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THIRTY YEARS IN ORGANOSILICON CHEMISTRY

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We began work in the organosilicon field in 1950. Since that date we have developed original general synthetic methods as well as preparing interesting novel products. We were interested throughout in organosilicon and pure organic synthesis. A large part of our work was published in French. This partly explains why some of it has been repeated by others without reference to our reports, and this is one reason why we offer here a general survey of our contributions to organosilicon chemistry and organic synthesis.

Contents

The studies are usually described in chronological order except in the last Section.

1. Reactions involving hydrogenosilanes

1.1. Hydrosilylation of compounds having a carbon—carbon double bond

In our first researches in organosilicon chemistry we utilized the hydrosilation of carbon—carbon double bonds [1] in functional derivatives such as unsaturated fatty acids [2—12], allylic esters [13] or unsaturated ethers [14,15]. Thus we prepared C-silylated acids, esters, ethers, amides, lactones, etc. having a branched long chain. Either $HSiCl_3$ or $HSiR_3$ was used as the hydrosilylating reagent. Later we reported hydrosilylation of methylcyclohexene [16] and terpenes such as limonene [17,18], α- [19] and β-pinenes [20,21]. Through these studies we were able to propose a convenient route to $\Delta(1,7)$-*p*-menthene [22,23] which had previously been very difficult to prepare. This reaction con-

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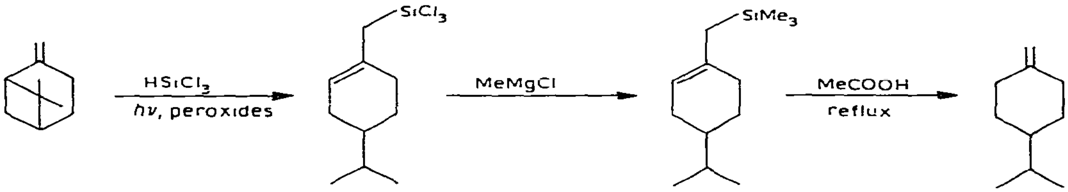
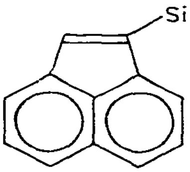
stituted one of the first examples of the use of organosilicon intermediates in pure organic synthesis:



Very recently, hydrosilylation of acenaphthylene [24] gave us, after subsequent oxidation



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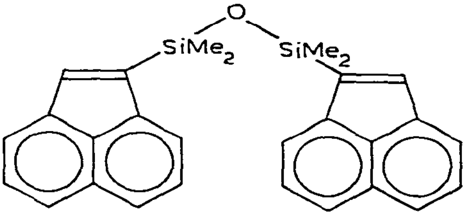
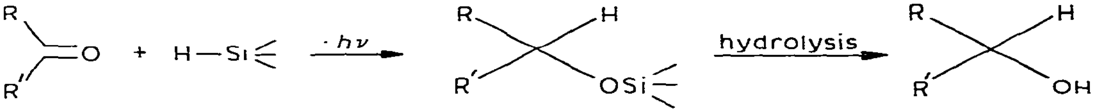


The latter can undergo a reversible cyclomerisation involving a color change, endowing this compound with interesting photochromic properties.

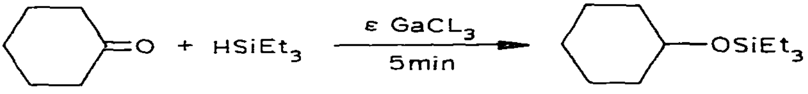
1.2. Action of hydrogenosilanes on $\gt C{=}O$, $\gt C{=}N{-}$ *or* $-C{\equiv}N$ *bond-containing compounds*

Since hydrosilylation of carbon—carbon multiple bonds was so well known, it was surprising to find that a similar reaction with carbonyl derivatives had not been described in 1957. We found at that time that hydrosilylation of ketones with $HSiCl_3$ or $HSiPh_3$ occurred upon UV irradiation [25,26]. The corresponding alcohols are formed upon hydrolysis, and so hydrosilylation constitutes an efficient reduction process:



$H{-}Si{\lessgtr} = HSiCl_3$ or $HSiPh_3$

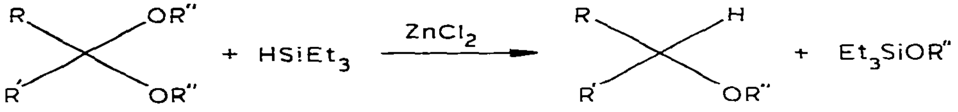
We investigated the stereochemistry of this reaction [27—29] which was widely developed [27—33], and generalized it for aldehydes [34—36], benzil [37], and even an acylsilane [38]. Upon UV irradiation, hydrosilylation occurs by a radical mechanism. We extended the reaction to triethylsilane but in the presence of $ZnCl_2$, involving a polar hydrosilylation process [39]. Later we showed that $InCl_3$ and especially $GaCl_3$ induce a very fast hydrosilylation of some ketones [40]:



We discovered the first examples of hydrosilylation of carbonyl derivatives, but we note that a few months after our first report Gilman et al. described a thermal process for hydrosilylation of ketones [41].

We also investigated hydrosilylation of α,β-unsaturated aldehydes and ketones [42] which was widely utilized by Frainnet et al. [42]. We also observed that hydrostannylation was possible upon UV irradiation [43—45], and the same conditions were used for hydrogermylation [46].

The reducing properties of Et_3SiH were used to convert acetals into the corresponding ethers [47]:



We then studied the behaviour of γ- and δ-lactones [48], amides [49,50], imino-ethers and imines [50], and observed that use of triethylsilane permits the conversion of primary amides into the corresponding amines or nitriles [49]. Moreover we investigated hydrosilylation of nitriles [51] and dinitriles [52]. For instance PhCN afforded the corresponding N-silyl imine in satisfactory yield [51].

$$PhCN + HSiEt_3 \xrightarrow{ZnCl_2} PhCH{=}NSiEt_3 \xrightarrow{H_3O^+} PhCHO$$

These studies were carried out in collaboration with Frainnet et al. [53], who extended the work in this field.

Our results for the above-mentioned reactions were summarized in a review [54].

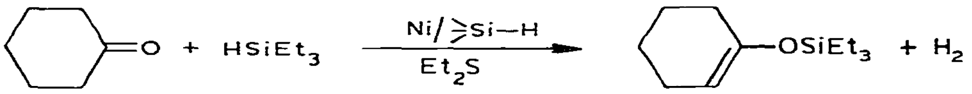
We should point out that asymmetric hydrosilylation of carbonyl derivatives was used in the synthesis of optically active alcohols in the presence of optically active catalysts or (and) hydrogenosilanes [55]. In our case asymmetric synthesis by hydrosilylation [56] or stannylation [57] of menthyl crotonate was successful, but involved hydrometallation of the $-\overset{|}{C}{=}\overset{|}{C}-$ bond.

1.3. Other reactions involving hydrogenosilanes

Being aware of the great interest in hydrogenosilanes as reagents we proposed original routes to these compounds from chlorosilanes [58—61] or disilanes [62—66]. (These reactions permitted us to prepare novel Si—Al bond-containing derivatives [66] and to convert industrial disilane residues into useful reagents [63—65]).

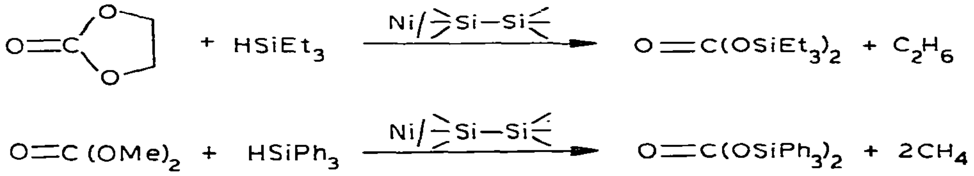
We also studied the conversion of chlorohydrogenosilanes into alkyl [67] or alkoxyhydrogenosilanes [68].

Among the novel properties of hydrogenosilanes we observed the reduction of oxygenated compounds of silver [69] and the insertion of sulfur into the $\geqslant$Si—H bond [70]. The most important reaction observed was the reduction of anhydrous $NiCl_2$ by refluxing with Et_3SiH [42,71—73] to give a pyrophoric nickel which is much more active than Raney Ni as a hydrogenation catalyst [74a]. This reduced nickel also catalyses the conversion of aldehydes and ketones into the corresponding alkoxysilanes or enoxysilanes [42,72,73] when inhibited by PhSH or Et_2S, e.g.:



Moreover, sterically hindered halo derivatives such as ArCHCl-t-Bu are reduced to ArCH(t-Bu)CH(t-Bu)Ar by Et_3SiH using $\mathrm{Ni}/{\geqslant}\mathrm{Si{-}H}$ as catalyst [74b].

