

Review

Acylsilanes and Their Applications in Organic Chemistry

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Estudos sobre o emprego de acilsilanos em rotas sintéticas e as novas metodologias de preparação desenvolvidas nos últimos anos, tornaram estes organo-silanos importantes reagentes para síntese de compostos orgânicos. Esta revisão apresenta algumas aplicações recentes e vários métodos desenvolvidos para síntese de acilsilanos.

Current studies concerning the use of acylsilanes in a variety of organic synthetic routes and the improved methodologies of their preparation have turned organosilanes into important reagents for organic chemistry. This review discusses the recent employment of acylsilanes in organic synthesis and also effective methods for their preparation.

Keywords: organosilicon compounds, Brook rearrangement, carbonyl compounds, stereocontrol

Introduction

Acylsilanes (RCOSiR'_3) are compounds that have the silicon directly attached to the carbonyl group, exhibiting unique chemical properties. The use of acylsilanes in organic synthesis has increased significantly over the last few years due to the discovery of valuable new reactions and the improvement of acylsilane synthesis methods. The substantial effect of the electronic properties and the bulk of trimethylsilyl group may be used to control the stereochemistry of reactions¹. One of the well-established uses of acylsilanes in organic synthesis is as an aldehyde equivalent, in which a stereoselective nucleophilic attack on the carbonyl group, α to a chiral center, is followed by stereospecific replacement of the silyl group by hydrogen. Moreover, acylsilanes can be used as ester equivalents for chirality induction, since acylsilanes can be smoothly oxidized to esters. The enantioselective reduction and the cyclization reaction of acylsilanes appear to have substantial synthetic potential. In the first part of this review we present some physical properties of acylsilanes as well as some classical reactions involving organosilicon compounds. In the second part, we present some new work in this area as a complement to the previous reviews²⁻⁷ and finally, in the third part, useful methods of acylsilane synthesis.

Physical properties and classical reactions of the acylsilanes

In the organosilicon compounds class, the acylsilanes

are compounds that present particular physical and chemical properties. The spectral data of acylsilanes are well described in the reviews by Brook² and Page and co-workers³. The inductive effect of the silicon favors the polarization of the carbonyl group, which absorbs at a lower frequency than simple ketones in the infrared and ultraviolet spectra. In ¹³C NMR spectroscopy, the signals for the carbonyl carbon are quite different from the corresponding ketones, appearing at higher δ values. The anisotropy effect and electronegativity differences also lead to higher δ values in the ¹H NMR spectra for hydrogens attached to the α -carbon of acylsilanes (except for α,β -unsaturated). Table 1 shows some examples of IR and NMR spectral data for acylsilanes. Another interesting characteristic of acylsilanes is the abnormally long Si-CO bond (1.926 Å), first observed by Trotter⁸ based on X-ray analysis, which can be compared to the analogous bond length in C-CO (1.51 Å)² compounds. The same authors determined that the carbonyl bond length is essentially normal, despite the low vibrational frequency.

Table 1. Infrared C=O absorption and NMR data of some acylsilanes^{2,3}.

Acylsilane	IR $\nu_{\text{C=O}}$ (cm ⁻¹) ^a	¹³ C NMR δ C=O ^a	¹ H NMR δ CHCO ^a
MeCOSiMe ₃	1645 (1710)	247.6 (215)	2.20 (2.08)
PhCOSiMe ₃	1618 (1675)	233.6 (207)	—
MeCOSiPh ₃	1645	240.1	2.30 (2.01)
PhCOSiPh ₃	1618 (1692)	—	—
t-BuCOSiMe ₃	1636	249.0 (215)	—
Me ₃ SiCOSiMe ₃	1570	318.2	—
PhCH ₂ COSiMe ₃	1635	—	3.77 (3.55)
CH ₂ =CHCOSiMe ₃	1641	237.0	6.28 (6.88)

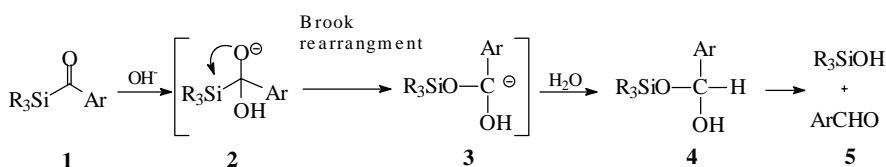
^aValues in parenthesis are for analogues in which the silicon atom has been replaced by carbon.

Studies have shown that acylsilanes in general behave as ordinary ketones. However, in some cases, these compounds have abnormal chemical behavior. Due to the intrinsic properties already mentioned, these compounds should undergo many unusual reactions. For example, in reactions of aroylsilanes with nucleophiles, the Brook rearrangement⁹ is very common. An example is the known hydrolysis of aroylsilanes **1** to the corresponding aldehydes **5**, promoted by traces of OH⁻ (Scheme 1).

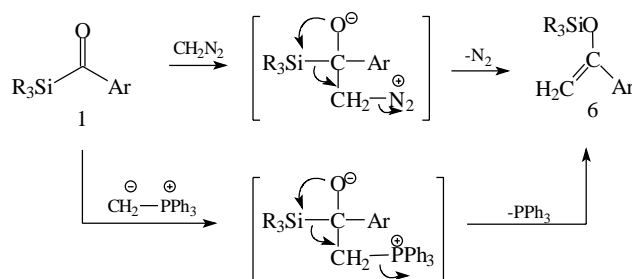
The Brook rearrangement, after carbonyl addition of a nucleophilic reagent, is commonly observed in aroylsilanes due to the relative stabilization of the carbanion intermediate **3** by the aromatic ring. Two classical examples in this context are presented in Scheme 2, where the silyloxyalkene **6** is formed only when an anion-stabilizing group is attached to the carbonyl group².

Brook investigated the great reactivity of acylsilanes

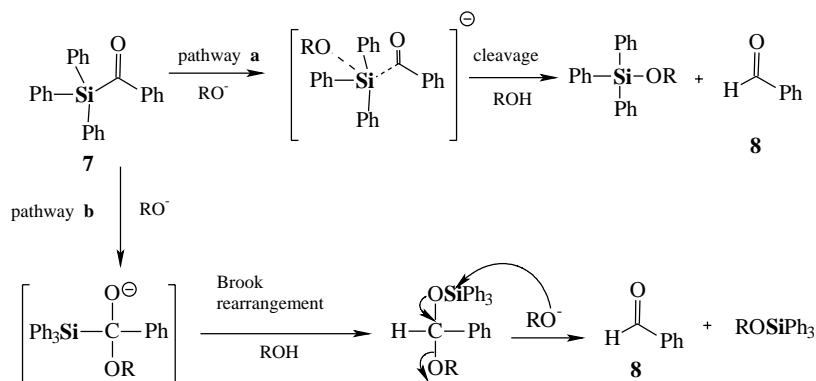
towards nucleophilic addition^{9,10}. His work is historically important because it led to a better knowledge of the reaction pathway. A nucleophilic attack of alkoxide ion on the silicon atom of acylsilane **7** was initially proposed for the formation of aldehyde **8** (Scheme 3, pathway a). Later, Brook proposed another competitive pathway, which involves a nucleophilic attack by the alkoxide ion at the carbonyl group of **7** (Scheme 3, pathway b). Using the optically active acylsilane (-)-**9** in reactions with different alkoxide ions, **10** was reduced by LiAlH₄ to give (-)-**11** (Scheme 4). Although the optical purities of (-)-**11** were observed to be dependent on the bulk of the alkoxide ion (EtO⁻ 22% vs. *t*-BuO⁻ 65%), in all reactions with chiral acylsilane (-)-**9** the enantiomer (-)-**11** was predominant, showing the retention of configuration at silicon. Therefore the bulkier alkoxides find it more difficult to attack at silicon and, consequently, the attack at the carbonyl group becomes relatively easier¹¹.



Scheme 1.



Scheme 2.



Scheme 3.

Schemes 5 and 6 show recent examples of acylsilane reactions involving the Brook rearrangement. The acylsilane **12** reacts with amines to form the imine **13** or amins **14**¹². The acylsilane **15** reacts with cyanide anion under liquid-liquid ($\text{CH}_2\text{Cl}_2\text{-H}_2\text{O}$) phase-transfer catalytic conditions to form O-silylated cyanohydrin **17**¹³.

Novel work involving acylsilane chemistry

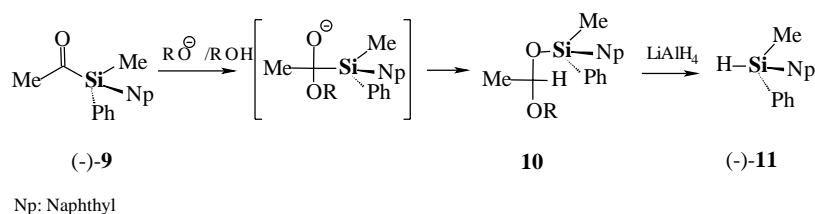
Herein some of the most important synthetic applications of acylsilanes will be presented, focusing especially on reports of the last ten years.

a. Stereocontrolled nucleophilic additions

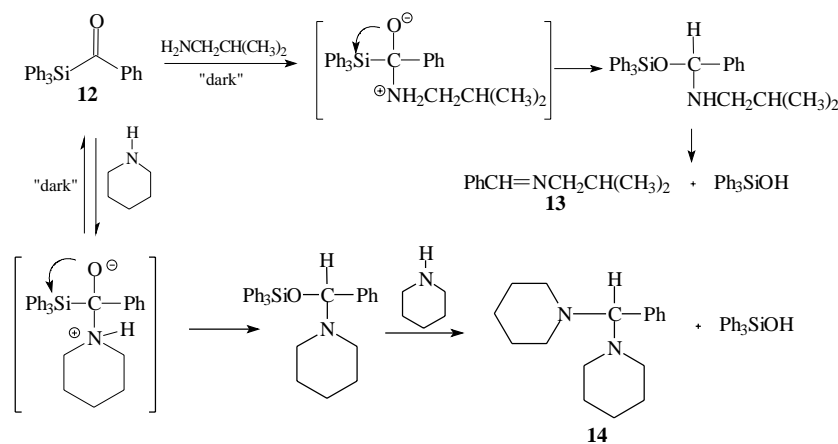
The first study involving enantioselective addition to acylsilanes was reported by Mosher¹⁴ in which he used an

optically active Grignard reagent to reduce benzoyltriphenylsilane and benzoyltrimethylsilane in low enantiomeric excess. Due to the relative facility that the silyl moiety can be removed and replaced by hydrogen, generally by the action of fluoride ion, acylsilanes can be considered as aldehyde equivalents in nucleophilic additions. Addition of nucleophiles can occur with a high Cram selectivity when the chiral center in the acylsilane is on the α -carbon, as in **18** (Scheme 7), and even in some cases where the chiral center is on the β -carbon¹, as in **19** (Scheme 8).

