

REACTIONS OF ALLYLSILANES AND APPLICATION TO ORGANIC SYNTHESIS

Hideki Sakurai

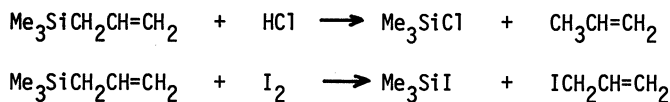
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Abstract - Allylsilanes undergo regiospecific reactions with a variety of electrophilic species, especially with carbon electrophiles to form a new carbon-carbon bond. An electrophile enters on the terminus of the allylic system and the cleavage of the carbon-silicon bond occurs to give a new allylic system in which the double bond is relocated adjacent to its original position. Allylsilanes also undergo conjugate addition to α,β -enones to give δ,ϵ -enones exclusively. High nucleophilicity of the double bond of allylsilanes together with these advantageous features render very useful applications in organic synthesis.

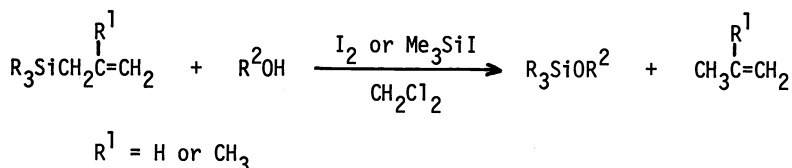
Recently, the use of organosilicon compounds as reagents and as intermediates in organic synthesis has become a field of considerable importance. Especially, useful organosilicon reagents for the carbon-carbon bond formation have been introduced into organic synthesis in the last decade. A variety of reactions of α -silyl carbanions, silyl enol ethers, arylsilanes, vinylsilanes, alkynylsilanes, allylsilanes, benzylsilanes, cyclopropylsilanes, homoallylsilanes and alkylsilanes has been extensively studied and applied to organic synthesis (Ref. 1). The chemistry of allylsilanes has proved that the reagents are particularly useful as applied to synthesis, because the reagents can provide synthetic strategies which may not be achieved with other reagents. Allyltrimethylsilane itself is quite stable toward oxygen and moisture. Generally speaking, organosilicon compounds are biologically inert except for a few examples. A variety of functionalities can be introduced into the allyl group, as demonstrated later in this article, and regiospecific transformation gives a desired product. These are virtues which give allylsilanes the premier place in organosilicon compounds as a synthetic reagent. In this report, reactions of allylsilanes studied mainly in this laboratory are described with emphasis upon application to organic synthesis.

CLEAVAGE OF THE SILICON-CARBON BOND WITH PROTON AND HETEROATOM ELECTROPHILES

Sommer, Tyler and Whitmore reported first the cleavage of the silicon-allyl bond of allyltrimethylsilane with proton and some heteroatom electrophilic reagents such as hydrogen chloride, bromine, iodine and sulfuric acid (Ref. 2). For example,

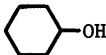
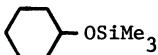
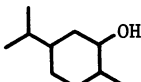
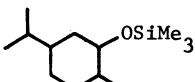
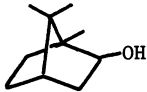
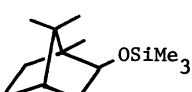
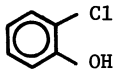
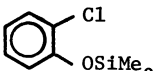


The latter reaction was used for the preparation of iodotrimethylsilane (Ref. 3). The reaction also provides a good method of protection of hydroxy functions when the reaction is carried out in the presence of alcohols, phenols and carboxylic acids in chlorinated hydrocarbon solvents (Ref. 4). A catalytic amount of iodine or iodotrimethylsilane is enough to complete the reaction. Representative results are listed in Table 1.



Silylation of hydroxy group with allylsilanes catalyzed by *p*-toluenesulfonic acid in acetonitrile has also been reported (Ref. 5).

TABLE 1. Conversion of alcohols and carboxylic acids into silyl derivatives with allylsilanes catalyzed by iodine.^a

Starting Compound	Allylsilane	Conditions Temp/°C(time/h)	Silyl ether	Yield(%)
ClCH ₂ CH ₂ OH	Me ₃ SiCH ₂ CH=CH ₂ (1)	60 (0.5)	ClCH ₂ CH ₂ OSiMe ₃	93
<i>n</i> -C ₄ H ₉ OH	<i>t</i> -BuMe ₂ SiCH ₂ CH=CH ₂	70 (1) ^b	<i>n</i> -C ₄ H ₉ OSiMe ₂ - <i>t</i> -Bu	90
<i>i</i> -C ₄ H ₉ OH	Et ₃ SiCH ₂ CH=CH ₂	60 (0.5) ^b	<i>i</i> -C ₄ H ₉ OSiEt ₃	93
HO(CH ₂) ₄ OH	<u>1</u>	60 (2) ^c	Me ₃ SiO(CH ₂) ₄ OSiMe ₃	83
<i>n</i> -C ₈ H ₁₇ OH	<u>1</u>	40 (1)	<i>n</i> -C ₈ H ₁₇ OSiMe ₃	95
<i>n</i> -C ₈ H ₁₇ OH	<u>1</u> ^d	60 (1)	<i>n</i> -C ₈ H ₁₇ OSiMe ₃	93
<i>n</i> -C ₈ H ₁₇ OH	Me ₃ SiCH ₂ C(CH ₃)=CH ₂	40 (1) ^e	<i>n</i> -C ₈ H ₁₇ OSiMe ₃	90
<i>sec</i> -C ₈ H ₁₇ OH	<u>1</u>	60 (2)	<i>sec</i> -C ₈ H ₁₇ OSiMe ₃	90
<i>sec</i> -C ₈ H ₁₇ OH	<u>1</u> ^f	80 (4) ^b	<i>sec</i> -C ₈ H ₁₇ OSiMe ₃	93
	<u>1</u>	30 (1)		93
	<u>1</u>	60 (1)		93
	<u>1</u>	60 (1)		94
PhCH ₂ OH	<u>1</u>	40 (2) ^d	PhCH ₂ OSiMe ₃	92
	<u>1</u>	60 (0.5)		95
<i>n</i> -C ₅ H ₁₁ CO ₂ H	<u>1</u>	60 (0.5) ^c	<i>n</i> -C ₅ H ₁₁ CO ₂ SiMe ₃	87
<i>sec</i> -C ₈ H ₁₇ OH	Et ₂ MeSiCH=CH ₂	80 (3) ^c	<i>sec</i> -C ₈ H ₁₇ OSiMeEt ₂	44

a) All reactions were catalyzed by iodine in CHCl₃ or CDCl₃ unless otherwise noted. b) In neat solution. c) In THF. d) Catalyzed by Me₃SiI. e) In CH₂Cl₂. f) Catalyzed by Br₂.

THE REACTION OF ALLYLSILANES WITH CARBON ELECTROPHILES.

REGIOSPECIFICITY IN THE REACTION

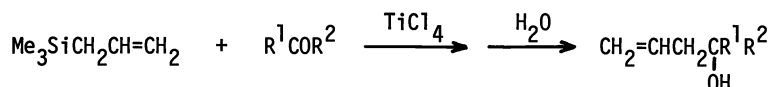
Reactions of allylsilanes with proton and heteroatom electrophiles are sometimes useful for organic conversions, but the formation of a C-C bond is of central importance in organic chemistry. Indeed, allylsilanes can be used for this purpose. We have reported the first carbon-carbon bond forming reactions of allyltrimethylsilane with bromotrichloromethane (Ref. 6). The high reactivity of allyltrimethylsilane compared to other ω-alkenylsilanes toward electrophiles has been noticed in the report.