Use of the nickel obtained from the reaction of $NiCl_2$ with Me_6Si_2 (see Section 4.1.) permitted the synthesis of the first bis(triorganosilyl) carbonates [75,76] e.g.:



These species generate CO_2 on heating [75].

2. New methods of forming silicon—carbon bonds. Development of C-silylated models

In order to provide novel species both for the development of organosilicon chemistry and for use as intermediates in pure organic synthesis our interest was to discover new methods of forming silicon—carbon bonds. First, we succeeded in the synthesis of ethynylsilanes [77]:

$$\mathrm{RC{\equiv}CH + HSiEt_3 \xrightarrow{\text{Na or NaH/HMPA catalyst}} RC{\equiv}CSiEt_3 + H_2}$$

$$\mathrm{RC{\equiv}CH + Me_3SiSiMe_3 \xrightarrow{\text{Na or NaH/HMPA catalyst}} RC{\equiv}CSiMe_3 + HSiMe_3}$$

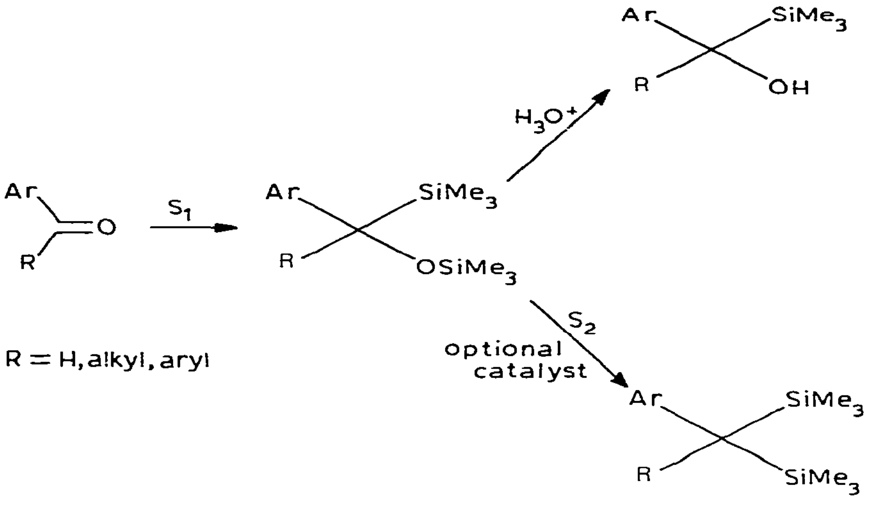
Later, ethynylchlorosilanes were obtained from RC≡CH, chlorosilanes and Et_3N, in the presence of CuCl as a catalyst [78].

Then we found an organometallic route to be especially convenient, and since 1969 we have reported numerous novel C-silylation reactions. A review [79] summarizes our results between 1968 and the beginning of 1976 (with about 100 references from our laboratories). We can now carry out direct C-silylation of most organic functional groups with either Me_3SiCl/Mg/HMPA (S_1) or with Me_3SiCl/Li/THF (S_2) as the silylation reagent, (The latter is used at 0—10°C).

This review will be restricted to some typical or recent results.

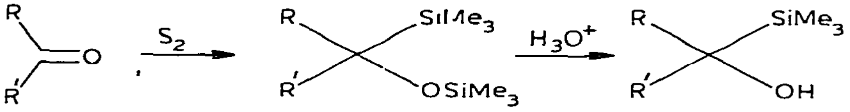
2.1. *Silylation of aldehydes and ketones*

Despite presumably different mechanisms [79], the reactions S_1 and S_2 show behaviour similar to that expected for organosilyl Grignard reagents.



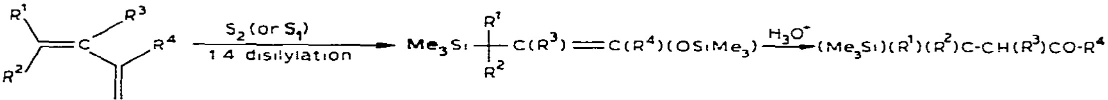
[80, 81]

[82–84]



[85, 86]

R, R′ = H, alkyl



enoxysilane [87-90]

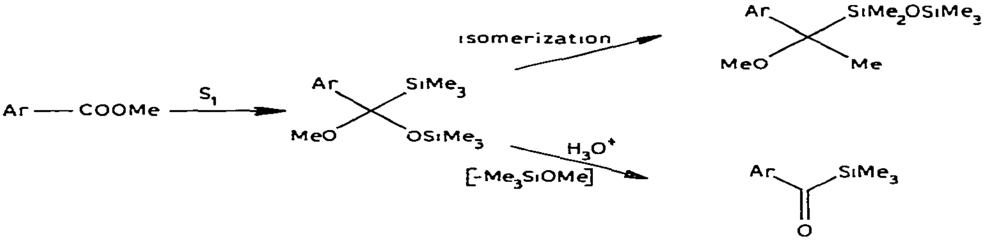
With α,β-unsaturated aldehydes 1,2-disilylation was observed:

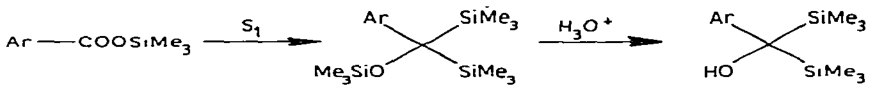
$$R^1C{\equiv}CCOR^2 \xrightarrow{S_1} (Me_3Si)(R^1)C{=}C{=}C(R^2)(OSiMe_3) \xrightarrow{H_3O^+} (Me_3Si)(R^1)C{=}CHCOR^2$$

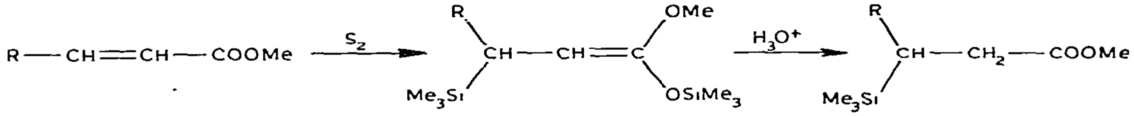
(with R^1 and R^2 appropriately chosen).

2.2. *Esters, acyl chlorides and amides*

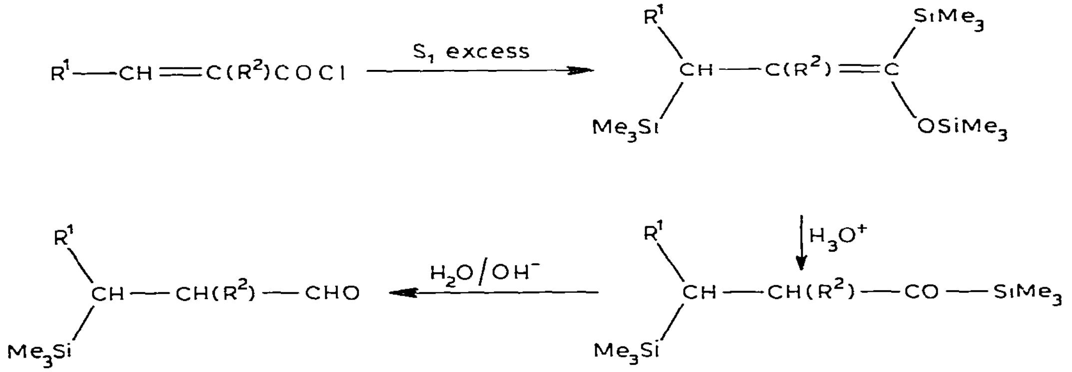
C-silylation reactions were extended to aromatic [92,93], α,β-ethylenic [94–96] or even saturated esters [96,97], e.g.:

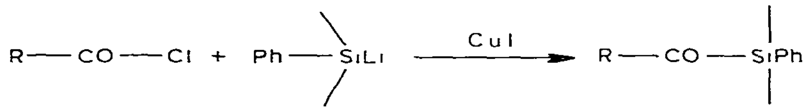






Likewise acyl chlorides underwent C-silylation [97—101].





Similarly aromatic [102,104], α,β-ethylenic [105] and saturated amides [106] afforded mono- or disilylated derivatives at a functional carbon atom. Formamide, for instance, gave $(Me_3Si)_2CH{-}N(SiMe_3)_2$, in which the free rotation around the C—N bond is sterically hindered at room temperature [106].

