions was used to introduce alkyl groups. For example, benzyltrimethylsilane was found to be a convenient reagent for the benzylation of aldehydes and ketones in the presence of fluoride ions.[194,197,198]

$$C_6H_5CHO + RSiMe_3 \xrightarrow[\text{THF, 20°C, 12h}]{SiO_2/TBAF} C_6H_5CH(OH)R$$

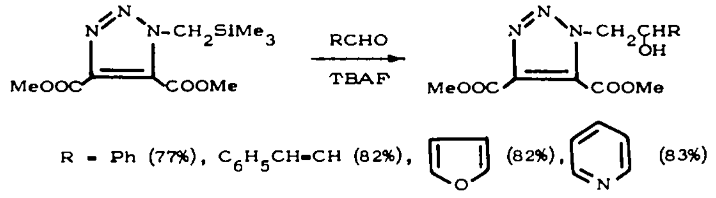
R = o-$NO_2C_6H_4CH_2$- (70%), 3,5-$Cl_2C_6H_3CH_2$- (70%), $C_6H_5CH{=}CHCH_2$- (50%),
4-$CH_2C_5H_4N$ (80%)

1-Phenyl(nitrophenyl)ethane was obtained in 60% yield by the reaction of (2-nitrobenzyl)trimethylsilane with benzylbromide in the presence of F^- ions.[194]

$$C_6H_5CH_2Br + RSiMe_3 \xrightarrow{SiO_2/TBAF} C_6H_5CH_2R$$

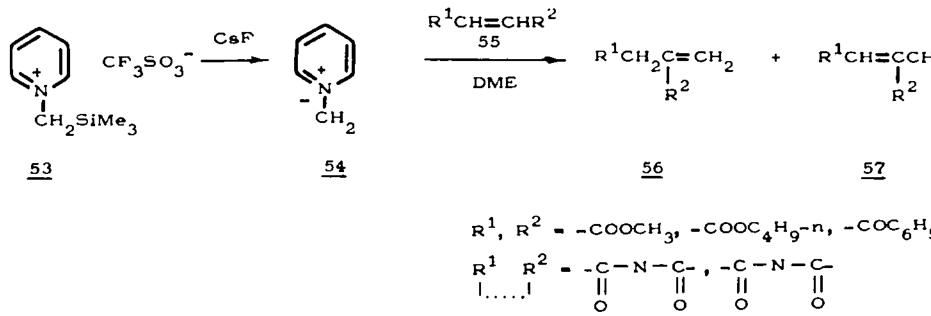
R = o-$NO_2C_6H_4CH_2$- (60%), 3,5-$Cl_2C_6H_3CH_2$- (50%), $C_6H_5CH{=}CHCH_2$- (40%)

The benzylation of some heterocyclic aldehydes was also carried out. The heterocyclic triazole reacted with aldehydes in the presence of TBAF to yield secondary alcohols (~ 80%) after hydrolysis.[198]



Benzyl, heteroaryl and allylsilanes react in the presence of CsF or silica gel/TBAF with electrophiles, such as δ-valero and ε-caprolactone, and with cyclohexen-2-one under mild conditions.[199] 2-Trimethylsilylthiasole (as well as 2-trimethylsilylbenzthiasole) easily reacts with benzaldehyde in the presence of fluoride ion to give secondary alcohols in high yields after hydrolysis.[200] The reaction is catalysed by KF in 18-crown-6 and by CsF or TBAF on silica gel. Lactones and α,β-unsaturated ketones also react similarly to form benzthiasole derivatives with long-chain alkyl substituents in position 2.

Pyridinium methylide (**54**), prepared *in situ* from *N*-(trimethylsilylmethyl)pyridinium triflate (**53**) and CsF, reacts with electron-deficient olefins **55** in 1,2-dimethylethane to give exomethylene compounds **56** in variable yields together with different amounts of trisubstituted olefins **57**.[201]



The conversion of disubstituted olefins **56** into trisubstituted olefins **57** is easily achieved using a catalytic amount of triethylamine in chloroform at room temperature. A general method has been reported[202] for transfer of an $ArCOCH_2^-$ group to electrophilic centres leading to a novel synthesis of a variety of mono- or α,γ and α,δ-dicarbonyl compounds (some of them not readily available) using the conventional routes. This method is based on the high reactivity of the aromatic β-ketosilanes towards a number of carbon electrophiles in the presence of F^- ions.

$$C_6H_5C(O)CH_2SiMe_3 \xrightarrow{E,\ F^-} C_6H_5C(O)CH_2E$$

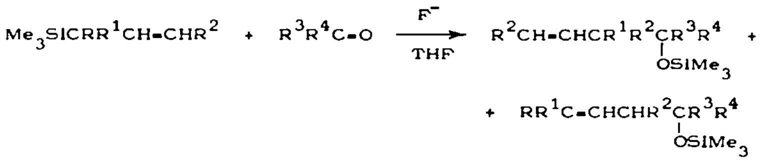
Details of these reactions are given in Table 3. The reactions with various electrophiles proceeded smoothly in reasonably good yield and were found to be regioselective. In addition to the usual

Table 3. Reactions of $C_6H_5COCH_2SiMe_3$ with eletrophiles in THF, catalysed by CsF[202]

Electrophile	Product	Reaction time (h)	Yield (%)
PhCHO	PhCOCH=CHPh	4	90
$CH_2CH_2CH_2CH{=}CHC{=}O$	$PhCOCH_2CHCH_2CH_2CH_2COCH_2$	6	80
$PhCH_2Br$	$PhCOCH_2CH_2Ph$	12	70
$CH_2{=}CHCH_2Br$	$PhCOCH_2CH_2CH{=}CH_2 + PhCOCH(CH_2CH{=}CH_2)_2$	15	30 + 30
$PhCOCH_2Br$	$PhCOCH_2CH_2COPh$	16	40
$PhCOSiMe_3$	$PhCOCH{=}CHPh + PhCOCH_2COPh$	8	20 + 40
2-Furyl$COSiMe_3$	2-FurylCH=CHCOPh + 2-Furyl$COCH_2COPh$	2	10 + 40

carbonyl derivatives, organic bromides interact with β-ketosilanes. The use of α-ketosilanes as electrophiles is also noteworthy.

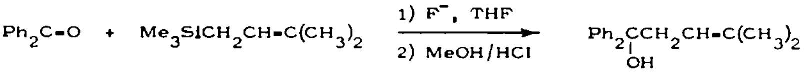
The allyl–silicon bond of allyltrimethylsilane is readily cleaved by TBAF to give a new allylic anionic species. The addition of allylsilanes to electrophiles is one of the most useful C—C bond formation reactions.[203] The reactions of allylsilanes with carbonyl compounds under the nucleophilic catalysis conditions were carried out for the first time by Sakurai and his co-workers[196] in 1978. Allylsilanes were found to undergo addition to the C=O group of aldehydes and ketones in mild conditions (60°C, 4–48 h) under the influence of fluoride ions (5% molar TBAF) yielding the adducts (60–90%).



$$Me_3SiCRR^1CH{=}CHR^2 + R^3R^4C{=}O \xrightarrow[THF]{F^-} R^2CH{=}CHCR^1R^2\underset{\displaystyle OSiMe_3}{\underset{|}{C}}R^3R^4 + RR^1C{=}CHCHR^2\underset{\displaystyle OSiMe_3}{\underset{|}{C}}R^3R^4$$

$R{=}R^1{=}R^2{=}H$; $R{=}R^1{=}H$, $R^2{=}CH_3$; $R{=}R^2{=}H$, $R^1{=}CH_3$;
$R{=}R^1{=}CH_3$, $R^2{=}H$

In this reaction allylsilanes form the corresponding ambident allyl anions which then attacks the electrophilic carbon atom of the carbonyl group (preferentially by the less substituted carbon atom of the anionic species). Thus, allylation of benzophenone by ν,ν-dimethylallyltrimethylsilane occurs solely with participation of the primary carbon atom of the allylic system.



$$Ph_2C{=}O + Me_3SiCH_2CH{=}C(CH_3)_2 \xrightarrow[2)\ MeOH/HCl]{1)\ F^-,\ THF} Ph_2\underset{\displaystyle OH}{\underset{|}{C}}CH_2CH{=}C(CH_3)_2$$

(87%)

The reaction is catalysed by fluoride ion and examples are listed in Table 4.

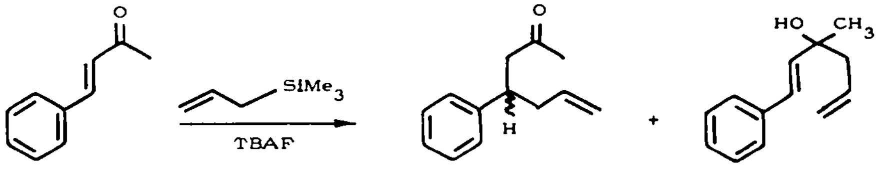
The interaction of butanal with α-methylallyltrimethylsilane leads to the formation of a mixture of isomeric products.

$$Me_3SiCH(CH_3)CH{=}CH_2 + CH_3(CH_2)_2CHO \xrightarrow{F^-} \underset{(41\%)}{CH_3(CH_2)_2CH(OH)CH_2CH{=}CHCH_3} + \underset{(30\%)}{CH_3(CH_2)_2CH(OH)CH(CH_3)CH{=}CH_2}$$

Table 4. Reaction of allylsilanes with carbonyl compounds catalysed by TBAF in THF at reflux[196]

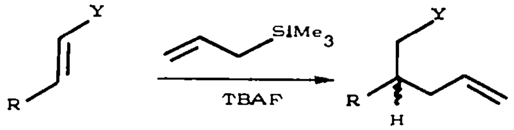
Allylsilane	Carbonyl compound	Products	Yield (%)
$Me_3SiCH_2CH{=}CH_2$	$CH_3(CH_2)_2CHO$	$CH_3(CH_2)_2CH(OH)CH_2CH{=}CH_2$	83
	$CH_3(CH_2)_3CHO$	$CH_3(CH_2)_3CH(OH)CH_2CH{=}CH_2$	92
	PhCHO	$PhCH(OH)CH_2CH{=}CH_2$	93
	$PhCOCH_3$	$PhC(OH)(CH_3)CH_2CH{=}CH_2$	60
$Me_3SiCH_2CH{=}C(CH_3)_2$	PhCOPh	$Ph_2C(OH)CH_2CH{=}C(CH_3)_2$	87

When the electrophile is an α,β-unsaturated ketone then conjugate addition and 1,2-addition take place competitively, e.g., treatment of *E*-4-phenyl-3-buten-2-one (**58**) with trimethylallylsilane and TBAF in THF gives the 1,4- and 1,2-addition products (**59a** and **59b**) in 24 and 50% yields respectively.[199]



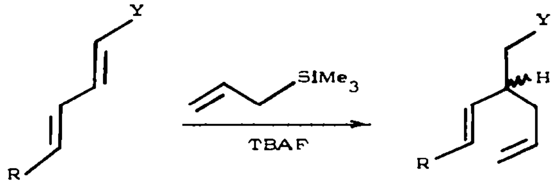
58 59a 59b

The question whether the allylic nucleophile generated by fluoride ion from trimethylallylsilane exhibits high selectivity for conjugate addition with less electrophilic Michael acceptors has been examined.[204] Under fluoride catalysis conditions, only 1,4-conjugate addition was observed for either α,β-unsaturated esters or nitriles.



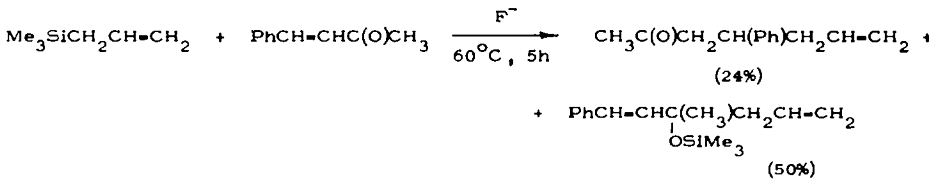
R = C_6H_5, Y = $COOCH_3$ (90%); R = C_6H_5, Y = CN (65%); R = C_6H_5, Y = $CONEt_2$(80%);
R = H, Y = $COOCH_2C_6H_5$ (65%); R = $COOCH_3$, Y = $COOCH_3$ (80%);
R = CH_3, Y = COOEt (27%); R = $(CH_3)_3C$, Y = COOEt (80%);
R = $(CH_3)_3C$, Y = CN (65%); R = 2-Furyl, Y = CN (91%); R = 2-Furyl, Y = COOEt (83%);
R = 2-Furyl, Y = COOEt (83%).

This method also afforded exclusively the 1,4-adduct in allylation reactions with polyene esters and nitriles.



R = C_6H_5, Y = CN (37%); R = C_6H_5, Y = COOEt (63%);
R = CH_3, Y = COOEt (31%)

The use of α,β-enones as electrophiles leads to the conjugate 1,4-addition as well as 1,2-addition.



$$Me_3SiCH_2CH{=}CH_2 + PhCH{=}CHC(O)CH_3 \xrightarrow[60^{\circ}C,\ 5h]{F^-} \underset{(24\%)}{CH_3C(O)CH_2CH(Ph)CH_2CH{=}CH_2} + \underset{(50\%)}{PhCH{=}CH\underset{OSiMe_3}{C}(CH_3)CH_2CH{=}CH_2}$$

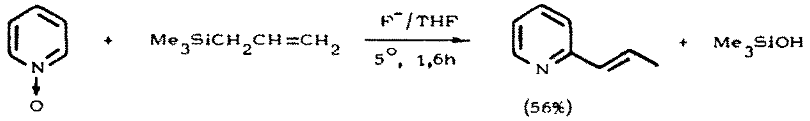
Aldehydes react more easily than ketones, while nitriles, epoxides and esters do not react even after prolonged boiling. For example, methyl laevulinate is allylated regioselectively only at the keto group (Table 4).

The fluoride ions generate the active species from allyltrialkylsilanes. These react with carbonyl compounds yielding secondary alcohols after hydrolysis. The reaction of 2-(trifluoromethyl)-allyltrimethylsilane with carbonyl compounds in the presence of TBAF or CsF[188] leads to unsaturated alcohols.

$$CH_2{=}C(CF_3)CH_2SiMe_3 + RR^1C{=}O \xrightarrow[DMF]{CsF} CH_2{=}C(CF_3)CH_2CRR^1(OSiMe_3)$$

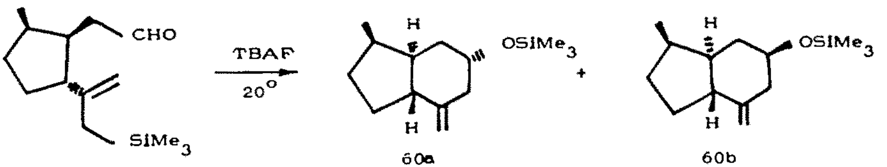
$R = C_6H_5$, $R^1 = C_6H_5$, CH_3; $R = C_2H_5$, $R^1 = C_2H_5$, $CH_3CH_2CH_2$

The reaction with pyridine *N*-oxide leads to 2-propenylpyridine (56%).[205] The proposed mechanism involves coordination of the silicon atom with the oxygen atom of the *N*-oxide group followed by rearrangement of the dihydropyridine silyl ether.[205]



The catalytic amount (0.1 equivalents) of TBAF is quite sufficient for the reaction to proceed. The reaction includes the stage of intermediate formation of 1,2-adduct, further elimination of Me_3SiOH and isomerization of 2-allylpyridine to 2-propenylpyridine. *N*-Oxides of 3-methyl- and 4-methylpyridine react similarly.

The ability of allylsilanes to be added to the C=O group under conditions of nucleophilic catalysis provides the basis for the new method of intramolecular cyclization of some unsaturated aldehydes.[206,207]

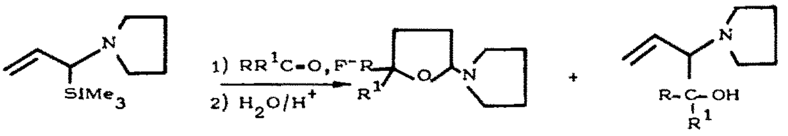


60a 60b

This intramolecular allylation yields axial and equatorial isomers of exocycloolefins, the yield of the equatorial isomer **60b** being 82%. The presence of Lewis acids as catalysts in this reaction leads mainly to the axial isomer **60a**. Thus, with $SnCl_4$ and $BF_3 \cdot Et_2O$ as Lewis acids, the ratios of the isomers **60a** (axial) and **60b** (equatorial) are 59 : 41 and 85 : 15 respectively.

Intramolecular allylation under conditions of nucleophilic catalysis (0.2 equivalents of TBAF) has been successfully used by Trost and Vincent for the synthesis of muskone and analogous reactions.[208]

The presence of the pyrrolidino-substituent in compound **61** inhibits the reactions of electrophiles activated by Lewis acids. Such deactivation was not observed in the case of β-amino-γ-trimethylsilyl crotonate esters.[209] The formation of a stable amino–Lewis acid complex in this case leads to a lack of reaction for compound **61**.[210] Activation of compound **61** by CsF or TBAF promotes the reaction with carbonyl compounds (Table 5).

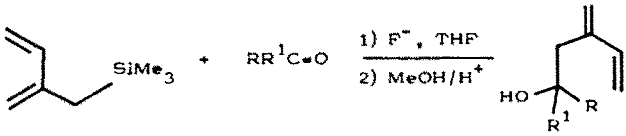


61 62 63

Table 5. Reactions of compounds **61** with carbonyl compounds (20°C) catalysed by fluoride ion[210]

Carbonyl compounds	Catalyst	Solvent	Reaction time (h)	Yield of (62 + 63) (%)	Ratio 62 : 63
PhCHO	CsF	DMF	30	55	2 : 3
PhCHO	TBAF	THF	72	53	1 : 1
$(CH_3)_2CHCHO$	CsF	DMF	30	30	2 : 3
$(CH_3)_2CO$	CsF	DMF	30	40	3 : 2
$Ph(CH_3)CO$	CsF	DMF	30	40	3 : 2
$Ph(CH_2CH_3)CO$	TBAF	DMF	24	40	1 : 1

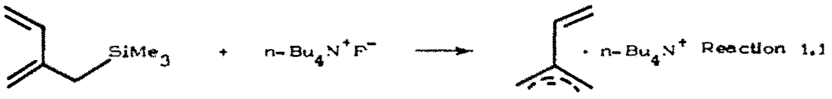
In 1983 Sakurai and his co-workers carried out the isoprenylation reaction of a number of aldehydes and ketones with 2-(trimethylsilyl)-methyl-1,3-butadiene in the presence of a catalytic amount of TBAF.[211]



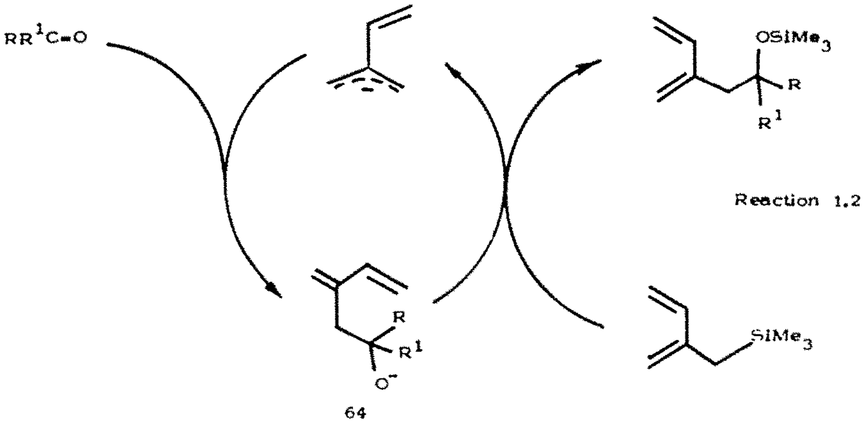
In the case of isovaler aldehyde (20°C, 30 min) and 3-methyl-2-butenal (35°C, 2 h), the reaction leads to ipsenol and ipsdienal respectively, which are components of pheromones.

Sakurai and his co-workers had suggested that the reactions of allylsilanes with carbonyl compounds, initiated by fluoride ion,[196] proceed by a mechanism analogous to the catalytic mechanism. Later,[111] the same authors suggested an alternative autocatalytic mechanism on the basis of the fact that isoprenylation of benzophenone takes place quantitatively even at 50°C (boiling point of Me_3SiF is 16.4°C) (Scheme 3).

The first stage is initiation (Reaction 1.1):



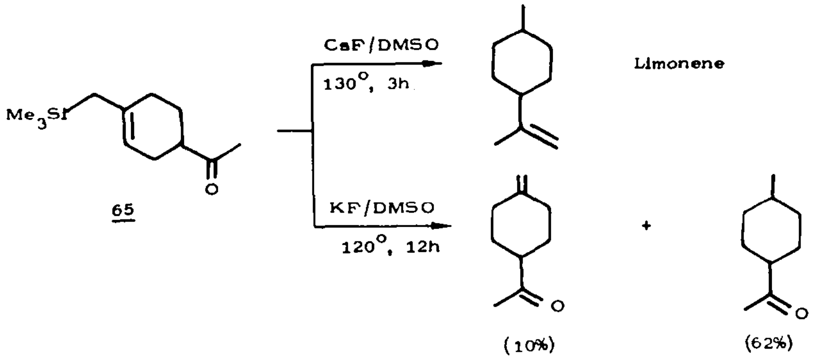
The second stage is autocatalytic mechanism (Reaction 1.2):



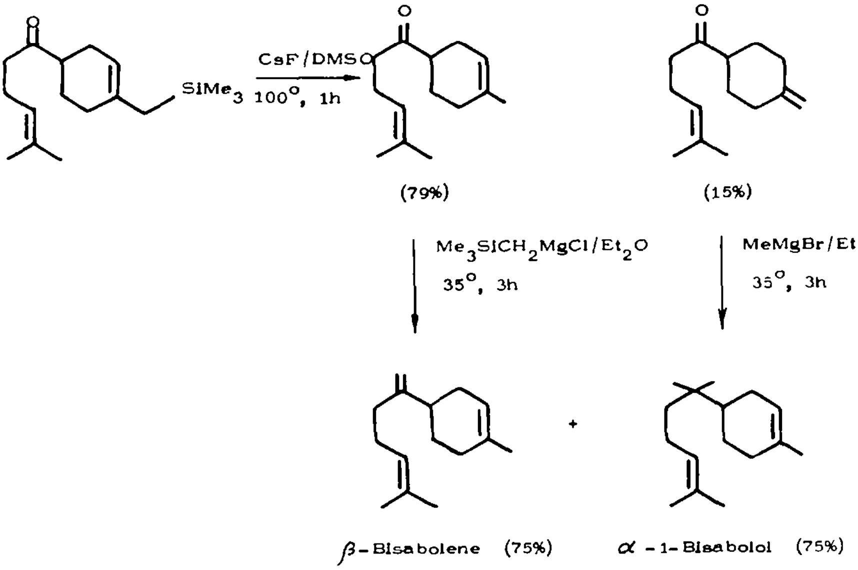
64

Scheme 3.

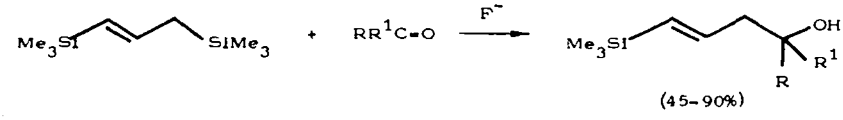
According to this mechanism (Scheme 3) the interaction (S_N2-Si-type reaction) of allylsilane and fluoride ion leads to Me_3SiF and the allyl anion. The latter then undergoes addition to the C=O group to give the alkoxy anion **64**. The alkoxy anion **64** then reacts with allylsilane to yield the final product and regenerate the allyl anion. As follows from Scheme 3, the role of the fluoride ion consists only in the initial generation of the allyl anion. In this process the fluoride ion forms Me_3SiF and so does not participate any further in the reaction. Thus, both the catalytic (Reaction 1.1.) and autocatalytic (Reaction 1.2) mechanisms include the stage of allyl anion generation. The authors,[111] however, do not preclude participation of the hypervalent allylsilicon intermediate of the $[CH_2{=}CH\,CH_2Si(F)Me_3]^-$ type as a nucleophile in the reaction. But without investigation of the reaction kinetics, the real structure of such intermediates, and the mechanism of their formation and further transformation are just the subject of speculation. Future work in this field will be directed towards the elucidation of the mechanism and the development of new synthetic methods for the preparation of useful products by a waste-free technology. The product **65** is itself an allylsilane and can be used for terpene synthesis.



Further applications in terpene syntheses are illustrated below.

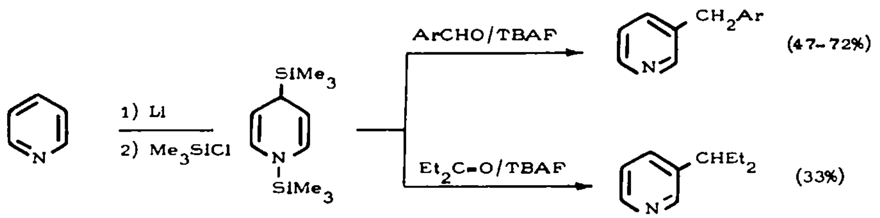


TBAF in THF was found to be an effective catalyst in the reaction between aldehydes and 2-trimethylsilylmethyl-1,3-butadiene leading to the formation of alcohols.[211] The allyl anion is more stable than the vinyl anion. This is indicated by the easy formation of the allyl anion in the reaction of trimethylallylsilane with fluoride ion in the gas phase.[212] Moreover, cleavage of only the allylic Si—C bond by the fluoride ion occurs in 1,3-bis(trimethylsilyl)propene although it is both a vinyl- and an allyl-silane. The easier cleavage of the C_{sp^3}—Si bond by the fluoride ion in compounds with a protected silicon-containing group in comparison with the C_{sp^2}—Si bond makes it possible to obtain unsaturated alcohols containing the SiR_3 substituent at the double bond.[213] The reaction of these silanes with carbonyl compounds (THF, 25°C, 3–16 h) followed by protolysis of the reaction mixture leads to *E*-1-trimethylsilylbut-1-en-4-ols.[214]

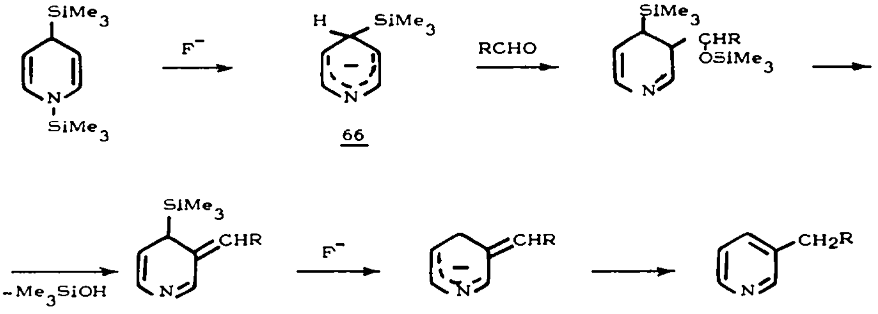


$R = H$, $R^1 = CH_3$, $n\text{-}C_6H_{13}$, C_6H_5 ;
$RR^1 = -(CH_2)_4-$, $-(CH_2)_5-$

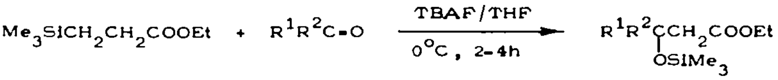
The reaction of the allyl carbanion with aldehydes may be regarded as the basis of an elegant method for the synthesis of 3-alkylpyridines.[215]



The key stage of the transformation of dihydropyridine to 3-alkylpyridine is, evidently, alkylation of the carbonyl compound by the carbanion (anionic σ-complex **66**). This corresponds to the addition of the trimethylsilyl anion at position 4 of pyridine.



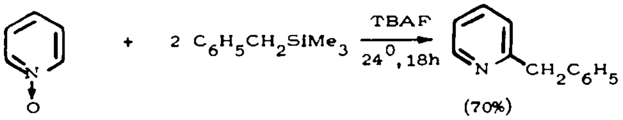
The reaction of aldehydes and ketones with carbalkoxymethyltrialkylsilanes is a route to β-oxycarbonyl compounds.[216,217]



$$Me_3SiCH_2CH_2COOEt + R^1R^2C{=}O \xrightarrow[0^\circ C,\ 2\text{–}4h]{TBAF/THF} R^1R^2\underset{OSiMe_3}{C}CH_2COOEt$$

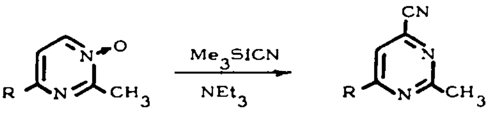
$R^1 = H$, $R^2 = C_6H_5CH{=}CH-$ (81%), $C_4H_9CH{=}CH-$ (82%), $CH_3CH{=}CH-$ (69%), Ph (76%); $R^1{=}R^2 = C_6H_5$ (88%)

Several 2-substituted pyridines are formed in the reaction of benzyltrimethylsilane with pyridine *N*-oxide in the presence of TBAF.[218]



(70%)

Pyridine, quinoline and isoquinoline *N*-oxides are easily cyanated by Me_3SiCN in the presence of triethylamine. Thus, pyridine *N*-oxide reacts with this compound to form 2-cyanopyridine (80%).[219] 4-Cyanopyridine is obtained in small amounts (~ 0.5%). Instead of Me_3SiCN, a mixture of Me_3SiCl and NaCN may be used. It is interesting to note that 3-hydroxpyridine *N*-oxide reacts with Me_3SiCN to form 2-cyano-3-hydroxypyridine (73%). The same picture is observed when this reagent reacts with substituted pyrimidine *N*-oxides.[220]



(71–90%)

R = H, CH_3, C_6H_5, OCH_3

2-$Me_3SiCH_2C_6H_4COOMe$ undergoes cyclization with olefins in $(Me_2N)_3P{=}O$ containing CsF to give α-tetralones.[221] TBAF initiates the reaction of (η^5-cyclopentadienyl)(trimethylsilyl)iron with benzylchloride and 1-bromobutane.[222]

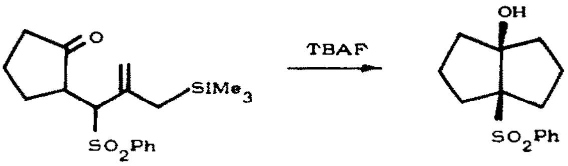
$$C_p(CO)_2(SiMe_3)Fe + RHal \xrightarrow{TBAF/THF} C_p(CO)_2(R)Fe$$

$$RHal = C_6H_5CH_2Cl \ (50\text{–}89\%),\ C_4H_9Br \ (45\text{–}85\%)$$

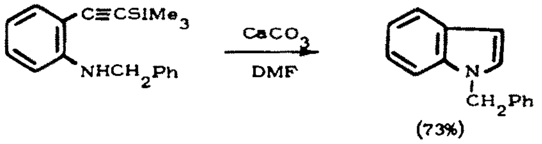
Introduction of the propargyl group by this method is accompanied by isomerization of the intermediate carbanion leading mainly to the formation of allene derivatives.[219] The reaction of propargyltrimethylsilane with acrolein and benzaldehyde yields vinylpropargylcarbinol and phenylpropargylcarbinol (20% and 30% respectively). At the same the corresponding allene-containing alcohols may be obtained similarly with a 70–80% yield. Propargylcarbinols cannot be obtained from aliphatic aldehydes (R^1 = Me, Et, Pr, Bu, t-Bu).

$$HC{\equiv}CCH_2SiMe_3 + R^1R^2C{=}O \longrightarrow CH_2{=}C{=}CH\underset{OH}{C}R^1R^2 + HC{\equiv}CCH_2\underset{OH}{C}R^1R^2$$

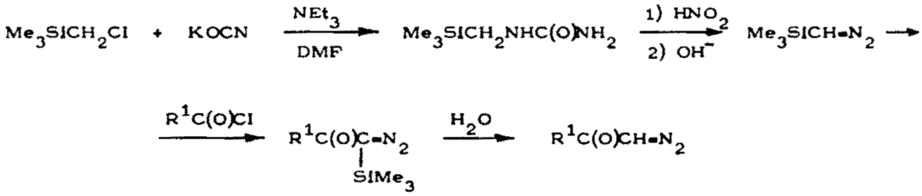
This approach was used for the intramolecular cyclization ; formation of the cyclic compound takes place simultaneously with elimination of the Me_3Si group.[196,206,208]



Cyclization also takes place in the case of other basic agents, such as $CaCO_3$.[214]



Organosilicon reagents possess certain advantages over standard reagents. For example, trimethylsilyldiazomethane, which can be easily obtained from (chloromethyl)trimethylsilane, is much more stable than diazomethane. It reacts with carboxylic acid chlorides forming intermediate α-trimethylsilyldiazoketones. The latter are highly reactive: their protolysis leads to α-diazoketones which yield benzyl esters of homologated acids by the Wolff rearrangement.[223,224]



$$Me_3SiCH_2Cl + KOCN \xrightarrow[DMF]{NEt_3} Me_3SiCH_2NHC(O)NH_2 \xrightarrow[2)\ OH^-]{1)\ HNO_2} Me_3SiCH{=}N_2 \longrightarrow$$

$$\xrightarrow{R^1C(O)Cl} R^1C(O)\underset{SiMe_3}{C}{=}N_2 \xrightarrow{H_2O} R^1C(O)CH{=}N_2$$

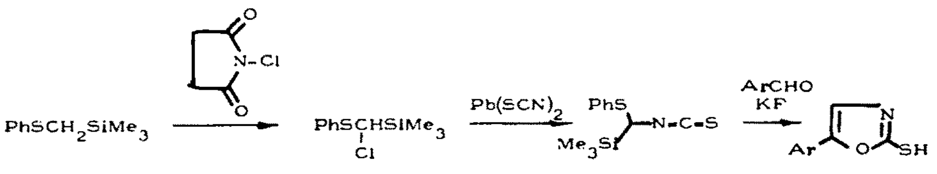
$$R^1 = c\text{-}C_6H_{11},\ C_6H_5CH_2CH_2,\ C_6H_5,\ \text{1-Naphthyl},\ \text{2-Thiophenyl}$$

Primary, secondary and tertiary alcohols, on treatment with Me_3SiCl in the presence of NaCN and NaI, form the corresponding nitriles.[225]

$$ROH \xrightarrow[DMF,\ 60\text{–}65^\circ C]{NaCN/Me_3SiCl/NaI} RCN \quad (64\text{–}98\%)$$

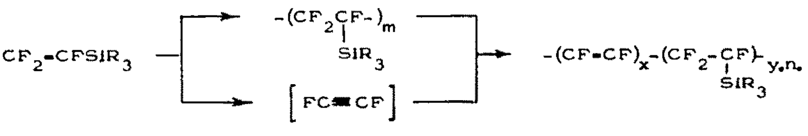
$$R = t\text{-}C_4H_9,\ n\text{-}C_6H_{13}CH(CH_3)\text{–},\ c\text{-}C_6H_{11}(CH_3)\text{–}$$

The α-trimethylsilylisothiocyanate prepared from **67** via **68** yields 2-mercapto-5-phenyloxazole by treatment with benzaldehyde and potassium fluoride.[226]

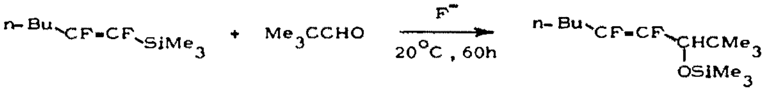


67 68

The fluoride ion catalyst is assumed to work[200] in the polymerization of triethyl(trifluorovinyl)silane either by elimination of fluorotriethylsilane from the polymer intermediate or, alternatively, by elimination of fluorotriethylsilane from triethyl(trifluorovinyl)silane giving difluoroacetylene which then copolymerizes with triethyl(trifluorovinyl)silane under the reaction conditions.