The high reactivity of allyltrimethylsilane may be explained by $\sigma(\text{Si-C})-\pi$ conjugation (Ref. 7, 8), and we have recognized that allyltrimethylsilane must be a useful intermediate for carbon-carbon bond formation. Therefore, the study on the reaction of allylsilanes has been undertaken extensively.

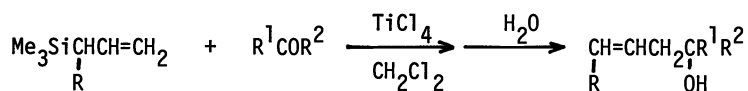
When the work in this laboratory was in progress, Calas *et al.* have reported the addition of allyltrimethylsilane to activated carbonyl compounds such as α -chloroacetone and chloral in the presence of a Lewis acid such as AlCl_3 , GaCl_3 and InCl_3 (Ref. 9). Abel and Rowley also reported the reaction of allylic derivatives of both silicon and tin with perhalogenoacetones (Ref. 10).

We have found that allyltrimethylsilane undergoes a smooth reaction with carbonyl compounds in a general pattern shown below.



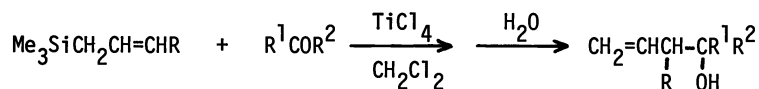
We have published the first paper of this series in 1976 describing that (1) a wide variety of aliphatic and aromatic carbonyl compounds can enter the reaction with allylsilanes very smoothly provided that carbonyl compounds are activated by TiCl_4 , and (2) regiospecific transposition occurs always in the allylic part in the reaction (Ref. 11).

The reaction of allyltrimethylsilane (1) with carbonyl compounds proceeds very rapidly to give γ,δ -unsaturated alcohols in the presence of a Lewis acid such as TiCl_4 , AlCl_3 , SnCl_4 and $\text{BF}_3 \cdot \text{OEt}_2$. The synthetic utility of the reaction is displayed by the regiospecific transformation of the allylic part to a carbonyl function, in which the carbon-carbon bond formation occurred exclusively at the γ -carbon of allylsilanes. The following examples indicate the regiospecificity of the reaction.



2 ; R=Me

3 ; R=Ph

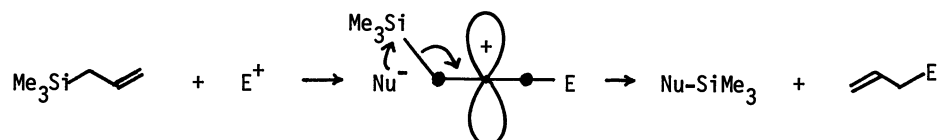


4 ; R=Me (*cis* and *trans*)

5 ; R-Ph (*trans*)

The reaction of allylsilanes, 2 and 3, gave *trans* predominant mixtures of two stereoisomers, respectively, while *cis* and *trans*-4 and *trans*-5 afforded branched homoallyl alcohols exclusively. Examples of the reaction are listed in Table 2 (Ref. 11).

The reaction of allylsilanes with an electrophile may be represented in the following general scheme in which the electrophile attacks at the γ -carbon of the allyl system to generate a cation stabilized by a neighboring C-Si bond through $\sigma-\pi$ conjugation.



It is interesting to compare the reaction of allyltrimethylsilane with that of homoallyltrimethylsilane (Ref. 12).

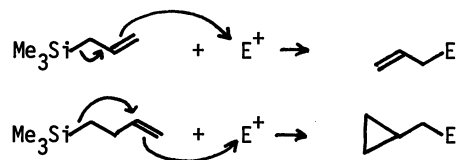
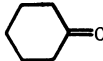
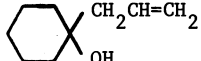
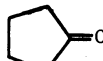
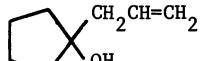


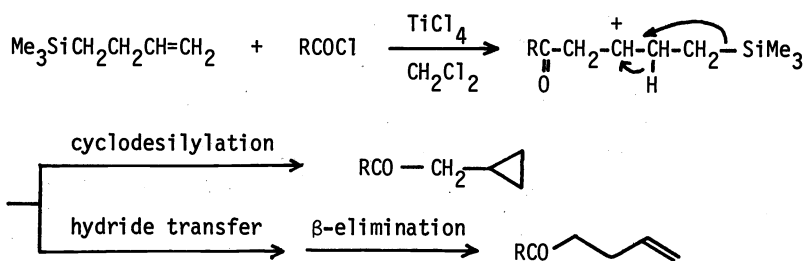
TABLE 2. Synthesis of γ,δ -unsaturated alcohols

Allylsilane	Ketone or Aldehyde	Reaction time(min)	Product	(% yield)
<u>1</u>	$\text{CH}_3(\text{CH}_2)_2\text{CHO}$	0.5	$\text{CH}_2=\text{CHCH}_2\underset{\text{OH}}{\text{CH}}\text{CH}_2\text{CH}_2\text{CH}_3$	(87)
<u>1</u>	$(\text{CH}_3)_2\text{CHCHO}$	10	$\text{CH}_2=\text{CHCH}_2\underset{\text{OH}}{\text{CH}}\text{CH}(\text{CH}_3)_2$	(54)
<u>1</u>	$\text{CH}_3(\text{CH}_2)_5\text{CHO}$	1	$\text{CH}_2=\text{CHCH}_2\underset{\text{OH}}{\text{CH}}(\text{CH}_2)_5\text{CH}_3$	(91)
<u>1</u>	$\text{CH}_3(\text{CH}_2)_6\text{CHO}$	1	$\text{CH}_2=\text{CHCH}_2\underset{\text{OH}}{\text{CH}}(\text{CH}_2)_6\text{CH}_3$	(86)
<u>1</u>	$\text{Ph}(\text{CH}_2)_2\text{CHO}$	1	$\text{CH}_2=\text{CHCH}_2\underset{\text{OH}}{\text{CH}}(\text{CH}_2)_2\text{Ph}$	(96)
<u>1</u>	PhCHO	1 ^a	$\text{CH}_2=\text{CHCH}_2\underset{\text{OH}}{\text{C}}\text{HPh}$	(58)
<u>1</u>	$(\text{CH}_3)_2\text{CO}$	1	$\text{CH}_2=\text{CHCH}_2\underset{\text{OH}}{\text{C}}(\text{CH}_3)_3$	(83)
<u>1</u>	$(\text{CH}_3)_2\text{CHCH}_2\text{COCH}_3$	1	$\text{CH}_2=\text{CHCH}_2\underset{\text{OH}}{\text{C}}(\text{CH}_3)\text{CH}_2\text{CH}(\text{CH}_3)_2$	(44)
<u>1</u>		3		(70)
<u>1</u>		3		(44)
<u>3a</u>	$\text{CH}_3(\text{CH}_2)_2\text{CHO}$	1	$\text{CH}_3\text{CH}=\text{CHCH}_2\underset{\text{OH}}{\text{C}}\text{H}(\text{CH}_2)_2\text{CH}_3^b$	(89)
<u>3a</u>	$(\text{CH}_3)_2\text{CO}$	1	$\text{CH}_3\text{CH}=\text{CHCH}_2\underset{\text{OH}}{\text{C}}(\text{CH}_3)_2$ (<i>cis:trans</i> =37:63)	(72)
<u>3b</u>	$\text{CH}_3(\text{CH}_2)_2\text{CHO}$	0.5	$\text{PhCH}=\text{CHCH}_2\underset{\text{OH}}{\text{C}}\text{H}(\text{CH}_2)_2\text{CH}_3^c$	(54)
<i>trans</i> - <u>5a</u>	$\text{CH}_3(\text{CH}_2)_2\text{CHO}$	0.5	$\text{CH}_2=\text{CHCH}(\text{CH}_3)\underset{\text{OH}}{\text{C}}\text{H}(\text{CH}_2)_2\text{CH}_3$	(83)
<i>trans</i> - <u>5a</u>	$(\text{CH}_3)_2\text{CO}$	0.5	$\text{CH}_2=\text{CHCH}(\text{CH}_3)\underset{\text{OH}}{\text{C}}(\text{CH}_3)_2$	(45)
<i>cis</i> - <u>5a</u>	$\text{CH}_3(\text{CH}_2)_2\text{CHO}$	0.5	$\text{CH}_2=\text{CHCH}(\text{CH}_3)\underset{\text{OH}}{\text{C}}\text{H}(\text{CH}_2)_2\text{CH}_3$	(71)
<i>cis</i> - <u>5a</u>	$(\text{CH}_3)_2\text{CO}$	0.5	$\text{CH}_2=\text{CHCH}(\text{CH}_3)\underset{\text{OH}}{\text{C}}(\text{CH}_3)_2$	(51)
<u>5b</u>	$\text{CH}_3(\text{CH}_2)_2\text{CHO}$	0.5	$\text{CH}_2=\text{CHCH}(\text{Ph})\underset{\text{OH}}{\text{C}}\text{H}(\text{CH}_2)_2\text{CH}_3$	(87)