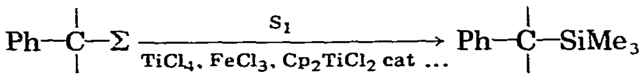
2.3. Imines, iminoyl chlorides and nitriles

Imines [107], iminoyl chlorides [108] and nitriles [107,109—112] were easily C-silylated and the reaction with nitriles was used to synthesize polysilylated enamines [108,109] or α-silylated nitriles [111,112].

2.4. Other functional benzylic, allylic or propargylic derivatives

Enoxysilanes in which the double bond is conjugated with a phenyl group underwent disilylation of the double bond [113,114], whereas epoxystyrene gave the derivative resulting from disilylation of styrene [115].

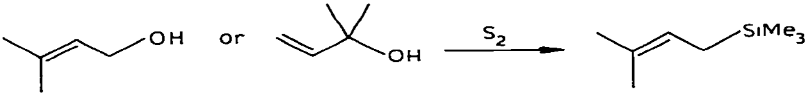
The S_1 reagent brings about reductive silylation of benzylic alcohols, alkoxysilanes, ethers, esters or amines [82—84]:

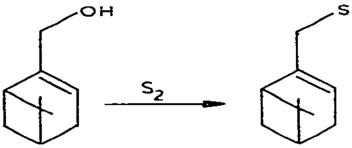


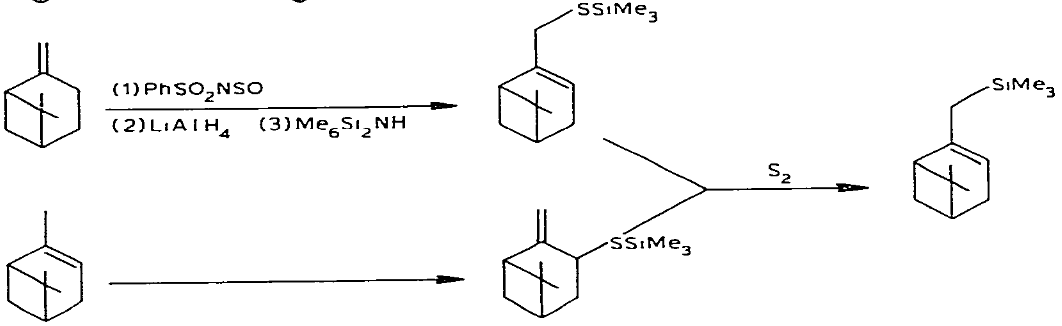
$$\mathrm{Ph{-}\overset{|}{\underset{|}{C}}{-}\Sigma} \xrightarrow[\mathrm{TiCl_4,\ FeCl_3,\ Cp_2TiCl_2\ cat\ \ldots}]{S_1} \mathrm{Ph{-}\overset{|}{\underset{|}{C}}{-}SiMe_3}$$

Σ = OSi$\leqslant$, OR, OCOR, NMe$_2$ ...

Ph_2CHOH was also converted into $Ph_2CHGeMe_3$ [84]. Allylic functional derivatives exhibited similar behaviour, but the reductive silylation generally occurs with allylic rearrangement [83,84]. At the present time we are developing original methods for synthesizing allylsilanes based on the reductive silylation of allyl alcohols [116] or thiols [117] by the S_2 reagent. E.g.:



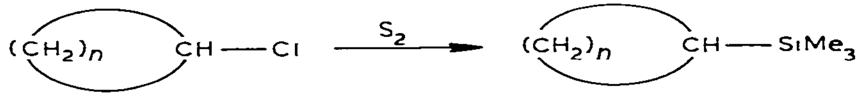


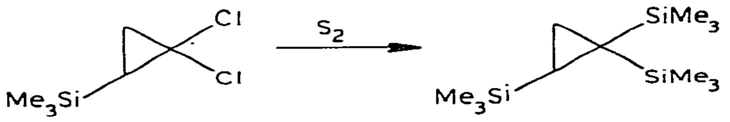


Further, by using S_2 as silylating reagent, $HC{\equiv}CCH_2OH$ or better $HC{\equiv}C{-}CH_2OMe$ were easily converted into the interesting species $Me_3SiC{\equiv}CCH_2SiMe_3$ [118].

2.5. *Halogenated derivatives*

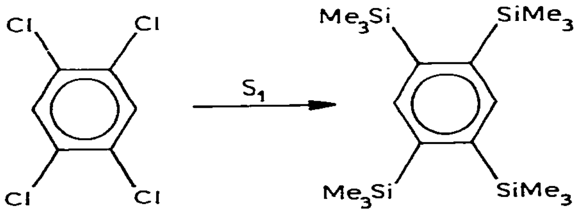
Use of the S_2 reagent has provided a convenient synthesis of trimethylsilyl- or bis(trimethylsilyl)-cycloalkanes:





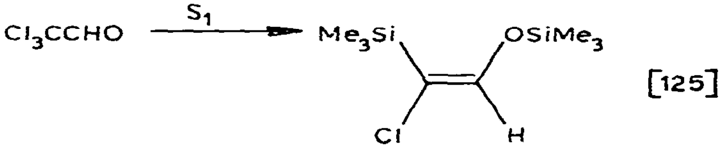
[120]

The S_1 reagent afforded allenylsilanes in its reaction with propargyl halides [121]. The S_2 reagent is especially convenient for complete [122—124] or partial silylation [123—125] of polyhalogenated derivatives giving high yields:



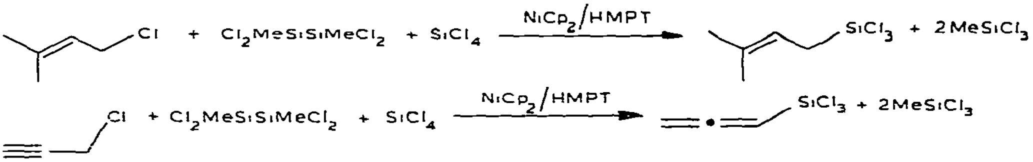
[122]

$MeCCl_3 \xrightarrow{S_1} MeCCl_2SiMe_3$ [123]



[125]

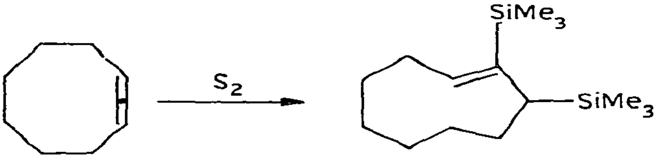
Recently we reported a novel method for the synthesis of allyl-, benzyl-, [126,127] and allenyl-trichlorosilanes [128] involving reaction of allyl, benzyl and propargyl chlorides, respectively, with $Cl_2MeSiSiMeCl_2$ or the methylchlorodisilane residues from the industrial synthesis of Me_2SiCl_2, in the presence of $SiCl_4$:



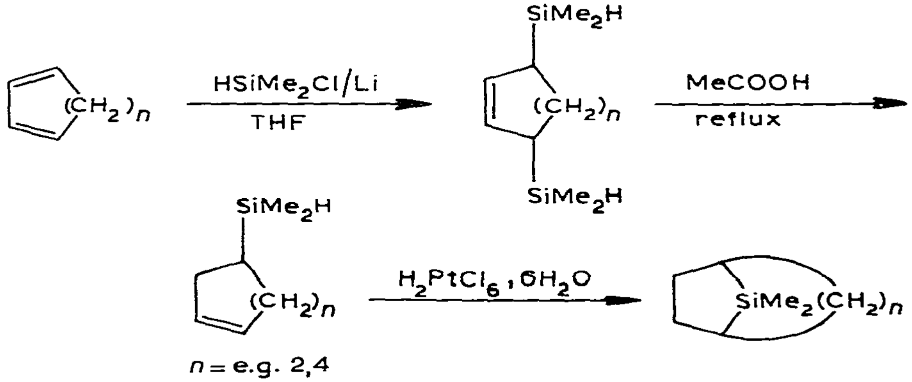
Thus we devised a convenient synthesis of  etc., and suggested a catalytic cycle to explain the role of the catalyst [127,128].