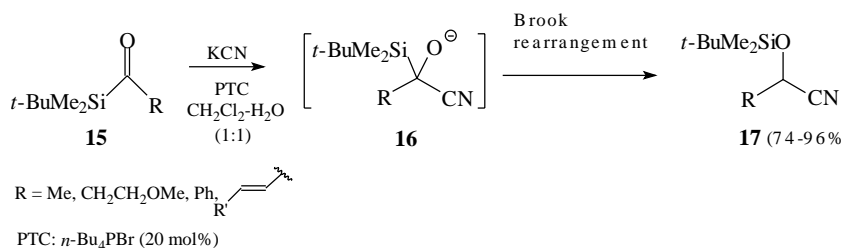
In general, the protodesilylation (replacement of the R_3Si moiety by H) occurs with a high level of stereoselectivity through the Brook rearrangement¹⁵. Two recent examples are shown in the Schemes 8 and 9 in which high stereocontrol was obtained in asymmetric induction in the syntheses of calcitriol lactone derivatives **20**¹⁶ and β -aminoalcohols **21** and **22**¹⁷. Scheme 10 illustrates a key



Scheme 4.



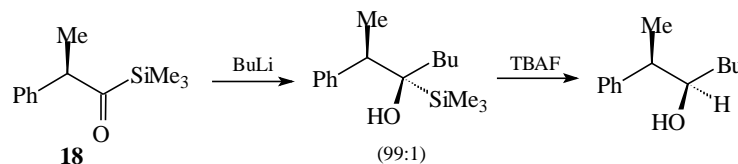
Scheme 5.



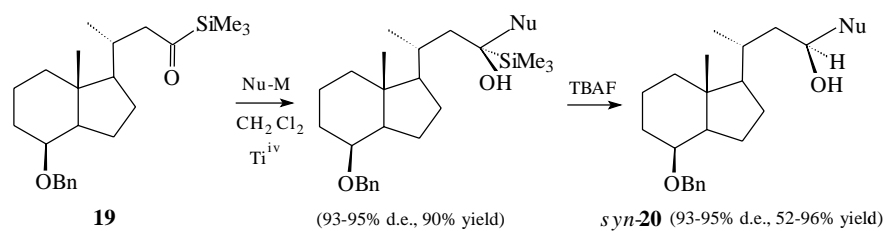
Scheme 6.

step of Corey's total synthesis of pentacyclic triterpene **24** of the β -Amyrin family¹⁸. The addition of 2-propenyl-lithium to acylsilane **23**, followed by a Brook

rearrangement and coupling with allylic bromide, resulted in the *Z*-olefin in an overall yield of 82% with excellent stereoselectivity (> 95%).

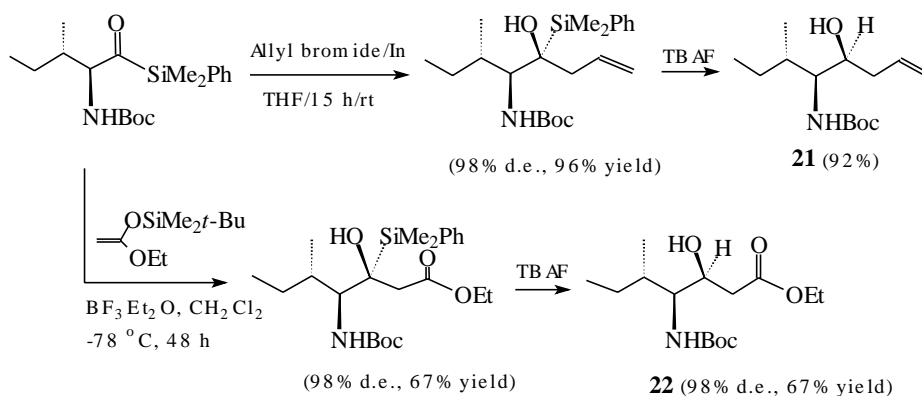


Scheme 7.

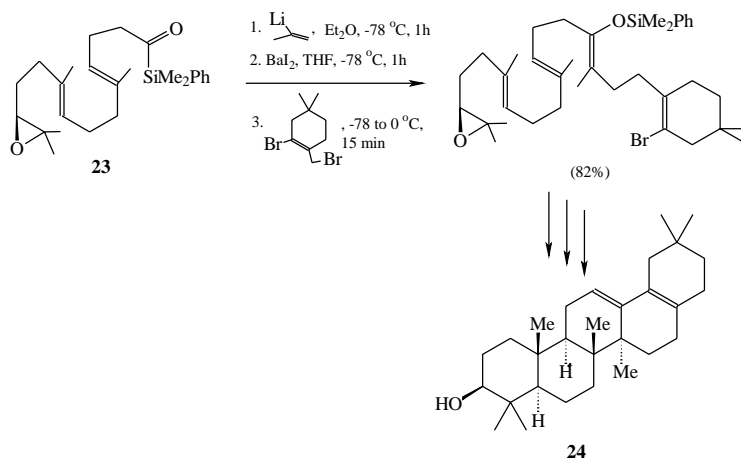


Nu-M = Allyl-SiMe₃, Methallyl-SiMe₃

Scheme 8.



Scheme 9.



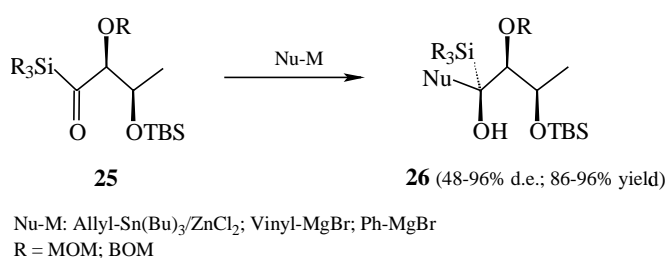
Scheme 10.

Syn- α -alkoxy-(β -silyloxy)acylsilanes **25** undergo chelation-controlled addition reactions with vinyl and phenyl Grignard reagents affording all-*syn* triols **26** with diastereoselectivities up to >98:2 (Scheme 11)^{19,20}.

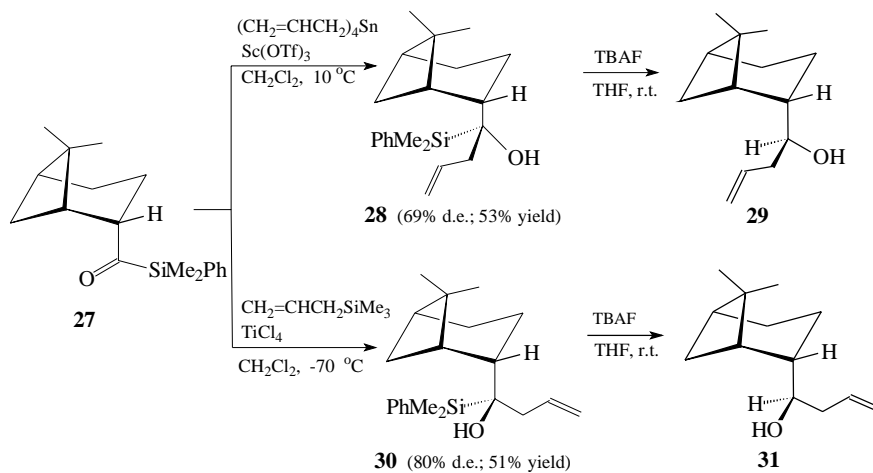
The allylation reaction of acylsilane **27** has been applied to a stereoselective synthesis of allyl myrtanols **29** and **31** (Scheme 12)²¹. In this case, the reaction of **27** with tetraallyltin/Sc(OTf)₃ provides an asymmetric induction opposite to that observed by using allyltrimethylsilane/TiCl₄. The configurations of **28** and **30** were tentatively assigned taking into account that the protodesilylation generally proceeds with complete

retention of configuration^{15,22}. The B-allyl(diisopinocampheyl)-borane has been also used for asymmetric allylation of acylsilanes **32** (Scheme 13)²³.

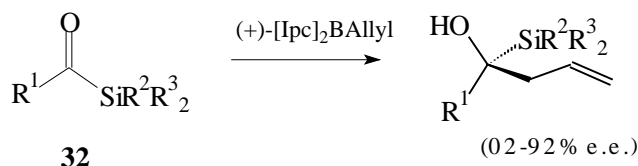
The addition of alkyl and phenyl lithium^{24,25} or Grignard reagents (Scheme 14)²⁶ to acylsilanes **33** having a chiral center at silicon is also diastereoselective. High diastereoselective excesses are obtained with Grignard reagents by means of a chelate-controlled reaction pathway involving intermediate **34** (Scheme 15)²⁴. Cyclopropanediol monosilyl ethers **36** and **37** are obtained with good diastereoselectivity from reaction of benzoylsilane **35** with lithium enolates derived from methylketones (Scheme 16)²⁷.



Scheme 11.



Scheme 12.



R¹ = 4-CF₃-C₆H₄, 4-Me-C₆H₄, cyclopentyl

R², R³ = Me, Et, Ph

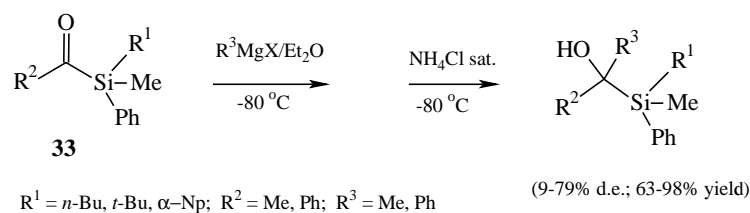
(+)-[Ipc]₂BAllyl: (+)-B-allyl diisopinocampheylborane

Scheme 13.

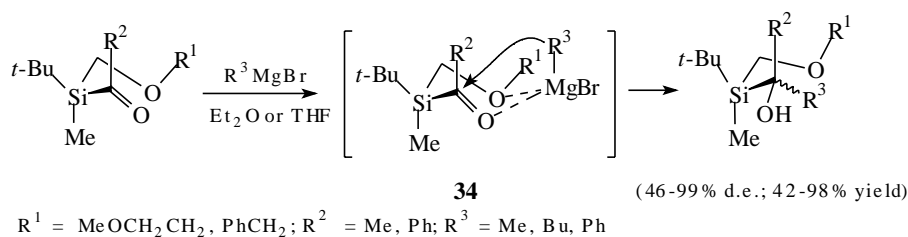
Ethynyl triphenylsilyl ketone **38** undergo stereospecific Michael addition with silylated nucleophiles²⁸, dialkylcuprates²⁹ and tributylstannyl-cuprate³⁰ to afford only one double bond isomer of β -functionalized propenylsilanes depending on the type of nucleophile used. An interesting application of these reactions is the preparation of a variety of α,β -unsaturated acylsilanes **40** by reaction of **38** with trimethylsilyl iodide yielding **39**, which undergoes stereospecific palladium-catalyzed coupling with tin compounds (Scheme 17)³¹.

b. Stereocontrolled aldol reactions

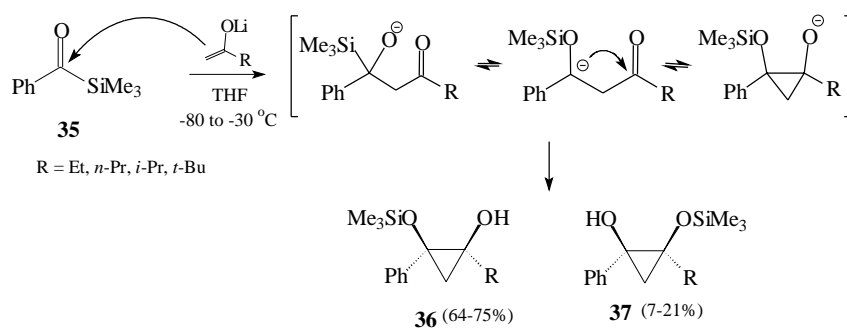
Lithium enolates of propanoyl silanes **41** react with aryl and alkyl aldehydes to afford mainly *syn*- β -hydroxyacylsilanes **42**, which can be converted into **43** as the major product (Scheme 18) in 31-68% overall yields³². While benzaldehyde gives a modest *syn/anti* ratio, isobutyraldehyde gives good diastereoselectivity (*syn/anti* > 20). Aldehydes having a chiral center on the α -carbon react with **41**, giving **44** in good diastereoselectivity.