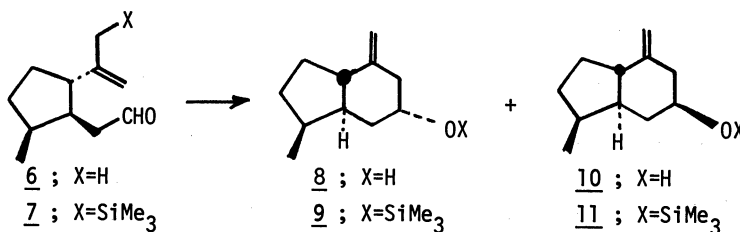
a) $\text{BF}_3 \cdot \text{OEt}_2$ was used as a Lewis acid. b) A *cis* and *trans* mixture.

c) A *trans* isomer.

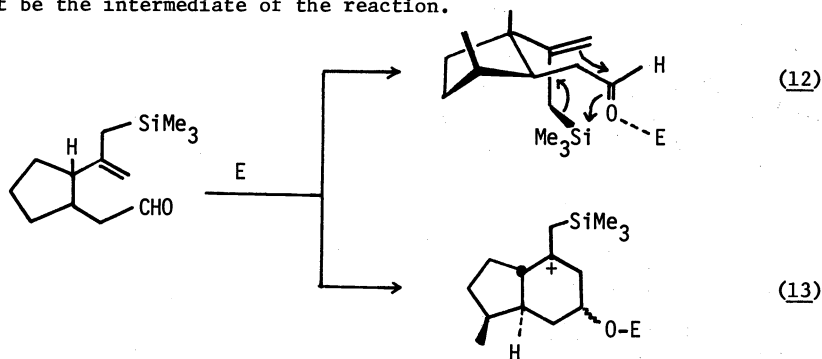
The reaction of 3-butenyltrimethylsilane with a variety of aliphatic, aromatic and olefinic acid chlorides in the presence of titanium tetrachloride gave the corresponding cyclopropylmethyl ketones together with 3-butenyl ketones as minor product.



The stereochemistry of intramolecular addition of allylsilane to a carbonyl group was examined (Ref. 13).

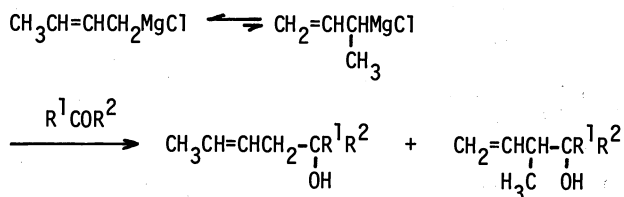


Although 6 gave only the axial alcohol isomer (8) under thermal and Lewis acid-catalyzed conditions where a concerted mechanism was considered, the corresponding silyl derivative (7) gave a mixture of axial (9) and equatorial (10) compounds. The production of the equatorial isomer may eliminate the concerted process as a major contribution to the mechanism through the cyclic transition state (12) (Ref. 13). Instead, a β -silyl cationic species (13) must be the intermediate of the reaction.

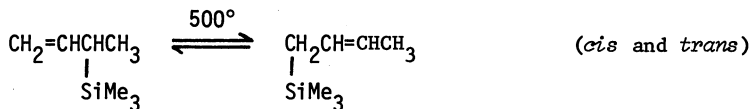


THERMAL REACTIONS OF ALLYLSILANES

Allylation of carbonyl compounds can be performed with allyl Grignard reagents. However, substituted allyl Grignard reagents are in equilibrium between two positional isomers and in principle afford two products. For example,

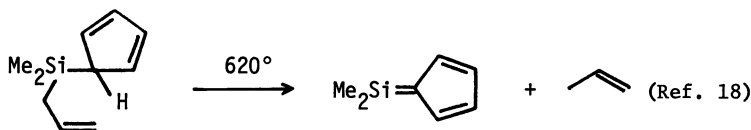
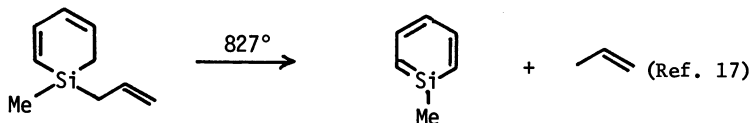
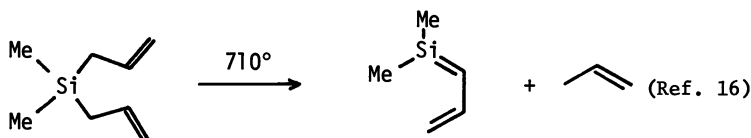


1,3-Silyl migration in the allylsilane system takes place just like allyl Grignard reagents and other allylmethyl compounds, but only at high temperature (Ref. 14) and at ordinary temperature, the localized σ -bond structure of allylsilanes is quite stable, so that each positional isomer of allylsilanes can be separated and used individually for the reaction (Ref. 15).

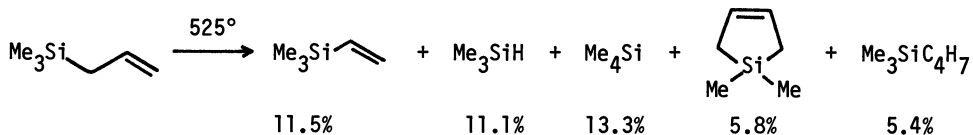


The thermal stability of allylsilanes at temperatures up to 200°–300° is one of the most important factors of allylsilanes as synthetic reagents, but at higher temperatures allylsilanes undergo a variety of interesting thermal reactions.