2.6. Unsaturated hydrocarbons

Mono-olefins are not very reactive either with reagent S_2 at 0—10°C [129] or with reagent S_1 at 100—110°C [130]. A saturated product was formed at 200°C [130]. From the readily available 1,2-cyclononadiene, a compound having the *trans* cyclononene skeleton was obtained by vicinal disilylation, [131]:



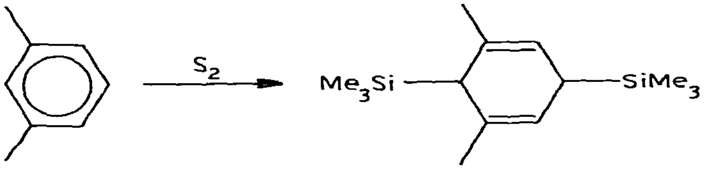
We have extended the previously known [132] 1,4-disilylation of conjugated dienes [133,134]. Using Me_2SiCl_2 as the chlorosilane we considerably improved the synthesis of 3-sila-1-cyclopentenes [134]. Moreover conjugated trienes were found to react at the 1,4- (and not 1,6-) position [134,135]. Recently we reported a one-step synthesis of a sila-tropadiene [135]. We have also proposed a a new route to sila-bicyclic derivatives [135]:



Similarly styrene underwent disilylation at the carbon—carbon double bond [136]. With acetylene, silylation continued progressively to give a heptasilyl derivative [137].

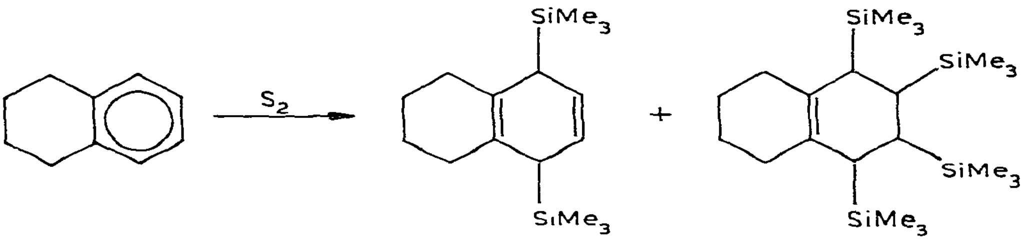
Although there were a few earlier reports of the disilylation of some aromatic compounds (benzene [138], for instance), we decided to study such silylation further;

(a) Benzene, alkylbenzenes, *m*- or *p*-dialkylbenzenes underwent 1,4 reductive disilylation in high yield using the S_2 reagent [139,140]. e.g.:

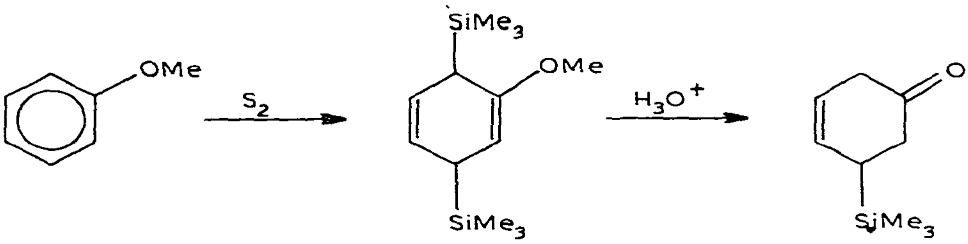


The products generally aromatize in the presence of air, but under special conditions aromatization can be accompanied by loss of one of the Me_3Si groups. In the case of the derivatives obtained by 1,4-desilylation of *m*-xylene, we observed a spontaneous *endo*-peroxidation by triplet oxygen, which is very rarely observed with such species [141].

(b) *o*-Dialkylbenzenes gave a mixture of 1,4-disilyl and 1,2,3,4-tetrasilyl derivatives [140,142]. e.g.:

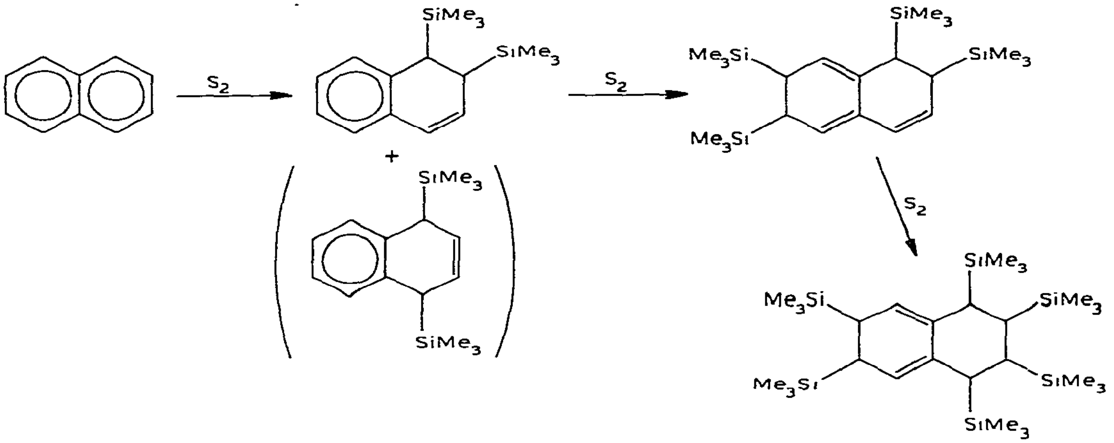


(c) Phenols, phenoxysilanes and related compounds gave novel δ-silylated β,γ-unsaturated ketones e.g. [143]:

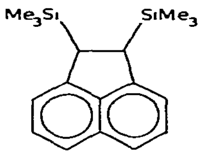


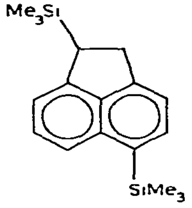
Thus we have synthesized a sila-analogue of an *ortho*-menthenone [144].

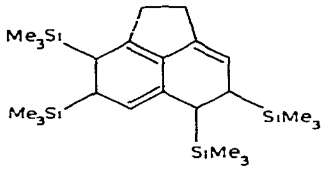
(d) The reaction was extended to polyaromatics e.g. [145,146]:

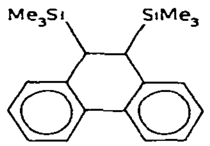


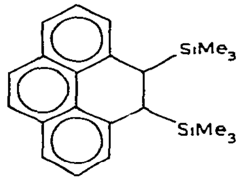
The following were also synthesized [24,146]:

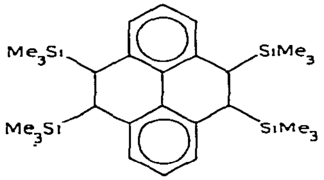


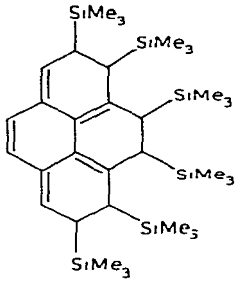






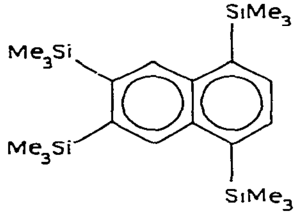






et

Using the silylation/oxidation process, we prepared [24,146]:



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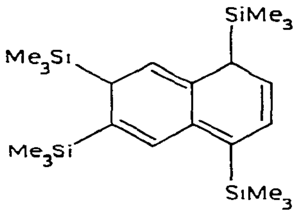

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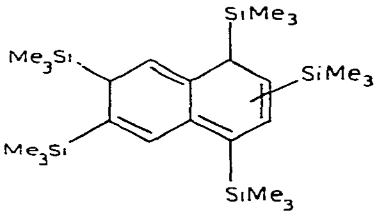

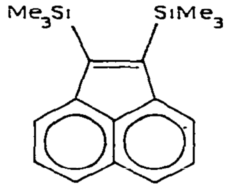

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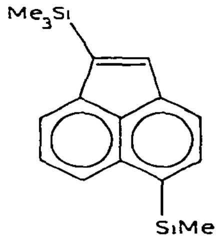
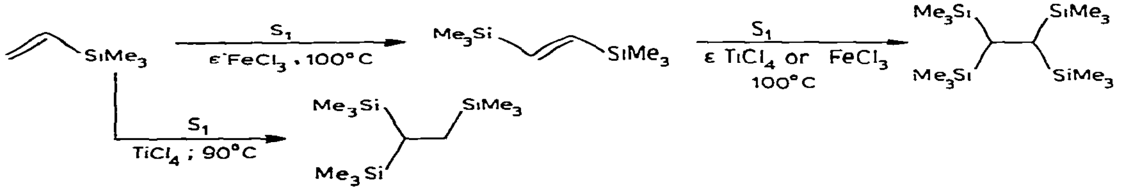


These constitute new intermediates; the obtained dihydro- and tetrahydronaphthalenes have novel structures. Our investigations in this field are continuing.