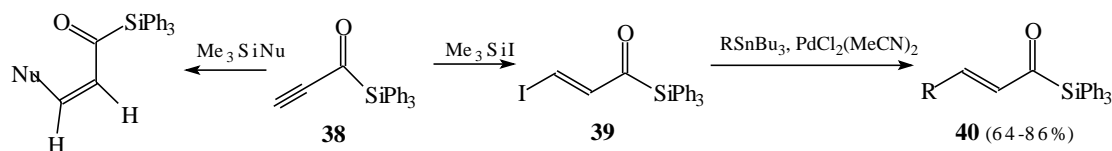
Scheme 14.



Scheme 15.



Scheme 16.



Nu = H₂N, MeNH, SPh

R = Me₃SiC≡C, CH₂=C(OEt), CH₂CH, 2-furyl, BOCNHCH₂CH=CH, Ph₃SiCOCH=CH

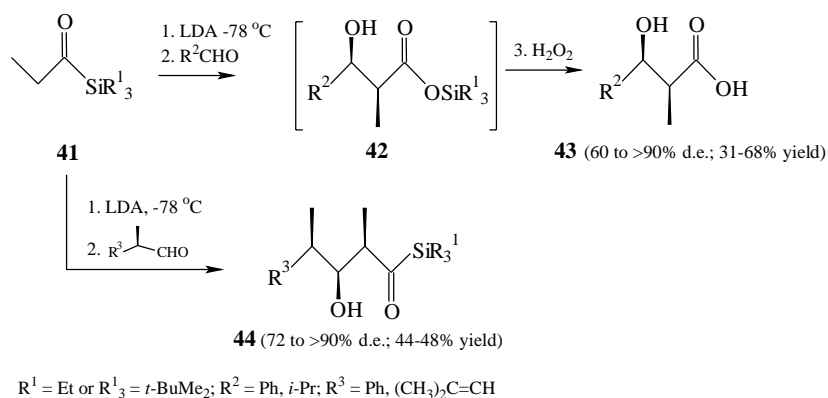
Scheme 17.

Stereoselective intramolecular aldol reaction was performed with bis-acylsilanes under Lewis acid activation to give *cis*- β -hydroxyacylsilanes³³.

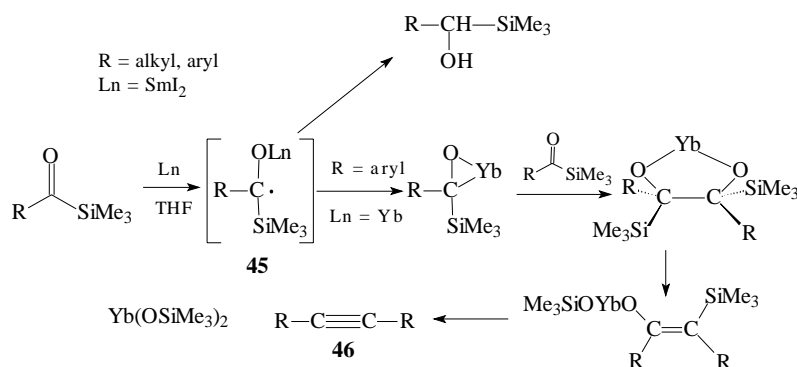
c. Acylsilanes in radical reactions

Lanthanoids, especially ytterbium and samarium, promote several kinds of reactions with alkanoyl and aroylsilanes. The mechanism of these reactions is always dependent on the metal and on the group attached to the carbonyl group (Scheme 19). An interesting point is the

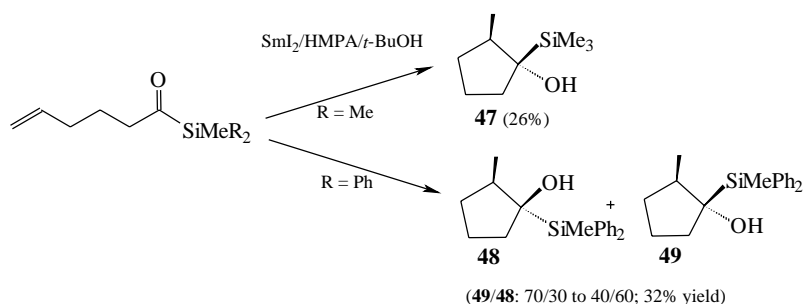
production of acetylene derivatives **46**, which are probably formed by the addition of a silyl-radical **45** to another acylsilane molecule and involve two consecutive Brook rearrangements³⁴. Other reactions such as intramolecular radical cyclization reactions of acylsilanes (Scheme 20), aldol reactions (Scheme 21) and pinacol couplings (Scheme 22) take place mediated by SmI_2 ³⁵. The example presented in Scheme 20 shows an interesting *cis*-stereoselectivity observed for the cyclization of the acyltrimethylsilyl group (giving **47**), while the diphenylmethylsilyl group gave poor (**48:49**) stereoselectivity.



Scheme 18.



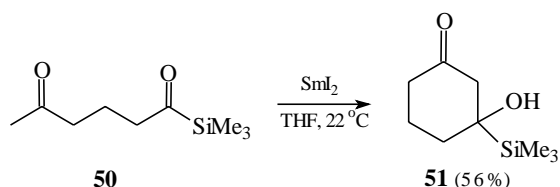
Scheme 19.



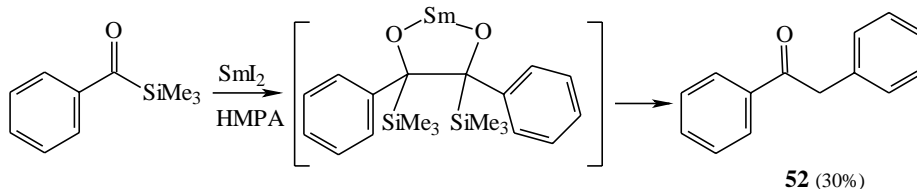
Scheme 20.

Trialkyltin radicals can promote intramolecular cyclization of acylsilanes **53-55** with alkyl, aryl and vinyl radicals, affording cyclopentyl silyl ethers **56** and **57** and enol silyl ether **58** (Scheme 23)³⁶ by a mechanism involving a radical Brook rearrangement, as shown in the example outlined in the Scheme 24^{36c}. An interesting application of the tandem cyclization-addition reaction of acylsilanes is the diastereoselective

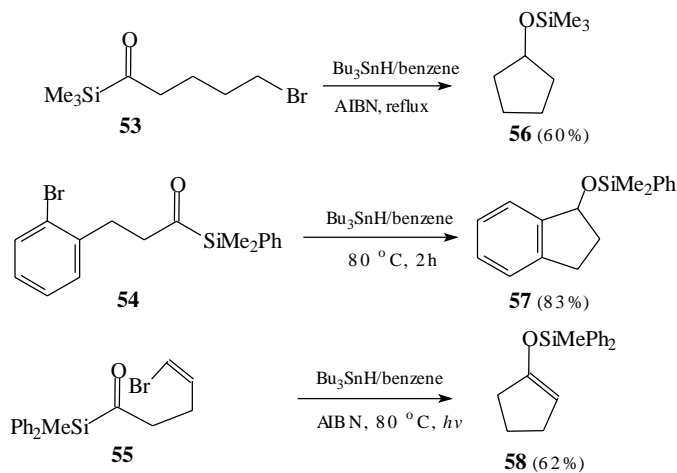
synthesis of *endo* bicyclic alcohol **60** from acylsilane **59** (Scheme 25)^{36a}. On the other hand, bicyclic spiro-lactones **62** and **63** are obtained in the reaction of **61** with methyl acrylate and tributyltin hydride or $\text{CH}_2=\text{C}(\text{CO}_2\text{Et})\text{CH}_2\text{SnBu}_3$ (Scheme 26)³⁷. For other examples see Tsai³⁸, including tandem cyclizations with acylsilanes containing C=C or C^oC groups attached at the silicon atom.



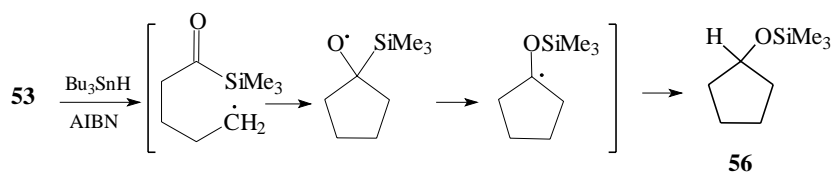
Scheme 21.



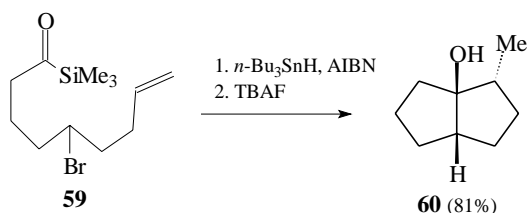
Scheme 22.



Scheme 23.



Scheme 24.

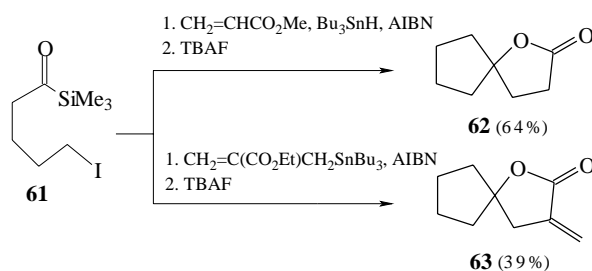


Scheme 25.