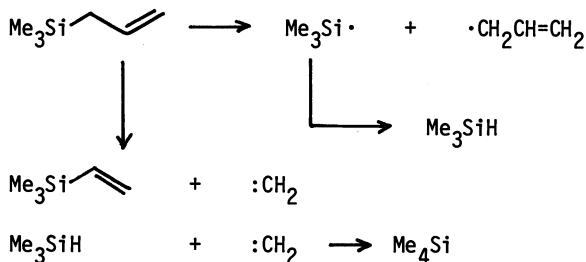
Retro ene reactions have been applied successfully to generate silicon-carbon double bonded species, *inter alia*:



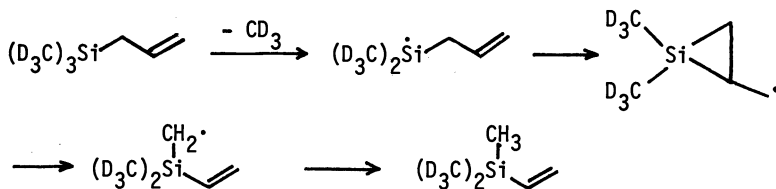
The vapor phase thermolysis of allyltrimethylsilane resulted in the formation of vinyltrimethylsilane, tetramethylsilane, trimethylsilane and other products (Ref. 19).



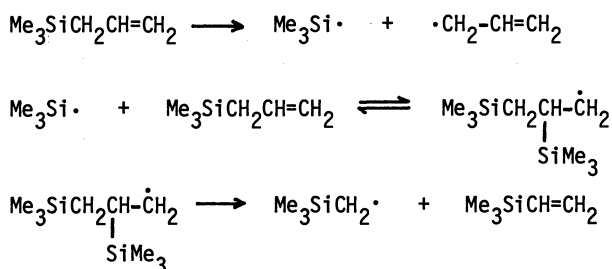
We have proposed a methylene transfer mechanism in addition to free radical reactions to account the results.



Recently, Neider, Chambers and Jones have reexamined the reaction with $(\text{CD}_3)_3\text{SiCH}_2\text{CH}=\text{CH}_2$ and concluded that the mechanism of the thermal conversion of allyltrimethylsilane to vinyltrimethylsilane does not involve methylene extrusion (Ref. 20). Instead, a mechanism initiated by loss of a methyl radical from silicon is claimed based on the result that vinyltrimethylsilane contained 2.67 protons in the methyl position.



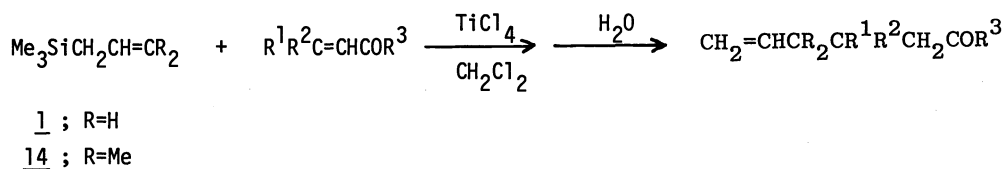
The preferential loss of methyl to allyl seems to be rather strange and indeed the labeling experiment of Jones *et al.* turned out erroneous (Ref. 21). No loss of a methyl group from the silicon atom was confirmed. The fact fits both the methylene extrusion mechanism and the following alternative free radical mechanism.



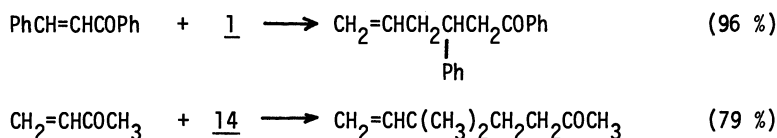
Intermediacy of the $\text{Me}_3\text{SiCH}_2\cdot$ radical explains the formation of Me_4Si and butenyltrimethylsilane. Attack of the trimethylsilyl radical on the terminus of 1 resulted in the identity reaction. Anyhow, generation of the trimethylsilyl radical by Si-allyl cleavage seems to be important (Ref. 21).

CONJUGATE ADDITION OF ALLYLSILANES TO α,β -ENONES

Now back to the synthetic application of the reaction, we have found the second important feature of the reaction of allylsilanes is its regiospecific conjugate addition to α,β -enones (Ref. 22, 23).

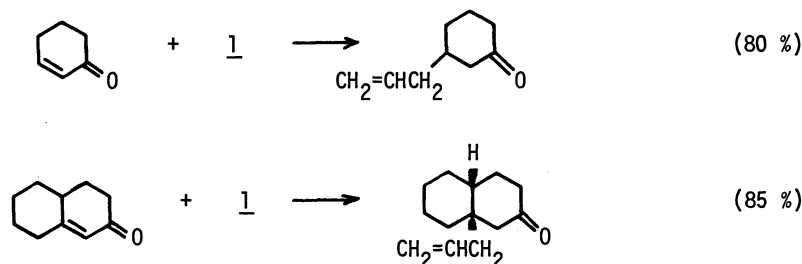


Thus, allylsilane gives δ,ϵ -enones exclusively in the reaction with α,β -enones. The regio-specific transposition in the allylic part was also observed.



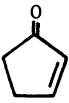
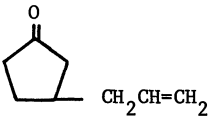
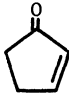
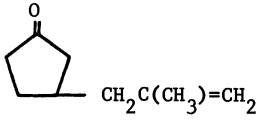
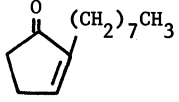
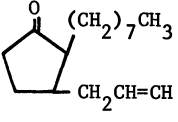
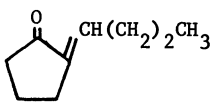
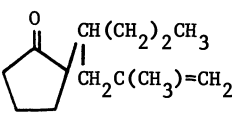
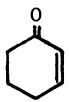
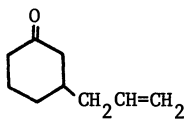
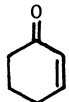
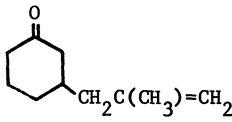
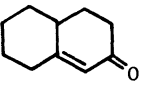
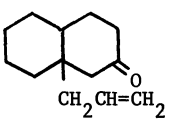
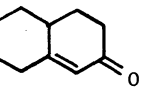
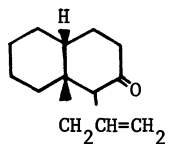
Other examples are listed in Table 3 (Ref. 23).

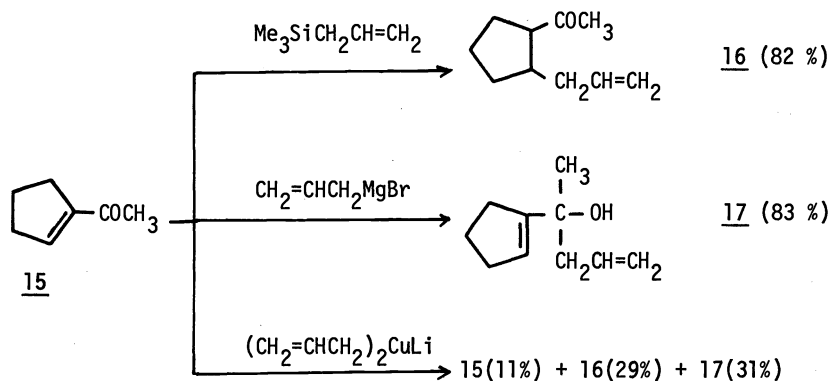
This reaction provides the first instance of stereoselective direct introduction of the angular allyl group to a fused cyclic α,β -enone, $\Delta^{1,9}$ -2-octalone.