We also successfully silylated allyltrimethylsilane with the reagent S_1 using $TiCl_4$ or $FeCl_3$ as catalyst, and have also carried out di- and tri-silylation of vinyltrimethylsilane [84,147]:

(allylic hydrogen substitution with rearrangement)



The sterically hindered tetrasilyl-derivative adopts a *gauche* conformation at room temperature. This conformational preference is attributed to a distortion of the tertiary carbons from tetrahedral geometry because of steric repulsion between the geminal trialkylsilyl groups [149].

3. Organosilicon routes in organic synthesis

There were two aspects of our use of organosilicon derivatives in pure organic synthesis, (i) organosilicon compounds as reagents; (ii) organosilicon compounds as precursor substrates.

3.1. Organosilicon compounds as reagents

Hydrogenosilanes were found to be versatile reducing agents as shown in Section 1. The S_1, S_2 and $Me_3SiCl/Mg/THF$ (S_3) reagents are considered separately.

In the presence of a catalytic amount of $GaCl_3$, use of trialkylchlorosilanes permitted demethylation of anisole [40]:

$$PhOMe + Me_3SiCl \xrightarrow[-MeCl]{GaCl_3\ catalyst} PhOSiMe_3 \xrightarrow{H_2O} PhOH$$

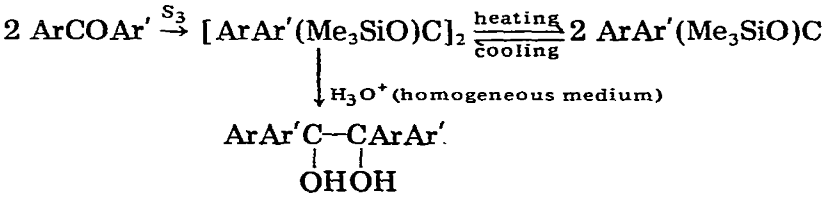
Similarly Bu_2O was converted into BuCl by refluxing with Et_3SiCl in the presence of $GaCl_3$. This work, which is never cited in more recent reports concerning demethylation of ethers or esters using Me_3SiI, was applied to the synthesis of a sila-analogue of stilboestrol [150]. Alkoxysilanes or siloxanes were found to be cleaved by acyl chlorides and anhydrides. Thus we obtained esters [151] or silyl derivatives of acids [152,153] and extended our work to syntheses [154,156,157] and structural studies [157,161—165], and to the cleavage [155,156,159,160] of C-silylated ether-oxides or alkoxysilanes.

Furthermore we have synthesized amines [167] and imines [168a] using hexamethyldisilazane or its derivatives as amination reagents. Use of $(Me_3Si)_2NH$ enables the conversion of certain esters and lactones into the corresponding nitriles [169]. We have also proposed two routes to trimethylsilylchlorosulfonate [171,172]. Later we showed that this reagent is a very mild and efficient sulfonating reagent, more versatile than SO_3, dioxan-SO_3 or pyridine-SO_3 (see Section 3.2). We must note here that $ClSO_3SiMe_3$ permits the conversion of esters into the corresponding acyl chlorides [173]:

$$RCOOR' + ClSO_3SiMe_3 \rightarrow RCOCl + R'OSO_3SiMe_3$$

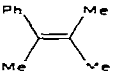
Chlorosilane/Mg (or Li) donor solvent systems (S_1, S_2, S_3)

(a) $Me_3SiCl/Mg/THF$ (S_3) converts aryl aldehydes and ketones into products which are a result of reductive dimerization accompanied by O-silylation [174a]. In the case of diarylketones the obtained bis(trimethylsilyl) pinacolates give colored free radicals when heated in an inert atmosphere:



$$\begin{array}{l} 2\,ArCOAr' \xrightarrow{S_3} [ArAr'(Me_3SiO)C]_2 \underset{\text{cooling}}{\overset{\text{heating}}{\rightleftharpoons}} 2\,ArAr'(Me_3SiO)C \\ \qquad\qquad\qquad \downarrow H_3O^+ \text{ (homogeneous medium)} \\ \qquad\qquad ArAr'\underset{OH}{C}-\underset{OH}{C}ArAr' \end{array}$$

The minimum temperature of formation and the color of free radicals depend on the nature of Ar and Ar′ and the steric hindrance from the substituents. $[Ph_2C(OSiMe_3)]_2$ was used as a catalyst for radical polymerisation of styrene [174b]. Use of the S_3 reagent also enabled us to prepare



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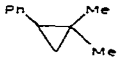
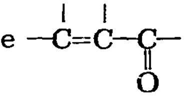


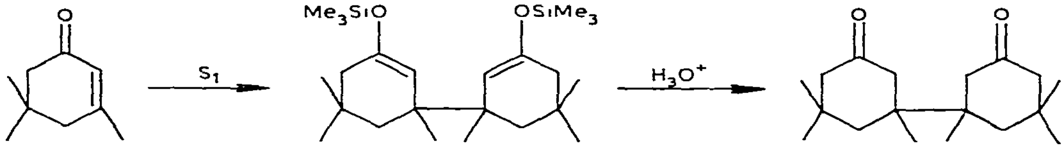
. from pivalophenone [175].

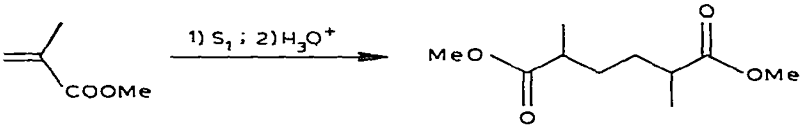
(b) The S_1 reagent produces ε-diketones [88—90], diesters [95], and diamides [105] from the α,β-unsaturated corresponding carbonyl derivatives, especially when the



$$-\overset{|}{C}=\overset{|}{C}-\underset{\underset{O}{\|}}{C}-$$

sequence is not conjugated with another group; e.g.:

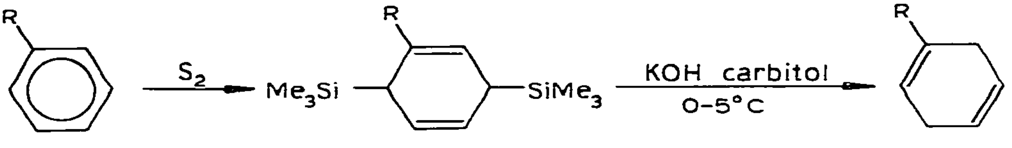




(c) The silylation/desilylation process provides a means of reducing esters or acyl chlorides to the corresponding aldehydes:

$$\mathrm{ArCOOMe\ or\ RCOCl} \rightarrow \mathrm{acylsilanes}\ [92,93,100] \xrightarrow{H_2O/OH^-\ [176]} \mathrm{aldehydes}$$

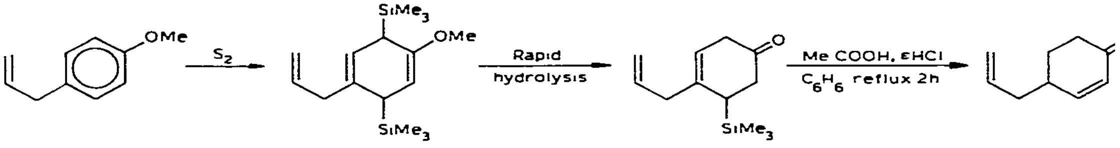
(d) The S_2 reagent produces 1,4-cyclohexadienic species from benzene and alkyl-substituted derivatives [139,140]:



R = H, Me

This reaction is easier to be carried out than the Birch reduction [177] in the case of benzene because the disilyl intermediate is readily separated from the C_6 hydrocarbons. Consequently the 1,4-cyclohexadiene can be easily obtained free from the other six member ring hydrocarbons. Similarly the S_2 system constitutes a good reagent for partial reduction of phenol derivatives to 2-cyclohexenones.

Thus we very easily prepared 2-cyclohexenone in high yield from anisole, and more notably 4-allyl-2-cyclohexenone, previously very difficult to obtain [178] from estragole [143]:



Recently this method was successfully used to prepare cryptone [179]. For simple cases, as mentioned above, the silicon route can largely compete with the Birch reduction. Unfortunately, attempts at partial reduction of the aromatic ring A of some steroids using the silylation/desilylation process were unsuccessful [180].