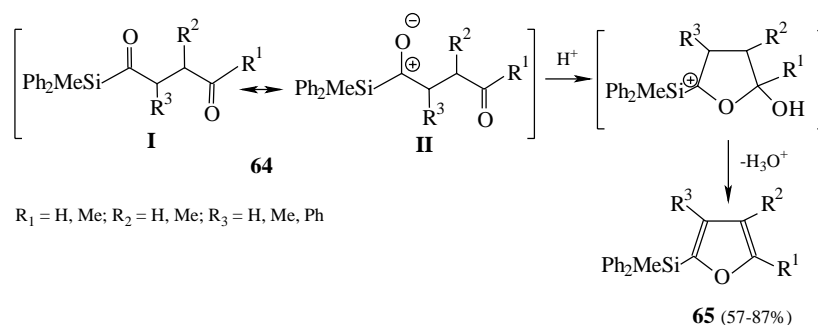
d. Cyclization reactions of acylsilanes

In addition to the examples cited above, many other cyclization reactions involving acylsilanes can be found in the literature. Carbonyl acylsilanes **64** provide furans **65** under milder conditions and in higher yields than the common cyclization reactions of dicarbonyl compounds. This advantage is derived from the high nucleophilicity of the carbonylic oxygen in acylsilanes, due to the

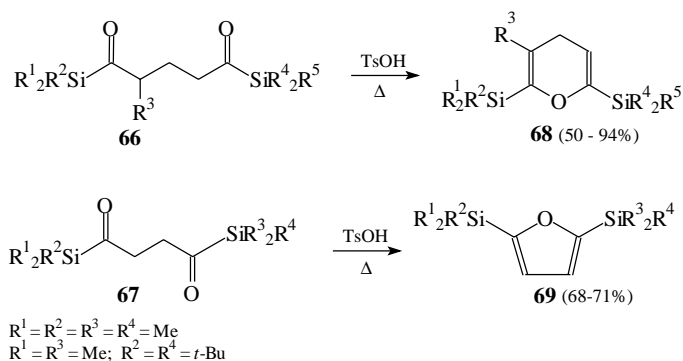
contribution of the polarized resonance form **II** (Scheme 27)³⁹. Scheme 28 presents examples of syntheses of disilylhydropyranes **68** and disilylfurans **69** through a similar cyclization of 1,5-bis-acylsilanes **66**⁴⁰ and 1,4-bis-acylsilanes **67**⁴¹ respectively, catalyzed by p-toluenesulfonic acid (TsOH). The nucleophilicity of the carbonylic oxygen in acylsilane is also observed in the cyclization of γ - and δ -haloacylsilanes **70** affording **71** in reasonable to good yield (Scheme 29)⁴².



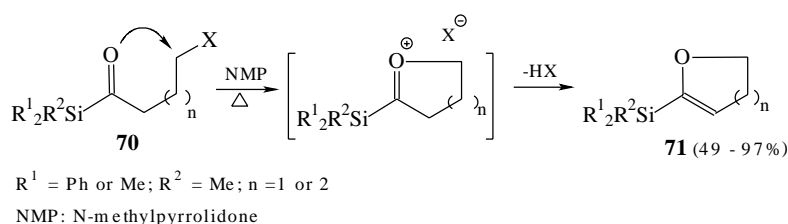
Scheme 26.



Scheme 27.



Scheme 28.



Scheme 29.

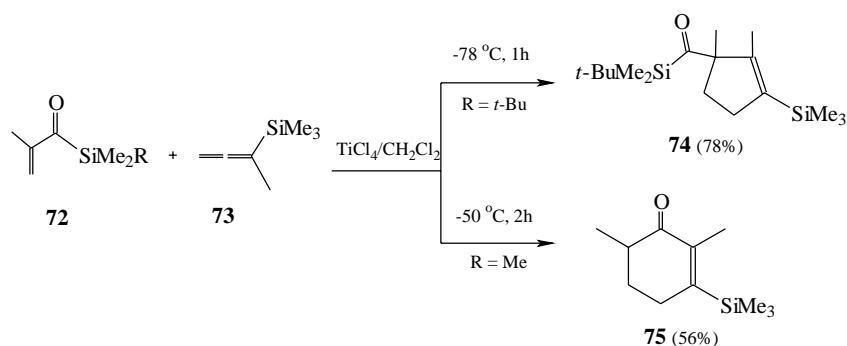
α,β -Unsaturated acylsilanes **72** combine with allenylsilanes **73** in presence of TiCl_4 to produce [3+2] or [3+3] annulation products **74** and **75** in good yield. The course of the annulation reactions can be controlled to produce either five- or six-membered rings by controlling the reaction temperature or by using an appropriate trialkylsilyl group in **72** (Scheme 30)⁴³, since the initially produced cyclopentene undergoes rearrangement at higher temperatures.

On the other hand, α,β -unsaturated acylsilanes **76** and lithium enolates of α,β -unsaturated methyl ketones **77** afford interesting [3+4]-annulation products **78** (Scheme 31)⁴⁴. These stereospecific reactions were proposed to occur by a concerted anionic oxy-Cope rearrangement through cyclopropanediolate intermediate **80**. The addition of cyanide

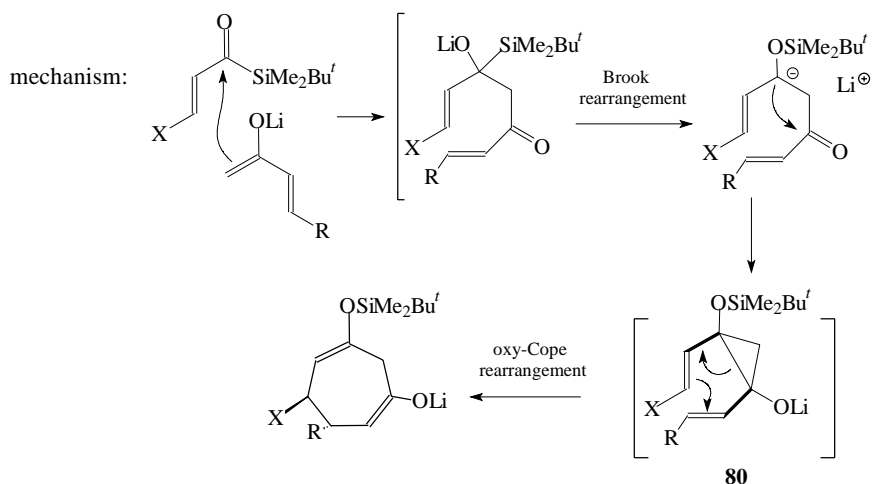
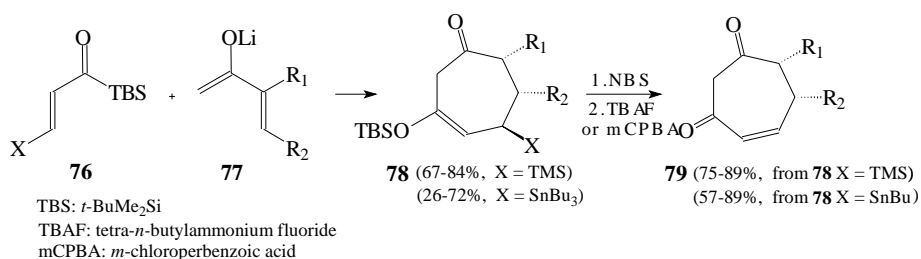
anion^{13,45} to acylsilane **81** (or phenyllithium in an analogous reaction)⁴⁶ produces a cyanohydrin which undergoes a Brook rearrangement, followed by an intramolecular alkylation to give cyclopropane **82** (Scheme 32).

e. Thioacylsilanes: preparation and synthetic applications

The replacement of the C=O with the C=S functionality in acylsilanes is possible by reacting acylsilanes such as **83** with $\text{H}_2\text{S}/\text{HCl}$ or by treatment with $(\text{Me}_3\text{Si})_2\text{S}$ under CoCl_2 catalysis⁴⁷. These highly reactive compounds are employed as unstable thioaldehyde equivalents and also to afford molecules containing the Si-C-S unit or to prepare sulfur heterocycles. Contrary to the thiocarbonyl analogues, the thioacylsilanes as **84** having an α -hydrogen



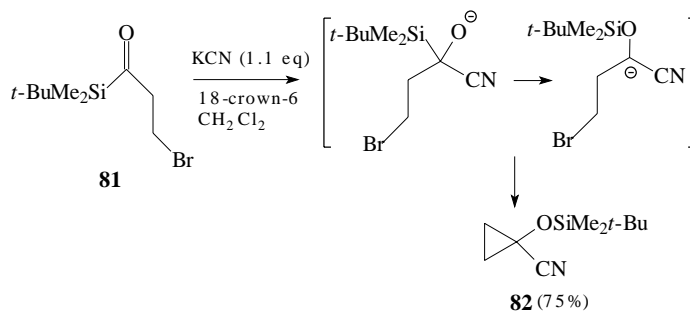
Scheme 30.



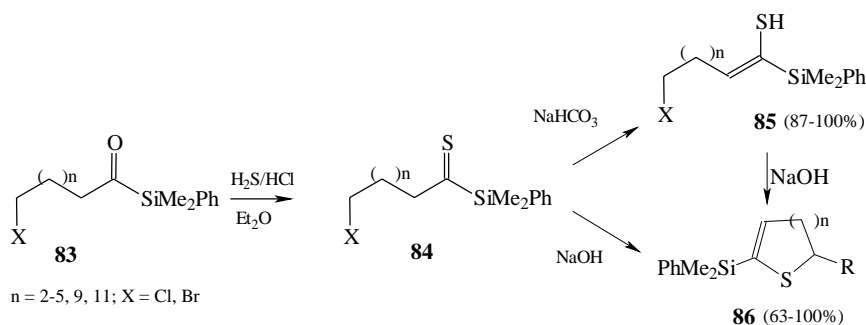
Scheme 31.

bonded to the C=S group exist in the thioenol tautomeric form affording compounds Z- α -silyl vinyl mercaptans⁴⁸, such as **85**. These are interesting molecules because two functional groups with opposite polarization are bonded to a single double bond. An example of these reactions is concisely outlined in Scheme 33 where halothioacylsilanes **84** are cyclized in the presence of a base to provide 2-silylthiocycloalkyl-2-enes **86** in good yields⁴⁹. These compounds react with acid chlorides, such as **88** and **90**, in presence of a Lewis acid to give interesting bicyclic **89**

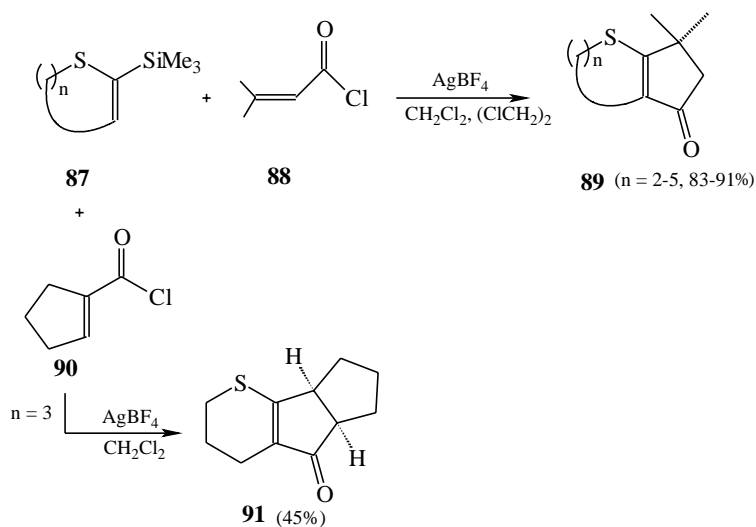
or tricyclic **91** structures depending upon the nature of the alkyl chloride (Scheme 34)⁵⁰. Scheme 35 presents some reactions of thioacylsilanes **92** containing the ferrocene moiety attached to the thiocarbonyl group⁵¹. Unlike ketones and common acylsilanes, which need long reaction periods and high temperatures for replacement of the C=O with the C=S functionality, acylsilanes containing ferrocene are converted readily into thioacylsilanes by Lawesson's⁵² reagent in high yields in a few minutes at room temperature.



Scheme 32.



Scheme 33.