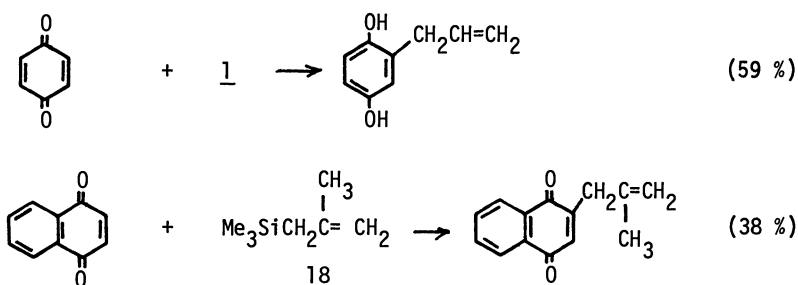
The following example demonstrates a marked contrast in the reaction of allyltrimethylsilane, allylmagnesium bromide and lithium diallylcuprate (Ref. 24). Allylmagnesium bromide undergoes only 1,2-addition and the cuprate gives less satisfactory results.

TABLE 3. Conjugate allylation of α,β -enones with allylsilanes.

Allylsilane	α,β -Enone	δ,ϵ -Enone	(% yield)
$\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$	$\text{CH}_2=\text{CHCOCH}_3$	$\text{CH}_2=\text{CH}(\text{CH}_2)_3\text{COCH}_3$	(59)
$\text{Me}_3\text{SiCH}_2\text{CH}=\text{C}(\text{CH}_3)_2$	$\text{CH}_2=\text{CHCOCH}_3$	$\text{CH}_2=\text{CHC}(\text{CH}_3)_2\text{CH}_2\text{CH}_2\text{COCH}_3$	(79)
$\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$	$(\text{CH}_3)_2\text{C}=\text{CHCOCH}_3$	$\text{CH}_2=\text{CHCH}_2\text{C}(\text{CH}_3)_2\text{CH}_2\text{COCH}_3$	(87)
$\text{Me}_3\text{SiCH}_2\text{C}(\text{CH}_3)=\text{CH}_2$	$\text{PhCH}=\text{CHCOCH}_3$	$\text{CH}_2=\text{C}(\text{CH}_3)\text{CH}_2\text{CH}(\text{Ph})\text{CH}_2\text{COCH}_3$	(69)
$\text{Me}_3\text{SiCH}_2\text{CH}=\text{CHCH}_3$	$\text{PhCH}=\text{CHCOCH}_3$	$\text{CH}_2=\text{CHCH}(\text{CH}_3)\text{CH}(\text{Ph})\text{CH}_2\text{COCH}_3$	(76)
$\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$	$\text{PhCH}=\text{CHCOPh}$	$\text{CH}_2=\text{CHCH}_2\text{CH}(\text{Ph})\text{CH}_2\text{COPh}$	(96)
$\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$			(70)
$\text{Me}_3\text{SiCH}_2\text{C}(\text{CH}_3)=\text{CH}_2$			(70)
$\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$			(54)
$\text{Me}_3\text{SiCH}_2\text{C}(\text{CH}_3)=\text{CH}_2$			(82)
$\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$			(80)
$\text{Me}_3\text{SiCH}_2\text{C}(\text{CH}_3)=\text{CH}_2$			(99)
$\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$			(85)
$\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$			(88)

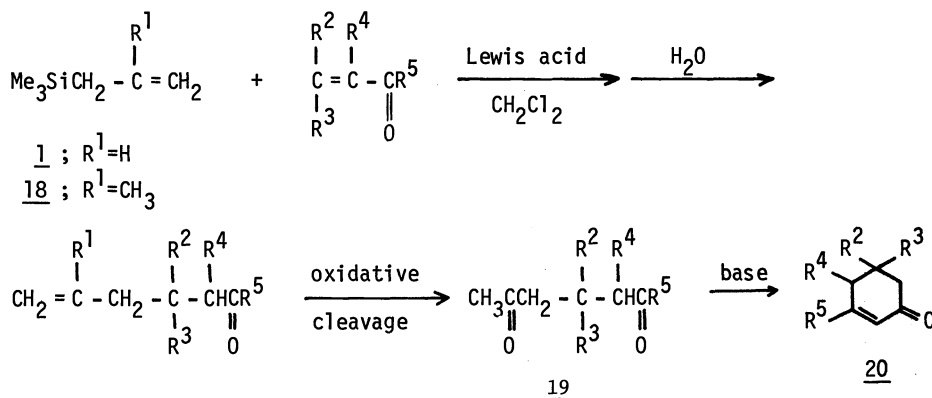


Quinones are allylated with allylsilanes as illustrated below (Ref. 25).

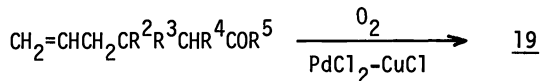


APPLICATIONS OF CONJUGATE ADDITION TO ANNEALATION AND DOUBLE ALKYLATION

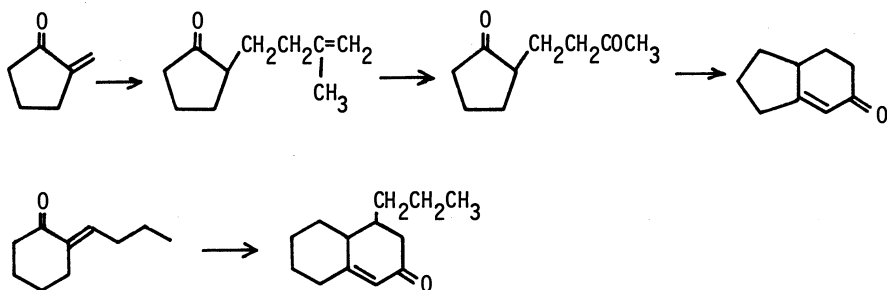
Since the conjugate addition of allylsilanes to α,β -enones is very specific, the reaction can be applied to a variety of syntheses. One example is a [3+3] annelation reaction (Ref. 26).



A β -methallyl group is introduced to α,β -enones to give δ,ϵ -enones which can be oxidized to 1,5-diketones (**19**) by the oxidation of the olefinic part. Ozone is the most convenient reagent for the purpose. Alternatively, introduction of an allyl group followed by the Wacker-type oxidation catalyzed by palladium chloride-cuprous chloride in DMF also affords 1,5-diketone.

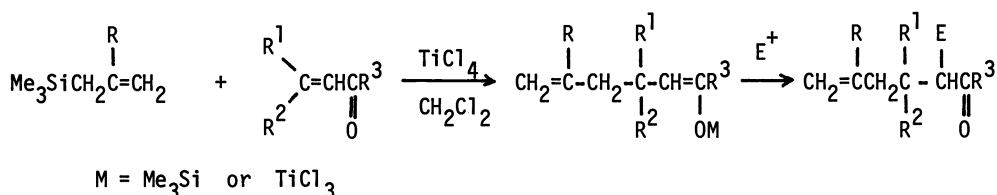


1,5-Diketones thus obtained can be converted to fused cyclic α,β -enones (**20**) readily under a basic condition. Examples are:

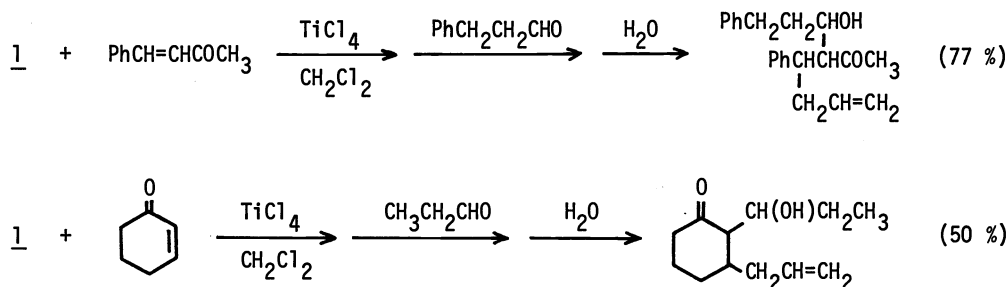


The characteristic feature of this annelation reactions stems in that the method consists of [3C+3C] reactions; namely a three carbon unit is introduced to an α -alkylidene-cycloalkanone which may be obtained selectively from a cycloalkanone. The method can avoid the use of rather unstable methyl vinyl ketone or its equivalent used in the [4C+2C] annelation reaction. An application of the method to the synthesis of (+)-Nootkatone, a grapefruit essence, has been reported (Ref. 27).