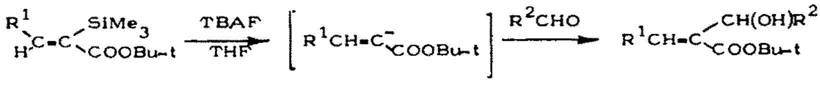
Under similar conditions, *trans*-(1,2-difluorohexene-1-enyl)trimethylsilane undergoes addition to the carbonyl group of pivalic aldehyde.[139]



$$\text{n-Bu}\diagdown CF{=}CF\diagdown SiMe_3 + Me_3CCHO \xrightarrow[20^\circ C,\ 60h]{F^-} \text{n-Bu}\diagdown CF{=}CF\diagdown CH(OSiMe_3)CMe_3$$

The reaction was supposed to occur through the formation of the intermediate *trans*-(1,2-difluorinealk-1-enyl) anion. The reactions of *E*-(1-cyanalk-1-enyl)-trimethylsilanes with carbonyl substrates (20°C, 30 min) initiated by TBAF are stereospecific and lead to *E*-2-(1-hydroxyalkyl)alk-2-ene-nitriles.[141] In these reactions the authors postulate the intermediate formation of *Z*-(1-cyanalk-1-enyl) anion interacting with electrophiles without any changes in configuration.

The fluoride ion-induced desilylation of *E*-2-trimethylsilyl-2-alkene-nitriles gives stereospecifically *Z*-1-cyano-1-alkenyl anion intermediates, which may be converted into *Z*-2-alkenenitriles or *E*-2-(1-hydroxyalkyl)-2-alkenenitriles with retention of configuration.[140,141] The authors of Ref. 227 describe the formation of α-carbanions of t-butyl-2-alkenoates by a similar desilylation and the reaction of these carbanions with aldehydes as electrophiles.



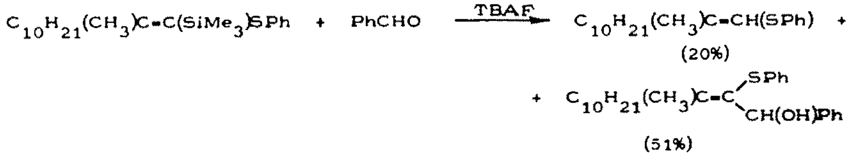
$R^1 = R^2 = \text{n-}C_3H_7CH(CH_3)\text{-}$ (75%);

$R^1 = \text{n-}C_3H_7CH(CH_3)\text{-}$, $R^2 = \text{c-}C_6H_{11}$ (77%)

The same situation is observed in the reaction between *trans*-1,2-difluoro-1-trimethylsilylhexene and the promoted form of 2,2-dimethylpropanal in DMSO leading to 2,2-dimethyl-4,5-difluorononene-4-ol-3[139] with a good yield. At the same time the stereochemical result of alkenylation of aldehydes by 1-trimethylsilyl-1-carb(t-butoxy)alkenes-1 in the presence of TBAF depends substantially on the structure of the initial silane. This dependence may be considered as the consequence of a configurational change of the vinyl anion in the process of desilylation.[138]

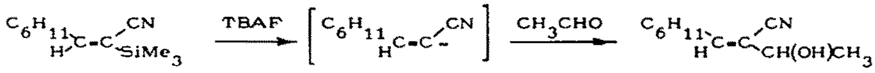
The greater number of reactions catalysed by fluoride ion involve the interaction of vinyl-silane derivatives with the fluoride ion and trapping of the vinyl anion formed (corresponding to the crypto-ion or a molecule with the Si—C polarized bond) by an appropriate electrophilic reagent.

If the vinyl anion is stabilized by some substituents (e.g., a phenylthio group), the reaction of alkenylation takes place in the presence of benzaldehyde.[131]



$$C_{10}H_{21}(CH_3)C{=}C(SiMe_3)SPh + PhCHO \xrightarrow{TBAF} C_{10}H_{21}(CH_3)C{=}CH(SPh)\ (20\%) + C_{10}H_{21}(CH_3)C{=}C(SPh)CH(OH)Ph\ (51\%)$$

The stability of vinyl anions is increased by the presence of CN groups or fluorine to atoms at the sp^2 carbon atom. This led to the synthesis of 2-cyanallyl alcohol derivatives by treatment of substituted 1-trimethylsilyl-1-cyanoethylene and acetaldehyde with TBAF in mild conditions.[141] Configuration of the initial olefinic fragment in this process remains unchanged.



4.2. *Reactions of ethinyl- and propargyl-silanes with carbonyl compounds*

The reaction of ethinylsilanes with carbonyl compounds under conditions of nucleophilic catalysis was first reported in 1976.[228] (Phenylethinyl)trimethylsilane was found to interact with ketones and aldehydes in mild conditions in the presence of the catalytic amounts of TBAF.[228,229]

$$PhC\equiv CSiMe_3 \; + \; RR^1C{=}O \xrightarrow{F^-} PhC\equiv CRR^1(OSiMe_3)$$

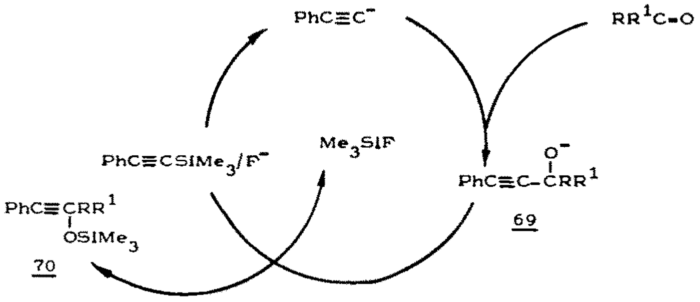
(60–90%)

$R = H$, $R^1 = Ph$, $t\text{-}Bu$, $n\text{-}C_7H_{15}$, $CH{=}C(CH_3)(CH_2)_2CH{=}C(CH_3)_2$;

$R = Ph$, $R^1 = Ph$, Et, $CH{=}CHPh$;

$RR^1 = -(CH_2)_5-$

This reaction with cyclohexanone occurs completely in 5 min at −20°C with an 87% yield of the product. The following mechanism is proposed.



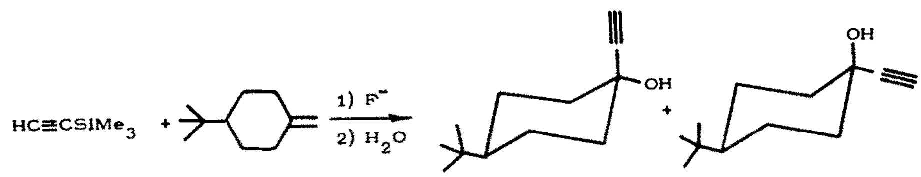
Reaction 1.3

Scheme 4.

The attack at $PhC\equiv CSiMe_3$ by the fluoride ion leads to the formation of Me_3SiF and the phenylacetylenide anion. The addition of the latter to the C=O group of the carbonyl compound gives the alkoxy anion **69** which then participates in an S_N2-Si type reaction with Me_3SiF yielding the final product **70** and regenerating the fluoride ion. At the final stage of the catalytic cycle the alkoxy anion **69** can interact either with Me_3SiF or with $Me_3SiC\equiv CPh$. In this case, product **70** is formed and the $PhC\equiv C$ carbanion is generated.

It is interesting that in the reaction of $PhC\equiv CSiMe_3$ with some ketones capable of enolization (acetophenone, β-ionone, benzalacetone) the yield of product **70** decreases to 5–12%. The formation of **70** is not observed at all in the reaction with pentanone, 2-cyclohexene-1-one and mesityl oxide. It is considered that deactivation of the catalytic cycle (Reaction 1.3) occurs as a result of enolization of these ketones.[229] The interaction between these ketones and the $PhC\equiv C^-$ carbanions leads to the less reactive enolate anion so that the rate of regeneration of the fluoride ion or the $PhC\equiv C^-$ ion considerably decreases.

To confirm the mechanism (Reaction 1.3), the authors[229] investigated the reaction between ethyltrimethylsilane and 4-tert-butylcyclohexane initiated by TBAF. The reaction was shown to produce a mixture of the isomers **71a** and **71b** (88%) with a 9 : 1 ratio. These isomers were obtained as a result of axial and equatorial attack on the carbonyl group by the acetylenide anion. A similar isomeric ratio was observed in the reaction of 4-t-butylcyclohexanone with sodium acetylenide.[230] On the other hand, the same reaction with bulkier nucleophiles than the hydride or acetylenide anions leads only to the products of equatorial attack on 4-t-butylcyclohexanone.[231] Hence, the authors[231] reached the conclusion that the reacting species is rather the relatively small "pure"



71a 71b

acetylenide anion of the $[RC{\equiv}C]^- \cdot NR_4^+$ complex than the bulky anion of the pentacoordinated silicon complex $[RC{\equiv}CSi(F)Me_3]^- \cdot NR_4^+$.

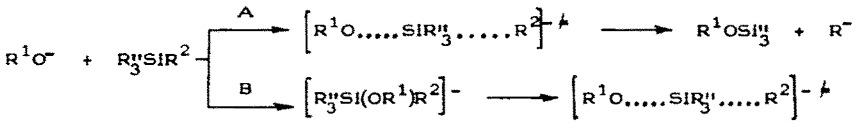
The gas-phase reactions of silanes with fluoride ion have been investigated.[221,222] The fluoride ion was shown to react rather fast with ethynyl-, allyl- and benzyl-trimethylsilanes, with substitution on the corresponding carbanions.

$$Me_3SiR \xrightarrow{F^-} \underset{\mathbf{72}}{Me_3Si(F)R^-} \xrightarrow[-Me_3SiF]{} R^-$$

$$R = C{\equiv}CR^1,\ CH_2CH{=}CHR^1,\ CH_2C_6H_5$$

According to this scheme, $Me_3SiC{\equiv}CCH_3$ and $Me_3SiC{\equiv}CH$ form the isomeric $CH_3C{\equiv}C^-$ and $HC{\equiv}C^-$ anions in a more than 90% yield. The reaction stops, however, at the stage of the ate-complex **72**, when the leaving carbanion R^- is unstable; e.g. with R = Me. In the case of trimethylphenylsilane, the ate-complex **72** is also the major reaction product, the yield of the phenyl anion being only 20%.

In 1965, Eaborn and Valton[232] investigated the kinetics of the cleavage of the silylacetylenic compounds $(XC_6H_4)_3SiC{\equiv}CPh$ (X = *p*-F, *p*-OCH$_3$, *p*-Cl, *m*-CH$_3$, *m*-Cl, H), $R_3SiC{\equiv}CH$ (R = Me, Et, Ph) by alkali in H_2O–CH_3OH at 30–50°C. The reaction rate shows first-order kinetics with respect to the organosilicon compound. Cleavage of (phenylethinyl)-trimethylsilane proceeds 2×10^7 times faster than that of benzyltrimethylsilane and this may be rationalized in terms of the relatively higher stability of the phenylethinyl anion. This is in accordance with the synchronous mechanism A, as well as the two-stage mechanism B where the second stage determines the kinetics of the process.



The common stage for both mechanisms is the fast interaction of the R^- carbanion with the solvent. The reaction rate of $Me_3SiC{\equiv}CPh$ is 280 times higher than that of $Et_3SiC{\equiv}CPh$. This may be attributed to the steric influence of Et groups towards solvation and, consequently, towards stabilization of the carbanion in the transition state. This is also the reason for lowering of the cleavage rate by substitution of Et groups by iso-Pr or Ph. The rate of hydrolysis for $(XC_6H_4)_3SiC{\equiv}CPh$ increases substantially with increase of the electron-withdrawing properties of X. This is in accordance with the presence of the effective negative charge on silicon in the transition stage.

The reactions of octyltrimethylsilane with carbonyl compounds, initiated by TBAF, occur more slowly than in the case of (phenylethinyl)-trimethylsilane.[228,229] This may also be explained in terms of the stability of the corresponding carbanions. The inductive effect of the aliphatic chain in the case of octyltrimethylsilane is less than that of the phenylethinyl group and this reduces the Si—C bond cleavage rate.

Holmes *et al.*[193] found that bis-(trimethylsilyl)acetylene and bis-(trimethylsilyl)-diacetylene attacks ketones and aldehydes in the presence of the catalytic amount (1–10 mol %) of the KF · 18-crown-6 complex.

$$Me_3Si(C{\equiv}C)_nSiMe_3 + RR^1C{=}O \xrightarrow{F^-} \underset{\mathbf{73}}{RR^1C(OSiMe_3)(C{\equiv}C)_nSiMe_3} \longrightarrow$$

$$\xrightarrow{RR^1C{=}O,\ F^-} \underset{\mathbf{74}}{RR^1C(OSiMe_3)(C{\equiv}C)_nC(OSiMe_3)RR^1}$$

$n = 1, 2;\quad R = H,\ R^1 = Ph,\ i\text{-}Pr;\quad R = R^1 = Ph;$

The type of products may be either mono- or di-adducts and depends upon the ratio of silane and carbonyl compounds. For example, the selective formation of monoadduct **73** in the reaction between benzaldehyde and bis-(trimethylsilyl)-acetylene was observed at a reagent ratio of 1 : 1. The authors do not mention the formation of the corresponding diadduct **74**. On the other hand, formation of a mixture of mono- and di-adducts with yields of 26% and 32% respectively in this reaction initiated by TBAF have been reported.[229] Hence, the reactivity of monoadduct **73** appears to be higher than that of the initial silane.

Pornet used fluoride ion catalysis to carry out the reactions of propargylsilanes with aldehydes and ketones.[219,233]

$$\underset{\underline{75}}{Me_3SiCH_2C{\equiv}CR} + R^1R^2C{=}O \xrightarrow[2)\ H_2O]{1)\ F^-} \underset{\underline{76}}{CH_2{=}C{=}CRC(OH)R^1R^2} + \underset{\underline{77}}{RC{\equiv}CCH_2C(OH)R^1R^2}$$

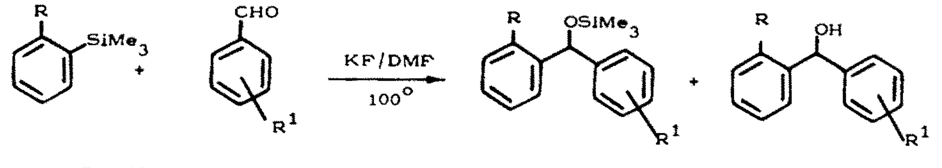
$R = H, CH_3$

This reaction was carried out in THF in the presence of the catalytic amounts (5 mol %) of TBAF. The major reaction products are the α-allenic alcohols. Propargylsilane **75** reacts with aliphatic aldehydes yielding only the α-allenic alcohols **76**. In the case of heptanal, the yield of the alcohol is about 70% (0°C, 1 h). Secondary aldehydes (of isostructure) are somewhat less reactive. Thus, the reaction with isobutyraldehyde requires heating up to 60°C for 16 h (53% yield). The reaction of propargylsilane **75** with ketones occurs even more slowly. In the case of diethylketone, the alcohol was obtained in only 15% yield (60°C, 16 h). Silane **75** reacts with acrolein (0°C, 4 h, yield 25%) and benzaldehyde (50°C, 16 h, yield 45%) to form mixtures of isomeric alcohols (**76** and **77**) with the relative content of acetylenic alcohol (type **77**) 20% and 30% respectively.

Trimethylsilyl-1-butyne-2 **75** is a less selective reagent in the same reactions.[233] Thus, in the reactions with aromatic and aliphatic aldehydes the relative yield of the acetylenic alcohols **77** in the reaction mixture reaches 15–30%. Ketones are an exception; for example, diethylketone and silane **75** yields only the α-allenic alcohol **76** (12%).

Pentafluorophenyltrimethylsilane reacts with benzaldehyde in the presence of fluoride ion forming phenyl(pentafluorophenyl)trimethylsiloxymethane.[234] On the basis of this evidence, Reutov has postulated a nucleophilically-assisted mechanism, $S_E1(N)$, for reactions of this type.[235] The addition of cyanomethyltrimethylsilane to aliphatic and aromatic aldehydes occurs at 160–180° when catalysed by sodium hydroxide and related compounds. Benzaldehyde reacted completely with $C_6F_5SiMe_3$ in ether in the presence of catalytic amount of the potassium cyanide-18-crown-6 complex in less than 5 h at room temperature. In the case of aryltrimethylsilanes containing electron-withdrawing substituents in the *ortho*-position, the reaction is observed only under the conditions of nucleophilic catalysis by KF or CsF.[236]

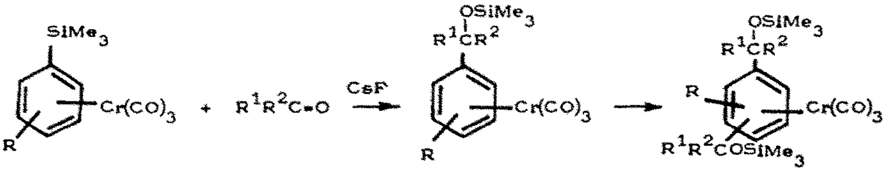
The synthetic application of base-catalysed carbodesilylation of aryltrimethylsilanes is illustrated by the reactions of 2-nitro- and 2-chloro-1-(trimethylsilyl)-benzene with aldehydes, ketones, acyl fluorides and anhydrides of carbon acids.[237] The new method is a useful alternative to the normal electrophilic substitution or the use of organometallic compounds for the synthesis of polysubstituted benzenes.



$R = NO_2, Cl;$

$R^1 = H, 4\text{-}Cl, 4\text{-}CH_3, 4\text{-}CH_3O, 2\text{-}Cl, 3\text{-}Cl$

The presence of the electron-donor substituents in the benzene ring of aryltrimethylsilanes leads to the necessity of their activation, e.g. by the preliminary formation of chromium tricarbonyl complexes.[238] For example, the silane **78** ($R = o\text{-}CH_3$) gives the adduct **79** (81%) in 15 min. With the silane **78** ($R = SiMe_3$) the obtained adduct **79** reacts with a second molecule of the carbonyl compound yielding the product **80**. The formation of 28–55% of η^6-(benzoyl)-tricarbonylchromium as a by-

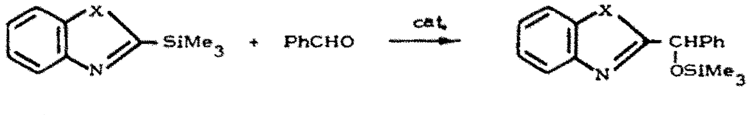


78 79 80

R = H, 2-CH$_3$, 2-Cl, 3-CH$_3$, 4-CH$_3$

product is observed in the reactions of silane **78** with enolizable carbonyl compounds (together with adducts of the **79** type). Thus, introduction of the Cr(CO)$_3$ group into the aromatic ring of arylsilane-containing electron-donor substituents increases the reactivity of the silane under nucleophilic catalysis. Coordination of the arene ring with the Cr(CO)$_3$ group by π-orbitals acts similarly to the introduction of an electron-withdrawing substituent. This makes the ring electron deficient which counteracts the destabilizing effect of the electron-donating CH$_3$ group in silane **78**.[239]

The influence of different bases on the cleavage of silicon–carbon bonds in aryl- and heteroaryltrimethylsilanes has been investigated using benzaldehyde as an electrophilic scavenger for the aryl and heteroaryl anions which are formed in this process.[236] The relative reactivity of various basic catalysts has been examined for the reactions of 2-(trimethylsilyl)-benzothiazole (Table 6).



X = S, NCH$_3$

Attack of the base at the Si atom was suggested to be the first stage in this reaction, with subsequent dissociation of the pentacoordinated intermediate as the rate determining step. The rapidly forming carbanion reacts further with benzaldehyde giving the final product. Silane **81** undergoes addition to the C=O group of benzaldehyde in the presence of 10 mol % CsF, TBAF or KF · 18-crown-6 (THF, 20°C, 12 h).[194,240] 2-Trimethylsilylbenzothiazole **81a** interacts with benzaldehyde without a catalyst by heating at 160°C for 40 h (75%).[234]

$$\underset{\underline{81}}{RSiMe_3} + PhCHO \xrightarrow{F^-} PhCH(OSiMe_3)R$$

R = PhCH$_2$, o-NO$_2$C$_6$H$_4$CH$_2$, 3,5-Cl$_2$C$_6$H$_4$CH$_2$,

In 1970 Gilman[234] discovered the "Grignard" reaction of pentahalophenyltrimethylsilanes with benzaldehyde (62–89%) under rather harsh conditions (170°C, 96 h).

$$ArSiMe_3 + PhCHO \xrightarrow{F^-} PhCH(OSiMe_3)Ar$$

Ar = C$_6$F$_5$, C$_6$Cl$_5$

Table 6. Influence of some catalysts on the reaction of benzaldehyde with 2-(trimethylsilyl)-benzothiazole[236]

Catalyst	Reaction temperature (°C)	Yield (%)
KF	100	100 (1 h)
KCl	100	5 (4 h)
Et$_4$N$^+$F$^-$ · 2H$_2$O	0	9 (30 min)
Et$_4$N$^+$Br$^-$	100	1 (2 h)
LiF	100	2 (19 h)
CsF	0	98 (30 min)
MeCO$_2$K	0	19 (30 min)
MeCO$_2$NBu$_4$	0	44 (30 min)
Me$_3$COK	−60	91 (15 min)
PhOK	−60	84 (15 min)
MeCO$_2$K	20	75 (15 min)

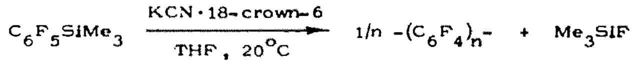
Phenyltrimethylsilane does not react in this way. Nucleophilic catalysis allows the reaction to proceed using mild conditions, e.g. $ArSiMe_3$ (Ar = 3-chloro-2,4,5,6-tetrafluoro, 3,5-dichloro-2,4,6-trifluoro-, 2,6-difluoro- and 2,6-dichlorophenyl) reacts at room temperature in the presence of fluoride ion (KF–DMF, 3 h).[234] *o*-, *m*-, *p*-F and *p*-$NO_2C_6H_4SiMe_3$, corresponding to less stable carbanions, do not react with benzaldehyde under these conditions.[234] On the other hand, Effenberger and Spiegler,[241] showed $XC_6H_4SiMe_3$ (X = *o*-NO_2, *o*-F, *o*-PhO, *o*-MeO, *o*-$PhSO_2$, *m*-Cl, *p*-Cl) to be active electrophilic reagents under nucleophilic catalysis. Thus, *o*-$NO_2C_6H_4SiMe_3$ (−60°C, 1 h) and *o*-$FC_6H_4SiMe_3$ (20°C, 1 h) reacted with benzaldehyde (92 and 76% respectively) in the presence of 5–10 mol % of *t*-BuOK in DMF. Harsh conditions are required for this reaction with *m*- and *p*-$ClC_6H_4SiMe_3$ (30 mol %) of t-BuOK, hexamethylphosphotriamide, 100°C, 3–4 h); alkylphenyl- or aminophenyl-trimethylsilanes seem to be inert in this reaction. The authors[240] note (without presenting any experimental data) that CsF, KF and TBAF are active initiators, almost as active as *t*-BuOK. They also found that ketones, acid anhydrides and CO_2 are able to react as electrophiles.

The higher acidity of the C—H bonds in fluorinated benzenes is connected with the electron-withdrawing properties of fluorine substituents[242] as is shown in the following series.[241]

C_6H_6 (pK_a 43), 1,2,3-$F_3C_6H_3$ (pK_a 34), 1,2-$H_2C_6F_4$ (pK_a 31), C_6HF_5 (pK_a 25)

Evidently, the strongest influence is produced by *ortho*-fluoro substituents. C_6HCl_5 has pK_a = 31. The inductive effect of fluoro substituents may be considered as the determining factor of stabilization of aryl anions. The reactivity changes in the above-mentioned examples appear to be directly connected with the stability of the corresponding aryl carbanions.

Under interphase catalysis (KCN·18-crown-6, 20°C), $C_6F_5SiMe_3$ in tetrahydrofuran yields a polymeric product. This indicates the generation of the $C_6F_5^-$ anion.[243]

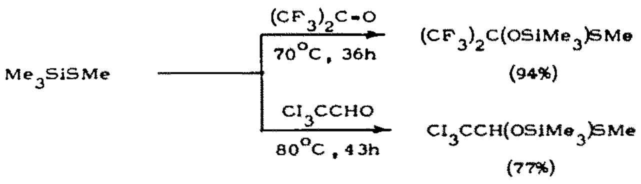


$$C_6F_5SiMe_3 \xrightarrow[\text{THF, } 20^\circ C]{\text{KCN}\cdot\text{18-crown-6}} 1/n\ -(C_6F_4)_n- \ + \ Me_3SiF$$

Protection of functional groups by means of organosilicon compounds has been one of the topical problems of organic synthesis. The possibilities for nucleophilic catalysis in the solution of these problems follows from the analysis of data on the reactions of organosilanes Me_3SiX with carbonyl compounds. $C_6F_5SiMe_3$ is considered to be the most active and selective deprotosilylating agent.[97,98] Its use under conditions of nucleophilic catalysis is advantageous as it allows protection of functional groups due to its advantages over the known reagents in that field. Thus, the use of $C_6F_5SiMe_3$ and $(C_6F_5)_2SiMe_2$ as reagents for the protection of functional groups under nucleophilic catalysis has certain advantages: (i) all transformations take place at 20°C in the usual aprotic solvents; (ii) the reactions occur regioselectively and practically in all cases there is an opportunity to control the degree of silylation; (iii) the reagents are able to silylate even relatively weak CH-acids (pK_a < 25); (iv) a homogeneous reaction mixture is obtained, which facilitates isolation of the main reaction product; (v) the by-product C_6HF_5 has a low b.p. These qualities allow us to consider $C_6F_5SiMe_3$ and $(C_6F_5)_2SiMe_2$ as possibly the most convenient of all the existing silylating agents.

4.3. *Reactions of thio- and seleno-silanes with carbonyl compounds*

One of the known properties of thiosilanes[244,245] is their ability to undergo addition (rather slow) to the C=O group of highly reactive carbonyl compounds (e.g. trichloroacetaldehyde and hexafluoroacetone) without catalysts.



The reaction of thiosilanes with less electrophilic carbonyl substrates (e.g. n-hexanal or isobutyraldehyde) requires more vigorous conditions.[246]

$$CH_3(CH_2)_4CHO + Me_3SiSEt \xrightarrow[\substack{\text{or}\\ \text{KCN}\cdot\text{18-crown-6, } 25^{\circ}\text{C}}]{120^{\circ}\text{C, 20h, (30\%)}} \underset{(82\%)}{CH_3(CH_2)_4CH(OSiMe_3)SEt}$$

In the same work,[246] Evans *et al.* discovered for the first time the influence of anion initiation on these addition processes when analogous reactions were carried out in the presence of catalytic amounts of n-Bu_4NCN or TBAF or KCN · 18-crown-6. n-Hexanal reacts exothermally at 25°C in the presence of anion initiators to form the mixed acetal (82%). Isobutyraldehyde and $PhSSiMe_3$ react similarly giving the same product (81%). Evans suggested a mechanism (Reaction 1.2, $X = SR$) for such reactions.

On the other hand,[246] aryl and alkylthiosilanes do not react with ketones (except the α,β-unsaturated ones) under conditions of anionic initiation. The authors explain this by the low value of the equilibrium constant for adduct formation (see Reaction 1.2, $X = SR$) or by the inefficiency of anionic catalysis for ketonic substrates; that is by the low value of the equilibrium constant for the intermediate alcoholate anion formation.