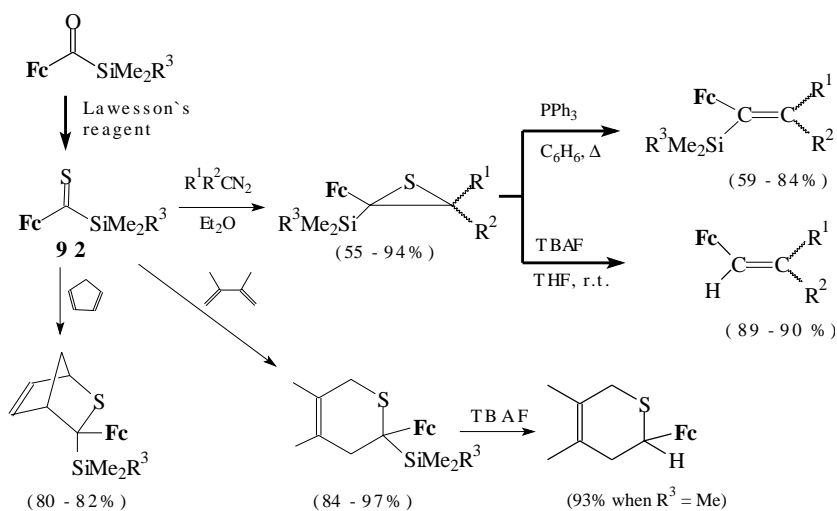


Scheme 34.

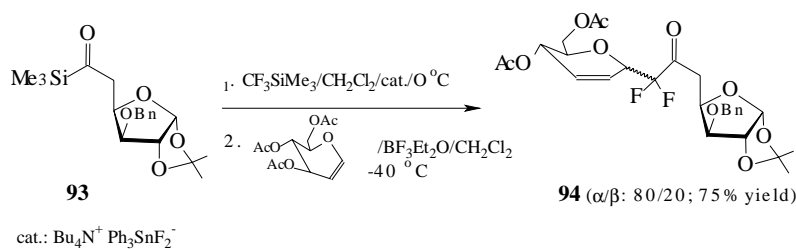
f. Acylsilanes derived from natural products

We have already described the application of acylsilanes for the synthesis of a pentacyclic triterpene, vitamin D₃ metabolites and in aminoalcohol synthesis. However, the use of acylsilane moiety in natural product synthesis is still very restricted and few examples are found in the literature. Scheme 36 shows an “acylsilane-sugar” **93** as the starting material to prepare C-difluorosaccharide **94**. Sugar chemistry may be a good option for the preparation of optically active silanes, little explored to date⁵³. The proposed mechanism of this condensation of the saccharides is based on the highly reactive

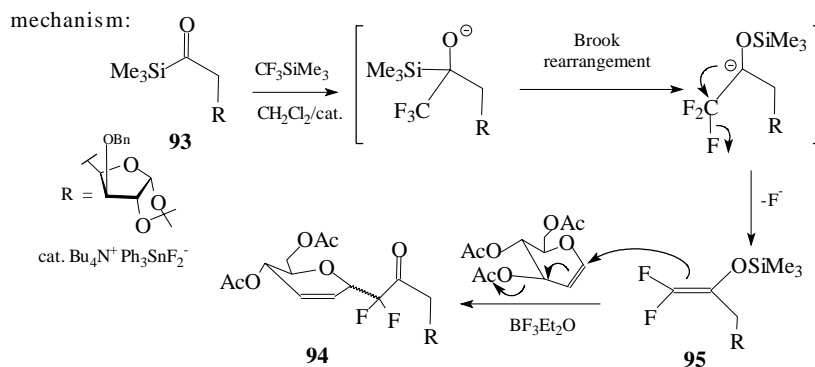
difluorosilyl enol ether **95**, formed by the reaction of acylsilane with trifluoromethylsilane, followed by Brook rearrangement and the subsequent loss of fluoride ion, as outlined in Scheme 37⁵⁴. The reaction of acylsilanes with trifluoromethyltrimethylsilane has been utilized to afford alicyclic 2-fluoro-1,3-diketone⁵⁵, 2,2-difluoro-1,5-diketone⁵⁶ and “difluoro-artumerone” **97**⁵⁷, a sesquiterpene derivative with antitumor activity, as shown in Scheme 38. The stereoselective synthesis of β- and γ-amino alcohols **100** and **101**, starting from a natural aminoacid and proceeding through the homochiral aminoacylsilanes **98** and **99**, reveals the great potential of these compounds as chiral building blocks (Scheme 39)⁵⁸.



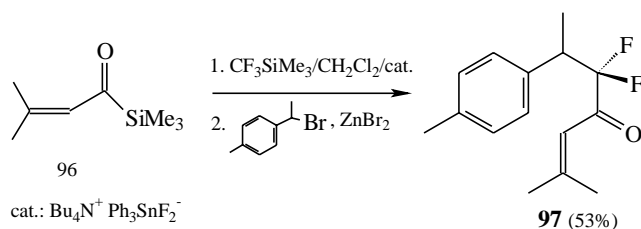
Scheme 35.



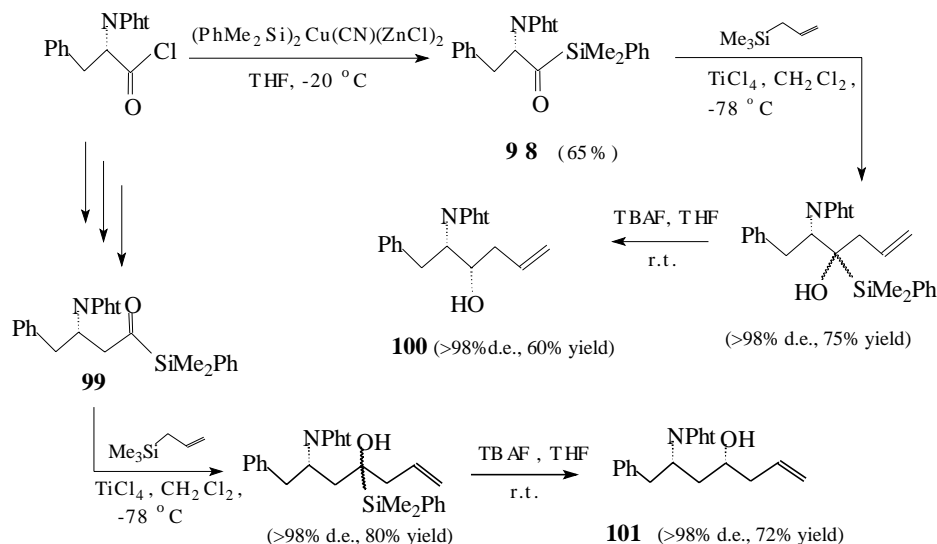
Scheme 36.



Scheme 37.



Scheme 38.



Scheme 39.

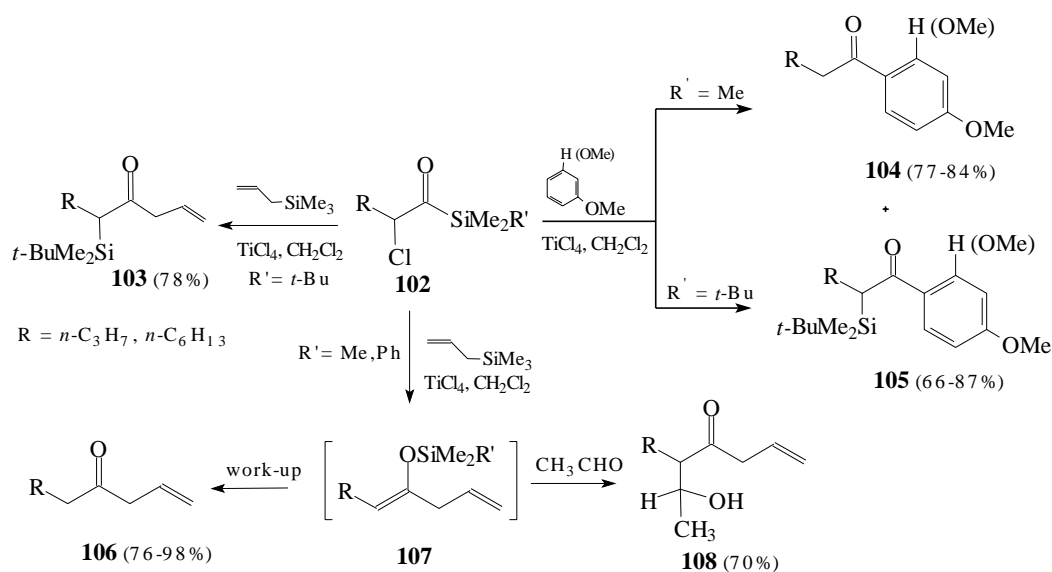
g. Reactions of α -haloacylsilanes

In spite of α -haloacylsilanes being little known, their reactions are very interesting due to a variety of products that they provide. Ketone enolates usually react with α -chloroacyltrimethylsilane under mild reaction conditions to give the corresponding 1,3-dicarbonyl compounds⁵⁹. Titanium tetrachloride promotes coupling reactions of α -chloroacylsilanes **102** to afford α -silyl ketones **103**, β,γ -unsaturated ketones **106** and Friedel-Crafts type products **104** and **105** (Scheme 40). The intermediate acyl cation equivalent **109** was proposed to be responsible for the formation of **103** (Scheme 41). An interesting observation in these reactions is the migration of silyl group and subsequent loss of this moiety, which happens when $\text{R}' = \text{Me}$ or Ph , but not *t*-butyl. Apparently, the formation of the intermediate silyl enol ether **107** is difficult when the silyl group is very bulky ($\text{R}' = t\text{-Bu}$). The presence of intermediate **107** was inferred from the aldol type products **108**⁶⁰ isolated upon addition of acetaldehyde to the reaction mixture. Another example involving these α -haloacylsilanes is presented in Scheme 42, where α -bromoacylsilane **110** reacts with zinc in a Reformatsky type reaction giving **111** with high diastereoselectivity⁶¹. The addition of

triethylborane to α -iodoacylsilane provides boron enolate that reacts with aldehydes to give aldol type adducts with good diastereoselectivity in reasonable yields⁶¹.

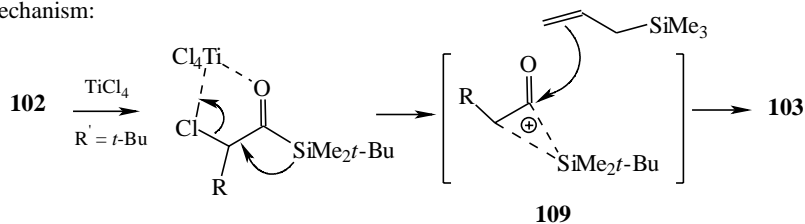
h. Acylsilane oxidation

The acylsilanes have a much smaller oxidation potential than aldehydes and ketones due to the large interaction of the C-Si bond with the lone electron pair of the carbonyl oxygen⁶². This characteristic allows the acylsilanes to suffer oxidation to the corresponding carboxylic acids mediated by peroxides⁶³, ozone⁶⁴ and electrochemistry⁶⁵. The oxidation of acylsilanes has been showing of great importance in organic synthesis, for example in chain homologation⁶⁶ and as a precursor for chiral esters (Scheme 43)⁶⁷. The most common method for oxidation of acylsilanes utilizes peroxides but the electrochemical method, although seldom applied, appears to be advantageous because it permits the direct preparation of acids, esters or nitrogen derivatives, depending upon the additive present during electrolysis. Recently, we introduced a new method for direct esterification of alkyl and arylsilanes by means of iron (III) ion or nitric acid oxidation in dilute alcohol solution (Scheme 44)⁶⁸.