Since the intermediate of the conjugate addition is an enolate, the reaction of the intermediate with carbon electrophiles results in the formation of an additional carbon-carbon bond formation (Ref. 28).



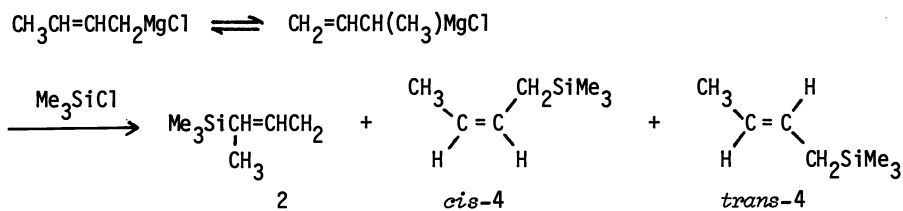
The reaction can be carried out in one-pot operation in good yields. Examples are:



REGIOSELECTIVE SYNTHESIS AND REACTIONS OF SUBSTITUTED ALLYLSILANES

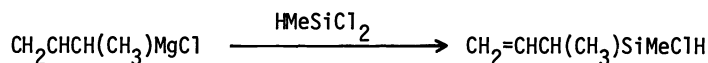
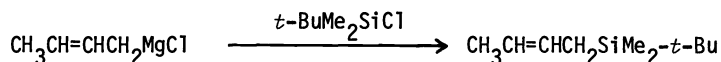
The most important and interesting character of the reaction of allylsilanes is its regio-specificity. In all cases, products are obtained exactly in a predictable fashion. Therefore, it is very important to develop the synthetic strategy for introduction of a functionality in the allyl group of allyltrimethylsilane. However, it is not necessarily an easy problem and therefore possibly becomes one of the major limitations of the use of allylsilanes in synthesis. We have been working to solve the problem and the situation will be improved in near future. The following are selected examples of these efforts.

The reaction of 2-butenylmagnesium halide with trimethylchlorosilane usually resulted in the formation of a mixture of α -methylallyltrimethylsilane and *cis*- and *trans*-2-butenyltrimethylsilane (Ref. 15).

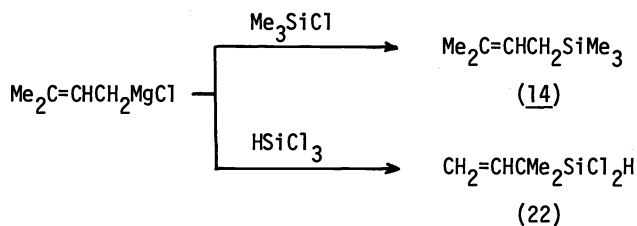


The ratio of 2 to 4 is approximately 50 to 50 under usual conditions with a *cis/trans* ratio of 2/3. However, the ratio of 2/4 can be changed to 92/8 at -30° in diethyl ether and to 34/66 at 0° in THF-HMPA with a *cis/trans* ratio of 97/3 (Ref. 29).

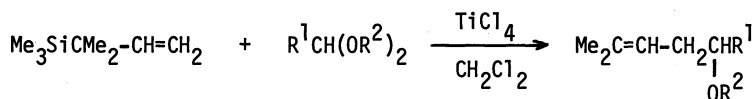
Regiospecific synthesis of 2-butenylsilane and α -methallylsilane may be achieved by the following procedure.



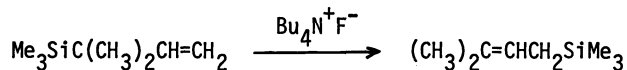
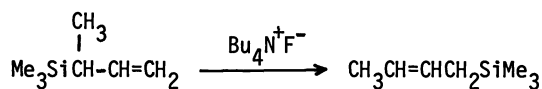
γ,γ -Dimethylallyltrimethylsilane (14) and α,α -dimethylallyltrimethylsilane (21) can also be prepared selectively (Ref. 30).



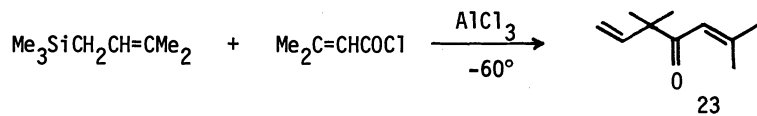
α,α -Dimethylallyltrimethylsilane is used as a reagent of regiospecific prenylation that is one of the important reactions for synthesis of various natural products.



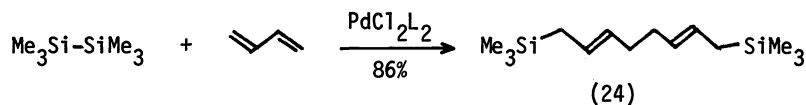
γ,γ -Dimethylallylsilane (14) can be prepared easily as described above. These γ -alkylated allylsilanes are also prepared by isomerization of α -alkylated allylsilanes with a catalytic amount of fluoride ion (Ref. 31).



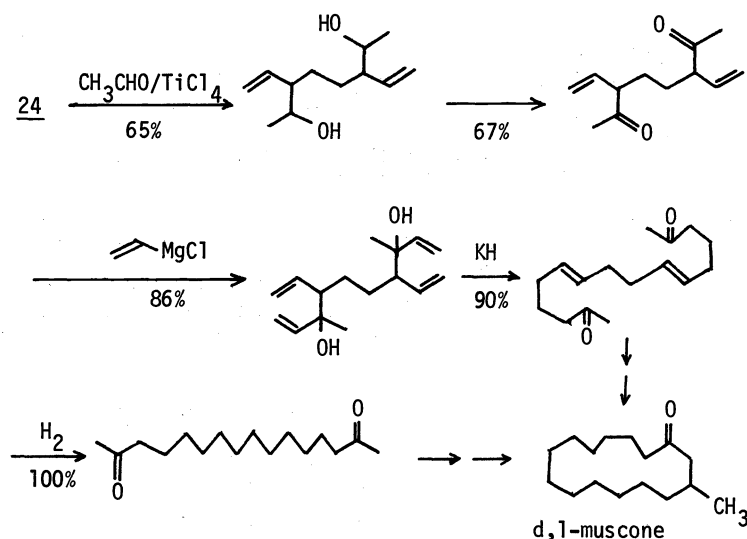
Synthesis of artemesia ketone (23) by the reaction of 14 is also reported (Ref. 32).



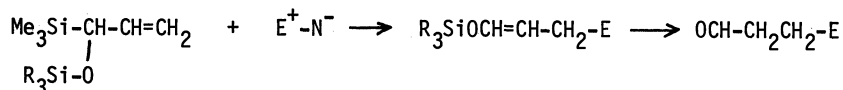
The palladium complex-catalyzed reaction of hexamethyldisilane with butadiene affords a 1:2 adduct (24) which is an interesting derivative of allylsilane (Ref. 33, 34).