Several reductions of halo derivatives were carried out using the S_1 reagent, e.g.;

$$\mathrm{Cl_3CCHO} \xrightarrow[(2)\ H_3O^+]{(1)\ S_1} \mathrm{ClCH_2CHO}\ [125]$$

$$\mathrm{PhCCl_3} \xrightarrow[\text{(2) Hydrolysis (first acidic then basic)}]{\text{(1) } S_1 \text{ (monosilylation giving } PhCCl_2SiMe_3)} \mathrm{PhCHO}\ [123]\ \text{etc...}$$

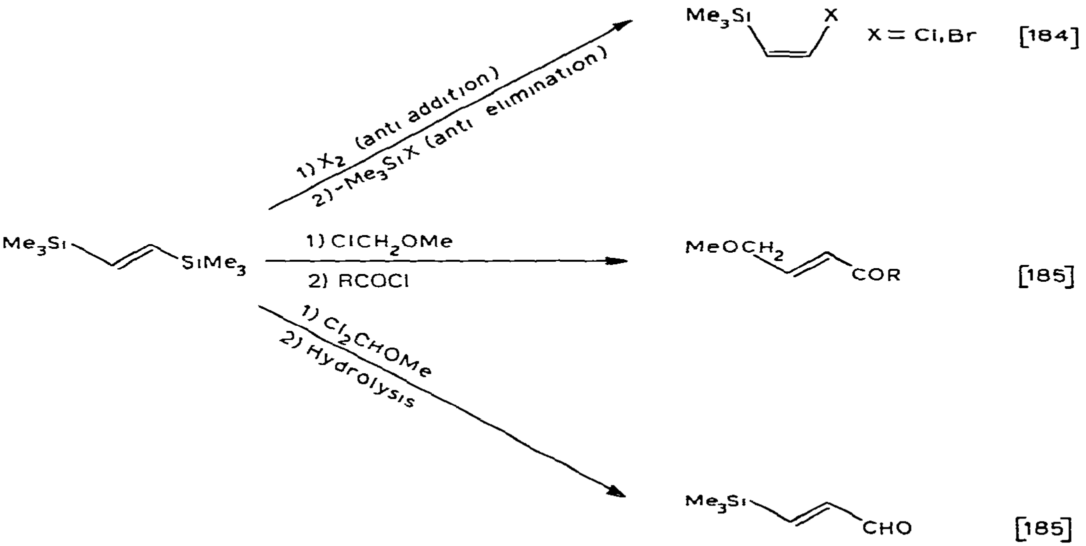
Addition of trimethylsilyl groups followed by protodesilylation thus constitutes a versatile route for the reduction of many functions.

3.2. Organosilicon compounds as precursor substrates

Vinyl-, cyclopropyl- and cyclopropylmethyl-, ethynyl-, allyl-, propargyl- and arylsilanes are considered next. Then the use of other compounds such as Me_3SiCH_2COOEt, $Me_3SiCH_2CONEt_2$, Me_6Si_2 and Me_4Si will be discussed.

3.2.1. *Vinylsilanes*

We were the first to report sulfonation (in 1966) [182] and acylation (in 1974) [183] reactions in these series, and we have used bis(trimethylsilyl)-1,2 ethylene for mono- or difunctionalizations:

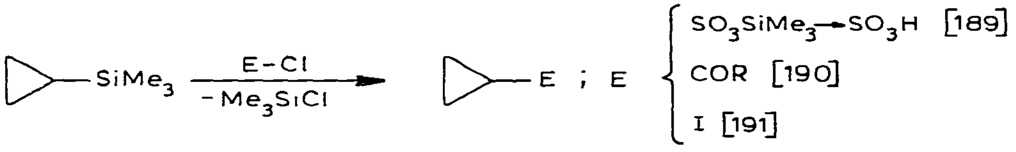


Acylations and methoxymethylations were carried out in the presence of a Lewis acid. It should be noted that the last reaction constitutes the first example of functionalization by replacement of —SiMe$_3$ by —CHO.

Radical addition of RSO$_2$Cl to vinylsilanes followed by elimination of HCl or Me$_3$SiCl led us to new sulfones [186]. We have also proposed a new route to vinylsilanes [187a] and to 1-trimethylsilyl-1,3-dienes which we have used in synthesis [188]. Furthermore, in one case we observed vinylation of chloral [107].

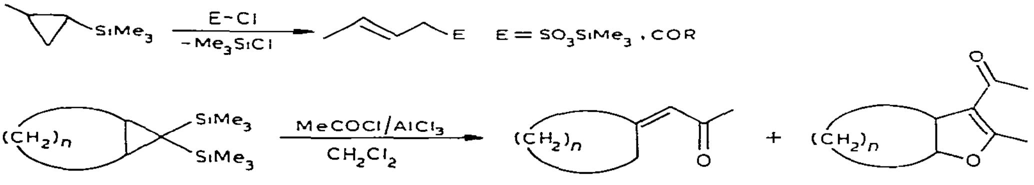
3.2.2. *Cyclopropyl- and cyclopropylmethylsilanes*

Use of cyclopropyltrimethylsilane permitted for the first time the functionalization of cyclopropane by electrophilic substitution without ring opening [189—191]:



In this way we synthesized the first cyclopropane sulfonic acid, and this reaction is especially convenient for the preparation of alkenyl cyclopropyl ketones.

Acylation of *trans*-bis(trimethylsilyl)cyclopropane was found to be regio and stereospecific. Cyclopropylsilanes bearing other substituents are also interesting intermediates for regiospecific substitutions [192,193].



$n = 3,4,6$

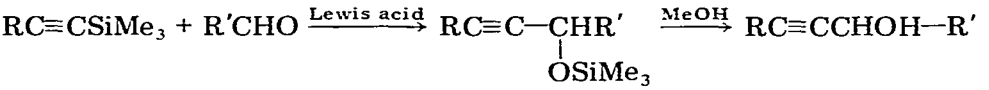
major product
(with $n = 6$ it isomerizes to β,γ-unsaturated ketone)

In addition, we have studied electrophilic substitution in the case of the cyclopropylmethyltrimethylsilanes (particularly acylation and sulfonation) produced by cyclopropanation of linear allylsilanes and 3-sila-1-cyclopentenes [192,194—196], and we obtained new unsaturated sulfonic acids, sultones and ketones (e.g. $MeCOCH_2C(COMe){=}CHMe$ [192]) as well as alkenylfluorosilanes.

3.2.3. *Ethynylsilanes (and allenylsilanes)*

Electrophilic replacement of $SiMe_3$, discovered by Birkofer et al. [167], has been extended to the synthesis of α,β-acetylenic amides [198a] or imines [198b]; phenyl isocyanate led to 4-silyl-2-quinolones [199]. We obtained our most important results in sulfonation reactions, which provided access to new classes of functional acetylenic derivatives [200—205], such as α-acetylenic sulfonic acids $RC{\equiv}CSO_3H$ (R = Ph, t-Bu, $SiMe_3$ [201] and even H, see $HC{\equiv}CSO_3H \cdot 2.5\ H_2O$ [203,204]) or trimethylsilyl esters of propargylic sulfonic acids from allenyl silanes and sometimes sulfonic acids themselves, e.g. $CH_2{=}C{=}CHSO_3H$ [202], $HC{\equiv}CCH_2SO_3SiMe_3$ [205], $CH_2{=}C(Me)C(SO_3SiMe_3){=}C(Ph)(SiMe_3)$ [205]. Using these reactions the first α,β-acetylenic sulfonamide, $Me_3SiC{\equiv}CSO_2NH_2$, was synthesized [206].

We have also shown that ethynylsilanes undergo addition reactions leading to propargylic alcohols [207a]:



$$RC{\equiv}CSiMe_3 + R'CHO \xrightarrow{\text{Lewis acid}} RC{\equiv}C{-}\underset{\displaystyle OSiMe_3}{\underset{|}{C}}HR' \xrightarrow{\text{MeOH}} RC{\equiv}CCHOH{-}R'$$

Allenylsilanes exhibit surprising behaviour, since, in contrast to the common allenes, their reaction involves allenic hydrogen bonded to the carbon which bears the silicon atom, and not an allylic hydrogen [207b].