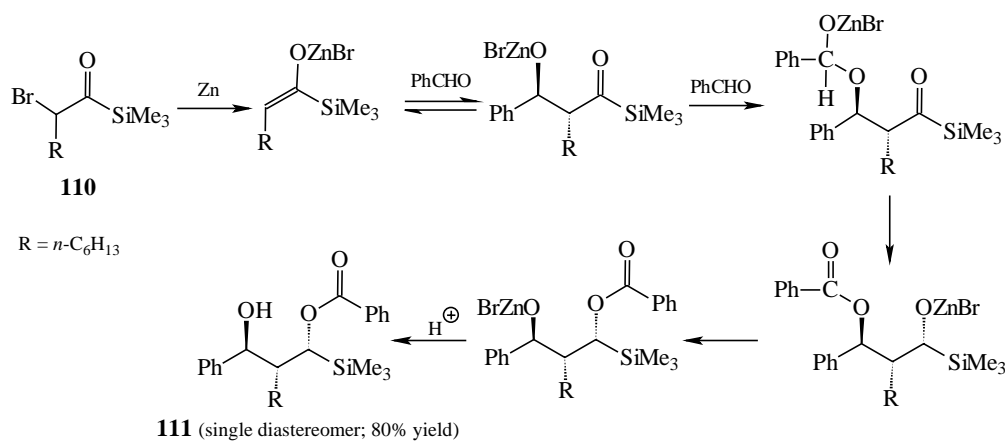


Scheme 40.

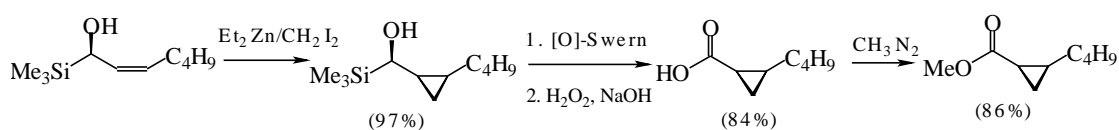
mechanism:



Scheme 41.



Scheme 42.



Scheme 43.

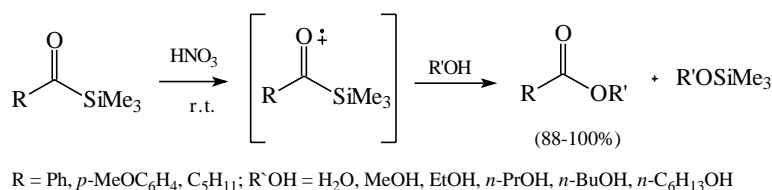
In this context, an important property of the acylsilanes is their oxidation through photoprocesses, affording compounds such as carboxylic acids (promoted by room light)^{69,70} or silylesters **112** and vinyloxysilanes **114** as principal products (Scheme 45)⁷¹. Also see Brook⁷² for other examples of classical photolyses reactions of acylsilanes.

i. Enantioselective reduction of acylsilanes

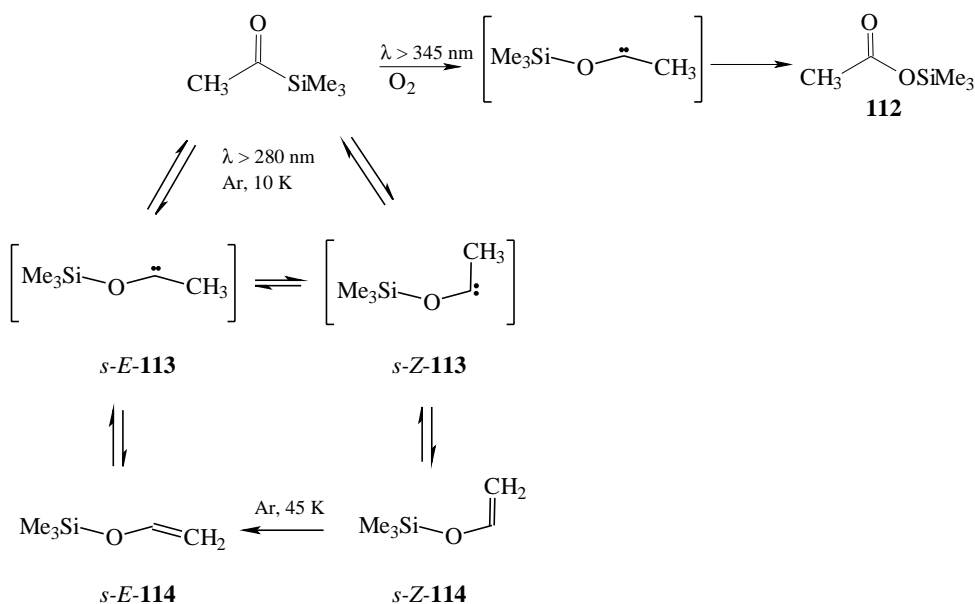
Chiral boranes have been used for enantioselective reduction of acylsilanes affording optically active alcohols (Scheme 46)^{73,74}. Compound **115** was used as homochiral building block in the synthesis of (+)-sesbanamide A²⁰. Scheme 47 shows an interesting reduction of α,β -unsaturated acylsilanes **116**, which is mediated by the chiral lithium amide **117** affording alcohols **118** in excellent enantiomeric excesses⁷⁵.

Because of the higher reactivity of the carbonyl group of acylsilanes compared to the analogous ketones, attributed mainly to the high polarization of the acylsilane carbonyl group, these compounds can react with weak nucleophiles. Therefore, these organosilanes

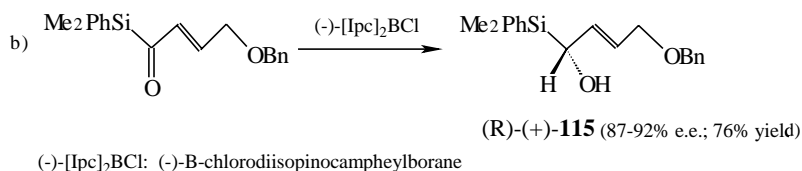
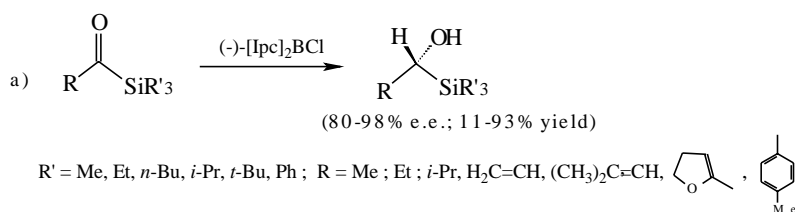
are important substrates for bioreductions, from which the corresponding α -hydroxysilanes can be obtained with high enantiomeric excesses by using a variety of isolated enzymes or microorganisms⁷⁶. Scheme 48 shows one of the first reports of this methodology, the acylsilane **119** being reduced by *Trigonopsis variabilis* 20 times faster than the analogue dimethylphenylpropanone⁷⁷. Although *Saccharomyces cerevisiae* is one of the most commonly used micro-organisms in enantioselective reductions of ketones, it is usually inert toward substrates possessing steric hindrance⁷⁸ or having electron-donating groups attached to the aromatic ring of the aroyl ketone⁷⁹. On the other hand, aroylsilanes such as **121** were reduced by this microorganism, affording the corresponding α -hydroxy-silanes **120** and **122** with enantiomeric excesses varying from 43 to 88%, Scheme 49⁸⁰. The disadvantage in using acylsilane bioreductions is the required lengthy period of reaction, which generally leads to the formation of by-products such as primary alcohols and carboxylic acids from C-Si bond cleavage. A radical oxidation of acylsilanes seems to be responsible for the formation of carboxylic acids⁸¹.



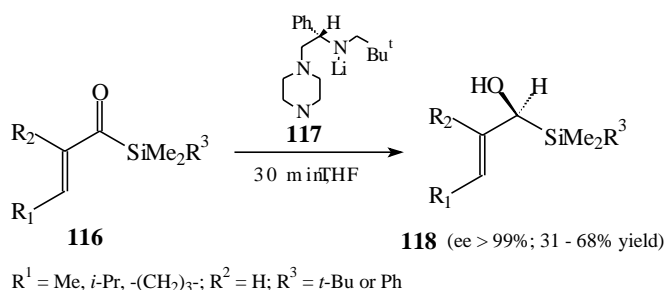
Scheme 44.



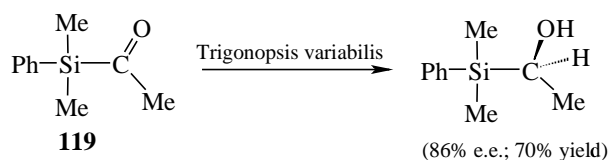
Scheme 45.



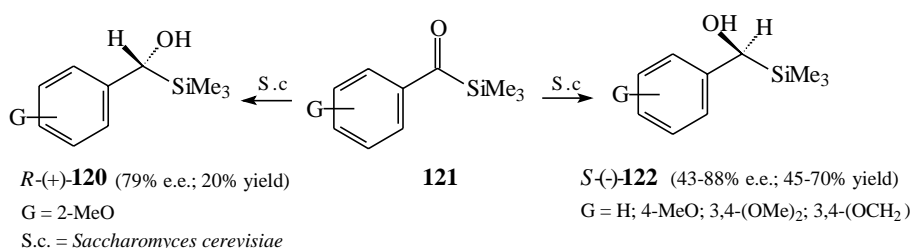
Scheme 46.



Scheme 47.



Scheme 48.



Scheme 49.

In Scheme 50 there is an interesting example of the bio-reduction of a racemic acylsilane (\pm)-**123** containing asymmetric silicon that was applied to afford chiral silyl compounds. Thus, acylsilane $(-)$ -**123**, prepared by oxidation of $(+)$ -**124**, was treated with phenyllithium, the asymmetric silyl group being a chiral inductor. After the Brook rearrangement promoted by KH, the silyl group was removed by tetrabutylammonium fluoride (TBAF), giving the enantiomerically enriched alcohol (R) - $(+)$ -**127**²⁵.

Chiral secondary silyl alcohols may also suffer thermal rearrangements through their acylated derivatives followed by oxidative cleavage^{74,82} that occurs with high stereocontrol⁸³, giving optically active alcohols.