The reactions of α,β-unsaturated aldehydes and ketones with $PhSSiMe_3$ and $EtSSiMe_3$ occur very slowly, even at higher temperatures. In the presence of the cyano-, fluoro- or thiolate anions, however, the addition is exothermic at 25°C. Only 1,4-addition was observed in all cases.[246]

$$CH_3CH{=}CHCHO + PhSSiMe_3 \xrightarrow[\substack{\text{or}\\ \text{KCN}\cdot\text{18-crown-6, } 25^{\circ}\text{C}}]{100^{\circ}\text{C, 48h,}} \underset{(90\%)}{PhSCH(CH_3)CH{=}CHOSiMe_3}$$

In 1978 Liotta *et al.*[247] investigated the reactivity of $PhSeSiMe_3$ with carbonyl compounds in the presence of triphenylphosphine. $PhSeSiMe_3$ was found to form quantitatively an adduct with isobutyraldehyde.

$$CH_3CH_2CH_2CHO + PhSeSiMe_3 \xrightarrow[55^{\circ}\text{C, 14h}]{PPh_3} \underset{(100\%)}{CH_3CH_2CH_2CH(OSiMe_3)SePh}$$

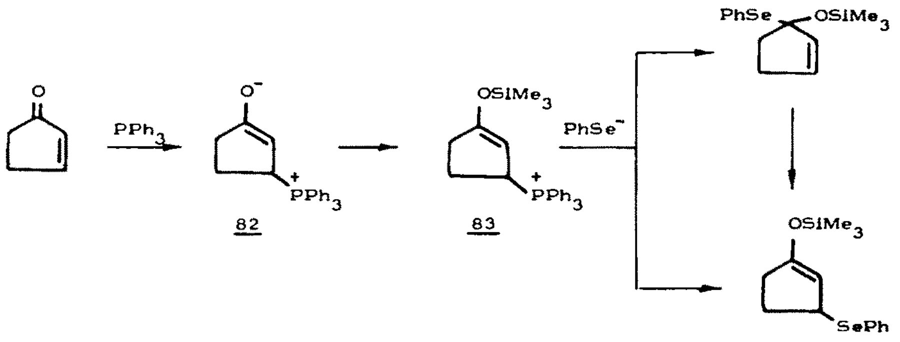
α,β-Unsaturated aldehydes react faster with $PhSeSiMe_3$ than their saturated analogues and form the 1,4-addition products. At the initial stage (30 min) of the reaction, however, the formation of 1,2- and 1,4-adducts in the ratio of 2:1 was observed. Then the relative amount of 1,4-isomer increases with the simultaneous decrease of the amount of 1,2-isomer. Thus, the formation of 1,2-adducts is kinetically controlled, whereas the 1,4-isomers are formed under thermodynamic control conditions.

$PhSeSiMe_3$ reacts with α,β-unsaturated ketones to yield 1,4-adducts.

$$RCH{=}CR^1R^2 + PhSeSiMe_3 \xrightarrow{PPh_3} R(Me_3SiO)C{=}CHC\overset{R^1R^2}{\underset{SePh}{}}$$

$R = CH_3$; $R^1{=}R^2{=}H$; $R{=}R^1{=}R^2{=}CH_3$

For example, the reaction with methylvinylketone and mesityl oxide, which occurred over 14.5 h, lead to the addition product in 89% and 70% yields.[246] Formation of 1,2-adducts was not observed in this case, but this possibility with the further fast isomerization to the corresponding 1,4-adducts cannot be excluded. The following mechanism for the reaction between $PhSeSiMe_3$ and unsaturated aldehydes and ketones was proposed.[247]

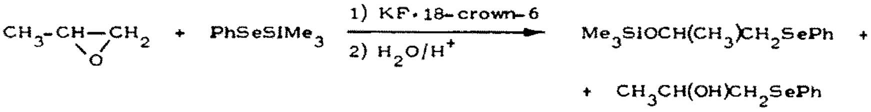


A similar mechanism had been postulated earlier[63] for the reaction of silicon pseudo-halides with unsaturated carbonyl compounds. Formation of phosphonium enolates of type **82** was proved by Evans by isolation of the crystalline phosphonium chloride **83** after treatment of the solution of methylvinylketone in benzene with one equivalent of Ph_3P and Me_3SiCl. δ-Butyrolactone reacts with (phenylseleno)trimethylsilane in the presence of KF in the 18-crown-6 medium to yield trimethylsilyl-4-phenylselenobutyrate.[248]

The reactivity of $PhSeSiMe_3$ under anionic catalysis was investigated by Detty in 1978.[248] The reactions occur in THF at 60–80°C or in CH_3CN in the presence of a catalytic amount (0.05 mol %) of KCN or KF complex with 18-crown-6. Under these conditions, the reaction with crotonaldehyde occurs (50%) and takes 18 h. Further treatment with diluted acid leads to a mixture of products (1 : 1).

$$CH_3CH{=}CHCHO + PhSeSiMe_3 \xrightarrow[2)\ H_2O/H^+]{1)\ KF\cdot 18\text{-crown-6}} PhSeCH(CH_3)CH{=}CHOSiMe_3 + PhSeCH(CH_3)CH_2CHO$$

The reaction of $PhSeSiMe_3$ with propylene oxide under the same conditions leads to opening of the cycle. The silylated compound appears to be the main product (85%).

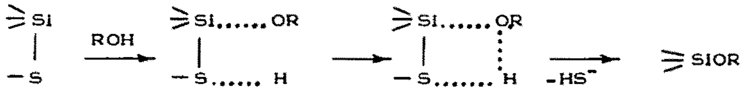


With an equimolar amount of KF, the reaction time is much shorter (4 h). Further treatment with dilute acid leads only to products without the Me_3Si group. In this case the quantitative formation of potassium phenylselenide takes place and this determines the reaction pathway.

$$PhSeSiMe_3 + KF \xrightarrow[60^{\circ}C]{18\text{-crown-6},\ THF} PhSeK + Me_3SiF$$

Anionic catalysis seems to be effective for generating Me_3SiS^- anions formed in the reaction between hexamethyldisilthiane and aldehydes initiated by the CN^- ion.[249] A catalytic amount (0.005 eq.) of KCN·18-crown-6 complex is sufficient for the initiation. The reaction leads to α,α'-bis(trimethylsiloxy)sulphides. The reaction of $(Me_3Si)_2S$ with isobutyraldehyde occurs during 48 h at 40°C.

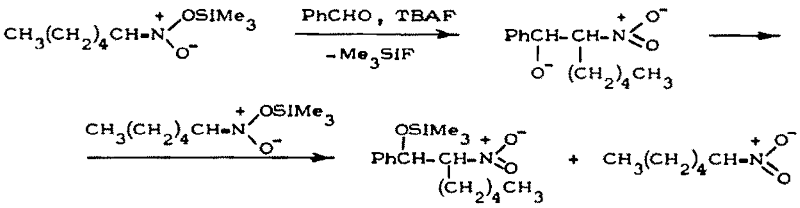
Organosilothianes undergo heterolytical cleavage by proton-donor reagents, such as β-diketones, oximes,[250] acids and amines.[251] The activity of these reagents decreases in the series $ROH > RNH_2 > RSH$ corresponding to the decrease of energy of Si—X bond formation in the silylation reaction.[250] The reaction is supposed to occur by simultaneous electrophilic attack on the heteroatom and nucleophilic attack on the silicon atom leading to a four-centred transition complex.[252]



The rate of alcoholysis of Si—S—Si bonds increases in the presence of catalytic amounts of nitrogen bases. The catalytic activity sequence for the bases DMF > pyridine > quinoline > morpholine corresponds to the decrease of the electronic density on the nitrogen atom.[253] In this case, the reaction is supposed to be of the ligand-change type involving a four-centred transition complex.

4.4. *Reactions of silylnitrates, α-silylalkylphosphonates, silyldialkylphosphonates, silyl-bis(dimethylamino)phosphites and other compounds*

Silylnitrates react with aliphatic and aromatic aldehydes under nucleophilic catalysis by TBAF to form 2-silyloxynitroalkanes.[254]



The reaction of t-butyldimethylsilylnitrates with aliphatic aldehydes, catalysed by fluoride ion, was shown to be a diastereoselective process leading to practically pure *erythro*-isomer. Lower diastereoselectivity was observed for benzaldehyde. The preferable formation of one diastereomer is connected with the transition state corresponding to minimal steric interactions.[255]

Kawashima showed in 1983[256] that the Si—C bond of α-silylalkylphosphonates **84** was easily cleaved by fluoride ion to form the carbanionoid species **85** which are very effective agents for the olefination of carbonyl compounds (the Emmons–Hurner reaction).

$$\underset{\underline{84}}{Me_3SiCHRP(O)(OMe)_2} \xrightarrow[-Me_3SiF]{F^-} \underset{\underline{85}}{\overset{-}{C}HRP(O)(OMe)_2} \xrightarrow{R^1R^2C=O} R^1R^2C=CHR$$

The KF · 18-crown-6 complex, TBAF, $Me_4N^+F^-$ and CsF were tested as fluoride ion sources. CsF and TBAF were shown to be the most active among them. This reaction yielded α-methylstilbene ($R = R^1 = C_6H_5$, $R^2 = CH_3$) from acetophenone (67%). It is interesting that LiF mainly deprotonates acetophenone and gives only a 5% yield of α-methylstilbene. On this basis the authors[256] consider the anion generated by desilylation of the initial compound to possess less basic properties than the lithium salt. The initial phosphonate reacts with benzaldehyde (CH_3CN, CsF, 80°C, 5 h) to form stilbene (85%) and dimethylbenzylphosphonate. On the other hand, α-trimethylsilylmethylphosphonate reacts with benzophenone to yield a mixture of 2,2-diphenylethenylphosphonate (30%), 1,1-diphenylethylene (20%) and dimethylmethylphosphonate (50%). The carbanion **86**, containing Me_3Si and phosphoryl groups in the α-position, reacts with carbonyl compounds forming vinylphosphonates **87**.[257]

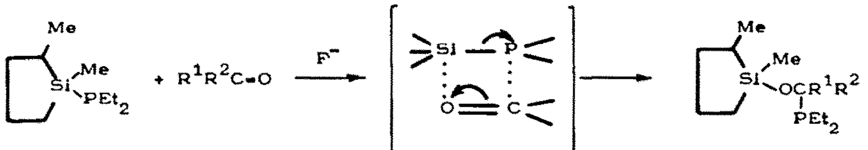
$$R^1R^2C=O + \underset{\underline{86}}{LiCH(SiMe_3)P(O)(OEt)_2} \xrightarrow[-Me_3SiOLi]{} \underset{\underline{87}}{R^1R^2C=CHP(O)(OEt)_2}$$

Dimethyl-2,2-diphenyl-2-trimethylsiloxyethylphosphonate in the presence of CsF quantitatively forms 1,1-diphenylethylene. Caesium ion as counter cation seems to be very effective for the formation of α-hydroxyalkylphosphonate. Use of potassium ions gave olefin in 30% yield.[258] It may be supposed that the generated phosphonate carbanion **85** removes a proton from the α-silylalkylphosphonate **88** to form the α-silylated carbanion **89** which is responsible for the formation of 2,2-diphenylethenylphosphonate in this reaction.

$$\underset{\underline{88}}{Me_3SiCH_2P(O)(OMe)_2} + \underset{\underline{85}}{\overset{-}{C}H_2P(O)(OMe)_2} \longrightarrow \underset{\underline{89}}{Me_3Si\overset{-}{C}HP(O)(OMe)_2} + CH_3P(O)(OMe)_2$$

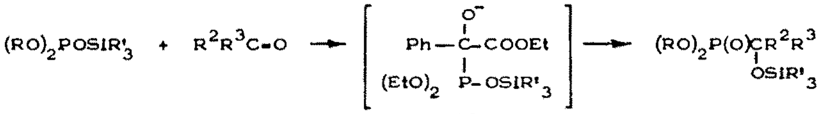
Desilylation of α-silylalkylphosphonium salts has very recently been shown to be a useful synthetic method for tri-substituted olefins.[259]

The nucleophilicity of phosphorus and the high affinity of silicon towards oxygen can explain the high reactivity of compounds with Si—P bonds in the reaction with carbonyl compounds. For example, 1,2-dimethyl-1-diethylphosphinosilacyclopentane **90** is easily added to the carbonyl group of aldehydes, ketones, heterocumulenes, ethylenic esters and nitriles.[260] The reactions studied from mixtures of geometrical isomers ($Z > E$ and $Z < E$) proceed via reaction at silicon via a four-centred concerted mechanism. The authors propose a four-centred coordinated mechanism. There is a certain analogy with the mechanism of Me_3SiCN addition to the C=O group under the influence of cyanide ion (see Reaction 1.2). In compounds **90** phosphorus acts as an X^- nucleophile and at the same time the phosphine group plays the role of the carrier of silicon to the alkoxy anion at the second stage (Reaction 1.2).



90

Much research on the reactions of trialkylsilyldialkylphosphites with carbonyl compounds[260-270] has appeared recently. These reactions lead to the corresponding α-trialkylsiloxydialkylphosphonates **91** and involve the initial attack of phosphite **92** on the carbonyl group to form the dipole **93** which is stabilized at the second stage of the Arbusov reaction by transformation of the phosphonate **91**. This is facilitated by the high mobility of the trialkylsilyl group.[261,262]



92 93 91

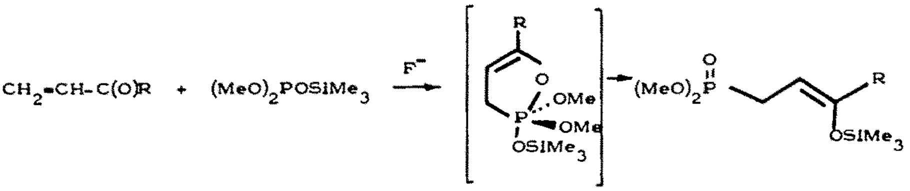
The reactions of these compounds with aldehydes and ketenes are exothermic and with ketones they occur by heating.[263-265]

Phosphite **92** (R = Et, R' = Me) forms diethyl-α-carbethoxy-α-trimethylsilylbenzylphosphate with ethyl benzoylformate[269] in accordance with the route involving the phosphonate–phosphate rearrangement of the initially generated dipole **93**. Evidently, the favourable conditions for the phosphonate–phosphate rearrangement with further migration of the Me_3Si group are created by the presence of two electron-withdrawing substituents on the α-carbon atom. The same rearrangement is observed in the reaction with benzoyl cyanide which yields a mixture of α-trimethylsiloxy-α-cyanobenzylphosphonate and α-trimethylsilyl-α-cyanobenzylphosphate.[266] The phosphonate-phosphate rearrangement was not observed in the reaction of phosphite **92** with diacetyl which yielded only diethyl-α-trimethylsilyloxy-α-acetoethylphosphonate in accordance with the equation mentioned above.[261] The reactions of phosphites **92** with α,β-unsaturated carbonyl compounds often lead to mixtures of the products of 1,2- and 1,4-addition.[261,264] Thus, crotonaldehyde reacts with trimethylsilyldimethylphosphite to form (90%) a mixture of 1,2- and 1,4-adducts in the ratio 3 : 1. Heating (200°C, 24 h) of each isomer does not lead to its transformation into the other.

$$CH_3CH{=}CHCHO + Me_3SiOP(OMe)_2 \xrightarrow{55^\circ C,\ 18h} (MeO)_2P(O)CHCH{=}CHCH_3 + $$

$$+ (MeO)_2P(O)CH(CH_3)CH{=}CHSiMe_3$$

The mechanism of formation of 1,2-adducts has been discussed above. 1,4-Adducts were shown to be only *Z*-isomers.[261] Moreover, α,β-unsaturated ketones, having the fixed transoid-configuration (e.g., cyclohexanone), do not form 1,4-addition products. These facts are in good accordance with the suggested mechanism of 1,4-adduct formation through the intermediate oxaphospholene **94**.[250]



94

Bis-(dimethylamino)triethylsilylphosphite **96** has a higher reactivity in the reactions with carbonyl compounds than dialkylsilylphosphites **92**. This is evidently connected with the higher nucleophilicity of phosphorus in phosphite **96**. The reaction between phosphite **96** and crotonaldehyde occurs during 30 min at 0°C and only the 1,2-addition product **95** is formed.[262]

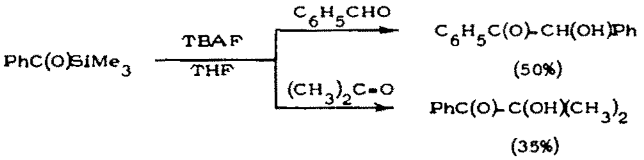
$$\underset{}{CH_3CH{=}CHCHO} + \underset{\mathbf{96}}{(Me_2N)_2POSiMe_3} \xrightarrow{0^\circ C,\ 0{,}5h} \underset{\mathbf{95}}{(Me_2N)_2P(O)CH(OSiMe_3)CH{=}CHCH_3} \quad (99\%)$$

1,1-Difluoro-2-oxyalkylphosphonates **97** were obtained in the reactions of carbonyl compounds with 1-trimethylsilyl-1,1-difluoromethylphosphonate in the presence of a catalytic amount of CsF.[271]

$$Me_3SiCF_2P(O)(OEt)_2 + C_6H_5CHO \xrightarrow[2)\ H_2O]{1)\ CsF} C_6H_5CH(OH)CF_2P(O)(OEt)_2$$

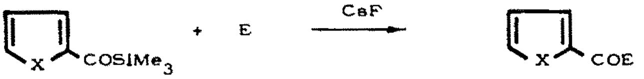
$\underline{97}$

Acylsilanes react with methyl iodide and n-butyl iodide in the presence of fluoride ion to give acetophenone (yield 55%) and valerophenine (35%).[158] The reaction of benzoyltrimethylsilane with TBAF in THF solution containing benzaldehyde, acetone or cyclohexanone gives benzoin (50%) and hydroxy ketone (35%) respectively. Three mechanisms for these reactions may be considered. The first involves the initial nucleophilic attack on the carbonyl carbon, carbon-to-oxygen-migration of the silyl group, protonation or alkylation of the resulting benzyl anion and collapse of the resulting geminal fluoro ether.[272] The second mechanism involves initial nucleophilic attack at silicon leading to a pentacoordinated silicon atom. The weakened carbon–silicon bond would then be cleaved by an appropriate electrophile. The third mechanism which one might consider is a direct reaction involving an acyl anion forming α-oxycarbonyl compounds.



Treatment of benzoyltrimethylsilane with KF in DMSO or with TBAF in THF yields benzaldehyde. The same process with the addition of alkyl halides to the reaction mixture yields alkylarylketones.[191]

The behaviour of aroylsilanes and allied substrates as the source of nucleophilic acyl anions has been studied.[191,273] The authors[273] investigated the reactions of pyrroyl, thienoyl and furoyl anions (generated by fluoride ions and compounds **98**) with various electrophiles.



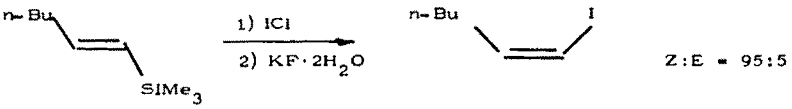
$\underline{98}$ (10–68%)

$X = O, S, NCH_3$

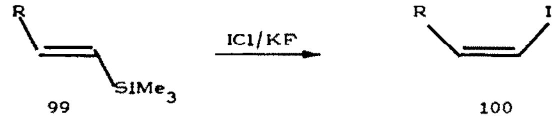
$E = PhCHO, CH_3(CH_2)_2CHO, PhCOCH_2Br, PhCH{=}CHCH_2I$

With the most reactive electrophiles, such as benzaldehyde, a clean transfer of the heteroacyl moiety was observed, whereas with aliphatic aldehydes the reaction proved to be successful only when long-chain derivatives such as butyraldehyde were used with 1,3-dimethylimidazolidin-2-one as solvent.

The reactions of compounds **98** with ketones were unsuccessful. The reactions employing allyl bromide as an electrophile afforded a complex reaction mixture in which only 2% of the expected product was formed. The reaction of iodine (chlorine, bromine) with vinyltrimethylsilane with Me_3SiI elimination leads to vinyliodide. *E*-1,2-Bis-(trimethylsilyl)-ethylene reacts with iodine in CCl_4 to give equal amounts of *Z*- and *E*-1-iodo-2-trimethylsilylethylene.[274] In the case of the reaction with chlorine and bromine, *Z*-isomers are obtained. The stereoselectivity of this reaction may be controlled by using silver trifluoroacetate and iodine in the presence of KF in DMSO. *Z*-1-Trimethylsilylhexene under these conditions gives *E*-1-iodohexene.[275] ICl is alco effective in this reaction leading mainly to *Z*-isomer.[276]



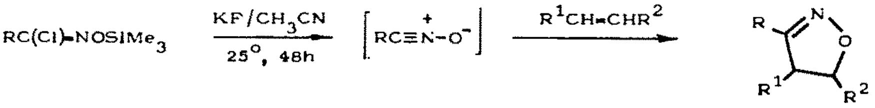
Treatment of vinylsilane **99** with ICl/KF leads to *Z*-vinyliodide **100** with a high yield.[277]



99 100

R = $CH_3(CH_2)_{12}$-, $(CH_3)_2CH(CH_2)_4$-

Treatment of *O*-(trimethylsilyl)-acetohydroxamoyl chloride **101** or *O*-(trimethylsilyl)-benzhydroxamoyl chloride with KF in CH_3CN containing various olefins resulted in the formation of Δ^2-isoxazolines **102**.[278]



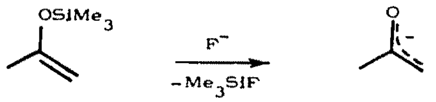
101 102

R = Me, R^1 = H, R^2 = n-C_6H_{13} (70%); R = Me, R^1 = H, R^2 = $SiMe_3$ (62%);
R = Me, R^1 = H, R^2 = Ph (76%); R = Me, R^1 = OCH_2CH_3 (70%);
R = Me, R^1 = H, R^2 = COOMe (88%); R = Me, R^1 = H, R^2 = CN (71%);
R = Me, R^1 = Me, R^2 = Me (44% cis, 47% trans); R = Ph, R^1 = H, R^2 = n-C_6H_{13} (72%);
R = Ph, R^1 = H, R^2 = OCH_2CH_3 (79%); R = Ph, R^1 = H, R^2 = CN (76%).

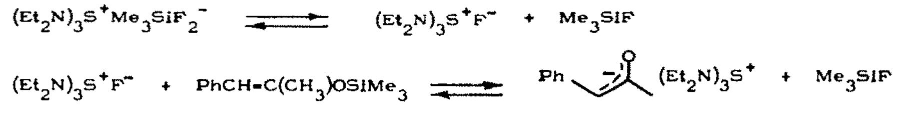
4.5. *Reactions of silyl enolates*

Silyl ethers of enols are widely used in organic synthesis[279–281] and nucleophilic catalysis considerably enhances their synthetic utility. Versatile methods for carbon–carbon bond formation have been developed based on silyl ethers of enols activated by fluoride ion. Various groups have reported alkylations, arylations, aldol condensations, acylations and Michael additions. The nucleophilic reactivity of such reagent combinations might be distinctly different from that of the classical metal enolates. In particular enhanced nucleophilicity might be attained without significantly increasing the basicity and this could lead to novel carbon–carbon bond-forming reactions.

The possibility of formation of the "pure" enolate anion was the subject of a number[229,282–287] of investigations of the reactions of silyl ethers of enols with electrophilic substrates under conditions of fluoride ion catalysis.



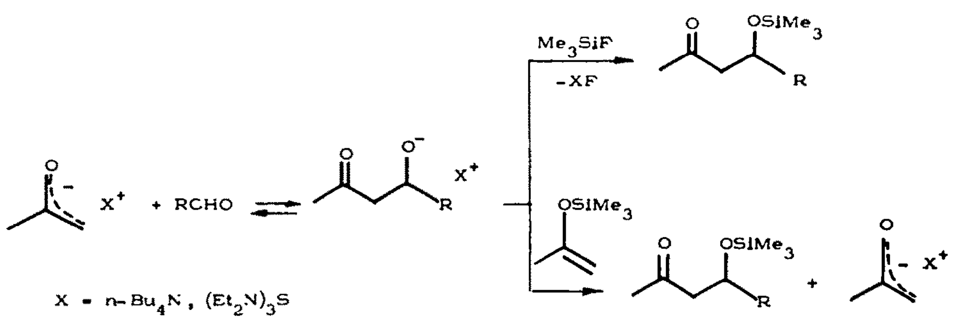
Direct evidence of this was obtained by Noyori *et al.*[285–287] They found that the reaction of tris-(diethylamino)-sulphonium difluorotrimethylsiliconate (TASF) with *Z*-trimethylsilyl ether of benzylmethylketone enol leads to TAS *Z*-enolate **103** isolated by means of a high-vacuum technique.



103

The NMR and quantum-chemical calculation data indicate a negligible interaction between the ions in **103** and the electroconductivity measurement in THF shows that the salt **103** is completely dissociated.

Silyl ethers of enols react in the presence of fluoride ions (TBAF or TASF) with aldehydes to form silyl ethers of aldols.[229,282,284,287] The mechanism of this reaction may be represented by a number of mobile equilibria.[285–287]

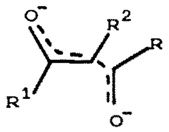


Scheme 5.

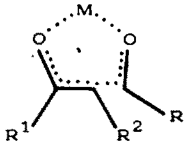
The interaction between the silyl ether of the enol and fluoride ion leads to generation of the "pure" enolate anion undergoing reversible addition to aldehyde giving aldol anion. The latter reacts with Me_3SiF or with silyl ether of enol to form the final product of the reaction.

Formation of the aldol product was not observed in the reaction of TAS-enolate **103** with aldehydes at −78°C and further treatment by water. But addition of either Me_3SiF or the silyl ether of the enol to the reaction mixture facilitates the aldol reaction and the product is obtained without difficulty. This observation may be explained in terms of the shift of the thermodynamic equilibrium to the left in the absence of Me_3Si donors. The metal enolate, unlike the "pure" enolate anion, leads easily to the formation of aldol products.[288,289]

The aldol reactions initiated by fluoride ions produce mainly *erythro*-aldols independent of the geometry (*E* or *Z*) of the silyl ether of enol. The *erythro*-selectivity is connected with the kinetic control at the stage of formation of the aldol anion. Thus, the silyl ether of cyclopentanone enol reacts with isobutyraldehyde at −78°C in the presence of 0.01 equivalents of TBAF to form only the *erythro*-adduct. Stereoisomerization was not observed under these conditions. Diastereoselectivity decreases at higher temperatures (up to −20°C) leading to the formation of a mixture of *erythro*- and *threo*-isomers (89 : 11) at −20°C. The transition state **104** was suggested[286–288] to explain the *erythro*-selectivity in the reactions initiated by the fluoride ion.



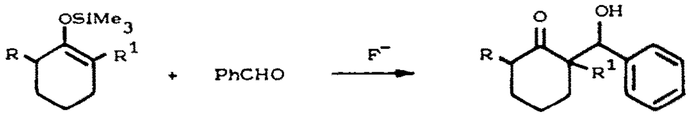
104



109

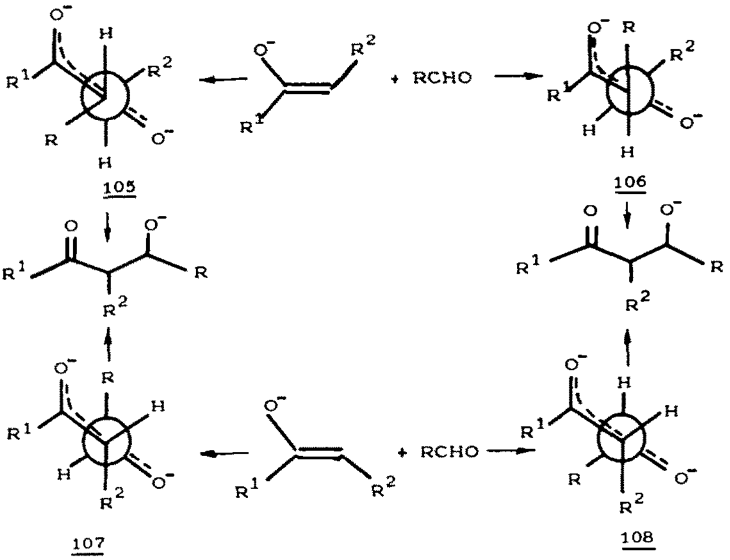
The *erythro*-transition state **105**, being the result of the interaction between aldehyde and the *E*-enolate anion, is more preferable than the *threo* one (**106**) because of the gauche-R,R^2-interaction in the latter. For the same reason the *erythro*-transition state **107** is more stable than the *threo* one (**108**, Scheme 6). These reactions, however, are not always kinetically controlled. The *erythro*-selectivity is always observed in the reactions of aliphatic aldehydes with silyl ethers or enols independently of the enol structure; but the analogous reactions of aromatic aldehydes with silyl ethers of enols of cycloalkanes or α-silylated ketones show a decrease or complete disappearance of the *erythro*-selectivity,[290,291] indicating that the stage of aldol anion formation could be thermodynamically controlled.

Stereoselectivity in the reactions between aldehydes and metal enolates directly depends on configuration of the latter; *Z*-enolates form products enriched by *erythro*-aldols and *E*-enolates form mainly *threo*-aldols. Stereoselectivity is determined by the relative stability of the corresponding diastereomeric transition state of type **107**.[288,289,292,293] The reactions of silyl ethers of enols catalysed by fluoride ions occur regiospecifically.[282]



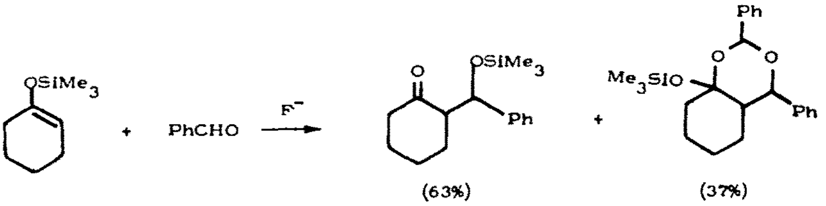
110 111

a, R = Me, R^1 = H; b, R = H, R^1 = Me



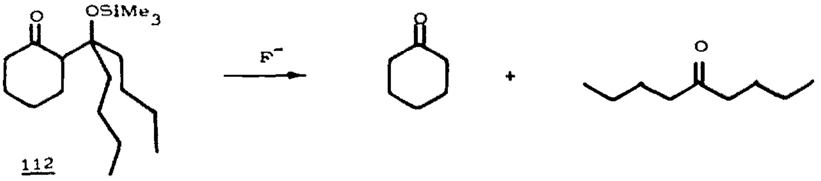
Scheme 6.

For example, enoxysilanes **110a** and **110b**, when treated with benzaldehyde (−30°C, 2 h, THF), are converted to the adducts **111a** (68% yield) and **111b** (62%) respectively. Alkylation of the silyl ethers of enols by alkyl halides in the presence of fluoride ion (TBAF, TASF) occurs similarly.[283,287] Silyl ethers of enols react with α,β-unsaturated aldehydes (−78°C, THF, TBAF) to form only the 1,2-addition products.[282,284] Silyl ethers of the enols of ketones containing bulky substituents are successfully used in the catalysed aldol reaction : in the non-catalysed reaction the use of these ethers leads to aldol products with low yields.[294] The yields of adducts, e.g., in the reactions (−25°C, 16–22 h, THF, TBAF) of silyl ethers of diisopropylketone and t-butylmethylketone enols with benzaldehyde, reach 59%.[284] In some cases the formation of 1,2-adducts of enoxysilane with the aldehyde is observed. Thus, the interaction between allyl ether of cyclohexanone enol and benzaldehyde leads not only to the usual 1,1-adduct, but also to the 1,2-adduct.[284]



In this case the aldehyde appears to be a more effective trap for the aldol anion than the silylating agent (Me_3SiF or enoxysilane). Formation of the 1,2-adduct may be avoided by introducing a greater amount of catalyst (5–20 mol %) or an excess of Me_3SiF into the reaction mixture. In the reaction between 1-trimethylsilyloxypentane and isobutyraldehyde addition of an excess of Me_3SiF leads to a considerably higher yield (increase from 3 to 53%) of the corresponding silyl ether of the aldol. The addition of Me_3SiCl decreases the reaction rate because of the destruction of the catalytic cycle.