3.2.4. *Allylsilanes*

As in the vinylsilane series, we described the first sulfonation [*] [194] and acylation [209a] reactions of allylsilanes. We also reported some methoxy-

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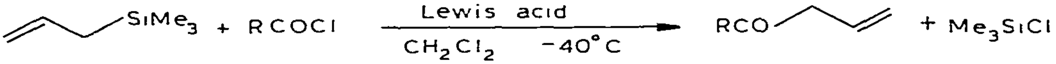
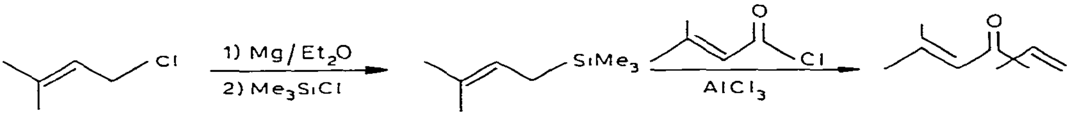
[*] P. Bourgeois, M. Duffaut and R. Calas described the sulfonation of $CH_2{=}CHCH_2SiMe_3$ in 1966 [108].

methylations of these species [209b]. The most remarkable applications of these reactions were:

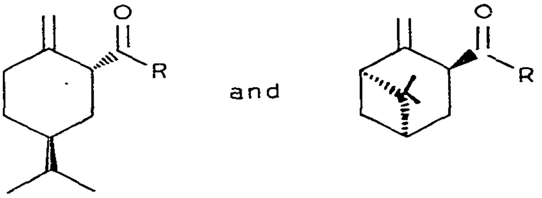
(i) The synthesis of non-substituted allyl ketones (the mild conditions avoid the isomerization to α,β-unsaturated ketones) [210]:



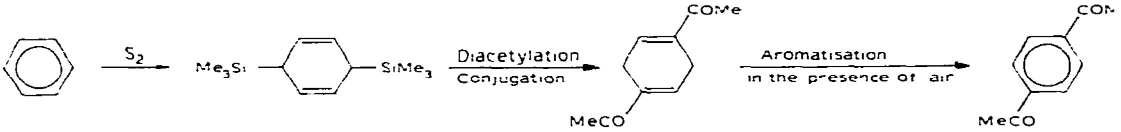
(ii) A two-step synthesis of Artemisia ketone [211] from isoprene hydrochloride and senecioyl chloride:



(iii) A synthesis of novel derivatives of p-menthene or pinene having a double bond in the exocyclic position [212]:



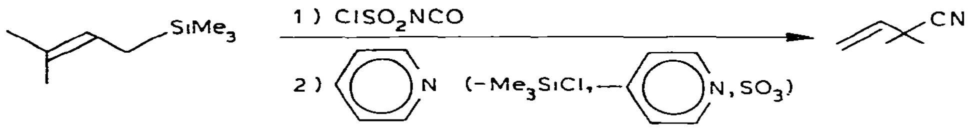
(iv) A two-step p-diacetylation of benzene and p-xylene [213]:

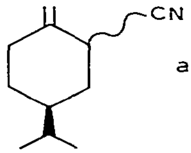


In our studies on electrophilic substitution in the 3-sila 1-cyclopentenes series [195,196,214], the reaction mechanisms were investigated and we provided evidence for the possible competition between the allylic C—H or C—Si bond cleavages.

In the addition reaction series of allylsilanes we described the first allylations of aldehydes and ketones [207a,215]; e.g.:

Moreover we observed addition reactions between allyl- (and even ethynyl-) silanes and chlorosulfonyl isocyanate which provide, via a four membered ring lactame, a regioselective synthesis of β,γ-unsaturated nitriles [216a]. E.g.:





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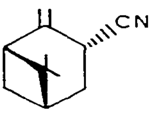


were similarly synthesized [216]

Allylsilanes undergo radical reactions with sulfonyl chlorides (to give allylsulfones and ene disulfones) [186]. Moreover, in the allylsilanes the ene reaction is oriented towards the reaction involving hydrogen bonded to the carbon atom which bears silicon [207].

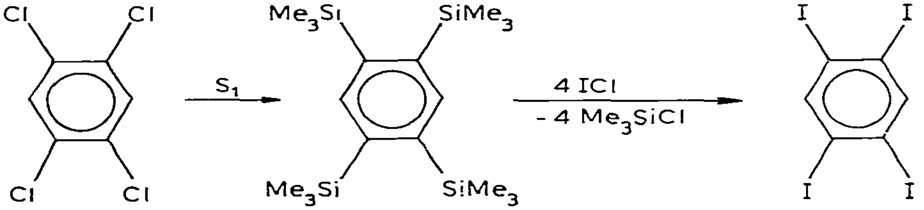
3.2.5. Propargylsilanes

Electrophilic substitution of Me_3Si in propargylsilanes enabled us to synthesize the first trimethylsilyl esters of α-allenic sulfonic acides and related compounds [202,203,205,217] as well as some α-allenic ketones such as $CH_2=C=CHCO\text{-t-Bu}$ [218]. In the addition reaction to chloral we observed a competition between $H—C_{acetylenic}$ and $Si—C_{propargylic}$ bonds in $HC\equiv CCH_2SiMe_3$, whereas with $Me_3SiC\equiv CCH_2SiMe_3$ only the $Si—C_{acetylenic}$ bond was cleaved in accordance with the proposed mechanism [215].

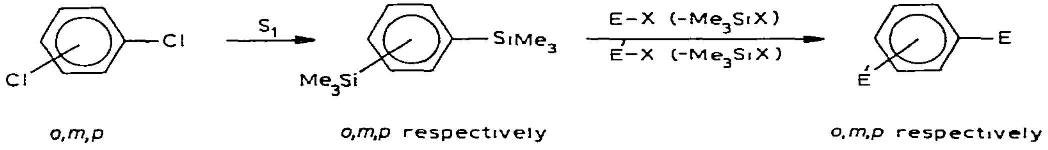
3.2.6. Arylsilanes

Following the initial work of Eaborn [219] we have developed novel electrophilic substitutions in the aromatic series oriented by the position of the Me_3Si group and not by the substitutent effects. Thus:

(i) we reported a convenient route for regioselective mono- and polyiodination of the benzene ring [220]; e.g.,

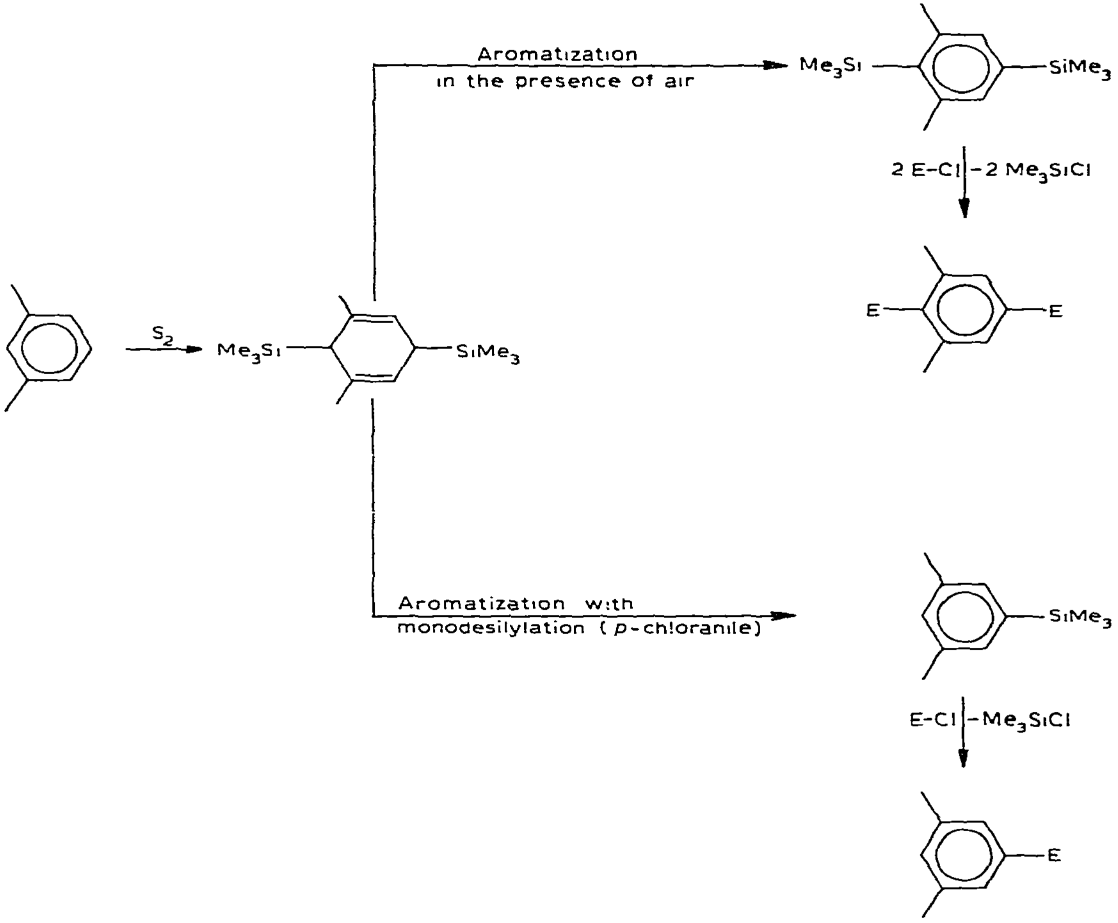


(ii) We described a process for a regioselective bifunctionalization of benzene [221]:

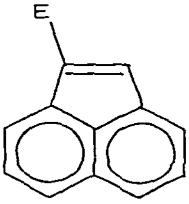


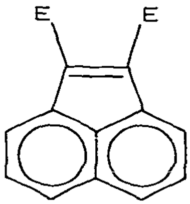
This permitted a two-step *para*-disulfonation of benzene [122] or a practical route to *o*-disubstituted benzenes [221] (e.g. *o*-nitrobenzene sulfonic acid etc.).