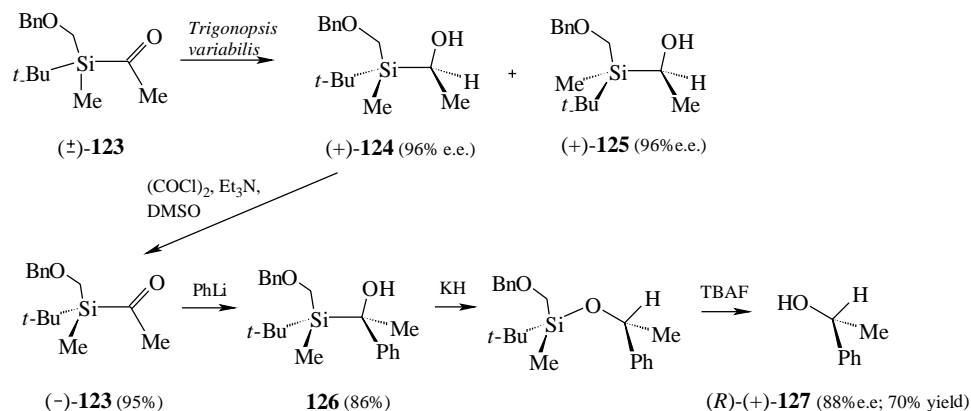
Synthesis of acylsilanes

In 1957, Brook reported the first synthesis of an acylsilane, benzoyltriphenylsilane, which was accomplished by the

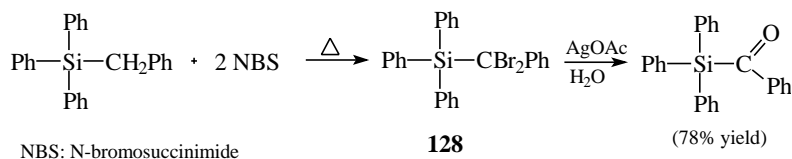
reaction of triphenylsilylpotassium with benzoyl chloride in only 6% yield. The same compound was prepared in much better yield by hydrolysis of dihalide compound **128** (Scheme 51)⁸⁴.

The biggest problem in the synthesis of acylsilanes is the instability of these compounds under many reaction

conditions which may lead to C-Si bond cleavage. In this review, some of the methodologies developed for acylsilanes synthesis will be introduced concisely. A useful summary is presented in the Chart, showing that some of the common organic functional groups may be used for the preparation of acylsilanes.



Scheme 50.



Scheme 51.

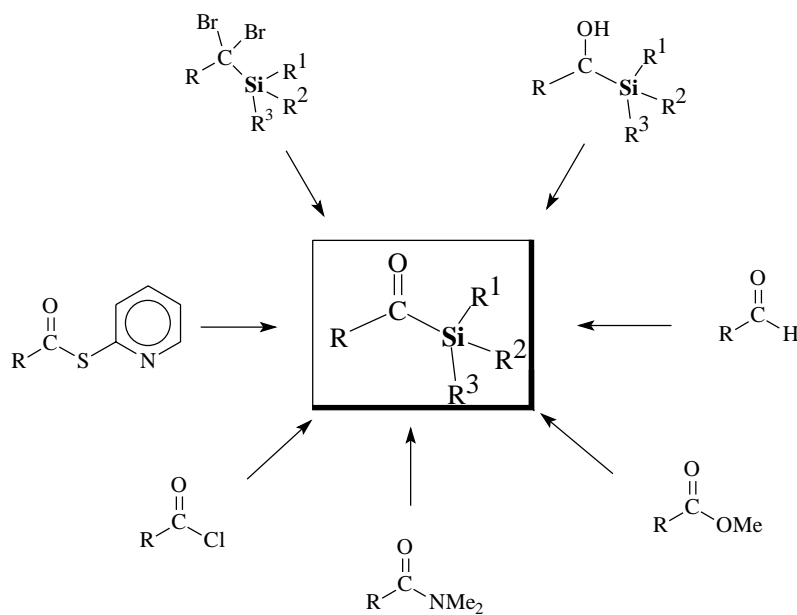


Chart.

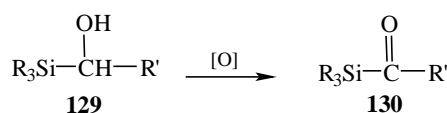
a. From α -silyl alcohols^{2,4}

α -Silyl alcohols can be prepared by several methods, such as the condensation of trialkylsilyl anions with aldehydes⁸⁵ and the transmetalation of trialkylstannanes followed by a reverse Brook rearrangement⁸⁶. The oxidation of α -silyl alcohol **129** with ordinary oxidizing reagents like permanganate and chromic acid leads to acylsilanes **130** (Scheme 52). However, this route has several limitations since Si-C bond cleavage may compete (Scheme 53)², and the products may suffer over-oxidation to carboxylic acids (Schemes 43 and 44). Very mild conditions, such as those present in Swern oxidation, are the most indicated options. In the example showed in Scheme 54^{87,3}, the "reverse Brook rearrangement" (**131**→**132**), followed by a mild oxidation, is employed for the synthesis of α,β -unsaturated acylsilanes **133**. Silylalcohol **135**, prepared by nucleophilic opening of epoxide **134**, was oxidized under extremely mild condition by the use of the Dess-Martin reagent, giving acylsilanes

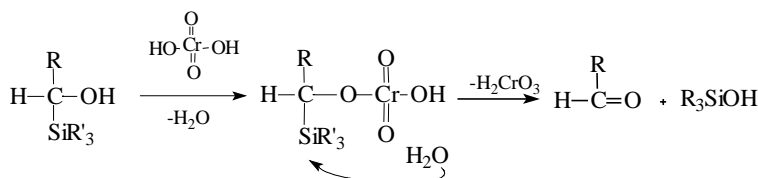
136 in good to excellent overall yields (Scheme 55)⁸⁸. Recently, we have found that potassium permanganate supported onto alumina transforms silylalcohols to aroylsilanes in good yields, without significant Si-C bond cleavage or over-oxidation to carboxylic acid⁸⁹.

b. From masked aldehydes

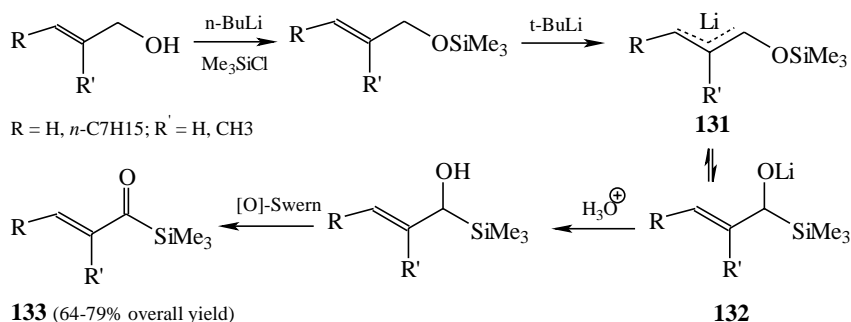
The addition of silyllithium reagents to aldehydes gives α -silyl alcohols, which may be oxidised to acylsilanes as commented above. However, aldehydes **137** are more commonly converted into acylsilanes **139** by the dithiane route (the umpolung methodology⁹⁰, Scheme 56). The hydrolysis of 2-silyl-1,3-dithianes **138** was first investigated in simultaneous work by Brook⁹¹ and Corey⁹², and it is one of the most useful methodologies for acylsilanes synthesis. The great advantage of this method is the variety of compounds that can be prepared, including aroylsilanes, alkanoylsilanes, and functionalized acylsilanes. In general, the first and second steps (Scheme 56) afford products in



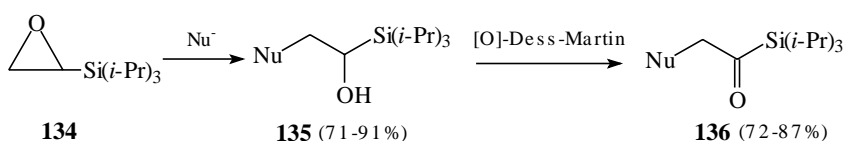
Scheme 52.



Scheme 53.



Scheme 54.



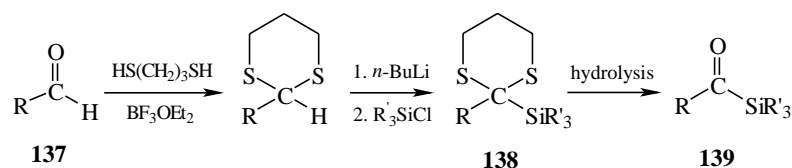
Scheme 55.

high yields, but the hydrolysis step may be problematic. Although there are many procedures for the regeneration of the masked carbonyl group in dithianyl compounds⁹³, the most frequently applied reagents for 2-silyldithianes **138** are mercury salts, the oldest methodology for hydrolysis. Generally, the hydrolysis with mercuric chloride is very slow, thus the product aroylsilanes may suffer degradation, as mentioned earlier. Other methods have been applied for the regeneration of the masked carbonyl group, giving acylsilanes in good yields. Among these, we may mention treatment with methyl iodide⁴¹, chloramine-T³³, I₂/CaCO₃⁹⁴, anodic oxidation⁹⁵ and oxidative hydrolysis mediated by N-bromosuccinimide (NBS)⁹⁶.

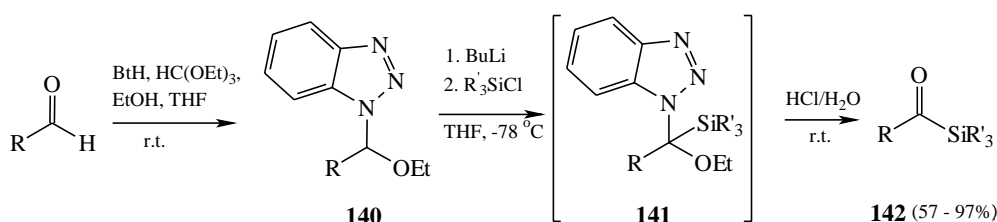
The benzotriazole derivatives **140** present a similar approach to the dithiane methodology, offering advantage in the hydrolysis step. The hydrolysis of intermediate **141** occurs *in situ* and under mild conditions, giving the desired aroyl, heteroaryl, alkenoyl and alkynoylsilanes **142** in excellent yields (Scheme 57)⁹⁷.

c. From esters and amides

The synthesis of acylsilanes by reductive silylation

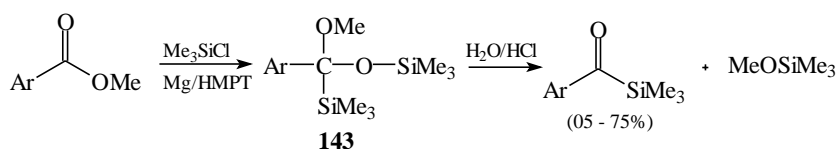


Scheme 56.

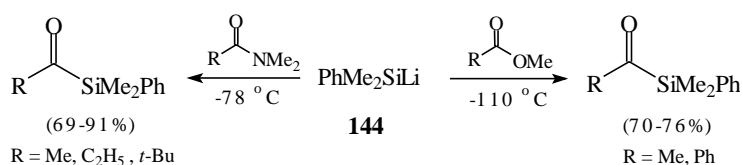


R = aryl and heteroaryl ; substituted alkenyl and alkynyl

Scheme 57.



Scheme 58.



Scheme 59.

is well known and proceeds by the reaction of esters with silyl-Grignard derivatives, forming silylacetals **143** (Scheme 58)⁹⁸. This method generally gives poor yields and hence has been seldom employed. One-pot synthesis of aroylsilanes based on reductive silylation of methylbenzoates using Mg/I₂/chlorosilane/NMP (1-methyl-2-pyrrolidinone) affords aroylsilanes in moderate yields⁹⁹.