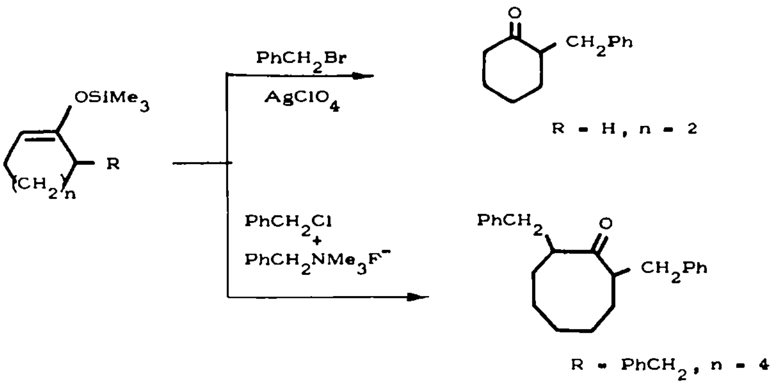
Silyl ethers of enols do not undergo addition to the C═O group of ketones (except benzyl) in the presence of TBAS at −78°C. Besides, the aldol product **112** dissociates in the presence of 12 mol % of TBAF to form cyclohexanone and 5-nonanone.



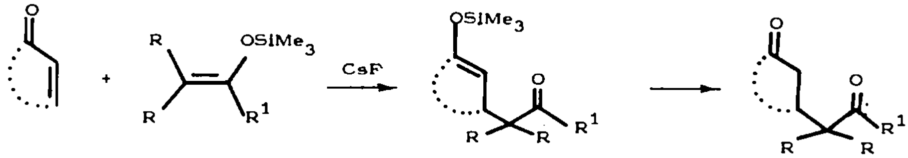
The addition of enoxysilanes to ketones may be carried out by using CsF in conditions of heterogeneous catalysis (without solvent, 60–100°C).[295] The interaction of silyl ethers of enols with ketones capable of enolization leads to a mixture of products.

$$RR^1C{=}CR^2OSiMe_3 + R^3R^4CHC(O)R^5 \rightleftharpoons RR^1CHC(O)R^2 + R^3R^4C{=}CR^5OSiMe_3$$

The Si—O bond in silyl ethers of enols is cleaved in the benzylation reactions involving the catalysis by $AgClO_4$ or fluoride ion,[296] as well as in cyclization reactions.

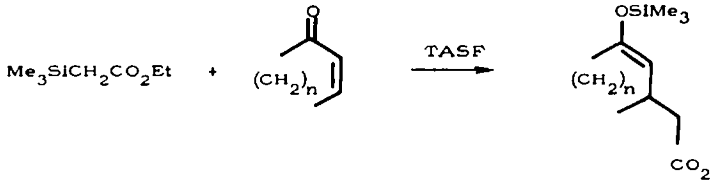


The Michael reaction is a well-known, important method for carbon–carbon bond formation. However, its synthetic use is essentially limited to the additions of stabilized anions such as those derived from malonates, cyanoacetates and acetoacetates. The reactions with simple, unstabilized enolates are often complicated by attendant side reactions, which include proton transfers, undesired condensations between reacting species and concomitant 1,2-additions. Some of these problems can be overcome by the use of modified enolates or by the use of masked carbonyl functionality. Yet another approach is to use silyl enol ethers as the functional equivalents of enolates.[297]



113 114 115

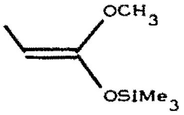
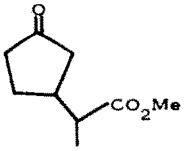
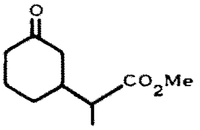
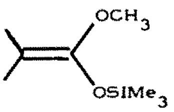
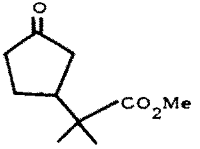
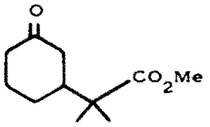
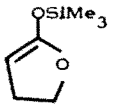
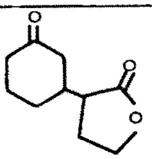
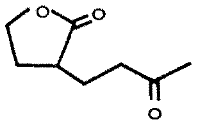
With CsF catalysis, however, the valuable intermediate silyl enol ethers **114** can be isolated. Ketene trimethylsilyl acetals **113** add to α,β-unsaturated ketones in the presence of catalytic amounts of TASF to give 5-(trimethylsiloxy)-4-pentenoic acid esters **114** (R^2 = O-alkyl). The yields are high and the addition proceeds exclusively in the 1,4-fashion (Table 7). The C-silyl compound ethyl-(trimethylsilyl)-acetate also participates in these reactions. This is not surprising because the C—$SiMe_3$ group is known to be displaced by fluoride ion.[282,284,297]



n = 1 (90%); n = 2 (62%)

The reaction of 1-(trimethylsiloxy)-cyclohexene with cyclohexanone (60°C, 11 h) with subsequent treatment by water leads to 55% yield of 2-(1-cyclohexenyl)-cyclohexanone.[295] The authors propose a mechanism excluding the intermediate formation of enolate anion. Non-enolizable ketones, such as fluorenone and benzophenone, form the products of addition of two enoxysilane molecules. For example, the reaction of benzophenone with the silyl ether of acetophenone (100°C, 8 h) leads to a 75% yield of diphenyl-(diphenacyl)-methane.

Table 7. TASF-catalysed additions of trimethylsilyl ketene acetals to α,β-unsaturated ketones[297]

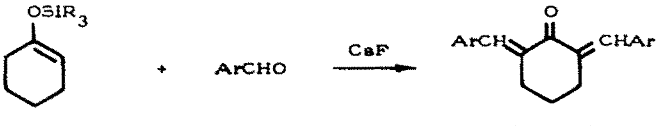
Silyl ketene acetal 113	Enone	Products 115	Yield, %
	cyclopentenone		82
	cyclohexenone		78
	cyclopentenone		75
	cyclohexenone		53
	cyclohexenone		58
	methyl vinyl ketone		74

Aldehydes react more easily with enoxysilanes than with ketones under heterogeneous catalysis. After treatment of the reaction mixture with water only the dehydration products were obtained from aromatic and aliphatic aldehydes.

$$\mathrm{RC(OSiMe_3){=}CH_2} \; + \; \mathrm{R^1CHO} \xrightarrow[\text{2) } H_2O/H^+]{\text{1) CsF}} \mathrm{RC(O)CH{=}CHR^1} \quad (75\text{–}95\%)$$

$R = Ph,\ t\text{-}Bu,\ R^1 = Ph,\ p\text{-}BrC_6H_4,\ C_6H_{13}$

The reaction with α,β-unsaturated aldehydes occurs similarly. The silyl ether of cyclohexanone reacts with aldehydes (including the α,β-unsaturated ones) under the same conditions to form only the 1,2-adducts.



$SiR_3 = SiMe_3,\ SiMe_2(OEt),\ SiMe(OEt)_2$

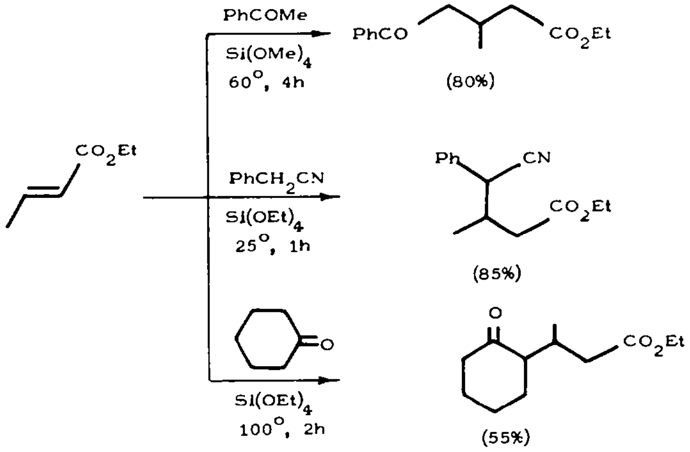
The reactions of enoxysilanes with enones and ethers of α,β-unsaturated carbon acids occur regioselectively by conjugated addition. After treatment of the reaction mixture, 1,5-dicarbonyl compounds **116** are isolated.

$$\mathrm{RC(OSiMe_3){=}CHR^1 + R^2CH{=}CHC(O)R^3 \xrightarrow{CsF} \underset{\underline{116}}{RC(O)CHR^1CHR^2CH_2C(O)R^3}}$$

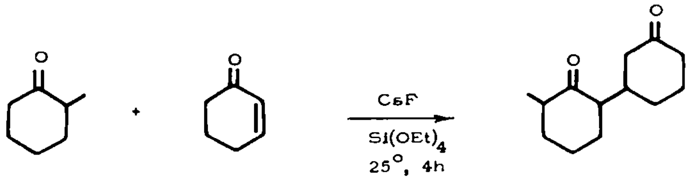
$\mathrm{R = Ph,\ t\text{-}Bu,\ R^1 = H;\ RR^1 = -(CH_2)_4-;}$

$\mathrm{R^2 = R^3 = Ph;\ R^2R^3 = -(CH_2)_3-;\ R^2 = Ph,\ R^3 = OEt}$

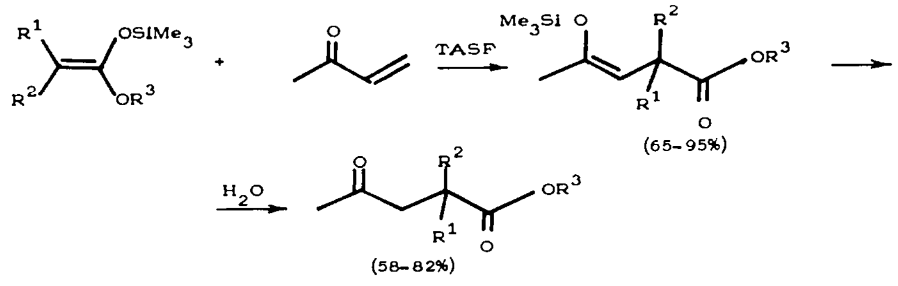
Corriu and his co-workers[291,298] have recently shown that tetraalkoxysilanes Si(OMe)$_4$ and Si(OEt)$_4$ are effective initiators of the Michael reaction under conditions of heterogeneous catalysis in the presence of CsF. The reactions of monoketones and arylacetonitriles with different kinds of Michael acceptors (α,β-unsaturated ketones, esters, nitriles) occur in the presence of stoichiometric amounts of CsF and Si(OR)$_4$ without a solvent. Addition of different kinds of ketones can occur even with hindered Michael acceptors such as pulegone or 3-methyl-2-butene nitrile. Only the 1,4-addition product is obtained except with hindered esters such as 3,3-dimethyl ethyl acrylate.



The proposed mechanism involves the formation of intermediate enoxysilane on the surface of the fluoride salt. Like enolizable ketones, arylacetonitriles can also act as donors in this reaction and α,β-unsaturated ketones, ethers and nitriles can act as acceptors. The reaction was found to be regiospecific. The addition of ketones takes place at the less substituted sp^3-carbon atom.



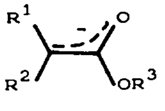
Aldehydes are not added to enols in these conditions but undergo the aldol condensation. The O-silylated acetals of ketones are easily added to α,β-unsaturated ketones under homogeneous fluoride ion catalysis.[299]



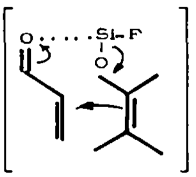
$\mathrm{R^1 = H,\ R^2 = R^3 = CH_3;\ R^1 = R^2 = R^3 = CH_3;}$

$\mathrm{R^1 = H,\ R^2R^3 = -(CH_2)_2-}$

1,4-Addition gives the ethers of 5-(trimethylsiloxy)-4-pentenic acids and after subsequent hydrolysis, 1,5-dicarbonyl compounds. In this case, the reaction route apparently includes the intermediate formation of the enolate anion **117** according to the mechanism discussed above. However, the authors also take into account the possibility of another reaction pathway involving the formation of the hypervalent silicon intermediates **118**.



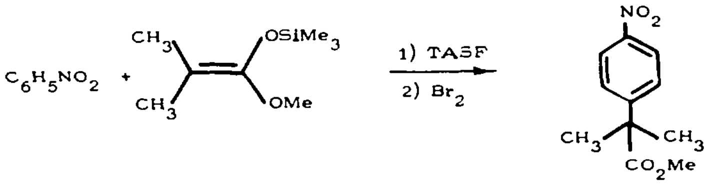
117



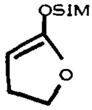
118

$CsF/Si(OCH_3)_4$ was successfully used for the reaction of 1,4-addition to α,β-unsaturated amides.[300]

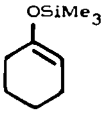
Addition of silyl ethers of enols and ketene silyl acetals to aromatic nitro compounds in the presence of TASF followed by oxidation of the intermediate dihydroaromatic nitronates gives α-nitroaryl ketones and esters respectively.[301,302]

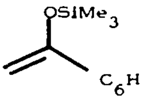


The following silicon organic compounds participate in this reaction:

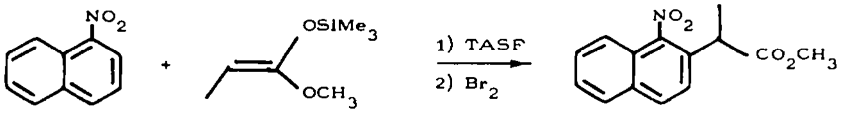


$Me_3SiCH_2CO_2Me$

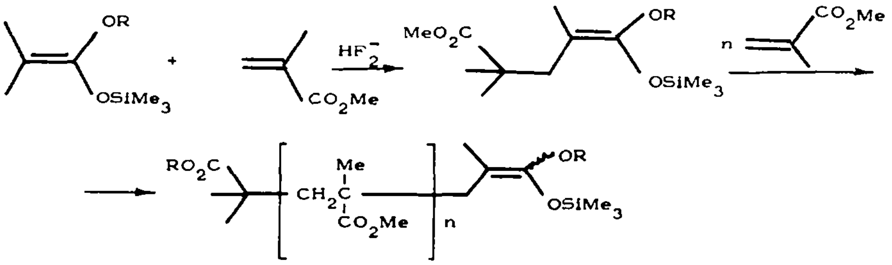




Nitronaphthalenes, nitroanthracene and various heterocyclic nitro compounds can also be used in this reaction. With 1-nitronaphthalene and 5-nitroisoquinoline the addition occurs predominantly at the *ortho* position.



Although the conjugate addition of silyl ketene acetals to α,β-unsaturated carbonyl compounds has been used in organic synthesis, application of this chemistry to polymer formation by sequential additions in novel. Such a process for the controlled polymerization of α,β-unsaturated esters, ketones, nitriles and carboxamides has been described.[303] This new method offers new dimensions in the design and construction of polymer chains from monomers. Scheme 7 illustrates the polymerization of methyl methacrylate with dimethylketene methyl trimethylsilyl acetal as initiator.

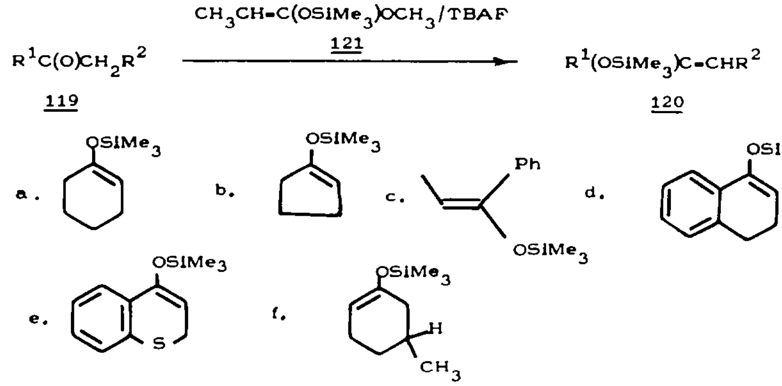


R = CH_3, $CH_2CH_2OSiMe_3$, $SiMe_3$

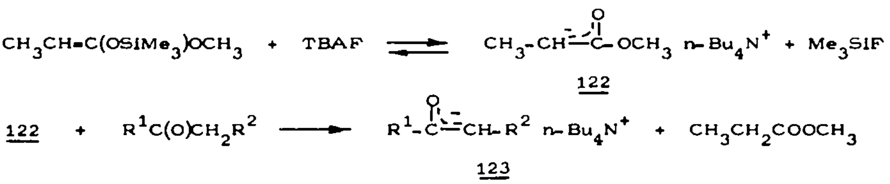
Scheme 7.

O-Silylated keteneacetals were found to be effective deprotosilylating reagents in the presence of fluoride ion.[304] For example, methyl-(trimethylsilyl)-acetal of methylketene readily reacts (THF, 20°C, 1–2 h) with cycloalkanones in the presence of TBAF to form silyl ethers of enols of cycloalkanones and methylpropionate.

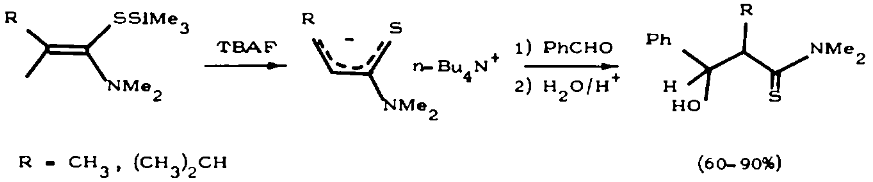
The O-silylation of ketones **119** leading to silyl ethers of enols **120** is generally carried out under weakly basic conditions. Equal amounts of reagent **121** and substrate **119** in THF containing a catalytic amount of TBAF are used. The silylation occurs completely within 1–2 h at 20°C (**113**) or even within 2 h at −80°C (**113f**).[302].



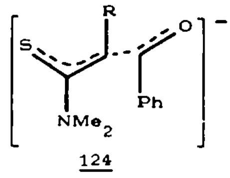
The formation of compounds **120** may be explained in terms of the following catalytic cycle involving the initial reversible formation of ammonium enolate **122**. This enolate **122** undergoes anionic exchange with ketone **119** to give ammonium enolate **123**. The latter is further O-silylated by reagent **121** and fluorotrimethylsilane.


$$CH_3CH{=}C(OSiMe_3)OCH_3 + TBAF \rightleftharpoons CH_3\text{-}CH{\cdots}C(O^-)\text{-}OCH_3\ n\text{-}Bu_4N^+ + Me_3SiF$$
122
$$\underline{122} + R^1C(O)CH_2R^2 \longrightarrow R^1\text{-}C(O^-){\cdots}CH\text{-}R^2\ n\text{-}Bu_4N^+ + CH_3CH_2COOCH_3$$
123

Z-*N*,*N*-Dimethyl-*S*-(trimethylsilyl)-ketene-*S*,*N*-acetals undergo addition to the carbonyl group of aldehydes in the presence of fluoride ion (TBAF).[305]



After treatment of the reaction mixture with water, *β*-hydroxythioamides mainly of the *erythro*-configuration were obtained. The intermediate formation of the enolate anion is observed in the reaction and the *erythro*-selectivity is connected with the acyclic transition state **124** similar to those discussed above for the reactions of "pure" enolate anions with aldehydes.



124

Silylnitronates react easily with aldehydes in the presence of TBAF to form mainly products of *erythro*-structure.[265,306]

$$R^1CH{=}N(O)OSiMe_3 + R^2CHO \xrightarrow{F^-} R^2CH(OSiMe_3)CHR^1{-}NO_2$$

Rationalization of the *erythro*-selectivity is based upon the transition stage **124**.[260,307] Alcohols and carboxylic acids were shown[308] to undergo alkylation and acylation by silyl ethers of enols under fluoride ion catalysis. Alkenylphenylketone and 1,3-diketones were obtained.

$$R^1CH{=}CHCH_2OH + PhC(OSiMe_3){=}CH_2 \xrightarrow[THF]{KF} \underset{(66\text{–}72\%)}{R^1CH{=}CHCH_2CH_2C(O)Ph}$$

R^1 = cis or trans-CH_3, trans-Ph

Trimethylsilyl ethers of enols react with carboxylic acids in the presence of KF and bis-(2,2,2-trifluoroethoxy)-diorganosulphuranes to form dicarbonyl compounds. Bis-(2,2,2-trifluoroethoxy) diorganosulphuranes serve in this case as acyl group carriers in the desilylation of trimethylsilyl ethers of enols.[309]

$$PhCOOH + Ph(OSiMe_3)C{=}CH_2 \xrightarrow[PhS(OCH_2CF_3)_3,\ 20^\circ C,\ 24h]{KF} \underset{(81\%)}{PhC(O)CH_2C(O)Ph}$$

The fluoride ion (CsF or $(C_6H_5CH_2)Me_3N^+F^-$) was shown[310] to promote the reaction between trimethylsilyl ethers of enols and aromatic and aliphatic sulphonyl fluorides, leading to enol sulphonates.

$$R^1R^2C{=}C(OSiMe_3)R^3 + R^4SO_2F \xrightarrow[-Me_3SiF]{F^-} R^1R^2C{=}C(OSO_2R^4)R^3$$

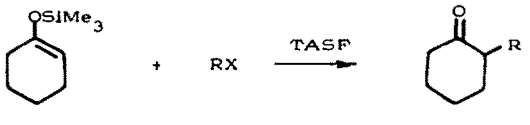
R^4 = C_6H_5, C_4F_9, CH_3

The fluoride ion-catalysed reaction of *F*-alkylacetylenes with various silyl enol ethers leads[311] to the corresponding F-alkinylated alcohols or 4-(1H-*F*-alkylidene)-1,3-dioxolane derivatives in good yields. This type of reaction is generally applicable to the synthesis of F-alkyl-substituted propargyl alcohols and α-hydroxy ketones. TBAF is the most efficient source of fluoride ion, CsF and KF being less effective. The results are summarized in Table 8.

$$\underset{\mathbf{124}}{R_FCF{=}CHP(O)(OEt)_2} \xrightarrow{TBAF} \left[R_FC{\equiv}CH\right] \xrightarrow{\substack{R^1R^2C{=}CH(OSiMe_3)\\ \mathbf{125}}} \underset{\mathbf{126}}{R_FC{\equiv}CCH(OH)CHR^1R^2}$$

Silyl enol ethers **125** derived from aldehydes readily undergo the reaction with *F*-alkylacetylene in the presence of TBAF yielding the corresponding acetylenic alcohols **126**. The reaction with silyl enol ethers obtained from ketones, however, proceeded slowly to give very low yields of products.

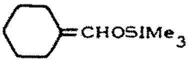
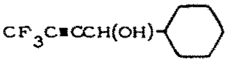
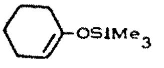
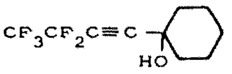
Tris(dialkylamino)-sulphonium enolates generated from TASF and enol silyl ethers are readily alkylated by various alkyl halides under mild conditions.[312]



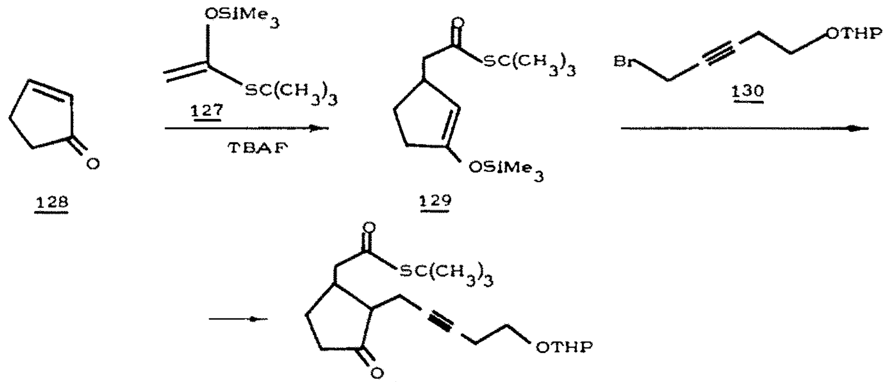
R = CH_3, X = I (95%); R = n-C_4H_9, X = I (59%);
R = $C_6H_5CH_2$–, X = Br (72%); R = $C_6H_5CH{=}CHCH_2$–, X = Br (61%);
R = $MeOOCCH_2$, X = Br (83%)

The unsolvated fluoride and enolate ions under such conditions can behave as naked, super-nucleophilic reagents: the overall C-alkylation reaction is accomplished at −78 to −30°C. It is shown that the lithium enolate of *S*-t-butyl thioacetate adds to 2-cyclopentenone in the *β*-position and that fluoride ions catalyse the 1,4-addition of the trimethylsilyl enol ether of *S*-t-butyl thioacetate

Table 8. Synthesis of F-alkyl-substituted propargyl alcohols **126**[311]

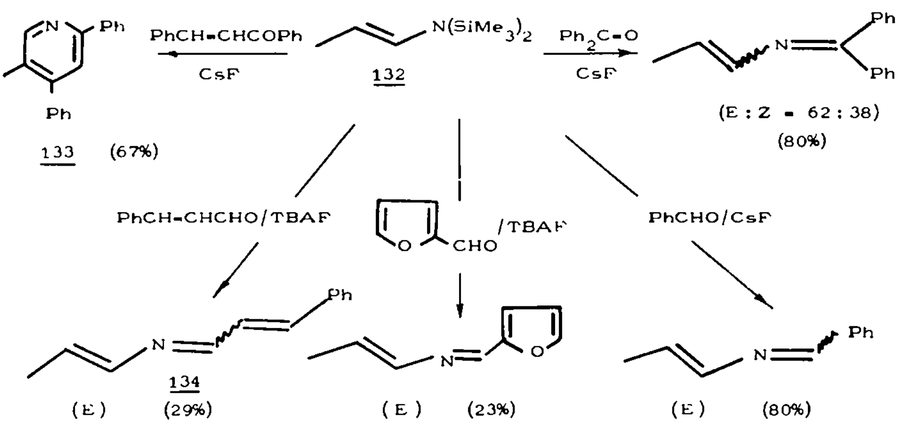
Alkenephosphonate	Silyl enol ether 125	Product 126	Yield,%
$CF_3CF{=}CHP(O)(OEt)_2$	$CH_3(CH_2)_4CH{=}CHOSiMe_3$	$CF_3C{\equiv}CCH(OH)(CH_2)_5CH_3$	34
-"-			45
$CF_3CF_2CF{=}CHP(O)(OEt)_2$	$CH_3CH_2CH{=}CHOSiMe_3$	$CF_3CF_2C{\equiv}CCH(OH)(CH_2)_2CH_3$	67
-"-	$CH_3(CH_2)_3CH{=}CHOSiMe_3$	$CF_3CF_2C{\equiv}CCH(OH)(CH_2)_4CH_3$	67
-"-	$CH_2{=}CHCH{=}CHOSiMe_3$	$CF_3CF_2C{\equiv}CCH(OH)CH{=}CHCH_3$	28
-"-			60
-"-	$CH_3(CH_2)_4CH{=}CHOSiMe_3$	$CF_3CF_2C{\equiv}CCH(OH)(CH_2)_5CH_3$	79
$CF_3(CF_2)_5CF{=}CHP(O)(OEt)_2$	$CH_3(CH_2)_4CH{=}CHOSiMe_3$	$CF_3(CF_2)_5C{\equiv}CCH(OH)(CH_2)_5CH_3$	81
-"-			85
$CF_3(CF_2)_7CF{=}CHP(O)(OEt)_2$	$CH_3(CH_2)_4CH{=}CHOSiMe_3$	$CF_3(CF_2)_7C{\equiv}CCH(OH)(CH_2)_5CH_3$	70
-"-			71

127 to 2-cyclopentenone **128** giving **129**. These novel versions of the Michael addition have been applied to a synthesis of jasmonoid compounds. Cleavage of the trimethylsilyl enol ether in **129** with TBAF produced the corresponding ketone enolate which could be trapped *in situ* by alkylation with 1-bromo-5(2′-tetrahydropyranoxy)-2-pentyne **130** to form **131**.[313]



4.6. *Reactions of* O- *and* N-*substituted derivatives of silicon*

Very interesting results were obtained by Corriu and his co-workers in the investigation of the reactions between *N*,*N*-bis-(silyl)enamines and electrophilic substrates which are initiated by fluoride ions.[60,314] *N*,*N*-Dialkylenamines reacted easily with electrophiles to form the C—C bond whereas *N*,*N*-bis-(silyl)enamines react as weak nucleophiles and do not interact with electrophiles in the absence of catalysts. The *N*,*N*-bis-(silyl)enamine **132** does not react with $PhCH_2Br$ and PhCOCl but it reacts easily with carbonyl compounds in the presence of catalytic amounts (5 mol %) of CsF (DMF, 80°C) or TBAF (THF, 20°C) to form 2-aza-1,3-dienes which are synthones for the preparation of six-membered heterocycles. In contrast with *N*,*N*-dialkyleneamines the formation of the C=N bond is observed. Good yields of products were obtained in the reaction of **132** with



Scheme 8.

benzaldehyde and benzophenone. Enolizing carbonyl compounds, however, gave lower yields as a result of the side reaction of aldol condensation.

The reaction with cinnamaldehyde leads to the azatriene **134**. Formation of the corresponding azatriene may also be supposed in the reaction of the silane **132** with chalkone; the cyclization of azatriene then leads to the substituted pyridine **133**. The formation of heterodienes (Scheme 8) may be explained in terms of the nitrogen nucleophilic attack on the carbonyl group with subsequent β-elimination of $(Me_3Si)_2O$. The role of the fluoride ion is weakening of the Si—N bond by means of nucleophilic attack on the silicon atom. In the opinion of the authors,[314] the reaction is controlled by disiloxane elimination.