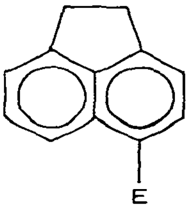
(iii) we carried out non classical 2,5-difunctionalization of toluene or *meta*-xylene and 5-functionalization of *meta*-xylene [222]; e.g.:

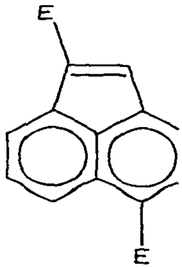


(iv) These methods were extended to the acenaphthylene (or acenaphthene) series, and we prepared various compounds such as [223]:









E : electrophile (reactions involved : halogenation, acylation, sulfonation)*

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* Only sulfonation in the latter case.

3.2.7. *Other compounds*

(a) We have used Me_3SiCH_2COOEt [187b,c] and $Me_3SiCH_2CONEt_2$ [224] as Reformatsky reagents, and from chloral and $Me_3SiCH_2CONEt_2$ we synthesized a compound which exhibits interesting pharmaceutical properties [224]:

$$Me_3SiCH_2CONEt_2 + Cl_3CCHO \xrightarrow[\text{(2) Hydrolysis}]{\text{(1) Addition}} Cl_3CCHOHCH_2CONEt_2$$

(b) We have used Me_6Si_2 [225—227] and Me_4Si [228,229] in methylation reactions. For example Me_6Si_2 converts acyl chlorides or anhydrides into methyl ketones [225—227]:

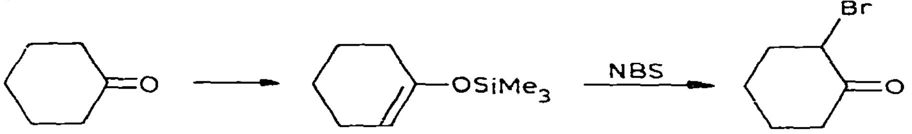
$$Me_3SiSiMe_3 + RCOCl \xrightarrow{AlCl_3} RCOMe + Me_3SiCl$$

Convenient syntheses of methanesulfonic acid have been developed using Me_6Si_2 [227] or Me_4Si [228,229]. Under special conditions Me_6Si_2 can be used for the methylation of Me_3SiCl [230].

The reducing properties of industrial disilane residues were used for the quantitative reduction of triphenyl phosphine oxide [231]:

$$Ph_3P(O) \xrightarrow[\text{disilane residues}]{\text{industrial}} Ph_3P$$

(c) Enoxysilanes were used as intermediates for the synthesis of α-haloketones [232]:



In this Section we have demonstrated that the organosilicon route is fruitful in organic synthesis both for the development of new methods or for the preparation of novel products, most notably for expensive sophisticated derivatives because:

(i) The organosilicon starting materials are readily available and the silicon group can be recovered and recycled.

(ii) The toxicity of organosilicon compounds is very low.

(iii) The organosilicon route needs only very mild conditions and therefore can be used in the case of sensitive species.

(iv) The yields are generally high.

(v) It offers the advantage of regio- (and sometimes stereo-) specificity.

For these reasons we are continuing our investigations in this field.

4. Miscellaneous reactions

4.1. *Investigations concerning disilanes*

We have described new methods of synthesizing mixed disilanes [233] (extended to digermanes [231]) and reported a practical synthesis of $(Me_2Si)_6$ [235]. We have described some reducing properties of disilanes (in addition to the uses mentioned above in Sections 1.3 [62—66], 2.5 [126—128] or 3.2.7

[225—227]). Thus we have observed that various disilanes (Me_6Si_2, $(Et_2MeSi)_2$ $[(MeO)_2MeSi]_2$ reduce some metallic salts (Ni, Cu, Ag, Hg and Fe salts) [236—238]:

$$NiCl_2 + Me_6Si_2 \xrightarrow{reflux} Ni + 2\ Me_3SiCl$$

Disilanes (as well as hydrogenosilanes) were observed to reduce $PhSO_2Cl$ [239] and NBS to give *N*-silylimides and Me_3SiBr [236].

Studies were also undertaken of the recovery and catalytic conversion of industrial disilanes residues into monochlorosilanes [63,240]. Physico-chemical properties of disilanes were investigated [241] and a ^{29}Si NMR study of methylchlorodisilanes is in progress [242].

4.2. *Silanols, siloxanes, alkoxysilanes*

We have devised a synthesis of silanediols in the alicyclic series [243] and of various functional [24,192,195,196,214,244,245] or nonfunctional [119,194] siloxanes, and of chlorosiloxanes [246]. We have published data on the physicochemical properties of disiloxanes (or digermoxanes) and alkoxysilanes (or germanes) [247]. It should be pointed out that siloxanes having two groups in the 1,3 positions with respect to an α-amino-acid function have been synthesized, and constitute a new class of C-silylated amino-acids [248].

In the heterocyclic series we worked on the synthesis of sila-(or stanna-) oxacycloalkanes [248]. Condensation of organo- (or diorgano-) dichlorosilanes with diols give products which exist either as monomers or dimers [250,251]. We have established rules which allow us to predict the structure of the product to be obtained. We have also studied the action of chlorosilanes on epoxides to produce β-chloroalkoxysilanes [252].

4.3. *Si—N bond containing compounds*

We have described some studies on diaminosilanes [253], silylimides [254] and even a primary hydrogenosilazane [255]. We have also investigated the action of hexamethyldisilazane on benzoyl disulfide [256], and obtained the trimethylsilyl derivatives of benzamide and thiobenzoic acid.

4.4. *Organosilicon compounds containing sulfur*

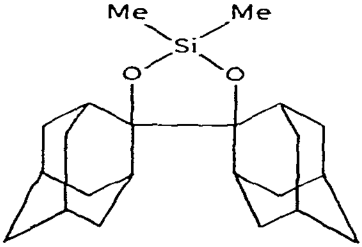
In addition to the previously mentioned publications on trimethylsilylchlorosulfonate, we have developed reactions of bis(silyl)sulfates [170—172], alkyltrimethylsilylsulfates [171,172] as well as silylesters of benzene sulfonic acid [257]. Use of compounds such as $PhSSiMe_3$ was found to allow the conversion of acyl chlorides or anhydrides into the corresponding thioesters [258] and of iminoyl chlorides into thioamides [259]. During these studies we observed the reduction of disulfides either by hydrogenosilanes or even chlorosilanes to give thiols. We also obtained silylesters of thiobenzoic acid from PhCOSSCOPh and hydrogenosilanes or silylamines (in the last the corresponding benzamide are formed [260].).

4.5. *Chlorosilanes and silylated hydrocarbons*

We briefly note here reports not previously mentioned. Chlorosilanes are reduced to the corresponding hydrogenosilanes by some Grignard reagents having reducing properties [261,262]. These reactions were extended to halo derivatives of germanium or tin [262]. The Grignard reagent prepared from chlorobenzene in PhCl as solvent also reduces Me_3SiCl, but it should be noted that $PhSiMe_3$ is formed if small amounts of a basic solvent are added [263]. The mechanisms of all these reactions were investigated.

Various silylated derivatives of chloroacetic esters [264] and *p*-cymene [265] were synthesized, as was $(i\text{-}Pr)_4Si$ which was the object of structural studies [266].

Finally, we note a surprising result observed in the silylation of adamantanone using Me_3SiCl or $Me_2SiCl_2/Li/THF$, which is that Me_3SiCl and Me_2SiCl_2 give the same silylated product [268]:



Formation of Me_4Si when Me_3SiCl is used supports the mechanism proposed for these reactions.

It will be clear from this review that our work was essentially oriented towards organosilicon and organic synthesis, although investigations of reaction mechanisms and structural studies were also undertaken. Our aim was to demonstrate that organosilicon chemistry today constitutes a large and interesting domain in itself and that organosilicon compounds can be versatile reagents or precursors in organic synthesis. The vast number of synthetic possibilities offered by organosilicon chemistry explains its extraordinary development during the last ten years. Our contribution is but one of many, and we see no signs of a slowing down in the future development of this field.

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