Compounds containing lithium attached to the silicon are extremely important reagents in organosilane chemistry. Dimethylphenylsilyllithium (**144**) is probably the most useful silyllithium for synthesis, due to the aryl group that gives good anion stability and to the fact that this reagent can be readily prepared from the corresponding chlorodimethylphenylsilane by its reaction with lithium in THF¹⁰⁰. On the other hand, trimethylsilyllithium is readily obtained by the reaction of hexamethyldisilane with methylolithium¹⁰¹. These compounds react with esters or amides to afford acylsilanes (Scheme 59)¹⁰². Amides appear to be more useful, giving better yields than the traditional reaction with esters, which require much lower temperatures.

In general, the reaction of silyllithium with esters affords disilyl alcohols as undesirable by-products due to double nucleophilic attack at the carbonyl group. However, these alcohols, such as **145**, have been oxidized by PDC (pyridinium dichromate)¹⁰², *tert*-butyl hypochlorite¹⁰³ and lead tetraacetate¹⁰⁴ (Scheme 60) to the corresponding acylsilanes. This latter method was recently reported, and involves a “radical Brook rearrangement” providing acylsilanes in good yield after treatment with silica gel.

d. From S-2-pyridyl esters

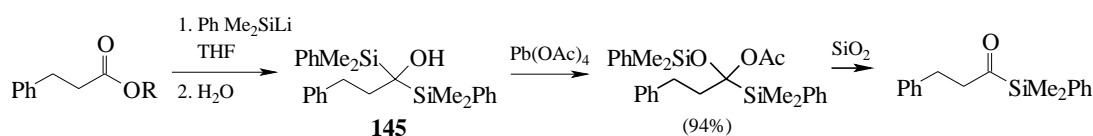
S-2-Pyridyl esters **146** react very smoothly with $\text{Al}(\text{SiMe}_3)_3$ in the presence of CuCN to afford acylsilanes in good to excellent yields (Scheme 61). This method may be applied to substrates having various groups such as alkoxy, acetal, ester, or an isolated double bond. Chiral centers α to the carbonyl group are not epimerized under the reaction conditions¹⁰⁵.

e. From acid chloride

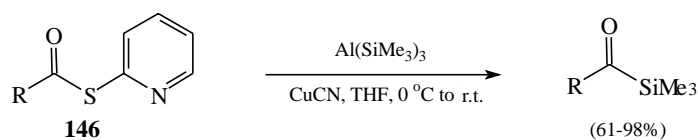
Treatment of silyllithium with acid chloride gives

acylsilanes. However, this procedure is not general due to the complex reaction mixtures that it provides. On the other hand, lithium silylcuprates like **148** react with a variety of acid chlorides, giving acylsilanes with good yields, offering advantages over the silyllithium methodology since fewer by-products are formed¹⁰⁶. These cuprates are traditionally obtained from the reaction of an alkylsilyllithium with CuCN or CuI¹⁰⁷. A limitation of this methodology is that high order cuprates are very reactive towards a variety of functional groups. The mixed Cu-Zn complex **147** is less reactive than ordinary cuprates, and therefore this type of complex has been applied to the synthesis of acylsilanes containing cyano, halo, ester and other groups (Scheme 62)^{6,108}.

Yamamoto and co-workers¹⁰⁹ prepared aroylsilanes by reaction of disilanes (compounds with Si-Si bond) with benzoyl chloride under palladium catalysis. However this method is not suitable for aliphatic acylsilanes, giving low yields of products. The methodology presented in Scheme 63 is a good alternative, providing both aroyl and alkanoylsilanes by reacting the acid chlorides **149** with the polarised Si-Sn bond of **150** (weaker than the Si-Si bond in the disilanes)¹¹⁰.

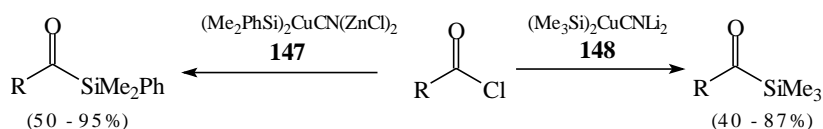


Scheme 60.

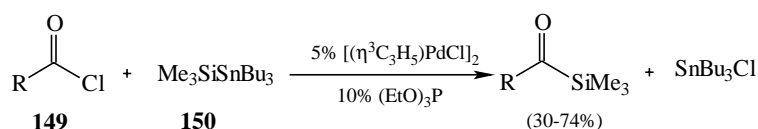


R = C₉H₁₉; Ph; PhCH=CH; TBDMSO(CH₂)CH; BOMOCH₂(CH₂)CH; Ph(CH₂)₃CH

Scheme 61.



Scheme 62.



R = *n*-C₄H₉, *n*-C₇H₁₅, C₄H₉(Et)CH, *c*-C₆H₁₁, Ph, *o*-ClC₆H₄, *p*-CH₃OC₆H₄

Scheme 63.

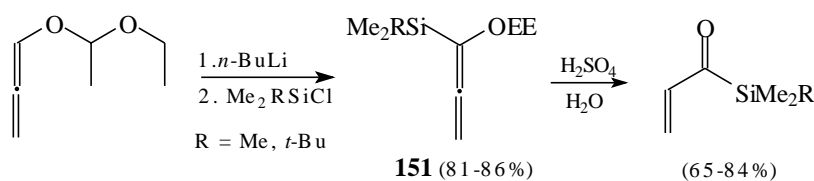
f. From other organic functionalities

The application of α,β -unsaturated acylsilanes as building blocks for organic synthesis is well known in such important reactions as the Diels-Alder one¹¹¹, thermal rearrangements and cyclizations, as commented above. A common method for alkenoysilane synthesis goes through the allenylsilanes **151** and is known as Reich's procedure (Scheme 64)¹¹³. Scheme 65 summarizes another method for the preparation of α -substituted- α,β -unsaturated acylsilanes **155** from silylpropargyl derivative **152** in a methodology involving silyloxy allene formation, a "reverse Brook rearrangement" (**153**→**154**) followed by the addition of an aldehyde.

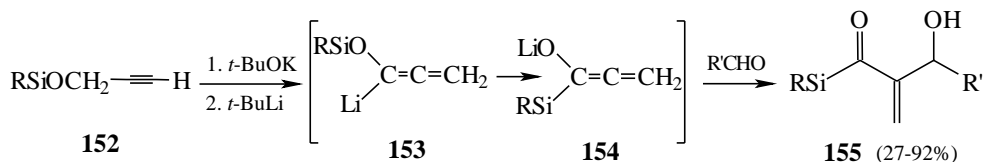
Several methods for the preparation of haloacylsilanes are reported in the literature, such as bromination of silyl enol ethers¹¹⁵ and halogenation of alkyl enol ethers¹¹⁶ with N-bromosuccinimide (NBS) or N-chlorosuccinimide (NCS). The reaction of ketones with silyl carbanion **156**,

which is obtained from an ethereal solution of *t*-BuMe₂SiCHBr₂ and lithium diisopropylamide, provides silyloxiranes **157** which undergo rearrangement, yielding α -bromoacylsilanes **158** in reasonable yields (Scheme 66)¹¹⁷. This method is a recent example of an α -bromoacylsilane preparation, where the formation of 2-silyloxiranes **157** is proposed by the authors, based on a known method for synthesis of α -iodo, α -fluoro, α -bromo and α -chloroacylsilanes **160** from silyloxiranes **159** (Scheme 67)⁶¹.

Acylsilane **164** could be prepared in a one-pot procedure from vinyl ether **161** by the reaction of intermediate **162** with trialkyl silyl chloride in pentane at -78 °C, followed by mild acid hydrolysis of **163** (Scheme 68)^{32,118}. Starting with allylic alcohol **165**, acylsilane **23** was prepared in a one pot procedure (Scheme 69)¹⁸. This acylsilane was used in the Corey's total synthesis of triterpenes as presented earlier in Scheme 10.

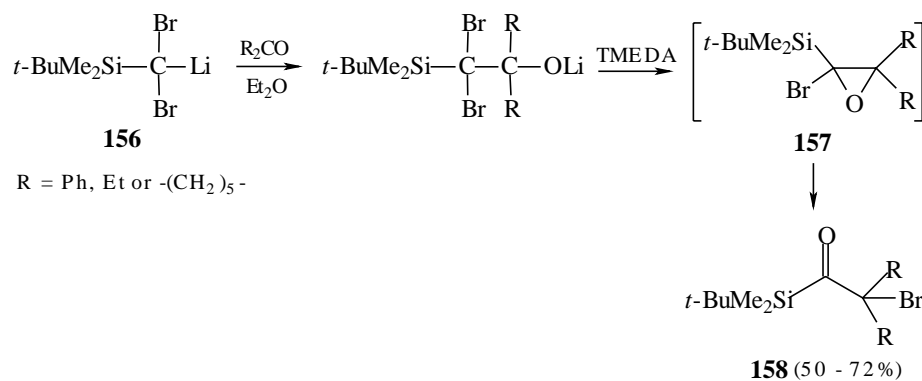


Scheme 64.

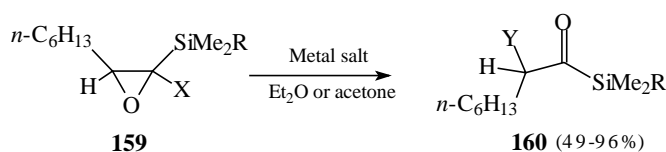


R = TBDM (*t*-BuMe₂) or TIP (triisopropyl)

Scheme 65.

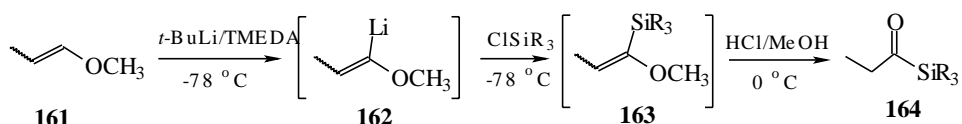


Scheme 66.



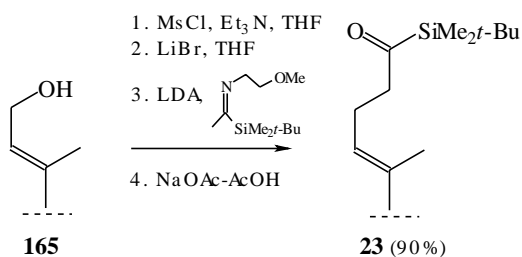
R = Ph, Me, *t*-Bu
 X = Cl or Br
 Y = Cl, Br, I or F
 Metal salts: ZnCl₂, ZnBr₂, NaI, AgBF₄

Scheme 67.



R = *t*-BuMe₂, Et, *n*-Pr

Scheme 68.



Scheme 69.

Conclusion

In this review we have resumed the most significant articles, published in the last ten years, involving acylsilanes, both from the point of view of their preparation and their application as versatile tools in organic syntheses. The research in this area has increased significantly over the last few years due to the discovery of valuable new reactions and the improvement of acylsilane synthesis methods. It is possible to visualise that in the near future the acylsilanes will be a well-known tool for the use of organic synthetic chemists.

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