N,*N*-Bis-(silyl)-enamines react even with *N*,*N*-dimethylformamide in the presence of methoxide ions forming enamidines.[314]

$$RCH_2CH{=}CHN(SiMe_3)_2 + HC(O)NMe_2 \xrightarrow{NaOMe} \underset{(60\text{–}82\%)}{RCH_2CH{=}CH\text{–}N{=}CHNMe_2}$$

$$R = H,\ SiMe_3$$

The reaction of *N*,*N*-bis-(trimethylsilyl)-3-trimethylsilylpropan-1-ylamine leads only to formation of the product of Si—N bond cleavage. Aminosilanes react readily with alkyl halides in the presence of sodium methoxide under conditions giving *N*-alkylamines in good yields (Table 9).[314]

$$\underset{\mathbf{135}}{RNHSiMe_3} + R'X + NaOMe \xrightarrow[(5:1)]{THF\text{–}diglime} \underset{\mathbf{136}}{RNHR'}$$

In the direct reaction of aminosilanes with alkyl halides, silylammonium salts are not formed, probably because of their low basicities, which result from the interaction of the lone electron pair

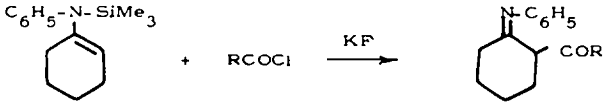
Table 9. Selective conversion of primary amines to secondary amines using aminosilanes[314]

Aminosilanes **135**	Alkyl halides	Temperature (°C)	Time (h)	Yield of **136** (%)
cyclo-$C_6H_{11}NHSiMe_3$	EtBr	40	15	64
	n-PrBr	40	18	56
	n-BuBr	40	18	53
	CH_2CHCH_2Br	40	15	68
	$PhCH_2Br$	40	18	67
$PhNHSiMe_3$	EtBr	r.t.	20	43
	n-PrBr	40	20	48
	EtI	40	18	64
	n-BuBr	40	18	55
	$CH_2{=}CHCH_2Br$	40	24	72
	$PhCH_2Br$	THF only reflux	5	84

of nitrogen with the vacant *d*-orbitals of silicon. A probable mechanism for this selective N-alkylation is shown below.

$$RNHSiMe_3 + NaOMe \longrightarrow RNH^-Na^+ \xrightarrow[-Me_3SiOMe]{R'X} RNHR'$$

(*N*-Vinyl-*N*-phenyl)-aminosilanes **137** react with acyl chlorides in the presence of KF dissolved in crown-ethers to yield 2-ketoimines **138**.[315]

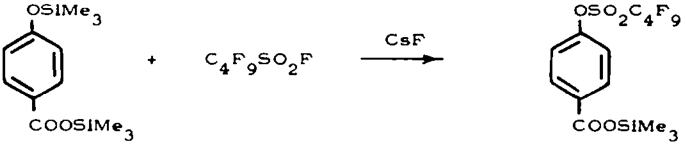


137 138

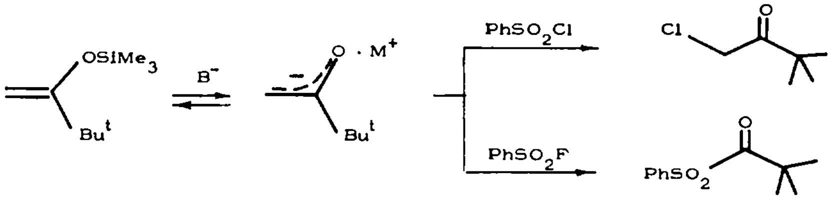
R = C_6H_5 (90%), $(CH_3)_2CHCH_2$ (89%), i-Pr (93%),

n-C_7H_{15} (92%), $CH_3CH{=}CH$ (81%), C_2H_5O (84%)

1-*N*-Trimethylsilyl-*N*-phenyl)-amino-6-methylcyclohexene is transformed by benzoyl chloride and KF to *N*-phenylimine-2-benzoyl-6-methylcyclohexanone (94%). The reaction has been supposed to involve difluorosilylation of enaminosilane by fluoride ion and further addition of the acyl group at the carbon atom. In these cases the substituted phenyl group reacts with polyfluoroalkylsulphonyl fluoride, while the trimethylsilyloxycarbonyl group remains inert, thus providing the possibility of obtaining mixed esters of benzoic and alkylsulphonic acids.[310]

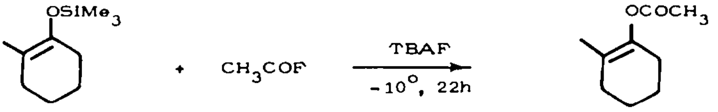


The role of the base is important. The use of CsF or $Alk_4N^+F^-$ leads to the vinylsulphonate only. However, in the presence of $LiN(Pr\text{-}i)_2$, $NaN(Pr\text{-}i)_2$ all three possible products are obtained.



In the absence of KF the reaction leads to the N-acylation product and after hydrolysis gives a mixture of ketone and amide.

Silyl ethers of enols react with acyl halides in the presence of TBAF or KF · 18-crown-6 complexes, to form vinyl esters of carboxylic acids. High regiospecificity is observed. The interaction occurs under mild conditions and gives a high yield.[304]

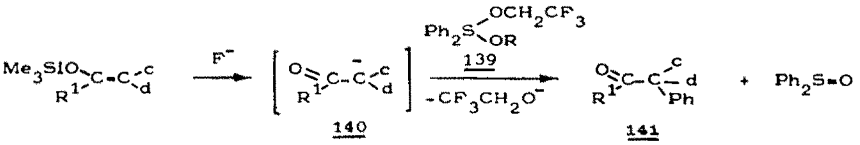


Trimethylsilyl ethers of enols react with ROCOF in the presence of benzyltrimethylammonium fluoride in THF giving enol carbonates. This occurs (90%) with high regio- and stereo-specificity. Thiocarbamates can also be obtained in this reaction when the KF · 18-crown-6 complex is used as a base. The reactivity of TBAF and the NaF · 18-crown-6 complex is insufficient.[315]

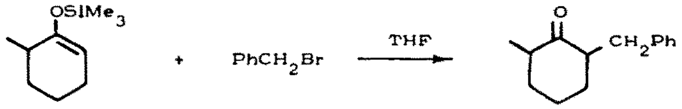
$$Me_2C{=}CHOSiMe_3 + PhSC(O)F \xrightarrow{KF\cdot 18\text{-}crown\text{-}6,\ 23h} Me_2C{=}CHOC(O)SPh$$

(69%)

Alkoxytrimethylsilanes react with benzenesulphonyl fluoride in the presence of TBAF, forming the corresponding benzenesulphonates (28–70%).[307] Aryl esters of perfluoroalkanesulphonic acids are obtained in higher yields by heating perfluoroalkanesulphonyl fluorides with alkyloxytrimethylsilane in the presence of KF or CsF.[316] On the basis of the reactions of acyl halides containing an activated halogen atom with silyl ethers of enols in the presence of fluoride ion there has been developed a method for the introduction of alkyl substituents in the α-position to carbonyl groups. Instead of alkyl halides, organosulphuranes may be used. The role of sulphuranes is in the formation of the alkoxy-derivatives of the type of **139**, which then react with the carbanions generated from silyl ethers of enols.[309] An enolate anion **140**, generated from the trimethylsilyl ether–KF system, readily attacked the alkoxysulphurane **139** forming compound **141**.

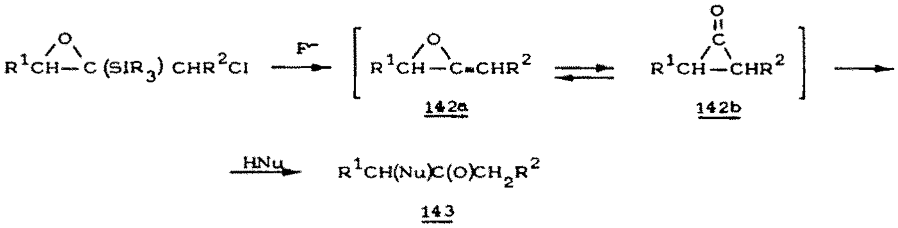


Tetraalkylammonium fluoride is a more active catalyst for these reactions. By this method the following substituents can be introduced into the α-position of carbonyl compounds: benzylic,[295,317] allylic[318] and propargylic.[319] The reaction also occurs with less active electrophiles, such as methyl iodide, butyl iodide and methyl bromoacetate. The following products were obtained from 1-trimethylsiloxy-6-methylcyclohexene.



20°, 1h cis (9%)
50°, 30 min, trans (80%)

Cleavage of the Si—C bond in (α-chloromethyl)-oxyranylsilanes by fluoride ion is accompanied by β-elimination of Me_3SiCl and leads to the formation of the allenoxide–cyclopropanone system **142**. This was confirmed by isolation of 1,3-dipolar cycloaddition products and by opening of the cyclopropanone ring during the reaction in the presence of conjugated dienes and nucleophilic reagents respectively.[137-139]



R=R^1 = Ph, R^2 = H, R=Me, R^1 = H, Me, i-Pr, t-Bu, n-$C_{10}H_{21}$, R^2 = H;
R = Me, R^1 = H, R^2 = n-$C_{10}H_{21}$, p-MeC_6H_4;
X = CH_2, O, NC(O)OMe;
Nu = Cl_3CCOO, HO, MeO, PhO, EtS, $(i\text{-}Pr)_2N$

When the reaction is carried out in methanol (20°C, 24 h), quantitative formation of product **143** occurs (Nu = OCH_3). The authors[137] did not observe formation of the products of silane protodesilylation; their absence indicates the reaction mechanism to be of the E_2-Si type.

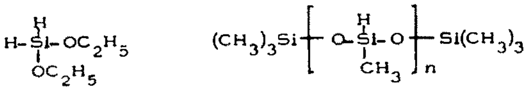
5. FLUORIDE ION NUCLEOPHILIC CATALYSIS OF SOME CHEMICAL REACTIONS

5.1. *Reduction*

Organosilicon hydrides are frequently used as reducing agents toward electrophilic carbon centres. The formation of alkoxysilanes from organosilicon hydrides and certain aldehydes and ketones, as shown by Vol'pin and his co-workers, requires the presence of fluoride ion.[56,61]

$$R_2C{=}O + R'_3SiH \xrightarrow{F^-} R'_3SiOCHR_2$$

Corriu *et al.* have subsequently shown that the fluoride ion may be used even under heterogeneous reaction conditions without solvent. This provides a useful selective procedure for the reductions of aldehydes, ketones and even esters to alkoxysilanes which yield alcohols by hydrolysis.[57,60,63–66] The reduction of aldehydes and ketones with trialkylsilanes has been recognized as a useful synthetic method for a number of years. Quite recently the reduction was shown to be catalysed by fluoride ion under neutral conditions.[320] 1-Naphthylsilane is an even more active reducing agent and benzophenone is reduced in the presence of CsF at 50°C into (1-naphthyloxy)-diphenylmethane in quantitative yield.[60] However, these silanes are not easily available and the silanes, R_3SiH, have a comparatively low reactivity. Ethoxysilanes $(EtO)_3SiH$ and $(EtO)_2MeSiH$ have been considered to be more useful reducing agents, which are easily obtained from the available trichloro- and methyldichlorosilanes.[66] $(EtO)_2MeSiH$ and polymethylhydroxysiloxane have become widely used reagents for reduction.



$$H{-}\overset{H}{\underset{OC_2H_5}{Si}}{-}OC_2H_5 \qquad (CH_3)_3Si{-}\left[O{-}\overset{H}{\underset{CH_3}{Si}}{-}O\right]_n{-}Si(CH_3)_3$$

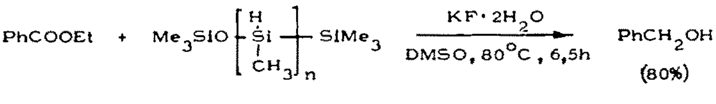
The ease of reduction was shown to decrease in the series: aldehydes > ketones > esters. Polymethylhydrosiloxane in the presence of potassium formate reduces aldehydes more rapidly than ketones. This differential reactivity may be used to carry out selective reduction of an aldehyde group in the presence of a keto function. Examples of the reduction products are presented in Table 10. Esters can also be converted to alcohols by ethoxysilanes in the presence of alkali metal fluorides.[63,65]

$$PhCOOEt \xrightarrow[60^\circ C,\ 0{,}5h]{(EtO)_3SiH/CsF} PhCH(OEt)OSi(OEt)_3 \xrightarrow{(EtO)_3SiH}$$

$$\longrightarrow PhCHOSi(OEt)_3 + EtOSi(OEt)_3 \longrightarrow \underset{(90\%)}{PhCH_2OH} + \left[(EtO)_3Si\right]_2O$$

This process may be realized for all types of esters—aliphatic, unsaturated and aromatic. The results of the reduction to alcohols are comparable with those for $LiAlH_n(OR)_{4-n}$ as the reducing agent. The methods described above have several advantages: the reducing agent is synthetically easily available; CsF returns unchanged after the reaction; the reaction occurs without solvent. The results of the reduction depend: (i) on the nature of the silane and of the carbonyl compound; (ii) on the type of fluoride being used; (iii) on the reaction temperature. The reducing ability of silanes decreases as follows: $(EtO)_3SiH > Me(EtO)_2SiH > Ph_2SiH_2$. For example, benzaldehyde is reduced at 20°C by $(EtO)_3SiH$ in the presence of KF. For the reduction of acetophenon, a more powerful fluoride ion donor, CsF, is required. And the reduction of ethyl benzoate occurs in the presence of CsF only at 60°C.[60]

The reduction rate increases in the presence of solvents. Thus, potassium fluoride used in combination with a solvent is able to reduce ethyl benzoate.

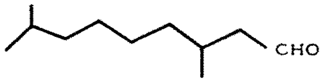
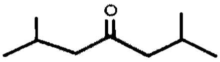
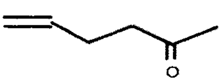
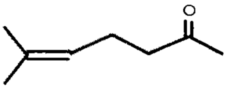
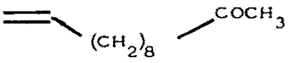


$$PhCOOEt + Me_3SiO\left[\overset{H}{\underset{CH_3}{Si}}\right]_n SiMe_3 \xrightarrow[DMSO,\ 80^\circ C,\ 6{,}5h]{KF\cdot 2H_2O} \underset{(80\%)}{PhCH_2OH}$$

The observed order of reactivity of carbonyl groups in aldehydes, ketones and esters permits a highly selective reduction of aldehydes in the presence of ketones and esters or of a mixture of ketones. The required conditions may be determined by varying the temperature and the fluoride.

$$C_6H_5CHO \xrightarrow[25^\circ C,\ 36h]{(EtO)_3SiH,\ KF} \underset{(100\%)}{C_6H_5CH_2OH}$$

Table 10. Reduction of carbonyl compounds by silylation of diethoxymethylsilane in the presence of KF[66]

Carbonyl Compounds	Yield,%
C_6H_5CHO	90
$C_6H_5COCH_3$	78
$(C_6H_5)_2C=O$	87
$n\text{-}C_6H_{13}CHO$	85
	68
	75
	85
	80
	65
	77

The reduction of substituted aromatic aldehydes and ketones containing C=O bonds, nitro and amino groups, etc., occurs only at C=O groups, the others being unreactive.

$$4\text{-}NO_2C_6H_4CHO + (EtO)_3SiH \xrightarrow[100^\circ C,\ 2h]{KF} \underset{(80\%)}{4\text{-}NO_2C_6H_4CH_2OH}$$

The carbonyl groups of α,β-unsaturated aldehydes and ketones are selectively reduced in the presence of CsF.[64,321]

$$PhCH{=}CHCHO + (EtO)_3SiH \xrightarrow[25^\circ C,\ 24h]{KF} \underset{(95\%)}{PhCH{=}CHCH_2OH}$$

Silanes R_2SiH_2 react with α,β-unsaturated carbonyl compounds in the presence of $(Ph_3P)_3RhCl$ giving a mixture of the products of 1,2- and 1,4-addition. The reduction in the presence of KF or CsF leads to 1,2-adducts only. The role of the fluoride ion involves coordination with the silicon atom thereby facilitating Si—H bond cleavage.

A reasonable explanation of the role played by the fluoride ion in these reactions is given in Scheme 9. The initial interaction of fluoride ion with organosilicon hydride leads to a kinetically active pentavalent anion (**9a**). The latter then interacts with the ketone forming the fluorosilane and the oxy-anion as a result of hydride transfer (**9b**). The latter is able to attack the fluorosilane molecule to give the observed alkoxysilane product and the initial fluoride ion (**9c**). In accordance with that Scheme, the pentavalent silicon anion acts as an excellent hydride transfer agent.

$$R'_3SiH + F^- \rightleftharpoons R'_3SiHF^- \qquad (a)$$

$$R'_3SiHF^- + R_2C{=}O \longrightarrow R'_3SiF + R_2CH\text{-}O^- \qquad (b)$$

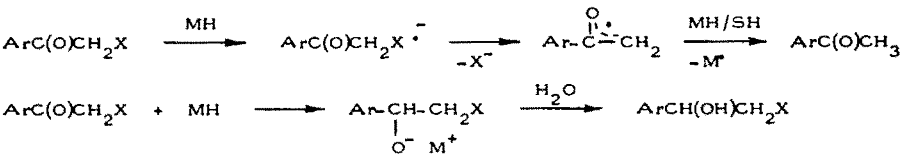
$$R'_3SiF + R_2CH\text{-}O^- \longrightarrow R'_3SiOCHR_2 + F^- \qquad (c)$$

Scheme 9.

Another possible route of reaction involving hydride transfer between the silane and the ketone molecule to form a silylenium cation has been demonstrated not to occur.[322]

$$R_2C{=}O + R_3SiH \longrightarrow R_2CH{-}O^- + R_3Si^+$$

The authors[323] have made an attempt to identify the most probable route of reduction. They have shown the catalytic effect of TBAF using ketones containing CF_3 groups as models. Thus, the reduction of α,α,α-trifluoroacetophenone with phenyldimethylsilane in DMSO has been shown[324] to lead, after subsequent hydrolysis, to the corresponding alcohol (22%). When TBAF (5%) was added its role as a catalyst leads to the alcohol in 86% yield. In the same work the detection of the EPR signals of the radical anions of 2,6-di-t-butylbenzoquinone (or phenylcyclopropyl ketones or butyrophenone) has been found during reduction of these ketones by $PhMe_2SiH$/TBAF in DMSO. The detailed investigation of these processes led to the conclusion that the pentavalent complex of **9a** type is an excellent hydride reducing agent and even with moderate acceptors (i.e., α-fluoroacetophenone or cyclopropylphenyl ketone) acts as a single-electron transfer agent giving minor amounts of radical-derived reduction products. α-Fluoroacetophenone under the action of silane/TBAF (40°C, 12 h) gives a mixture of 2-fluoroethanol (73–89%) and acetophenone (0.6–3.5%), the latter being formed as shown in the Scheme.



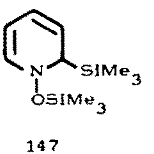
The fluoride ion-promoted reaction of *R*-(+)-α-naphthylphenylsilane **145** with several prochiral aromatic ketones **146** has been examined and the stereochemical outcome at both the silicon and carbon centres has been determined.[325]

$$\underset{\underline{145}}{Np(Me)PhSiH} + \underset{\underline{146}}{ArC(O)R} \longrightarrow Np(Me)PhSiOCHRAr \xrightarrow[-Np(Me)PhSiH]{} ArRCHOH$$

$Ar = C_6H_5$, $R = CH_3$	16,4% (S),	6,6% (S)
$Ar = 4\text{-}NO_2C_6H_4$, $R = CH_3$	11,3% (S),	12,7% (S)
$Ar = C_6H_5$, $R = CF_3$	13,2% (S),	11,2% (R)

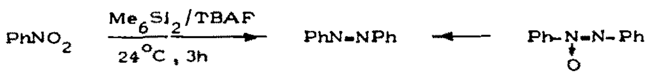
Vorbruggen *et al.* and Hwu *et al.* have used hexamethyldisilane with TBAF in THF or in HMPT for the reduction of *N*-oxides of pyridine derivatives.[321,326]

Quinoline and isoquinoline *N*-oxides form the corresponding heteroaromatic compounds (72 and 92% respectively). One mechanism suggested[321] for the reaction between pyridine *N*-oxide and hexamethyldisilane in the presence of TBAF involves the silylation of pyridine *N*-oxide with fluorotrimethylsilane giving the disilylated intermediate **147** and fluoride ion.



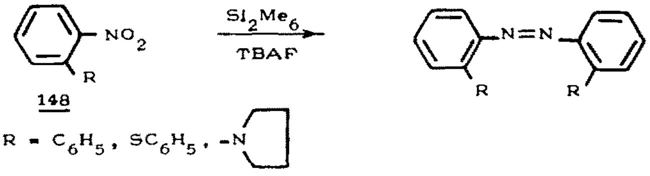
147

The reduction of aromatic nitro compounds with hexamethyldisilane and fluoride ion in THF at 24°C gives the corresponding azo- and azoxy-compounds in high yields.[327] Azoxybenzene is converted to azobenzene in a 95% yield in a similar way.



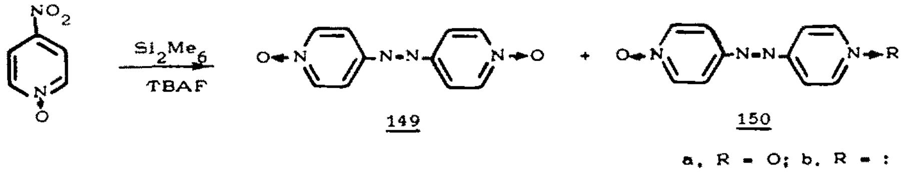
$$PhNO_2 \xrightarrow[24^{\circ}C,\ 3h]{Me_6Si_2/TBAF} PhN{=}NPh \longleftarrow Ph{-}\underset{\downarrow\atop O}{N}{=}N{-}Ph$$

Bulky *ortho*-substituents inhibit the reduction of **148** to the corresponding substituted azobenzenes.



The reduction of *o*-nitrobenzaldehyde in THF at 24°C occurs only in the presence of equivalent amounts of TBAF to form *o*-nitrobenzyl alcohol (80%); azo- and azoxy-compounds are not formed in this case.

Reduction of the polar and insoluble 4-nitropyridine *N*-oxide in *N*,*N*-dimethylimidazolin-2-one as a solvent leads to the azoxy compound **149** (52%).



As by-products, a mixture of **150a** and **150b** was obtained. Their formation is connected with the dimerization of the intermediate nitrosopyridine *N*-oxide.

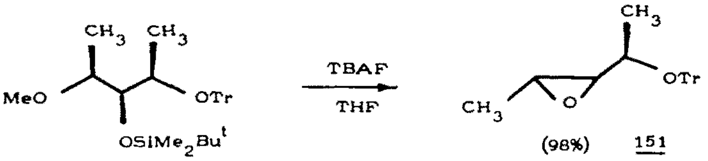
Selective reduction of the nitro group by the Si_2Me_6–TBAF system occurs in 4-nitropyridine *N*-oxides.[328] The authors[328] established that disilylperoxides in the presence of KF or CsF are easily converted to symmetric dialkyltritetramethyldisiloxane at 20°C. Without nucleophilic catalysis this reaction is observed only at 100°C.

$$(4\text{-}XC_6H_4)Me_2SiOOSiMe_2(C_6H_4X\text{-}4) \xrightarrow[0-60^{\circ}C]{MF/i\text{-}PrOH} (4\text{-}XC_6H_4)Me_2SiOSiMe_2(C_6H_4X\text{-}4)$$

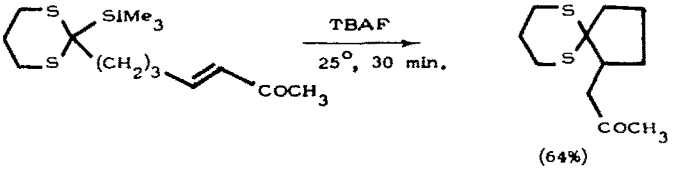
X = H, Cl, Me, OMe

5.2. *Synthesis of carbocyclic and heterocyclic compounds from organosilicon compounds under nucleophilic catalysis conditions*

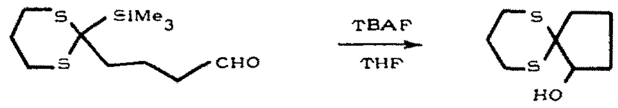
Organosilicon compounds have been widely used for the synthesis of cyclic compounds. For example, 1,3-dehydrohalogenation of α-halogen carbonyl compounds leads to cyclopropanone derivatives in good yields.[329] 1-Methoxy-2-silyloxy derivatives react with TBAF to form oxiranes **151**.



TBAF is an excellent reagent for the synthesis of spirodithiaalkanols from ω-(2-trimethylsilyl-1,3-dithian-2-yl)-alkanes. The reaction includes intramolecular cyclization of intermediate dithianyl anion with participation of an ω-aldehyde functional group.[330] Formation of the cycles containing 4–6 carbon atoms facilitates the reaction.

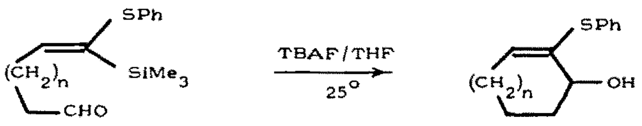


Spiroalcohols **152** are obtained in the same way.[330]



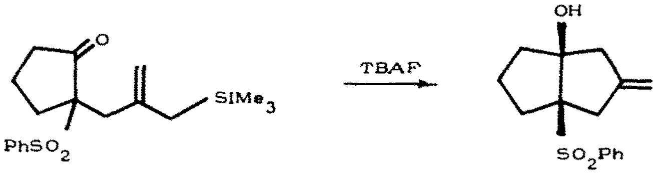
152

Intramolecular cyclization also occurs with participation of vinylsilanes which produce the stable vinyl anion by the action of fluoride ion. In this way 2-phenylthiocycloalken-2-ols-1 **153** were obtained. In the absence of anion-stabilizing substituents at the double bond, desilylation was observed instead of cyclization.[331]



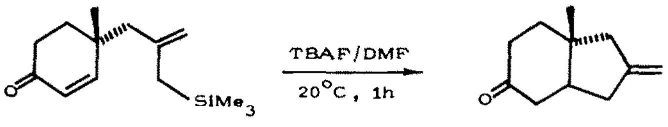
153

Intramolecular cyclization leads to five-membered carbocyclic compounds. The presence of a trialkylsilyl group in the δ-position of the carbonyl compounds leads to the elimination of Me_3SiF by fluoride ion. The carbanion centre formed in this way undergoes intramolecular attack at the carbon atom of the carbonyl group. Thus, in the example given below, heating for a short time with TBAF yields the bicyclo[5,5,0]octane derivatives **154** (94%).[208]



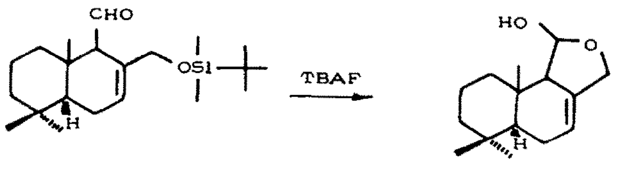
154

The cyclopentane fragment is obtained by the intramolecular Michael reaction of α,β-unsaturated carbonyl compounds containing the $SiMe_3$ group in the 5 position.[332]



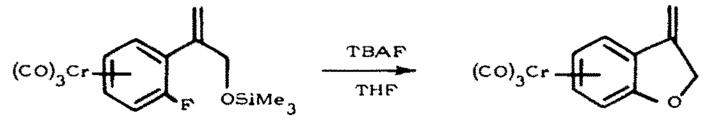
(63%)

A crucial step in the synthesis of (±)-drimenin was the reaction between TBAF and an allyl silyl ether. This yielded the lactol **155** which was oxidized to the corresponding lactone, (±)-drimenin.[333]



155 (78%)

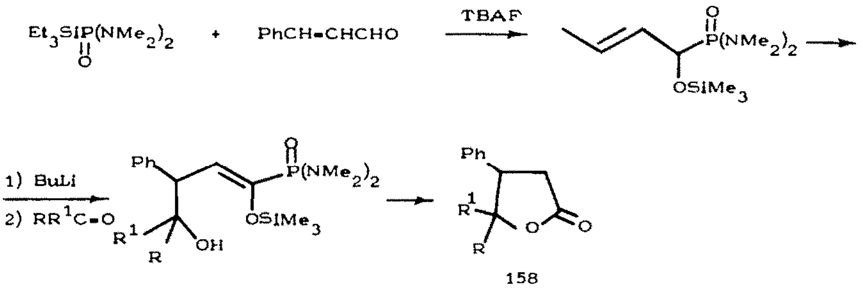
Desilylation of tricarbonyl-η^6-2-fluoro-(1-trimethylsiloxyprop-2-en-2-yl)benzene chromium **156** with TBAF in THF results in cyclization yielding the 3-methylene-2,3-dihydrofuran tricarbonylchromium complex **157**.[334]



156

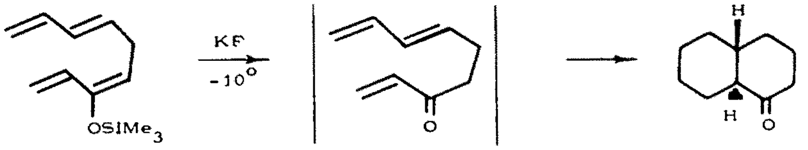
157 (89%)

A method of synthesis of γ-butyrolactone derivatives **158** (55–70%) from α,β-unsaturated aldehydes and silylated phosphamide $Et_3SiP(O)(NMe_2)_2$ in the presence of TBAF and THF has been developed.[335]



158

Six-membered carbocycle formation was observed in the desilylation of 3-triethylsiloxydeca-1,3,7,9-tetraene **159** by KF in methanol. The deca-1,7,9-trien-3-one is unstable under the reaction conditions and intramolecular cycloaddition leads to bicyclodecenone **160**.[336,337]



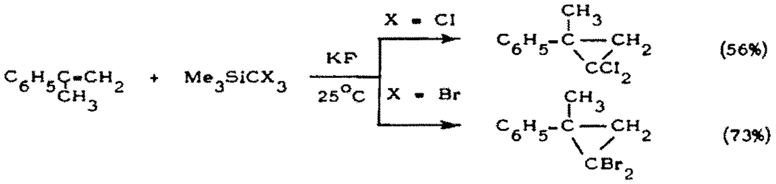
159

160 (78%)

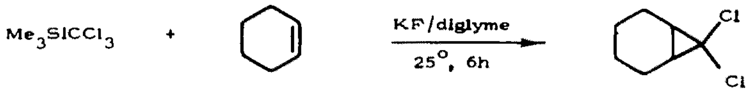
N,N-Bis-(trimethylsilyl)-1-aminopropene-1, $CH_3CH{=}CHN(SiMe_3)_2$, reacts with chalcone, PhCH$=$CHCOPh, in the presence of CsF to form 5-methyl-2,4-diphenylpyridine.[314]

5.3. *Formation of carbenes from organosilicon compounds and their reactivity*

Carbenes are the highly reactive products of 1,1-elimination (α-elimination) and organosilicon derivatives are widely used for generating carbenes. For example, trimethyl-(trihalomethyl)-silanes dissociate in the presence of KF to form carbenes which react with olefins giving derivatives of *gem*-dichloro and dibromo-cyclopropanes in good yields.[338] The reaction may be improved by adding crown-ethers.