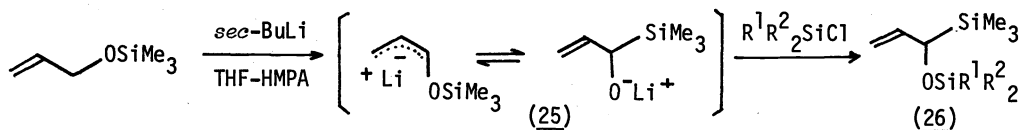
The following is a route to d,l-muscone from 24 (Ref. 34).



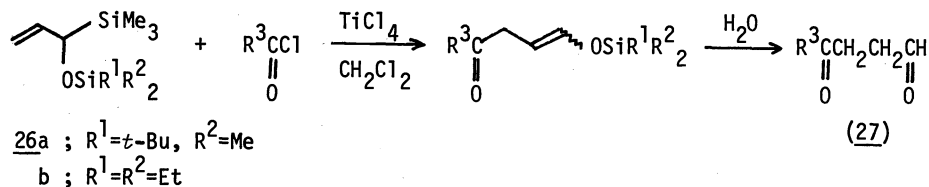
Introduction of a siloxy group at the α -carbon of allyltrimethylsilane could result in the formation of a silyl enol ether which should give a carbonyl compound on hydrolysis.



Silylation of an allyloxy carbanion (25) with chlorosilane occurred exclusively at oxygen to give the desired α -siloxyallylsilane (26) (Ref. 35).



The reaction of 26 with acid chlorides in the presence of titanium tetrachloride gave the corresponding γ -keto aldehydes (27) after hydrolysis, as shown in Table 4 (Ref. 35).



2-Alkoxy carbonylallyltrimethylsilanes (28) are prepared from diethyl malonate by the following scheme.

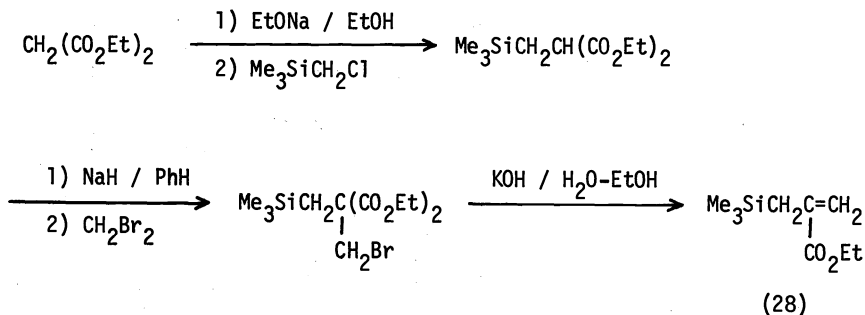
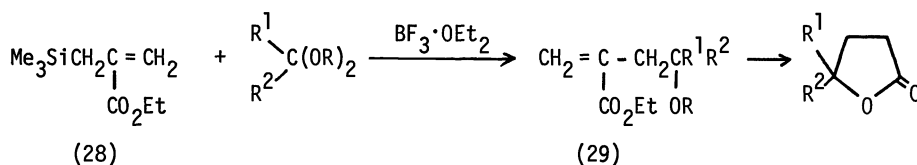


TABLE 4. Reactions of 26 with acid chloride.

Acid Chloride		Product	(% yield)
$(\text{CH}_3)_2\text{CHCOCl}$	<u>26a</u>	$(\text{CH}_3)_2\text{CHCOCH}_2\text{CH}_2\text{CHO}$	(80)
$\text{CH}_3(\text{CH}_2)_3\text{COCl}$	<u>26a</u>	$\text{CH}_3(\text{CH}_2)_3\text{COCH}_2\text{CH}_2\text{CHO}$	(45)
$(\text{CH}_3)_2\text{CHCH}_2\text{COCl}$	<u>26a</u>	$(\text{CH}_3)_2\text{CHCH}_2\text{COCH}_2\text{CH}_2\text{CHO}$	(63)
$(\text{CH}_3)_3\text{CCOCl}$	<u>26b</u>	$(\text{CH}_3)_3\text{CCOCH}_2\text{CH}_2\text{CHO}$	(79)
$\text{CH}_3(\text{CH}_2)_5\text{COCl}$	<u>26a</u>	$\text{CH}_3(\text{CH}_2)_5\text{COCH}_2\text{CH}_2\text{CHO}$	(65)
$\alpha\text{-C}_6\text{H}_{11}\text{COCl}$	<u>26a</u>	$\alpha\text{-C}_6\text{H}_{11}\text{COCH}_2\text{CH}_2\text{CHO}$	(65)
$(\text{CH}_3)_2\text{C}=\text{CHCOCl}$	<u>26a</u>	$(\text{CH}_3)_2\text{C}=\text{CHCOCH}_2\text{CH}_2\text{CHO}$	(58)

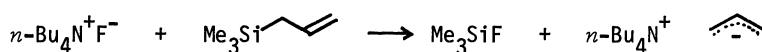
The reaction of 28 with acetals gives 29 which can be converted to α -methylene- γ -lactones, smoothly (Ref. 36).



FLUORIDE ION CATALYZED ALLYLATION OF CARBONYL COMPOUNDS.

CHEMOSELECTIVITY IN THE REACTION

Since the silicon-fluoride bond is remarkably strong with a bond dissociation energy of α . 140 kcal/mole, fluoride ion displays strong nucleophilic affinity specifically to a silicon atom. We found that this can be applied in allylsilane chemistry. The allyl-silicon bond of allyltrimethylsilane is readily cleaved with tetra-*n*-butylammonium fluoride (TBAF) to give a new allylic anion species (Ref. 37).



The allyl anion undergoes addition to aldehydes and ketones. The reaction is catalytic in fluoride ion and the following scheme illustrates the mechanistic rationale. Representative results are listed in Table 5.

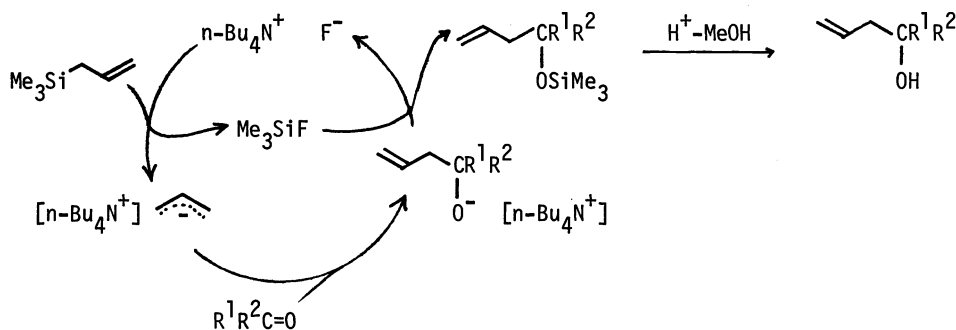

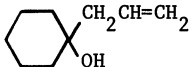
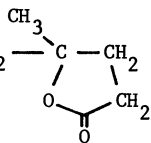


TABLE 5. Reaction of allylsilanes with carbonyl compounds catalyzed by tetra-*n*-butylammonium fluoride in THF at reflux