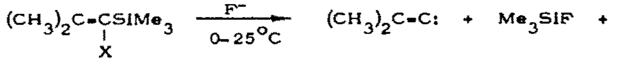


A convenient reagent for the fluoride-induced generation of dichlorocarbene under extremely mild conditions is (trichloromethyl)-trimethylsilane.[338]



(80%)

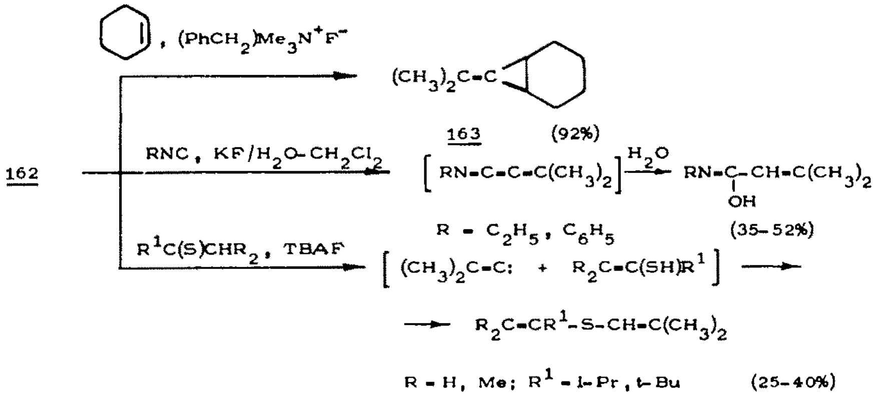
Strong bases (such as potassium t-butoxide, alkyllithium or lithium alkoxides) are usually used to generate alkylidene carbenes from primary alkenyl halides or from alkenyl triflates. In the case of base-sensitive intermediates, catalysis by TBAF should be used. Thus, (1-chloro-2-methyl-propen-1-yl)-trimethylsilane **161** in the presence of TBAF in diglyme forms isopropylidene carbene which reacts with unsaturated compounds.[339,340]



$$(CH_3)_2C{=}C(X)SiMe_3 \xrightarrow[0-25^\circ C]{F^-} (CH_3)_2C{=}C: + Me_3SiF + X^-$$

X = Cl (161), CF_3SO_3 (162)

Anionic cleavage of α-chlorovinyltrimethylsilane and α-(trifluoromethylsulphonyloxy)-vinyltrimethylsilane initiated by fluoride ion ($KF \cdot 18$-crown-6, $PhCH_2Me_3N^+F^-$, $Me_4N^+F^-$) is accompanied by α-elimination and leads to vinylidene carbene formation.[341,342] A source of F^- is KF which should be present in stoichiometric amounts. Of all known methods of generating $(CH_3)_2C{=}C:$, this one is the most convenient and mild. The rate of formation of vinylidene carbene from silane **161** is approximately 40 times higher than from silane **162**, because CF_3SO_3 is a more active leaving group. In both cases formation of 4–15% of $(CH_3)_2C{=}CHX$ is observed and this product is formed as a result of the intermediate reaction of the $(CH_3)_2C{=}CX^-$ carbanion with moisture in the reaction mixture.[343] The carbene reacts with alkenes yielding the corresponding isopropylidene propane adducts, such as **163** in the case of cyclohexene. Isopropylidene carbene is easily generated from **162** in the presence of $KF \cdot 18$-crown-6 at 0°C, and in the presence of benzyltrimethylammonium fluoride at 20°C.[343–346] Isopropylidene carbene reacts with isonitriles to form amides of 2-methylcrotonic acid.[347] On the basis of the reaction between isopropylidene carbene and thioketones in the presence of TBAF a method has been developed for the synthesis of divinylsulphide derivatives.[343]

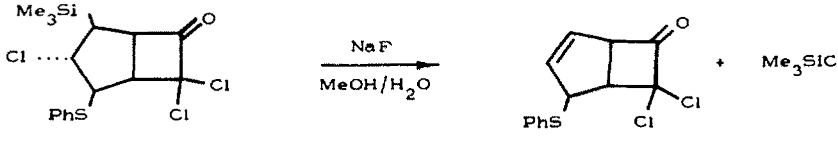


Recently the possiblity of the formation of C—C multiple bonds by 1,2-dehalosilylation (see Ref. 347) involving the elimination of R_3SiX (X = Br, Cl, etc.) has been examined. This method is especially useful for the synthesis of unsaturated compounds such as cyclopropenes and dicyclo bridged alkenes. Vinylsulphones are obtained (quantitative yields) by the reaction of TBAF with 1-phenylsulphonyl-1-chloro-2-trimethylsilylethanes at 20°C.[348]

$$Me_3SiCH_2CCl(R)SO_2Ph \xrightarrow[20^\circ C,\ 10\,min.]{TBAF/THF} CH_2{=}C(R)SO_2Ph \quad (99\%)$$

R = Et, Pr, Hex, All, Bz

Elimination of Me_3SiCl from compound **164** by fluoride ion (NaF), leads to the formation of cyclic allylphenylsulphide **165** (high yield).[349]



164 165

Elimination of $(Me_3Si)_2O$ from carboiminophosphine **166** results in the formation of a stable heteroallene, which contains tricoordinated phosphorus.[350]

$$t\text{-BuP(SiMe}_3\text{)-C(OSiMe}_3\text{)=N-Bu-}t \xrightarrow[-(Me_3Si)_2O]{NaOH,\ THF,\ 23^{\circ}C} t\text{-Bu-P=C=N-Bu-}t$$

166

Arylsulphenyl chloride was shown in Ref. 351 to react with vinyltrimethylsilane to yield adduct **167** which then undergoes elimination of Me_3SiCl forming arylvinylsulphide **168** under the action of KF.

$$PhSCl + Me_3SiCH{=}CH_2 \longrightarrow PhSCH(SiMe_3)CH_2Cl \xrightarrow[DMSO]{KF\cdot 2H_2O} PhSCH{=}CH_2$$

167 168

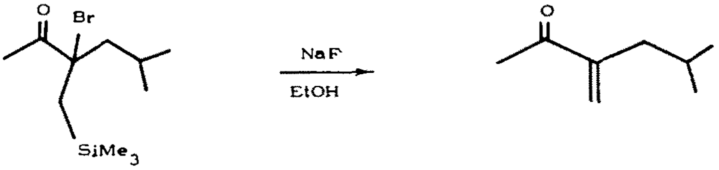
5.4. *Some chemical transformations of organosilicon compounds*

Elimination of Me_3SiCl rather than epoxide formation by HCl elimination occurs in the following reaction.

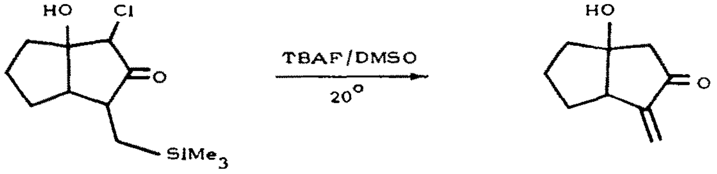
$$Me_3SiCH_2CCl(SO_2Ph)CH(OH)R \xrightarrow[THF]{TBAF} CH_2{=}C(SO_2Ph)CH(OH)R \quad (90\%)$$

$R = Pr,\ i\text{-}Pr,\ Ph,\ i\text{-}C_6H_{11},\ CH_2{=}CH$

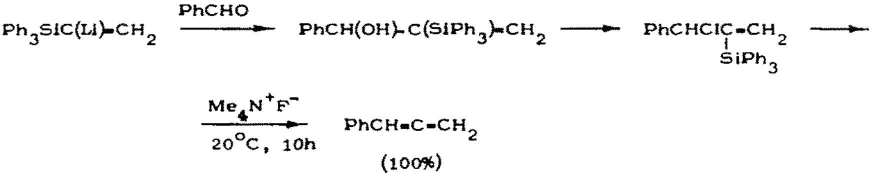
α,β-Unsaturated ketones are obtained by the reaction of NaF with carbonyl-containing β-haloalkylsilane[352,353] as a result of Me_3SiHal elimination.



This method has been used for the synthesis of cyclic α,β-unsaturated ketones containing *exo*-methylene C—C bonds.[353] Even labile oxyketones may be obtained by this reaction.



The reactions between vinylsilanes containing halogen atoms at the sp^3 hybridized carbon atom and fluoride ions lead to allenes.[341,354]

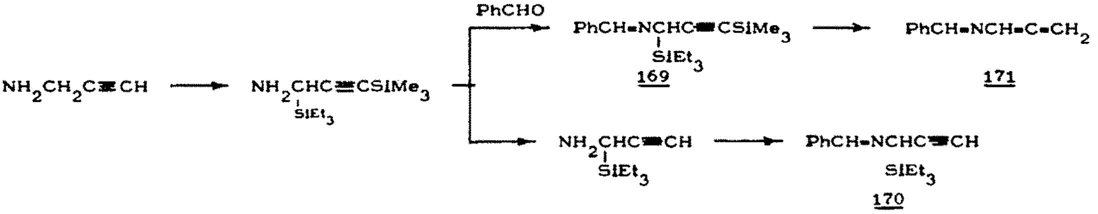


$$Ph_3SiC(Li){=}CH_2 \xrightarrow{PhCHO} PhCH(OH)\text{-}C(SiPh_3){=}CH_2 \longrightarrow PhCHCl\underset{SiPh_3}{C}{=}CH_2 \xrightarrow[20^{\circ}C,\ 10h]{Me_4N^+F^-} PhCH{=}C{=}CH_2 \quad (100\%)$$

The use of fluoride ion inhibits isomerization into alkynes which is a frequent side-reaction in the synthesis of allenes in strong basic media.[355]

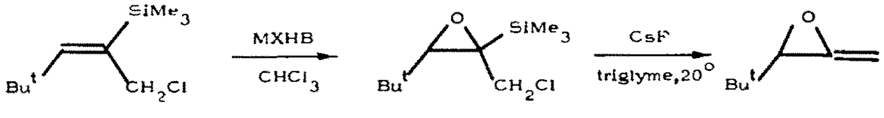
$$Me_3SiCH_2CH_2SO_2Ph \xrightarrow[2)\ RCHO\quad 3)\ H_3O^+]{1)\ R^1Li} Me_3SiCH_2C(SO_2Ph){=}CHR \xrightarrow{CsF} RCH{=}C{=}CH_2$$

A new method for the preparation of 2-aza-1,3-dienes involving protodesilylation of *N*-(1-triethylsilylallyl)-imines, induced by CsF, has been described.[342]

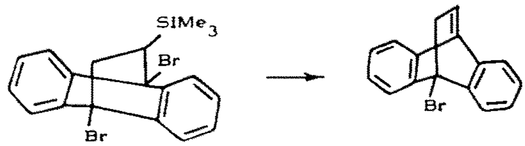


Protodesilylation of imines **169**, **170**, induced by CsF, occurs in either THF/H_2O/18-crown-6 or MeCN/H_2O (25°C, 1 h) and leads (70–85%) to 2-azatriene **171** and 2-azadiene **172**.

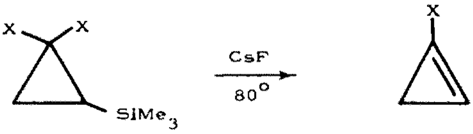
Another example illustrating the synthetic importance of 1,2-dehalosilylation under the action of fluoride ion is the synthesis of allene oxides, in particular of 2-epoxy-4,4-dimethylpent-1-ene.[356,357]



β-Elimination of this type, starting with a hard base attack on silicon, may be considered as the key process for the synthesis of many exotic molecules.[358]



Fluoride ion catalysis converts 1-trimethylsilyl-2-halogencyclopropane into cyclopropenes, which are characterized by Diels–Alder adducts with 1,3-diphenylisobenzofuran.

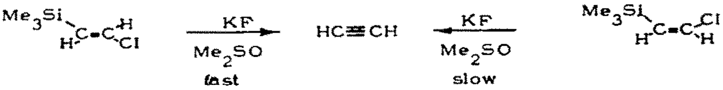


The presence of electron-withdrawing substituents in the vinyl fragment leads to a considerable increase in sensitivity of vinylsilanes towards nucleophilic reagents. Thus, *β*-chlorovinyltrimethylsilane is cleaved by KF in DMSO medium giving acetylene.[359]

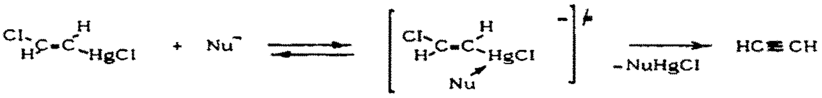
$$ClCH{=}CHSiMe_3 \xrightarrow[DMSO,\,25^{\circ}C]{F^-} HC{\equiv}CH + Me_3SiF + Cl^-$$

trans-*β*-Chlorovinyltrimethylsilane reacts to 95% in 20 h, whereas the *cis*-isomer reacts only to 10%. The authors suggest the E_2-Si mechanism involving the simultaneous cleavage of Si—C and C—Cl bonds taking place after attack at the silicon atom by fluoride ion.

The reaction of elimination, unlike substitution reactions, requires a limited range of bases and leaving groups.[360] Good leaving groups such as halogens are generally required. In most elimination reactions the nucleophile must have a high basicity. Alkoxides and amines are the most common nucleophiles but when the proton is replaced by silicon then the fluoride ion promotes elimination.



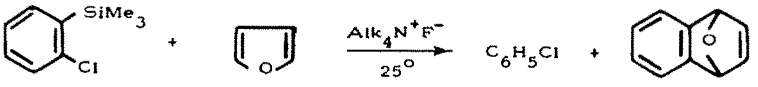
Cleavage of *trans*-β-chlorovinylmercury chloride by halogen anions[361] is accompanied by acetylene elimination. Reutov *et al.*[362] proposed an intermediate state structure similar to that of an S_E1-N reaction: stabilization of the carbanion centre is provided by elimination of chloride ion from the β-position thus leading to acetylene.



The same method was later used for the synthesis of allylacetylenes.[363]

R = C_4H_9 (57%), C_5H_{11} (73%), C_6H_{13} (84%)

1,2-Dehalosilylation by the fluoride ion occurs in 2-halogeno-phenyltrimethylsilanes yielding benzyne which was trapped as its adduct with furan.[364]



	C_6H_5Cl		
$Me_4N^+F^-$	12	31	(HMPA)
	39	32	(Furane)
$Et_4N^+F^-$	90		(HMPA)

o-Trimethylsilylphenyl triflate **173** generates the anionic intermediate **174** by fluoride-induced desilation under neutral conditions.[365] Elimination of the triflate group (giving benzyne) occurred in preference to protonation of **174** because of the excellent leaving ability of the triflate group (Table 11).[366]

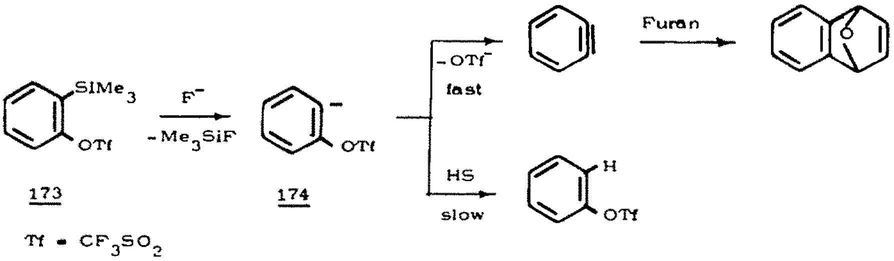
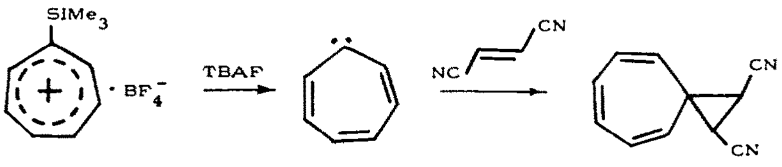


Table 11. Reactions of triflate **173** with furan at room temperature[366]

F^- reagents	Solvents	Moler ratio **173**: furan: F^-	Reaction time (h)	Yields of **173** (%)
$Me_4N^+F^-$	HMPT	1:4:2	4	42
	furan	1:15:2	2.5	86–96
	HMPT	1:4:2		51
	furan	1:excess:2	114	76
KF	HMPT	1:4:2	15	34
KF·18-crown-6	benzene	1:4:2	22	No reaction
CsF	HMPT	1:4:2	44	42
$Bu_4N^+F^-$	CH_3CN	1:4:1.5	3.5	61

The formation of tropylidene **176** from the silyltropylium salt **175** demonstrates the high affinity of the silicon atom towards the fluoride ion.[367]

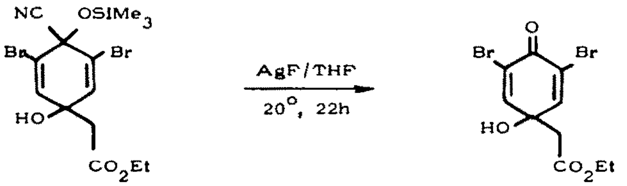


175 176

1,2-Dehalosilylation takes place in the reaction of CsF with trimethylsilylmethanesulphonyl chloride to form sulphene **177**.[368]

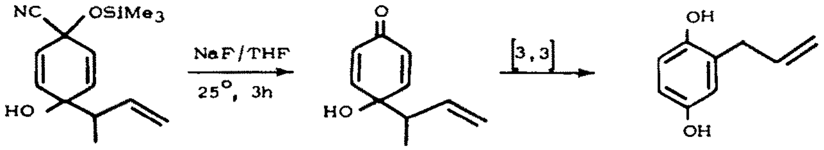
$$Me_3SiCH_2SO_2Cl \xrightarrow[20^{\circ}C,\ 2h]{CsF/CH_3CN} [CH_2{=}SO_2] \xrightarrow[Et_4N^+Cl^-]{Br_2} BrCH_2SO_2Cl$$

3-Methylsiloxy-3-cyano-1,4-cyclohexadienes **178** give cyclohexadienones **179** in the presence of AgF. This is a useful method for the protection of quinonoid carbonyl groups.[61,66]



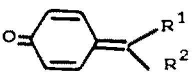
178 179 (77%)

[3,3]Sigmatropic transformations are observed with NaF leading to hydroquinone derivatives.[369]



(70%)

The synthesis of quinone methides **180** with electron-withdrawing groups R^2 is difficult but it can be achieved by trimethylsilyl protection.[370]



180

$R^1 = COOR,\ SO_2C_6H_5;\ R^2 = CH_2C_6H_5$

(2-Acyloxyalkyl)-triorganylsilanes are easily converted by fluoride ion into alkenes (20°C). γ-(1-Acetoxyhexyl)-γ-trimethylsilyl-butyrolactone reacted with TBAF in HMPA giving γ-hexylidenebutyrolactone.[371] β-Trimethylsilyl carbonates are cleaved by fluoride ion. β-Trimethylsilyl carbonates are protecting groups for OH and NH_2.[372]

$$ROH + Me_3SiCH_2CH_2OCOCl \xrightarrow[20^{\circ}C]{} Me_3SiCH_2CH_2OCOOR \xrightarrow[20^{\circ}C,\ 10\ min.]{TBAF/THF}$$

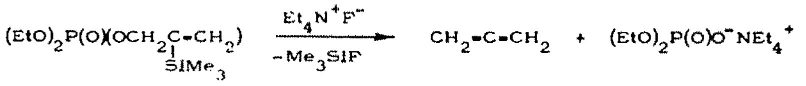
$$\longrightarrow ROH + CH_2{=}CH_2 + CO_2 + Me_3SiR$$

ROH = cholesterol (94%), timidine (88%), 3-nitrophenol (94%)

The 2-trimethylsilylethyl substituents is used to protect the carboxyl groups of N-substituted amino acids. This group is stable under the wide-ranging conditions used in peptide synthesis. It is easily removed by TBAF: ethylene and trimethylfluorosilane are formed together with carboxylic acid. It is noteworthy that no racemization of the chiral centres of amino acids occurs in this reaction. The $CO_2CH_2CH_2SiMe_3$ group is used for the protection of NH functions.[373] Besides the amine, only gaseous products are formed (80–90%).

$$4\text{-}ClC_6H_4NHCOOCH_2CH_2SiMe_3 \xrightarrow[2)\ H_2O]{1)\ Et_4N^+F^-,\ 50^\circ C} 4\text{-}ClC_6H_4NH_2 + CH_2{=}CH_2 + CO_2 + Me_3SiF$$

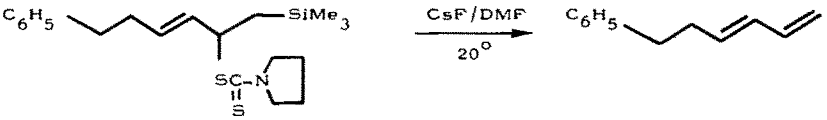
Esters of phosphoric acid **181** undergo elimination under the action of fluoride ion. Since allene **182** and trimethylfluorosilane evaporate from the heated reaction mixture this reaction is a good method for protecting phosphorus acids.[374]



$$(EtO)_2P(O)(OCH_2\underset{SiMe_3}{C}{=}CH_2) \xrightarrow[-Me_3SiF]{Et_4N^+F^-} CH_2{=}C{=}CH_2 + (EtO)_2P(O)O^-NEt_4^+$$

181 182

Stereo- and regio-selective syntheses of *E*-1,3-dienes using the transformation of the silylthiocarbamate **183** into the diene **184** induced by fluoride ion have been reported.[375]



183 184 (82%)

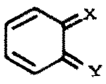
Kocienski uses 2-(phenylsulphonyl)-alkyltrimethylsilanes **185** to obtained terminal olefins **186**.[376]

185 186 (80%)

This reaction was successfully used by him for the synthesis of polyene antibiotics.[377-379] This method produces double bonds in cyclic compounds **187** (50–70%).[380,381]

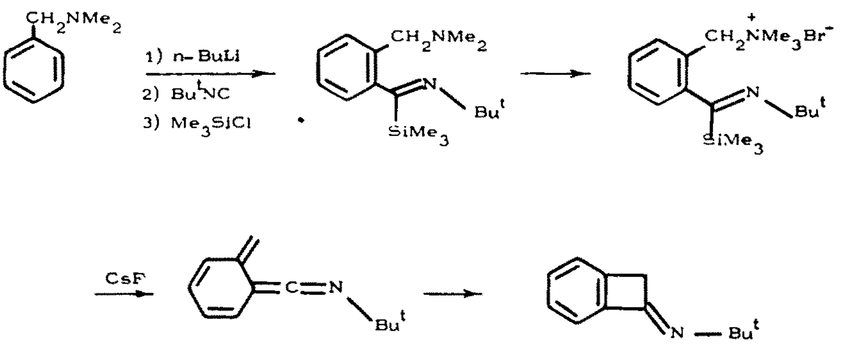
187

1,4-Elimination involving the silyl group which is induced by the fluoride ion provides a new methodology for the generation of *o*-quinodimethanes[382] and *o*-quinone methide imines **188**, whose Diels–Alder reactions are useful for convenient synthesis of polycycles.[383]



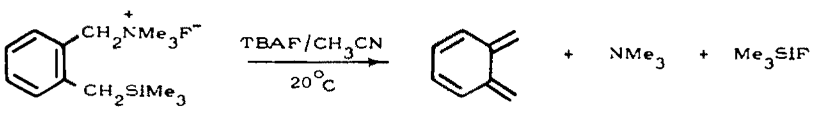
188 X = CH_2, Y = NR
189 X = CH_2, Y = C=NR
190 X = CH_2, Y = C=O
191 X = CH_2, Y = CH_2

α-(*N*-Alkylimino)-*o*-quinodimethane **189** and α-oxo-*o*-quinodimethane **190**, structurally related to **191** and **188**, have potential in organic synthesis because their Diels–Alder cycloadditions produce functionalized polycycles.[384] The first synthesis of α-(*N*-t-butylimino)-*o*-quinodimethane **192** by 1,4-elimination of the silicon-containing group has been described.[385]



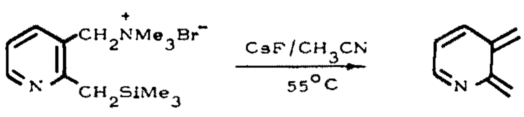
192

(α-Trimethylsilylakyl)-benzyltrimethylammonium halides **193** form *ortho*-xylylenes **194** under the action of TBAF or CsF.[382] These compounds possess high reactivity and easily take part in the Diels–Alder reaction in the presence of olefins.



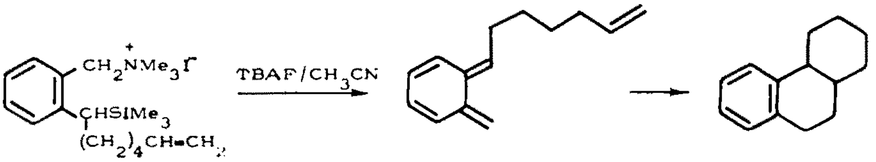
193 194

The pyridine analogue **195** was obtained by the same method.[382]



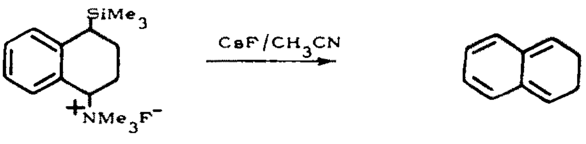
195

If the side chain of *ortho*-quinodimethane has a double bond, the intramolecular Diels–Alder reaction is observed. Thus, the reaction of TBAF in CH_3CN with *ortho*-(1-trimethylsilyl)-6-heptylbenzyltrimethylammonium iodide **196** leads to octahydrophenanthrene **197**.[386]



196 197 (77%)

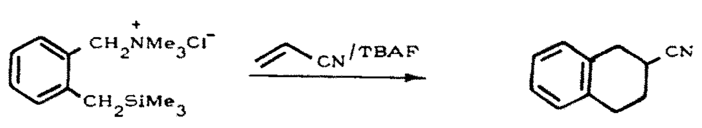
2,3-Dihydronaphthalene **198** forms the substituted tetralin **199**.



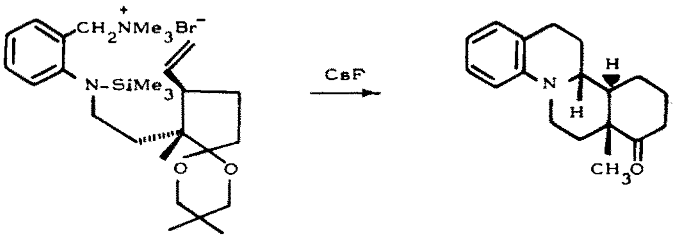
198 199

This approach was used in the synthesis of a part of the skeleton of hepherotoxine.[386]

Fluoride ion-induced 1,4-eliminations of activated benzylic systems such as **200** and **201** proceed under very mild conditions to liberate highly reactive *o*-quinomethides, which, under the proper conditions, can be trapped inter- or intra-molecularly.[383] This strategy now serves as the basis for the stereoselective synthesis of carbocyclic and heterocyclic natural products.

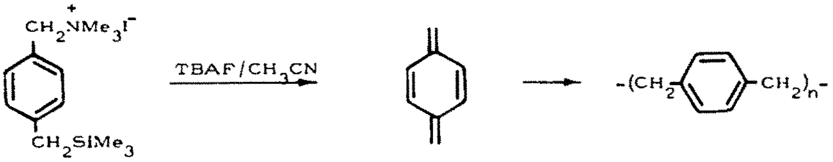


200



201

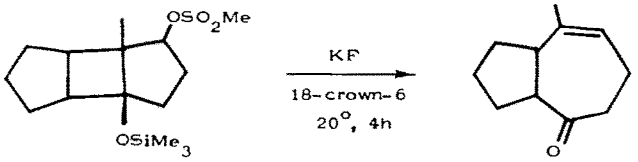
The above examples show the practical importance of this method of generating *ortho*-quinomethanes and their nitrogen-containing analogues for the synthesis of polycyclic compounds by the intra- and inter-molecular Diels–Alder reactions. Its possibilities are not exhausted only by the generation of *ortho*-quinodimethanes: the reaction of -*para*-(trimethylsilyl)-methylbenzyltrimethylammonium iodide **202** with TBAF in CH_3CN leads to the 1,6-elimination product—*para*-quinodimethane **203**.[387]



202 203 204 (51%)

Compound **203** gives mainly poly-*para*-xylene **204** depending upon the temperature.

Transformation of the tricyclic compound **205** into *cis*-hexahydroazulenone **206** may also be considered as an example of 1,4-addition induced by the fluoride ion.[388]



205 206 (78%)

1,4-Elimination initiated by fluoride ion occurs in the transformations of 4-phenylsulphonyl-1-trimethylsilyl-2-alkenes **207** into 1,3-dienes **208**.[389]

$$\mathrm{Me_3SiCH_2CH{=}CHCH(R){-}SO_2Ph} \xrightarrow[20^{\circ}\mathrm{C}\text{ },\ 20\ \mathrm{min.}]{\mathrm{TBAF/THF}} \mathrm{Me_3SiCH_2CH{=}CHCH(R)F} + \mathrm{PhSO_2^-} \ —$$

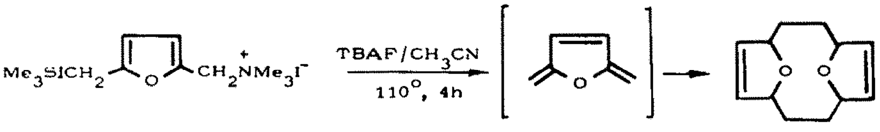
207

$$\longrightarrow \mathrm{CH_2{=}CHCH{=}CHR}$$

208

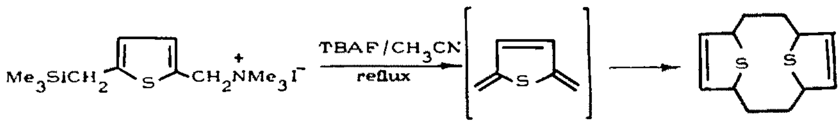
R = pentyl (83%); octyl (87%); benzyl (95%); δ-bromoctyl (99%)

Boiling compound **209** with TBAF in CH_3CN leads to 2,2-2,5-furanophane **210**.[387]



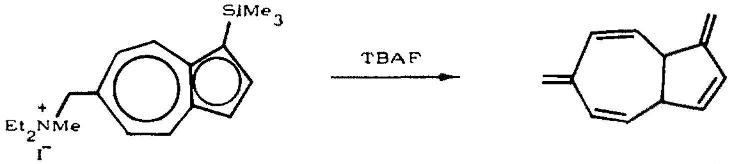
209 210 (73%)

The substituted thiophene is converted into 2,2-5,5-thiophenophane **211**.[387]



211

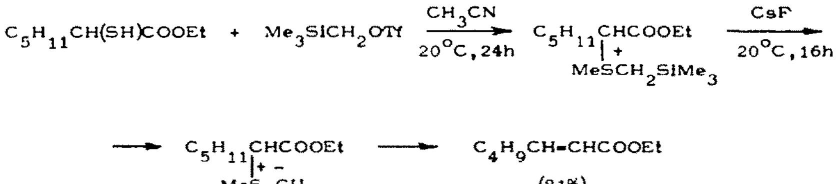
Two synthetic pathways affording *anti*-2,2(1,6)-azulenophane **212** via fluoride-induced 1,8-elimination compound **213** from trimethylsilyl tetraalkylammonium salts are described.[387]



213 212 (17%)

5.5. *Other reactions*

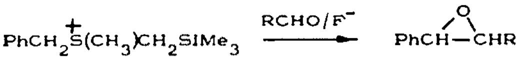
Fluorides of alkali metals have been shown to be convenient reagents for the generation of nitrogen-, phosphorus-, and sulphur-containing ylides. Desilylation of α-trimethylsilyl onium salts by fluoride ion has been widely utilized in recent years as a convenient method for preparing nitrogen and sulphur ylides.[391-396] A synthesis of olefins from thio-derivatives using diglyme as a solvent has been developed.[391]



$$C_5H_{11}CH(SH)COOEt + Me_3SiCH_2OTf \xrightarrow[20^\circ C,\,24h]{CH_3CN} C_5H_{11}\underset{MeSCH_2SiMe_3}{\underset{|\,+}{C}}HCOOEt \xrightarrow[20^\circ C,\,16h]{CsF} C_5H_{11}\underset{Me\overset{+}{S}-\overset{-}{C}H_2}{\underset{|}{C}}HCOOEt \longrightarrow C_4H_9CH{=}CHCOOEt$$

(81%)

Treatment of the sulphonium salt **214** with fluoride ion in the presence of an aldehyde produced only the disubstituted *trans*-epoxide **215**.[397]

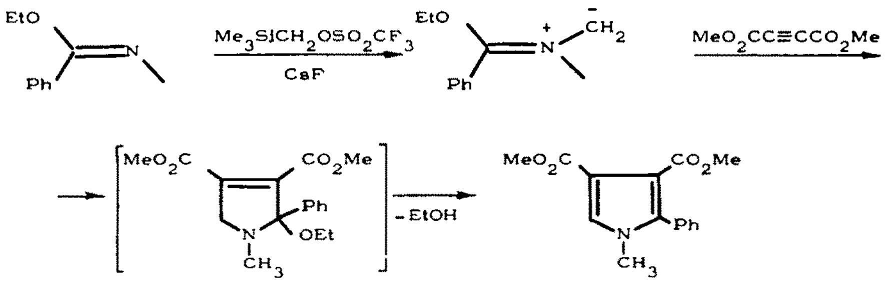


214 215

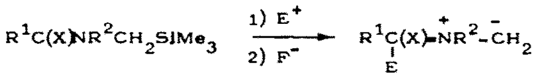
R = Ph, p-C_7H_8, Furanyl, Cinnamyl, C_2H_5, i-C_3H_7

The reaction of triflate with dimethylcyclododecylamine leads to *trans*-cyclododecane as a result of [3,2]-sigmatropic shift in the ylide.[391]

Desilylation by fluoride ion is especially convenient for the generation of azomethines for 1,3-dipolar cycloadditions. For this purpose the trimethylsilylammonium salt is treated in the presence of dipolarophile.[396,398,399]



The propensity of silicon to transfer to silylophiles when bound to electronegative carbon raised the possibility of desilylation of an intermediate such as **216** as a method for generating azomethine ylides **217**.[396]

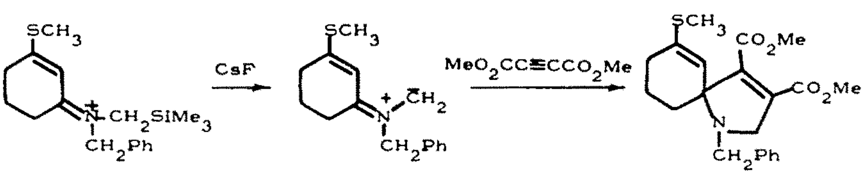


$$R^1C(X)NR^2CH_2SiMe_3 \xrightarrow[2)\ F^-]{1)\ E^+} R^1\underset{E}{C}(X)\overset{+}{N}R^2\text{-}\overset{-}{C}H_2$$

216 **217**

The CsF-induced desilylation reaction shows all the characteristics of a concerted cycloaddition, including stereospecificity when dimethyl fumarate and maleate are used as dipolarophiles. For example, treatment of *N*-methylbenzenecarboximidic acid ethyl ester with $Me_3SiCH_2OSO_2CF_3$, CsF and dimethylacetylenedicarboxylate produced dimethyl *N*-methyl-2-phenylpyrrole-3,4-dicarboxylate (48%).

The reaction of the azomethine ylide derived from *N*-(3-methylthio-2-cyclohexen-1-ylidene)-benzenemethanamine with CsF and dimethyl acetylenedicarboxylate proceeds smoothly and affords the cycloadduct dimethyl 1-benzyl-7-(methylthio)-1-azaspiro[4,5]deca-3,6-dienes-3,4-dicarboxylate (80%). With methyl propiolate, the cycloaddition reaction proceeds with complete regioselectivity giving methyl 1-benzyl-7-(methylthio)-1-azaspiro[4,5]deca-3,6-diene-4-carboxylate (70%).



The caesium fluoride-induced desilylation reaction of immonium salts derived from amides, thioamides and vinylogous amides provides access to reactive azomethine ylides in synthetically useful yields.

Some phosphorus ylides are rather inert in the Wittig reaction. But the reaction of the ylides **218** was shown to occur.[400]

$$\left[Ph_3PCR^1R^2SiMe_3\right]^+I^- \xrightarrow[20^\circ C]{CsF/DMF} \underset{218}{\left[Ph_3\overset{+}{P}\text{-}\overset{-}{C}R^1R^2\right]} \xrightarrow{R^3CHO} \underset{E/Z\ =\ 58/42}{R^1R^2C\text{=}CHR^3}$$

The intermediate formation of the pentafluorophenyl radical was observed in the reaction of XeF_2 with pentafluorophenyltrimethylsilane in the presence of CsF. Decafluorobiphenyl and pentafluorobenzene are the final products. The use of CsF is absolutely necessary. Substitution of at least one methyl group by fluoride facilitates the reaction and allows it to proceed in the absence of CsF.[401]

$$C_6F_5SiMe_3 + XeF_2 \xrightarrow[0^\circ C]{CsF/CH_3CN} \underset{2}{C_6HF_5} + \underset{1}{C_6F_5C_6F_5}$$
$$2 : 1$$

Organylfluorosilanes are converted to alcohols by reaction with oxidants, e.g. *m*-chloroperoxybenzoic acid (MCPB). The number of fluorine atoms bonded with silicon is the main factor in this reaction.[402] Thus, the relative reactivity of trifluorosilanes is higher than that of R_2SiF_2 and R_3SiF. $RSiF_3$ is oxidized by MCPB without KF.

$$R_nSiF_{4-n} \xrightarrow{MCPB/KF} ROH$$

$R = n\text{-}C_8H_{17}$, Ph, OEt;
$n = 1\text{–}3$

Theoretically, the difluorosilane derivatives can also be hydroxylated by MCPB, but in the absence of KF the reaction proceeds very slowly.[403] The rate of hydroxylation of R_2SiF_2 increases rapidly when catalytic quantities of KF are added. Under these conditions, oxidative cleavage occurs with a high yield and approximately 2 moles of KF are necessary to finish the reaction.

$$(C_8H_{17})_2PhSiF \xrightarrow[20^{\circ}C,\ 5h]{MCPB/2\ KF} \underset{(79\%)}{2\ C_8H_{17}OH} + \underset{(100\%)}{PhOH}$$

$$(C_8H_{17})_2SiF_2 \xrightarrow[20^{\circ}C,\ 5h]{MCPB,\ KF/DMF} \underset{(95\%)}{2\ C_8H_{17}OH}$$

The salts of pentafluorosiliconium also take part in hydroxylation by MCPB.[404]

$$K_2[PhSiF_5] \xrightarrow{MCPB/DMF} \underset{(64\%)}{PhOH}$$

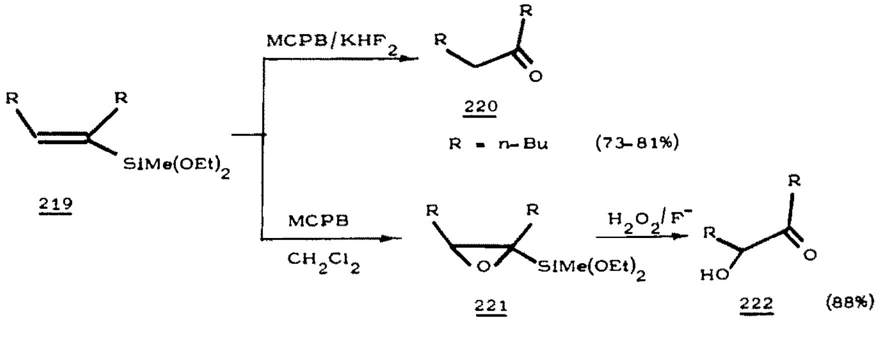
The choice of solvent produces a considerable influence on the yields of products of fluorosilane hydroxylation with KF as a catalyst and pentafluorosilicate hydroxylation by MCPB. Thus, depending on the solvents, the yields of octanol obtained from (n-$C_8H_{17})_2SiF_2$ (KF catalysis) were 15% (C_6H_6), 61% (THF) and 95% (DMF). Instead of the substituted fluorosilanes, the corresponding alkoxysilanes and chlorosilanes may react with MCPB and KF, but an excess of KF is required.[402]

$$4\text{-}EtOOCC_6H_4CH_2Si(OPr\text{-}i)_3 \xrightarrow[20^{\circ}C,\ 5h]{MCPB/KF} \underset{(75\%)}{4\text{-}EtOOCC_6H_4CH_2OH}$$

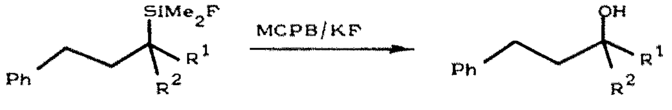
Chlorosilanes are less able to react with MCPB–KF than alkoxysilanes even in the presence of a large excess of KF, possibly due to the side-reaction of cleavage of Si—C bonds by MCPB.[405]

$$(C_8H_{17})_2SiCl_2 \xrightarrow[20^{\circ}C]{MCPB/KF} \underset{(45\%)}{2\ C_8H_{17}OH}$$

Direct oxidative cleavage of the alkenyl–silicon bond in **219** by MCPB/KHF_2 in DMF, as well as by 30% $H_2O_2/NaHCO_3$, gives 5-decanone **220** in high yields.[406] In contrast, treatment of **219** with the equivalent of MCPB in CH_2Cl_2 resulted in the formation of the corresponding epoxide **221** quantitatively, leaving the C—Si bonds intact. The carbon–silicon bonds in the epoxide were oxidized by 30% H_2O_2 in the presence of KHF_2 and $KHCO_3$ at room temperature forming 6-hydroxy-5-decanone **222** in high yield.



The fluorosilanes **223** reacted with three or more equivalents of MCPB in the presence of KF giving the corresponding alcohols **224**.[407]



223 224

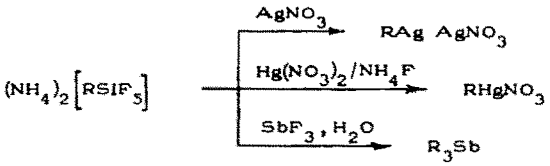
$R^1 = R^2 = H$ (74%);
$R^1 = H$, $R^2 = Me$ (70%);
$R^1 = R^2 = Me$ (75%)

The use of peracids or peroxids is limited to the substrates with functional groups which are not sensitive to such oxidizing reagents. Herein a novel C—Si bond cleavage reaction of organo-silanes **225** with trimethylamine-*N*-oxide to afford alcohols **226** stereospecifically has been reported.[408]

$$\underset{225}{RSiMe(OEt)_2} \xrightarrow{Me_3N\rightarrow O/KHF_2} \underset{226}{ROH}$$

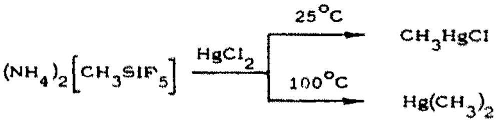
R = C_8H_{17} (96%), $MeOOC(CH_2)_{10}$ (79%), $PhO(CH_2)_3$ (79%), $Cl(CH_2)_5$ (71%), $Ph(CH_3)N(CH_2)_3$ (72%), $PhS(CH_2)_3$ (46%)

The reactions of metaldesilylation under the action of fluoride ions are based on the transformation of organyltrihalosilanes into the salts of pentafluorosiliconium. C—Si bonds in the latter are easily cleaved by electrophilic reagents, including the salts of heavy metals. The reaction requires comparatively mild conditions and R = alkyl, alkenyl or aryl groups. The examples of silver–mercury-desilylation[408] are shown below.



$$(NH_4)_2[RSiF_5] \begin{cases} \xrightarrow{AgNO_3} RAg\ AgNO_3 \\ \xrightarrow{Hg(NO_3)_2/NH_4F} RHgNO_3 \\ \xrightarrow{SbF_3,\ H_2O} R_3Sb \end{cases}$$

Ammonium methylpentafluorosilicate reacts with mercury dichloride at 25°C forming methylmercuric chloride and, at higher temperatures, dimethyl mercury.



$$(NH_4)_2[CH_3SiF_5] \xrightarrow{HgCl_2} \begin{cases} \xrightarrow{25^\circ C} CH_3HgCl \\ \xrightarrow{100^\circ C} Hg(CH_3)_2 \end{cases}$$

On the other hand, the treatment of potassium ethenyl- and trifluoroethenylpentafluorosilicates with copper sulphate and water leads to organic radical dimerization and formation of 1,3-butadiene and perfluoro-1,3-butadiene (87% and 49% yields respectively).[410]

Desilylation of alkylpentafluorosilicates of potassium $K_2[RCH_2CH_2SiF_5]$ proceeds with a good yield but it leads to small amounts of terminal olefin.[411]

$$K_2[C_{16}H_{33}CH{=}CHSiF_5] \xrightarrow{CuF_2 \text{ or } CuCl_2} C_{16}H_{33}CH{=}CH_2$$

6. CONCLUSION

Silylation and synthetic applications of organosilicon compounds show considerable advantages over the traditionally used reagents. They are connected, first, with conditions of the process and high stereo- and regio-selectivity of the reaction products. The analysis of main theoretical approaches to the mechanisms of the reactions occurring under nucleophilic catalysis shows the requirements for further investigation. Some considerations on the mechanism of action of the fluoride and cyanide ions has allowed investigators to make predictions. This is especially important for the solution of the key problem of organic synthesis—the creation of highly selective reagents. The use of nucleophilic catalysts is important from this point of view. The concept of participation of pentacoordinated silicon intermediates in the processes accompanying nucleophilic catalysis of organosilicon compounds proved to be suitable for the rationalization of the presented reactions.

Possible applications of silicon organic synthons in organic synthesis under nucleophilic catalysis conditions are far from exhausted. More new classes of compounds and types of reactions await discovery.

REFERENCES

[1] E. W. Colvin, *Silicon in Organic Synthesis*. I. Fleming, *Comp. Org. Chem.* **3**, 541 (1979), Butterworths, London (1981); P. D. Magnus, T. Sarkar and S. Djuric, *Comp. Organomet. Chem.* **7**, 515 (1982); I. Fleming, *Comp. Org. Chem.* **3**, 539 (1979); T. H. Chan and I. Fleming, *Synthesis* 761 (1979); L. A. Paquette, *Science* **217**, 793 (1982); M. Lalonde and T. H. Chan, *Synthesis* 817 (1985); R. Noyori, S. Murata and M. Sazuki, *Tetrahedron* **37**, 3899 (1981); P. Magnus, *Aldrichim. Acta* **13**, 43 (1980).

[2] W. P. Weber, *Silicon Reagents for Organic Synthesis*. Springer, Berlin (1983).

[3] A. E. Pierce, *Silylation of Organic Compounds*. Pierce Chemical Co., Rockford, Illinois (1968).

[4] G. G. Yakobson and V. V. Bardin, *Ftorid-ion in Organicheskoi Chimii*. Nauka, Novosibirsk (1986).

[5] J. K. Rasmussen, *Synthesis* 91 (1977).

[6] A. Hosomi, *Chem. and Chem. Ind.* (*Japan*) **36**, 84 (1983).

[7] X. Huang and Z. Chen, *Xyaxue Tongbao, Chemistry* 257 (1982).

[8] A. K. Banerjee, *J. Sci. Ind. Res.* **41**, 699 (1982).

[9] J. Dunogues, *Ann. Chim. Fr.* **8**, 135 (1983).

[10] H. Sakurai and Y. Okamoto, *J. Synth. Org. Chem. Japan* **40**, 525 (1982).

[11] V. A. Ponomarenko and M. A. Ignatenko, *Chemistry of Fluorosilicon Organic Compounds*. Science, Moscow (1979).

[12] Z. N. Parnes and G. I. Bolestova, *Synthesis* 991 (1984).

[13] A. Ricci, *Kem. Kozl.* **57**, 243 (1982).

[14] R. Oga, *Kagaky, Chemistry* (*Japan*) **39**, 214 (1984).

[15] T. Higama, M. Obayashi, I. Mori and H. Nozaki, *J. Org. Chem.* **48**, 914 (1983).

[16] L. Pauling, *The Nature of the Chemical Bond*, 3rd ed., Chapter 3. Cornell University Press, New York (1960).

[17] E. J. Corey and A. Venkateswarlu, *J. Am. Chem. Soc.* **94**, 6190 (1972).

[18] D. Schomburg and R. Frebs, *Inorg. Chem.* **23**, 1378 (1984).

[19] M. G. Voronkov, N. M. Deriglazov, E. I. Brodskaya, E. E. Kalistratova and L. I. Gubanova, *J. Fluorine Chem.* **19**, 299 (1982).

[20] R. J. P. Corriu and C. Guerin, *J. Organomet. Chem.* **198**, 231 (1980).

[21] K. Tamao, M. Mishima, J. Yoshida, M. Takahashi, M. Ishida and M. Kumada, *J. Organomet. Chem.* **225**, 151 (1982).

[22] R. J. P. Corriu, C. Guerin and J. J. E. Moreau, in *Topics in Stereochemistry* (eds E. L. Eliel, S. H. Wilen and N. L. Allinger), vol. XV, pp. 43–198. Wiley-Interscience, New York (1984).

[23] T. Higama, M. Obayashi and M. Sawahata, *Tetrahedron Lett.* 4113 (1983).

[24] J. Dunogues, R. Calas, J. Dedier and F. Pisciotti, *J. Organomet. Chem.* **25**, 51 (1970).

[25] J. Donogues, B. Arreguy, C. Biran and F. Pisciotti, *J. Organomet. Chem.* **63**, 119 (1973).

[26] D. R. Weyenberg, L. H. Toporcer and L. E. Nelson, *J. Org. Chem.* **33**, 1975 (1968).

[27] T. Higama and M. Obayashi, *Tetrahedron Lett.* 4109 (1983).

[28] H. Matsumoto, K. Ohkawa, I. Matsubars, T. Arai and Y. Nagai, *J. Organomet. Chem.* **264**, 29 (1984).

[29] L. Birkofer, A. Bitter and H. Wieden, *Chem. Ber.* **95**, 971 (1962).

[30] L. Birkofer and A. Ritter, *Angew. Chem.* **77**, 414 (1965).

[31] T. V. RajanBabu, G. S. Reddy and T. Fukunaga, *J. Am. Chem. Soc.* **107**, 5473 (1985).

[32] E. Nakamura, T. Murofushi, M. Shimizu and I. Kuwajima, *Tetrahedron Lett.* 1699 (1976).

[33] D. A. Evans, L. K. Truesdale and K. G. Grimm, *J. Org. Chem.* **41**, 3335 (1976).

[34] E. Nakamura, K. Hashimoto and I. Kuwajima, *Tetrahedron Lett.* 2079 (1978).

[35] E. Nakamura, K. Hashimoto and I. Kuwajima, *Bull. Chem. Soc. Japan* **54**, 805 (1981).

[36] P. Gariboldi, G. Jommi and M. Sisti, *J. Org. Chem.* **47**, 1961 (1982).

[37a] I. Kuwajima, E. Nakamura and K. Hashimoto, *Org. Synth.* 122 (1983); [b] E. Nakamura, T. Murofushi, M. Shimizu and I. Kuwajima, *J. Am. Chem. Soc.* **98**, 2346 (1976).

[38] I. Kuwajima and E. Nakamura, *Acc. Chem. Res.* **18**, 181 (1985).

[39] H. Taguchi, K. Shimoji, H. Yamamoto and H. Nazaki, *Bull. Chem. Soc. Japan* **47**, 2529 (1974).

[40] K. Shimoji, H. Taguchi, K. Oshima, H. Yamamoto and H. Nozaki, *J. Am. Chem. Soc.* **96**, 1620 (1974).

[41] S. L. Hartzell, D. F. Sullivan and M. W. Rathke, *Tetrahedron Lett.* 1403 (1974).

[42] O. A. Reutov, I. P. Beletzkaya and K. P. Butin, *CH-Acids*. Science, Moscow (1980).

[43] B. N. Dolgov, N. P. Charitonov and M. G. Voronkov, *Zh. Obshch. Khim.* **24**, 1178 (1954).

[44] K. A. Andrianov and L. M. Tartakovsky, *Izv. Akad. Nauk SSSR, Ser. Khim.* 2631 (1972).

[45] K. A. Andrianov, L. M. Tartakovsky, V. M. Kopilov and L. M. Sarafanova, *Izv. Akad. Nauk SSSR, Ser. Khim.* 1443 (1975).

[46] K. A. Andrianov, L. M. Tartakovsky, V. M. Kopilov and L. M. Sarafanova, *Zh. Obshch. Khim.* **45**, 112 (1975).

[47] I. S. Achrem, M. Dene and M. E. Vol'pin, *Izv. Akad. Nauk SSSR, Ser. Khim.* 932 (1973).

[48] J. Boyer, R. J. P. Corriu, R. Perz and C. Reye, *J. Organomet. Chem.* **148**, C1 (1978).

[49] J. Boyer, R. J. P. Corriu, R. Perz and C. Reye, *J. Organomet. Chem.* **157**, 153 (1978).

[50] L. Horner and J. Mathias, *J. Organomet. Chem.* **282**, 155 (1985).

[51] R. J. P. Corriu, R. Perz and C. Reye, *Tetrahedron* **39**, 999 (1983).

[52] M. Deneux, I. S. Achrem, D. V. Avetissan, E. I. Myssof and M. E. Vol'pin, *Bull. Chim. Soc. Fr.* 2638 (1973).

[53] J. Boyer, R. J. P. Corriu, R. Perz and C. Reye, *J. Organomet. Chem.* **172**, 143 (1979).

[54] J. Boyer, R. J. P. Corriu, R. Perz and M. Poirier, *Synthesis* 558 (1981).

[55] J. Boyer, R. J. P. Corriu, R. Perz and C. Reye, *J. Chem. Soc., Chem. Commun.* 121 (1981).
[56] J. Boyer, R. J. P. Corriu, R. Perz and C. Reye, *Tetrahedron* **37**, 2165 (1981).
[57] C. Chuit, R. J. P. Corriu, R. Perz and C. Reye, *Synthesis* 981 (1982).
[58] R. A. Benkesez, G. S. Li and E. C. Mozdzed, *J. Organomet. Chem.* **178**, 21 (1979).
[59] W. C. Groutas and D. Felker, *Synthesis* 861 (1980).
[60] I. Ojima and Shin-ichi Inaba, *Kagaku no Ryoiki* **31**, 127 (1977).
[61] D. A. Evans, J. M. Hoffman and L. K. Truesdale, *J. Am. Chem. Soc.* **95**, 5822 (1973).
[62] D. A. Evans, L. K. Truesdale and G. L. Carrol, *J. Chem. Soc., Chem. Commun.* 55 (1973).
[63] D. A. Evans and L. K. Truesdale, *Tetrahedron Lett.* 4229 (1973).
[64] D. A. Evans, G. L. Carrol and L. K. Truesdale, *J. Org. Chem.* **39**, 914 (1974).
[65] D. A. Evans and J. M. Hoffman, *J. Am. Chem. Soc.* **98**, 1983 (1976).
[66] D. A. Evans and R. Y. Wong, *J. Org. Chem.* **42**, 350 (1977).
[67] W. Lidy and W. Sundermeyer, *Chem. Ber.* **106**, 587 (1973).
[68] A. Takadate and J. Fishman, *J. Org. Chem.* **44**, 67 (1979).
[69] P. G. Gassman and J. Talley, *Tetrahedron Lett.* 3773 (1978).
[70] M. Oda, A. Yamamuro and T. Watabe, *Chem. Lett.* 1427 (1979).
[71] K. Deuchert, U. Hertenstein and S. Hunig, *Synthesis* 777 (1973).
[72] U. Hertenstein, S. Hunig and M. Oller, *Synthesis* 416 (1976).
[73] K. Deuchert, U. Hertenstein, S. Hunig and G. Wehner, *Chem. Ber.* **112**, 2045 (1979).
[74] S. Hunig and M. Oller, *Chem. Ber.* **113**, 3803 (1980).
[75] S. Veeraraghavan and F. D. Popp, *Synthesis* 384 (1980).
[76] I. Ojima, S. Inaba and K. Nakatsugawa, *Chem. Lett.* 331 (1975).
[77] I. Ojima, S. Inaba and Y. Nagai, *Chem. Lett.* 737 (1975).
[78] I. Ojima, S. Inaba and Y. Nagai, *J. Organomet. Chem.* **99**, C5 (1975).
[79] S. Inaba and I. Ojima, *J. Organomet. Chem.* **169**, 171 (1975).
[80] D. B. Sowerby, *J. Inorg. Chem.* **22**, 205 (1961).
[81] Weygand-Hilgetag, *Organisch-Chemische Experimentierkunst*, Johann Ambrosins Barth, Leipzig (1964).
[82] *Comprehensive Organic Chemistry*, vol. 2, Pergamon Press, Oxford (1982).
[83] G. L. Grunewald, W. J. Brouillette and J. A. Finney, *Tetrahedron Lett.* 1219 (1980).
[84] H. Neef and R. Muller, *J. Pract. Chem.* **315**, 367 (1973).
[85] E. J. Corey and G. S. Schmidt, *Tetrahedron Lett.* 731 (1980).
[86] B. A. Gostevsky, O. A. Vyazankina and N. S. Vyazankin, *Zh. Obshch. Khim.* **54**, 1209 (1984).
[87] B. A. Gostevsky, O. A. Krugloya, A. I. Albanov and N. S. Vyazankin, *Zh. Obshch. Khim.* **51**, 817 (1981).
[88] B. A. Gostevsky, O. A. Vazankina and N. S. Vyanzankin, *Zh. Obshch. Khim.* **53**, 1843 (1983).
[89] B. R. Davis, D. M. Gash, P. D. Woodgate and S. D. Woodgate, *J. Chem. Soc., Perkin I* 1499 (1982).
[90] E. W. Abel and C. A. Burton, *J. Fluorine Chem.* **14**, 105 (1979).
[91] A. A. Lazukina and V. P. Kukhar, *Zh. Org. Khim.* **49**, 2216 (1979).
[92] L. A. Lazukina and V. P. Kukhar, *Synthesis* 747 (1979).
[93] K. Nishiyama and N. Tanaka, *J. Chem. Soc., Chem. Commun.* 1322 (1983).
[94] O. Tsuge, S. Kanemasa and K. Matsuda, *Chem. Lett.* 1311 (1983).
[95] O. Tsuge, S. Kanemasa and K. Matsuda, *J. Org. Chem.* **49**, 2688 (1984).
[96] K. Nishiyama, H. Mikuni and M. Harada, *Bull. Chem. Soc. Japan* **58**, 3381 (1985).
[97] B. A. Gostevsky, O. A. Krugloya and N. S. Vyazankin, *Izv. Akad. Nauk SSSR, Ser. Khim.* 2425 (1978).
[98] I. D. Kalichman, B. A. Gostevsky, O. B. Bannikova, M. F. Lapin, O. A. Vyazankina and N. S. Vyazankin, *Izv. Akad. Nauk SSSR, Ser. Khim.* 1515 (1983).
[99] B. A. Gostevsky, O. A. Vyazankina, I. D. Kalichman, O. B. Bannikova and N. S. Vyazankin, *Zh. Obshch. Khim.* **53**, 229 (1983).
[100] N. Ishikawa and Ken-ichi Isobe, *Chem. Lett.* 435 (1972).
[101] B. A. Gostevsky, O. A. Krugloya, A. I. Albanov and N. S. Vyazankin, *J. Organomet. Chem.* **187**, 157 (1980).
[102] O. A. Krugloya, B. A. Gostevsky, I. D. Kalichman and N. S. Vyazankin, *Zh. Obshch. Khim.* **49**, 354 (1979).
[103] B. A. Gostevsky, O. A. Vyazankina, I. D. Kalichman, O. B. Bannikova and N. S. Vyazankin, *Zh. Obshch. Khim.* **53**, 2051 (1983).
[104] N. S. Vyazankin, O. A. Vyazankina, B. A. Gostevsky, I. A. Titova, V. A. Lopirev and I. D. Kalichman, *Zh. Obshch. Khim.* **54**, 461 (1984).
[105] B. A. Gostevsky, O. A. Vyazankina and N. S. Vyazankin, *Zh. Obshch. Khim.* **54**, 2613 (1984).
[106] C. Shih, E. L. Fritzen and J. S. Swenton, *J. Org. Chem.* **45**, 4462 (1980).
[107] G. Maier, M. Hoppe and H. P. Reisenauer, *Angew. Chem. Int. Ed.* **22**, 990 (1983).
[108] R. M. Williams, J. S. Dung, J. Jasey, R. W. Armstrong and H. Meyers, *J. Am. Chem. Soc.* **105**, 3214 (1983).
[109] R. J. Mills and V. Snieckus, *Tetrahedron Lett.* 479 (1984).
[110] R. J. Mills and V. Snieckus, *J. Org. Chem.* **48**, 1565 (1983).
[111] H. Sakurai, A. Hosomi, M. Saito, K. Sasaki, H. Igucki, Juh-ichi Sasata and Y. Araki, *Tetrahedron* **39**, 883 (1983).
[112] H. G. Koser, G. E. Renzoni and W. T. Borden, *J. Am. Chem. Soc.* **105**, 6359 (1983).
[113] J. Miller and G. Zweifel, *Synthesis* 128 (1983).
[114] A. B. Holmes, R. A. Raphael and N. K. Wellard, *Tetrahedron Lett.* 1539 (1976).
[115] C. M. Cimarusti, D. P. Bonner, H. Breuer, H. W. Chang, A. W. Fritz, D. M. Floyd, T. P. Kissick, W. H. Koster, D. Kronenthal, F. Massa, R. H. Mueller, J. Pluscec, W. A. Slusarchyk, R. B. Sykes, M. Taylor and E. R. Weaver, *Tetrahedron* **39**, 2577 (1983).
[116] C. S. Kraihauzel and J. E. Poist, *J. Organomet. Chem.* **8**, 239 (1967).
[117] P. J. Stang and M. Ladika, *Synthesis* 29 (1981).
[118] J. Dronin, F. Leyendecker and J. M. Conia, *Tetrahedron Lett.* 4053 (1975).
[119] K. Baum, C. D. Bedfold and R. J. Hunadi, *J. Org. Chem.* **47**, 2251 (1982).
[120] M. Ladika, P. J. Stang, M. D. Schiavelli and M. R. Hughey, *J. Org. Chem.* **47**, 4563 (1982).
[121] P. J. Stang, M. Hanack and L. R. Subramanian, *Synthesis* 85 (1982).
[122] S. Takahashi, Y. Kuroyama, K. Sonogashira and N. Hagihara, *Synthesis* 627 (1980).

[123] D. L. Bailey and A. N. Pines, *Ind. Eng. Chem.* **46**, 2363 (1954).
[124] T. H. Chan and W. Mychajlowskij, *Tetrahedron Lett.* 3479 (1974).
[125] T. H. Chan and W. Mychajlowskij, *Tetrahedron Lett.* 171 (1974).
[126] H. Oda, M. Sato, Y. Morizawa, K. Oshima and H. Nozaki, *Tetrahedron Lett.* 2877 (1983).
[127] S. Martin, R. Sauvetre and J.-F. Normant, *J. Organomet. Chem.* **303**, 317 (1986).
[128] R. Yamaguchi, H. Kawasaki, T. Yoshitome and M. Kawanisi, *Chem. Lett.* 1485 (1982).
[129] I. Hasan and Y. Kishi, *Tetrahedron Lett.* 4229 (1980).
[130] H. Tomioka, T. Suzuki, K. Oshima and H. Nozaki, *Tetrahedron Lett.* 3387 (1982).
[131] T. H. Chan, P. W. K. Lau and M. P. Li, *Tetrahedron Lett.* 2667 (1976).
[132] T. H. Chan, M. P. Li, W. Mychajlowski and D. N. Harpp, *Tetrahedron Lett.* 3511 (1974).
[133] T. H. Chan, B. S. Ong and W. Mychajlowski, *Tetrahedron Lett.* 3253 (1976).
[134] B. S. Ong and T. H. Chan, *Tetrahedron Lett.* 3257 (1976).
[135] I. Hasan and Y. Kishi, *Tetrahedron Lett.* 4229 (1980).
[136] W. E. Fristad, T. R. Bailey, L. A. Paquette, R. Gleiter and M. C. Bohm, *J. Am. Chem. Soc.* **101**, 4420 (1979).
[137] W. E. Fristad, T. R. Bailey and L. A. Paquette, *J. Org. Chem.* **45**, 3038 (1980).
[138] Y. Sato and S. Takenchi, *Synthesis* 734 (1983).
[139] S. Martin, R. Sauvetre and J. F. Normant, *J. Organomet. Chem.* **264**, 155 (1984).
[140] Y. Sato and Y. Niinomi, *J. Chem. Soc., Chem. Commun.* 56 (1982).
[141] Y. Sato and K. Hitomi, *J. Chem. Soc., Chem. Commun.* 170 (1983).
[142] G. Jones, *Org. React.* **15**, 204 (1967).
[143] A. Maercker, *Org. React.* **14**, 270 (1965).
[144] J. Boutagy and R. Thomas, *Chem. Rev.* **74**, 87 (1974).
[145] W. S. Wadsworth, *Org. React.* **25**, 73 (1977).
[146] T. H. Chan, *Acc. Chem. Res.* **10**, 442 (1977).
[147] G. W. Gokel, S. A. Dibaise and B. A. Lipisko, *Tetrahedron Lett.* 3495 (1976).
[148] J. C. Clinet and G. Linstrumelle, *Tetrahedron Lett.* 3987 (1980).
[149] D. P. Fox, J. A. Bjork and P. J. Stang, *J. Org. Chem.* **48**, 3994 (1983).
[150] M. J. Carter and I. Fleming, *J. Chem. Soc., Chem. Commun.* 679 (1976).
[151] I. Fleming and B. W. Au-Yeung, *Tetrahedron* **37**, 13 (1981).
[152] B. C. Berris and K. P. Vellhardt, *Tetrahedron* **38**, 2911 (1982).
[153] Y. Ikemi, R. Matsumoto and I. Uchida, *Heterocycles* **20**, 1009 (1983).
[154] D. Liotta, M. Saindane and W. Ott, *Tetrahedron Lett.* 2473 (1983).
[155] T. Acyama, S. Inone and T. Shiorri, *Tetrahedron Lett.* 433 (1984).
[156] K. Kawada, O. Kitagawa and Y. Kobayashi, *Chem. Pharm. Bull.* **39**, 3670 (1985).
[157] R. J. Mills and V. Snieckus, *Tetrahedron Lett.* 483 (1984).
[158] D. Schinzer and C. H. Heathcook, *Tetrahedron Lett.* 1881 (1981).
[159] E. J. Corey and A. Venkateswarlu, *J. Am. Chem. Soc.* **94**, 6190 (1972).
[160] K. K. Ogilvie, E. A. Thompson, M. A. Quilliam and J. B. Westmore, *Tetrahedron Lett.* 2865 (1974).
[161] K. K. Ogilvie, K. L. Sanada, E. A. Thompson, M. A. Quilliam and J. P. Westmore, *Tetrahedron Lett.* 2861 (1974).
[162] K. K. Ogilvie, S. L. Beancage and D. W. Entwistle, *Tetrahedron Lett.* 1255 (1976).
[163] K. K. Ogilvie, N. Theriault and K. L. Sadana, *J. Am. Chem. Soc.* **99**, 7741 (1977).
[164] K. K. Ogilvie, S. L. Beancage, D. W. Entwistle, E. A. Thompson, M. A. Quilliam and J. B. Westmore, *J. Carbohydr. Nucleosides, Nucleotides* **3**, 197 (1976).
[165] G. H. Dodd, B. T. Golding and D. V. Ioannov, *J. Chem. Soc., Chem. Commun.* 249 (1975).
[166] T. L. Chwang, R. D. Williams and J. E. Schieber, *Tetrahedron Lett.* 3183 (1983); *J. Chem. Soc., Perkin I* 2273 (1976).
[167] H. Seliger, D. Zeh and G. Azuru, *Chem. Ber.* **22**, 95 (1983).
[168] F. Franke and R. D. Guthrie, *Aust. J. Chem.* **31**, 1285 (1978).
[169] Y. Torisawa, M. Shibasaki and S. Ikegami, *Tetrahedron Lett.* 1865 (1979).
[170] K. K. Ogivie, S. L. Beaucage, A. L. Schifman, N. Y. Theriault and K. L. Sadana, *Can. J. Chem.* **56**, 2768 (1978).
[171] S. S. Jones and C. B. Reese, *J. Chem. Soc., Perkin I* 2762 (1979).
[172] L. A. Carpino and A. C. Sau, *J. Chem. Soc., Chem. Commun.* 514 (1979).
[173] S. Hanessian and P. Lavallee, *Can. J. Chem.* **53**, 2975 (1975).
[174] S. Hanessian and P. Lavallee, *Can. J. Chem.* **55**, 562 (1977).
[175] P. M. Kendall, J. V. Johnson and C. E. Cook, *J. Org. Chem.* **44**, 1421 (1979).
[176] P. Sieber, *Helv. Chim. Acta* **60**, 2711 (1977).
[177] H. Gerlach, *Helv. Chim. Acta* **60**, 3039 (1977).
[178] V. Pouzar, P. Drasar, I. Cerny and M. Havel, *Synth. Commun.* **14**, 501 (1984).
[179] C. B. Reese, R. C. Titmas and L. Yau, *Tetrahedron Lett.* 2727 (1978).
[180] A. G. Cardillo, M. Orena, S. Sandri and G. Tomasini, *Chem. Lett.* 643 (1983).
[181] W. Oppolzer, S. C. Burford and F. Marrazza, *Helv. Chim. Acta* **63**, 555 (1980).
[182] J. P. Marino and M. P. Ferro, *J. Org. Chem.* **46**, 1912 (1981).
[183] J. R. Heys, J. L. Nicks and P. H. Ruchle, *Steroids* **39**, 681 (1982).
[184] O. Tsuge, S. Kanemasa and K. Matsuda, *Chem. Lett.* 1131 (1983).
[185] T. Yoshisuke, O. Takeshi, S. Takehiro and T. Jun, *Heterocycles* **19**, 2021 (1982).
[186] G. Just, C. Luthe and H. Oh, *Tetrahedron Lett.* 1001 (1980).
[187] M. R. Detty, *J. Org. Chem.* **45**, 924 (1980).
[188] M. I. Lim and V. E. Marquez, *Tetrahedron Lett.* 4051 (1983).
[189] J. M. Muchowski and D. S. Solas, *Tetrahedron Lett.* 3455 (1984).
[190] R. J. P. Corriu, V. Huynh and J. J. E. Mareau, *Tetrahedron Lett.* 1887 (1984).
[191] A. Degl'Innocenti, S. Pike, D. R. M. Walton, A. Ricci, G. Saconi and M. Fiorenza, *J. Chem. Soc., Chem. Commun.* 1201 (1980).
[192] E. Nakamura and I. Kuwajima, *Angew. Chem. Int. Ed.* **8**, 498 (1976).
[193] A. B. Holmes, C. L. D. Jennings-White, A. H. Schulthess, B. Akinde and D. R. M. Walton, *J. Chem. Soc., Chem. Commun.* 840 (1979).

[194] A. Ricci, A. Degl'Innocenti, M. Fiorenza, M. Taddei, M. A. Spartera and D. R. M. Walton, *Tetrahedron Lett.* 577 (1982).

[195] F. Effenberger and W. Spiegler, *Angew. Chem. Int. Ed.* **20**, 265 (1981).

[196] A. Hosomi, A. Shirahata and H. Sakurai, *Tetrahedron Lett.* 3043 (1978).

[197] B. Bennetau and J. Dunogues, *Tetrahedron Lett.* 4217 (1983).

[198] B. Bennetau, M. Bordeau and J. Dunogues, *Bull. Chim. Soc. Fr.* 90 (1985).

[199] A. Ricci, M. Fiorenza, M. A. Grifagni and G. Bartolini, *Tetrahedron Lett.* 5079 (1982).

[200] T. Hiyama, K. Nishide and M. Obayashi, *Chem. Lett.* 1765 (1984).

[201] O. Tsuge, S. Kanemasa, S. Kuraoka and S. Takenaka, *Chem. Lett.* 281 (1984).

[202] M. Fiorenza, A. Mordini, S. Papaleo, S. Pastorelli and A. Ricci, *Tetrahedron Lett.* 787 (1985).

[203] H. Sakurai, *Pure Appl. Chem.* **54**, 1 (1982).

[204] G. Majetich, A. Casares, D. Chapman and M. Behnke, *J. Org. Chem.* **51**, 1745 (1986).

[205] H. Vorbruggen and K. Krolikiewicz, *Tetrahedron Lett.* 889 (1983).

[206] T. K. Sarkar and N. H. Andersen, *Tetrahedron Lett.* 3513 (1978).

[207] N. H. Andersen, D. A. McCrae, D. B. Grothjahn, S. Y. Gabhe, L. J. Theodore, R. M. Ippolito and T. K. Sarkar, *Tetrahedron* **37**, 4069 (1981).

[208] B. M. Trost and I. E. Vincent, *J. Am. Chem. Soc.* **102**, 5680 (1980).

[209] T. H. Chan and G. J. Kang, *Tetrahedron Lett.* 3011 (1982).

[210] R. J. P. Corrin, V. Huynh and J. J. E. Moreau, *J. Organomet. Chem.* **259**, 283 (1983).

[211] A. Hosomi, Y. Araki and H. Sakurai, *J. Org. Chem.* **48**, 3122 (1983).

[212] C. H. DePuy, V. M. Beirbaum, L. A. Flippin, J. J. Grabowski, G. K. King, R. J. Schmitt and S. A. Sullivan, *J. Am. Chem. Soc.* **102**, 5012 (1980).

[213] R. Corrin, N. Escudie and C. Guerin, *J. Organomet. Chem.* **264**, 207 (1984).

[214] J. Fujiwara, Y. Fukutani, H. Sato, K. Maruoka and H. Yamamoto, *J. Am. Chem. Soc.* **105**, 7177 (1983).

[215] O. Tsuge, S. Kanemasa, T. Naritomi and J. Tanaka, *Chem. Lett.* 1255 (1984).

[216] E. Nakamura, M. Shimizu and J. Kuwajjima, *Tetrahedron Lett.* 1699 (1976).

[217] J. Kuwajima, *J. Synth. Org. Chem. Japan* **34**, 964 (1976).

[218] H. Vorbruggen and K. Krolikiewcz, *Synthesis* 316 (1983).

[219] J. Pornet, *Tetrahedron Lett.* 455 (1981).

[220] H. Yamanaka, S. Nishimura, Soh-ichi Kaneda and T. Sakamoto, *Synthesis* 681 (1984).

[221] M. Aono, Y. Terao and K. Achiwa, *Chem. Lett.* 339 (1985).

[222] D. F. Marten and S. M. Wilburn, *J. Organomet. Chem.* **251**, 71 (1983).

[223] T. Aoyama and T. Shioiri, *Tetrahedron Lett.* 4461 (1980).

[224] T. Aoyama and T. Shioiri, *Chem. Pharm. Bull.* **29**, 3249 (1981).

[225] R. Davis and K. G. Untch, *J. Org. Chem.* **46**, 2985 (1981).

[226] I. Yamamoto, K. Okuda, S. Nagai, J. Motoyoshiya, H. Goton and K. Matsuzaki, *J. Chem. Soc., Perkin I* 435 (1983).

[227] Y. Sato and S. Takeuchi, *Synthesis* 734 (1983).

[228] E. Nakamura and I. Kuwajima, *Angew. Chem.* **88**, 539 (1976).

[229] I. Kuwajima, E. Nakamura and K. Hashimoto, *Tetrahedron* **39**, 975 (1983).

[230] G. F. Hennion and F. X. O'Shea, *J. Am. Chem. Soc.* **80**, 614 (1958).

[231] E. C. Assby and J. T. Laemmle, *Chem. Rev.* **75**, 52 (1975).

[232] C. Eaborn and D. R. Walton, *J. Organomet. Chem.* **4**, 217 (1965).

[233] J. Pornet and B. Randrianoelina, *Tetrahedron Lett.* 1327 (1981).

[234] A. F. Webb, D. S. Sethi and H. Gilman, *J. Organomet. Chem.* **21**, 61 (1970).

[235] O. A. Reutov, *Tetrahedron* **34**, 2827 (1978).

[236] F. Effenberger and W. Spiegler, *Chem. Ber.* **118**, 3872 (1985).

[237] F. Effenberger and W. Spiegler, *Chem. Ber.* **118**, 3900 (1985).

[238] F. Effenberger and K. Schollkopf, *Angew. Chem. Int. Ed.* **20**, 266 (1981).

[239] *Organicheskya synthesy segodnya zavtra.* Mir, Moskow (1984).

[240] F. H. Pinkerton and S. F. Thames, *J. Heterocycl. Chem.* **6**, 433 (1969).

[241] F. Effenberger and W. Spiegler, *Angew. Chem.* **93**, 287 (1981).

[242] V. M. Vlasov and G. G. Yakobson, *Uspechi Khimii* **43**, 1642 (1974).

[243] G. M. Brooke, R. D. Chambers, J. Heyes and W. K. R. Musgrave, *J. Chem. Soc.* 729 (1964).

[244] K. Iton, K. Matsuzaki and Y. Ishii, *J. Chem. Soc. C* 2709 (1968).

[245] E. W. Abel, D. J. Walker and J. N. Wingfield, *J. Chem. Soc. A* 1814 (1968).

[246] D. A. Evans, L. K. Truesdale, K. G. Grimm and S. L. Nesbit, *J. Am. Chem. Soc.* **99**, 5009 (1977).

[247] D. Liotta, P. B. Paty, J. Johnston and G. Zima, *Tetrahedron Lett.* 5091 (1978).

[248] M. R. Detty, *Tetrahedron Lett.* 5087 (1978).

[249] T. Aida, T. H. Chan and D. N. Harpp, *Tetrahedron Lett.* 1089 (1981).

[250] M. D. Mizipitslii, E. P. Lebedev and N. N. Furaev, *Zh. Obshch. Khim.* **52**, 2092 (1982).

[251] V. A. Baberina and E. P. Lebedev, *Zh. Obshch. Khim.* **48**, 125 (1978).

[252] D. V. Fridland, E. P. Lebedev and V. O. Reichfeld, *Zh. Obshch. Khim.* **47**, 1504 (1977).

[253] V. O. Reichfeld and E. P. Lebedev, *Zh. Obshch. Khim.* **40**, 2052 (1970).

[254] E. E. Colvin and D. Seebach, *J. Chem. Soc., Chem. Commun.* 689 (1978).

[255] D. Seebach, A. K. Beck, F. Lehr, T. Weller and E. Colvin, *Angew. Chem. Int. Ed.* **20**, 397 (1981).

[256] I. Kawashima, T. Ishii and N. Inamoto, *Tetrahedron Lett.* 739 (1983).

[257] F. A. Carey and A. S. Court, *J. Org. Chem.* **37**, 939 (1972).

[258] E. J. Corey and G. T. Kwiatkowski, *J. Am. Chem. Soc.* **88**, 5654 (1966).

[259] H. J. Bestmann and A. Bomhard, *Angew. Chem. Int. Ed. Engl.* **21**, 545 (1982).

[260] J. Escude, C. Couret, J. Dubac, J. Cavezzan, J. Satge and P. Hazezolles, *Tetrahedron Lett.* 3507 (1979).

[261] T. Ch. Gazizov, A. M. Kibardin, A. P. Pachinkina, Yu. I. Sudarev and A. N. Pudovik, *Zh. Obshch. Khim.* **43**, 679 (1973).

[262] D. A. Evans, K. M. Hurst, L. K. Truesdale and J. M. Takaes, *Tetrahedron Lett.* 2495 (1977).

[263] L. V. Nesterov, N. E. Krenisheva, R. A. Sabirova and G. N. Romanova, *Zh. Obshch. Khim.* **41**, 2449 (1971).

[264] Z. S. Novikova and I. F. Luzenko, *Zh. Obshch. Khim.* **40**, 2129 (1970).

[265] Z. S. Novikova, S. N. Matoshina, T. A. Sapozhnikova and I. F. Luzenko, *Zh. Obshch. Khim.* **41**, 2622 (1971).
[266] I. V. Konovalova, L. A. Burbaeva, N. S. Saifulina and A. N. Pudovick, *Zh. Obshch. Khim.* **46**, 18 (1976).
[267] A. N. Pudovick, E. S. Batueva and G. U. Zamaletdunova, *Zh. Obshch. Khim.* **42**, 2577 (1972).
[268] A. N. Pudovick, E. S. Batueva and G. U. Zamaletdunova, *Zh. Obshch. Khim.* **43**, 680 (1973).
[269] A. N. Pudovick, T. Ch. Gazizova and Yu. I. Sudarev, *Zh. Obshch. Khim.* **43**, 2086 (1973).
[270] A. M. Kubardin, P. I. Gryaznov, T. Ch. Gazizov and A. N. Pudovick, *Izv. Akad. Nauk SSSR, Ser. Khim.* 1205 (1983).
[271] M. Obayachi and K. Kondo, *Tetrahedron Lett.* 2327 (1983).
[272] A. G. Brook and N. V. Schwartz, *J. Org. Chem.* **27**, 2311 (1962).
[273] A. Ricci, A. Degl'Innocenti, S. Chimichi, M. Fiorenza and G. Rossini, *J. Org. Chem.* **50**, 130 (1985).
[274] J. P. Pillot, J. Dunogues and R. Calas, *Synth. Commun.* **9**, 395 (1979).
[275] R. B. Miller and G. McGarvey, *Synth. Commun.* **8**, 291 (1978).
[276] C. Huynh and G. Linstrumelle, *Tetrahedron Lett.* 1073 (1979).
[277] T. H. Chan and K. Koumaglo, *J. Organomet. Chem.* **285**, 109 (1985).
[278] R. F. Cunico and L. Bedell, *J. Org. Chem.* **48**, 2780 (1983).
[279] J. K. Rasmussen, *Synthesis* **91** (1977).
[280] *Obschaya organycheskaya Khimiya*, vol. 6. Khimia, Moskow (1984).
[281] P. Brownbridge, *Synthesis* 1 (1983).
[282] R. Noyori, K. Yokoyama, J. Sakata, I. Kuwajima, E. Nakamura and M. Shimizu, *J. Am. Chem. Soc.* **99**, 1265 (1977).
[283] I. Kuwajima, E. Nakamura and M. Shimizu, *J. Am. Chem. Soc.* **104**, 1025 (1982).
[284] E. Nakamura, S. Shimizu, I. Kuwajima, J. Sakata, K. Yokoyama and R. Noyori, *J. Org. Chem.* **48**, 932 (1983).
[285] R. Noyori, I. Nishida, J. Sakata and M. Nishizawa, *J. Am. Chem. Soc.* **102**, 1223 (1980).
[286] R. Noyori, I. Nishida and J. Sakata, *J. Am. Chem. Soc.* **103**, 2106 (1981).
[287] R. Noyori, I. Nishida and J. Sakata, *J. Am. Chem. Soc.* **105**, 1598 (1983).
[288] W. A. Kleschick, C. T. Buse and C. H. Heathcock, *J. Am. Chem. Soc.* **99**, 247 (1977).
[289] H. O. House, D. S. Crumrine, A. Y. Teranishi and H. D. Olmstead, *J. Am. Chem. Soc.* **95**, 3310 (1973).
[290] H. Takahaki, N. Yasuda, M. Asoaka and H. Talei, *Bull. Chem. Soc. Japan* **52**, 1241 (1979).
[291] J. Bouer, R. J. P. Corriu, R. Perz and C. Reye, *Tetrahedron* **39**, 117 (1983).
[292] D. A. Evans, J. V. Nelson and T. R. Tabe, *Topics Stereochem.* **13**, 1 (1982).
[293] P. A. Bartllet, *Tetrahedron* **36**, 2 (1980).
[294] A. T. Nielsen and W. J. Houlihan, *J. Org. React.* **16**, 1 (1968).
[295] J. Boyez, R. J. P. Corriu, R. Perz and C. Reye, *J. Organomet. Chem.* **184**, 157 (1980).
[296] G. Quadro, Span. Pat. 478504; *Chem. Abstr.* **91**, 140565 (1979).
[297] T. V. RajanBabu, *J. Org. Chem.* **49**, 2083 (1984).
[298] C. Chuit, R. J. P. Corriu and C. Reye, *Synthesis* **294** (1983).
[299] T. V. RajanBaby, *J. Org. Chem.* **49**, 2083 (1984).
[300] R. J. P. Corriu and R. Perz, *Tetrahedron Lett.* 1311 (1985).
[301] T. V. RajanBabu, G. S. Reddy and T. Fukunaga, *J. Am. Chem. Soc.* **107**, 5473 (1985).
[302] T. V. RajanBabu, B. L. Chenard and M. A. Petti, *J. Org. Chem.* **51**, 1704 (1986).
[303] O. W. Webster, W. R. Hertler, D. Y. Sogah, W. B. Farnham and T. V. RajanBabu, *J. Am. Chem. Soc.* **105**, 5706 (1983).
[304] R. A. Olofson and J. Cuomo, *Tetrahedron Lett.* 819 (1980).
[305] C. Goasdone, N. Goasdone and M. Gaudemar, *J. Organomet. Chem.* **263**, 273 (1984).
[306] D. Seebach, A. K. Beck, T. Mukhopadhyay and E. Thomas, *Helv. Chim. Acta* **65**, 1101 (1982).
[307] P. Ykman and H. K. Hall, *J. Organomet. Chem.* **116**, 153 (1976).
[308] T. Kubota, S. Miyashita, T. Kitazumi and N. Ishikawa, *J. Org. Chem.* **45**, 5052 (1980).
[309] T. Kitarume and N. Ishikawa, *Bull. Chem. Soc. Japan* **53**, 2064 (1980).
[310] E. Hirsch, S. Hunig and H. U. Reissig, *Chem. Ber.* **115**, 3687 (1982).
[311] T. Ishihara, Y. Yamasaki and T. Ando, *Tetrahedron Lett.* 79 (1985).
[312] R. Noyori, I. Nishida and J. Sakata, *Tetrahedron Lett.* 2085 (1980).
[313] H. Gerlach and P. Kunzler, *Helv. Chim. Acta* **61**, 2503 (1978).
[314] R. J. P. Corriu, V. Huynh, J. J. E. Moreau and M. Pataud-Sat., *Tetrahedron Lett.* 3257 (1982).
[315] T. Ando and H. Tsumaki, *Tetrahedron Lett.* 3073 (1982).
[316] H. Niederprum, P. Voss and V. Beyl, *Liebigs Ann. Chem.* 20 (1973).
[317] I. Kuwajima and E. Nakamura, *J. Am. Chem. Soc.* **97**, 3257 (1975).
[318] J. Orban and J. V. Turner, *Tetrahedron Lett.* 2697 (1983).
[319] H. Gerlach and P. Kunzler, *Helv. Chim. Acta.* **61**, 2503 (1978).
[320] M. Fujita and T. Hiryama, *J. Am. Chem. Soc.* **106**, 4629 (1984).
[321] H. Vorbruggen and K. Krolikiewicz, *Tetrahedron Lett.* 5337 (1983).
[322] J. B. Lambert and W. J. Schulz, *J. Am. Chem. Soc.* **105**, 1671 (1983).
[323] D. D. Tanner, G. E. Diaz and A. Potter, *J. Org. Chem.* **50**, 2149 (1985).
[324] D. Yang and D. D. Tanner, *J. Org. Chem.* **51**, 2267 (1986).
[325] J. L. Fry and M. A. McAdam, *Tetrahedron Lett.* 5859 (1984).
[326] Jin Ru Hwu and J. M. Wetzel, *J. Org. Chem.* **50**, 400 (1985).
[327] H. Vorbruggen and K. Krolikiewicz, *Tetrahedron Lett.* 1259 (1984).
[328] G. A. Razuvaev, V. A. Yablokov, A. V. Ganynahkin, N. V. Yablokova and G. S. Kalinina, *J. Organomet. Chem.* **165**, 281 (1979).
[329] T. Makata, M. Fukui, H. Ohtsuka and K. Oishi, *Tetrahedron Lett.* 2661 (1983).
[330] D. B. Grotjahn and N. H. Andersen, *J. Chem. Soc., Chem. Commun.* 306 (1981).
[331] K. Oshima and H. Nozaki, *Tetrahedron Lett.* 2877 (1983).
[332] G. Majetch, R. Desmond and A. M. Casares, *Tetrahedron Lett.* 1913 (1983).
[333] S. P. Tanis and K. Nakanishi, *J. Am. Chem. Soc.* **101**, 4398 (1979).
[334] P. J. Beswick and D. A. Widdowson, *Synthesis* 492 (1985).
[335] D. A. Evans, J. M. Takacs and K. M. Hurst, *J. Am. Chem. Soc.* **101**, 371 (1979).
[336] W. Oppolzer and R. L. Snowden, *Tetrahedron Lett.* 4187 (1976).
[337] W. Oppolzer, R. L. Snowden and D. P. Simmons, *Helv. Chim. Acta* **64**, 2002 (1981).
[338] R. F. Cunico and B. B. Chou, *J. Organomet. Chem.* **154**, C45 (1978).

[339] R. F. Cunico and Y. K. Han, *J. Organomet. Chem.* **105**, C29 (1976).
[340] R. F. Cunico and Y. K. Han, *J. Organomet. Chem.* **162**, 1 (1978).
[341] T. H. Chan, W. Mychajlowskij, B. S. Ong and D. N. Harpp, *J. Org. Chem.* **43**, 1526 (1978).
[342] Shyh-Fong Chen and P. S. Mariano, *Tetrahedron Lett.* 47 (1985).
[343] D. P. Fox, J. A. Bjork and P. J. Stang, *J. Org. Chem.* **48**, 3995 (1983).
[344] P. J. Stang and D. P. Fox, *J. Org. Chem.* **42**, 1667 (1977).
[345] P. J. Stang and J. A. Bjork, *J. Chem. Soc., Chem. Commun.* 1057 (1978).
[346] P. J. Stang and S. B. Christensen, *J. Org. Chem.* **46**, 823 (1981).
[347] T. H. Chan, *Acc. Chem. Res.* **10**, 442 (1977).
[348] C. N. Hsiao and H. Shechter, *Tetrahedron Lett.* 3455 (1982).
[349] B. W. Au-Yeung and I. Fleming, *J. Chem. Soc., Chem. Commun.* 81 (1977).
[350] O. I. Kolodiazhnyi, *Tetrahedron Lett.* 4933 (1982).
[351] F. Cooke, R. Moerck, J. Schwindeman and P. Magnus, *J. Org. Chem.* **45**, 1046 (1980).
[352] I. Fleming and A. Percival, *J. Chem. Soc., Chem. Commun.* 178 (1978).
[353] I. Fleming and J. Goldhill, *J. Chem. Soc., Chem. Commun.* 176 (1978).
[354] T. H. Chan and W. Mychajlowskij, *Tetrahedron Lett.* 171 (1974).
[355] J. J. Eisch and S. K. Due, unpublished data.
[356] T. H. Chan and B. S. Ong, *J. Org. Chem.* **43**, 2994 (1978).
[357] I. Fleming and N. K. Terrett, *Tetrahedron Lett.* 4153 (1983).
[358] T. H. Chan and D. Mussuda, *J. Am. Chem. Soc.* **99**, 936 (1977).
[359] R. F. Cunico and E. M. Dexheineer, *J. Am. Chem. Soc.* **94**, 2868 (1972).
[360] C. E. Peishoff and W. L. Jorgensen, *J. Org. Chem.* **50**, 1056 (1985).
[361] A. N. Nesmeyanov, A. E. Borisov and I. S. Savejeva, *Izv. Akad. Nauk SSSR, Ser. Khim.* 286 (1968).
[362] O. A. Reutov, I. P. Beletzkay and V. U. Sokolov, *Mechanism Reaction of Metalloorganic Compounds.* Khimiy, Moskow (1972).
[363] R. Yamaguchi, H. Kawasaki, Y. Yoshitomep and M. Kawanisi, *Chem. Lett.* 1485 (1982).
[364] R. F. Cunico and E. M. Dexheimer, *J. Organomet. Chem.* **59**, 153 (1973).
[365] Y. Himeshima, T. Sonoda and H. Kobayashi, *Chem. Lett.* 1211 (1983).
[366] P. J. Stang, M. Hanack and L. R. Subramanian, *Synthesis* 87 (1982).
[367] M. Reiffe and R. W. Hoffmann, *Tetrahedron Lett.* 1107 (1978).
[368] E. Block and M. Aslam, *Tetrahedron Lett.* 4203 (1983).
[369] L. S. Hegedns and D. A. Evans, *J. Am. Chem. Soc.* **100**, 3461 (1978).
[370] A. J. Guildford and R. W. Turner, *Synthesis* 46 (1982).
[371] F. T. Luo and E. Negishi, *J. Org. Chem.* **48**, 5144 (1983).
[372] C. Gioeli, N. Balgobin, S. Josephson and J. B. Chattopadhyaya, *J. Org. Chem.* **46**, 969 (1981).
[373] E. Fell, L. A. Carpino, J. H. Tsao, H. Ringsdorf and G. Hettrich, *J. Chem. Soc., Chem. Commun.* 358 (1978).
[374] T. H. Chan and M. DeStefano, *J. Chem. Soc., Chem. Commun.* 161 (1978).
[375] T. Hayashi, M. Yanagiba, Y. Matsuda and T. Oishi, *Tetrahedron Lett.* 2665 (1983).
[376] P. J. Kocienski, *Tetrahedron Lett.* 2649 (1979).
[377] P. J. Kocienski, *J. Org. Chem.* **45**, 2037 (1980).
[378] P. J. Kocienski and M. Todd, *J. Chem. Soc., Perkin I* 1777 (1983).
[379] P. J. Kocienski and M. Todd, *J. Chem. Soc., Perkin I* 1783 (1983).
[380] L. A. Paquette, R. V. Williams, R. V. C. Carr, P. Charumiling and J. F. Blound, *J. Org. Chem.* **47**, 4566 (1982).
[381] R. V. C. Carr, R. V. Williams and L. A. Paquette, *J. Org. Chem.* **48**, 4976 (1983).
[382] Y. Ito, M. Nakatsuka and T. Saegusa, *J. Am. Chem. Soc.* **104**, 7609 (1982).
[383] Y. Ito, S. Miyata, M. Nakatsuka and T. Saegusa, *J. Am. Chem. Soc.* **103**, 5250 (1981).
[384] B. L. Chenard, C. Slapak, D. K. Anderson and J. S. Swenton, *J. Chem. Soc., Chem. Commun.* 179 (1981).
[385] Y. Ito and T. Saegusa, *Tetrahedron Lett.* 5139 (1984).
[386] Y. Ito, E. Nakajo, M. Nakatsuka and T. Saegusa, *Tetrahedron Lett.* 2881 (1983).
[387] Y. Ito, S. Mijata, M. Nakatsuka and T. Saegusa, *J. Org. Chem.* **46**, 1043 (1981).
[388] L. F. Tietze and H. Runchert, *Angew. Chem. Int. Ed.* **19**, 830 (1980).
[389] C. N. Hsiao and H. Shechter, *Tetrahedron Lett.* 1219 (1984).
[390] K. Rudolf and T. Koenig, *Tetrahedron Lett.* 4835 (1985).
[391] E. Vedejs and G. R. Martinez, *J. Am. Chem. Soc.* **101**, 6452 (1979).
[392] T. Cohen, Z. Kasraych, K. Susuki and L.-C. Yu, *J. Org. Chem.* **50**, 2965 (1985).
[393] R. Smith and T. Livinghouse, *J. Org. Chem.* **48**, 1554 (1983).
[394] E. Vedejs and F. G. West, *J. Org. Chem.* **48**, 4773 (1983).
[395] O. Tsuge, S. Kanemasa and K. Matsuda, *Chem. Lett.* 1411 (1985).
[396] A. Padwa, G. Hoffmanns and M. Tomas, *J. Org. Chem.* **49**, 3313 (1984).
[397] A. Padwa and J. R. Gasdaska, *J. Org. Chem.* **51**, 2857 (1986).
[398] E. Vedeja and G. R. Martinez, *J. Am. Chem. Soc.* **102**, 7993 (1980).
[399] A. Padwa, G. Hoffmanns and M. Tomas, *Tetrahedron Lett.* 4303 (1983).
[400] H. J. Bestmann and A. Bomhard, *Angew. Chem. Int. Ed.* **21**, 545 (1982).
[401] V. V. Bardin, I. V. Stennikova, G. G. Furin and G. G. Yakobson, *Izv. Akad. Nauk SSSR, Ser. Khim.* 946 (1985).
[402] K. Tamao, T. Kakui, M. Akita, T. Iwahara, R. Kanatani, J. Yoshida and M. Kumada, *Tetrahedron* **39**, 983 (1983).
[403] K. Tamao, N. Ishida and M. Kumada, *J. Org. Chem.* **48**, 2120 (1983).
[404] K. Tamao, T. Kakui and M. Kumada, *J. Am. Chem. Soc.* **100**, 2268 (1978).
[405] K. Tamao, T. Iwahura, R. Kanatani and M. Kumada, *Tetrahedron Lett.* 1909 (1984).
[406] K. Tamao and K. Maeda, *Tetrahedron Lett.* 65 (1986).
[407] I. Fleming, R. Henning and H. Plaut, *J. Chem. Soc., Chem. Commun.* 29 (1984).
[408] H. Sakurai, M. Ando, N. Kawada, K. Sato and A. Hosomi, *Tetrahedron Lett.* 75 (1986).
[409] R. Muller and Ch. Dathe, *Chem. Ber.* **98**, 235 (1965).
[410] R. Muller, M. Dressler and Ch. Dathe, *J. Prakt. Chem.* **312**, 150 (1970).
[411] J. I. Yoshida, K. Tamao, T. Kakui and M. Humada, *Tetrahedron Lett.* 1141 (1979).