Allylsilane	Carbonyl Compound	Products	(% yield)
$\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$ (1)	$\text{CH}_3(\text{CH}_2)_2\text{CHO}$	$\text{CH}_3(\text{CH}_2)_2\underset{\text{OH}}{\text{CH}}\text{CH}_2\text{CH}=\text{CH}_2$	(83)
$\underline{1}$	$\text{CH}_3(\text{CH}_2)_3\text{CHO}$	$\text{CH}_3(\text{CH}_2)_3\underset{\text{OH}}{\text{CH}}\text{CH}_2\text{CH}=\text{CH}_2$	(92)
$\underline{1}$	PhCHO	$\text{Ph}\underset{\text{OH}}{\text{CH}}\text{CH}_2\text{CH}=\text{CH}_2$	(93)
$\underline{1}$			(60)
$\underline{1}$	PhCOCH ₃	$\text{Ph}\underset{\text{OH}}{\text{C}}(\text{CH}_3)\text{CH}_2\text{CH}=\text{CH}_2$	(60)
$\underline{1}$	$\text{CH}_3\text{COCH}_2\text{CH}_2\text{CO}_2\text{CH}_3$	$\text{CH}_2=\text{CHCH}_2$  (30)	(71)
$\text{Me}_3\text{SiCH}_2\text{CH}=\text{CMe}_2$ (14)	PhCOPh	$\text{Ph}_2\underset{\text{OH}}{\text{C}}\text{CH}_2\text{CH}=\text{C}(\text{CH}_3)_2$	(87)

A variety of aldehydes and ketones are effective to this allylation reaction, although aldehydes are more reactive than ketones. On the contrary, nitriles, epoxides and esters do not react with this reagent even by heating for a prolonged time. Therefore, methyl levulinate, for example, can be allylated chemoselectively only at the keto group but not at the ester group to give a lactone (30) in 71% yield.

THE REACTION OF ALLYLSILANES WITH ACETALS.

A PROBLEM OF CATALYSIS

As carbon electrophiles, aldehydes, ketones, enones, quinones and acid chlorides are most commonly used in the reaction with allylsilanes for carbon-carbon bond formation, but the use of other electrophilic species such as chlorosulphonyl isocyanate (Ref. 38), chloromethyl methyl ether (Ref. 39), and *t*-alkyl halides (Ref. 40,41) has been reported. We have found that allylsilanes react with various acetals including aliphatic, alicyclic and aromatic acetals or with ethyl orthoformate in the presence of titanium tetrachloride to afford the corresponding homoallyl ethers in good yields (Ref. 42).

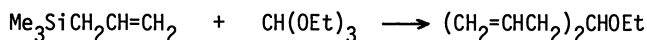
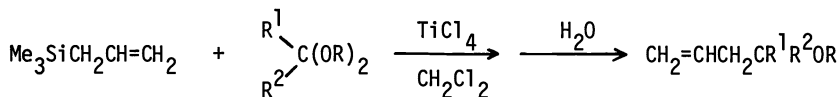
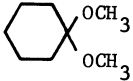
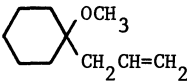
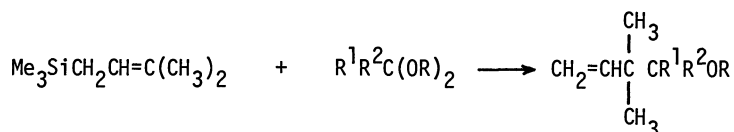


TABLE 6. Synthesis of homoallyl ethers

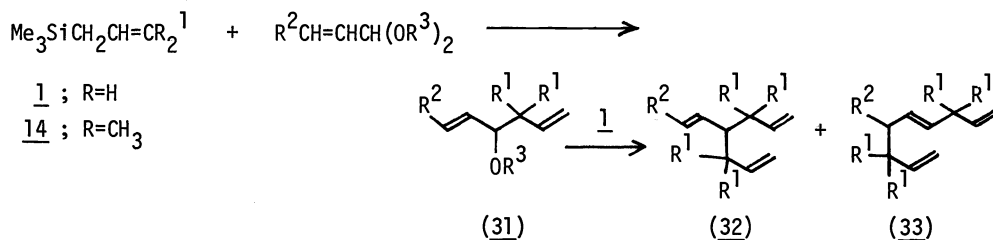
Allylsilane	Acetal	Product	(% yield)
<u>1</u>	$\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{OCH}_3)_2$	$\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{OCH}_3)\text{CH}_2\text{CH}=\text{CH}_2$	(77)
<u>1</u>	$\text{PhCH}_2\text{CH}_2\text{CH}(\text{OCH}_3)_2$	$\text{PhCH}_2\text{CH}_2\text{CH}(\text{OCH}_3)\text{CH}_2\text{CH}=\text{CH}_2$	(93)
<u>1</u>	$\text{BrCH}_2\text{CH}(\text{OCH}_2\text{CH}_3)_2$	$\text{BrCH}_2\text{CH}(\text{OCH}_2\text{CH}_3)\text{CH}_2\text{CH}=\text{CH}_2$	(90)
<u>1</u>	$\text{CH}_3(\text{CH}_2)_2\text{CHBrCH}(\text{OCH}_3)_2$	$\text{CH}_3(\text{CH}_2)_2\text{CHBrCH}(\text{OCH}_3)\text{CH}_2\text{CH}=\text{CH}_2$	(91)
<u>1</u>	$\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{OCH}_2\text{CH}_3)_2$	$\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{OCH}_2\text{CH}_3)\text{CH}_2\text{CH}=\text{CH}_2$	(76)
<u>1</u>			(71)
<u>1</u>	$(\text{CH}_3)_2\text{C}(\text{COH}_3)_2$	$(\text{CH}_3)_2\text{C}(\text{OCH}_3)\text{CH}_2\text{CH}=\text{CH}_2$	(98)
<u>1</u>	$\text{CH}(\text{OCH}_2\text{CH}_3)_3$	$\text{CH}(\text{OCH}_2\text{CH}_3)(\text{CH}_2\text{CH}=\text{CH}_2)_2$	(24)
<u>14</u>	$\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{OCH}_3)_2$	$\text{CH}_3(\text{CH}_2)_3\text{CH}(\text{OCH}_3)\text{C}(\text{CH}_3)_2\text{CH}=\text{CH}_2$	(80)

The regioselectivity in relocation of the allyl system was also observed.



Examples are listed in Table 6.

The reaction of allylsilanes with α,β -unsaturated acetals is rather complicated (Ref. 43): in the presence of titanium tetrachloride diallylated compounds are formed, while monoallylated compounds were obtained selectively by the reaction promoted by aluminum trichloride or a boron trifluoride-ether complex (Table 7).

TABLE 7. Reaction of allylsilane with α,β -unsaturated acetals

Allylsilane	Acetal		Lewis acid	% yield		
	R ²	R ³		<u>31</u>	<u>32</u>	<u>33</u>
<u>1</u>	Ph	Et	TiCl ₄	0	41	37
<u>1</u>	Ph	Et	AlCl ₃	70	0	0
<u>1</u>	Ph	Et	BF ₃ ·OEt ₂	45	0	0
<u>14</u>	Ph	Et	TiCl ₄	0	4	33
<u>1</u>	n-Pr	Et	TiCl ₄	0	0	21
<u>1</u>	n-Pr	Et	AlCl ₃	27	0	0

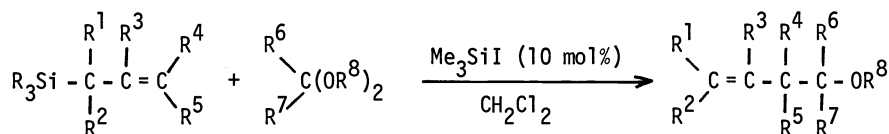
The effect of the Lewis acid on the allylation may be explained in terms of the difference in the coordinating ability between Lewis acid to acetals as shown below.



Titanium tetrachloride can coordinate to both alkoxy groups, while aluminum chloride can activate only one of them. As a result, the second allylation takes place smoothly with titanium tetrachloride as an activator to give diallylated compounds, while with aluminum chloride the second allylation is difficult.

In the reaction of allylsilanes with carbon electrophiles, an equivalent amount of a Lewis acid, usually titanium tetrachloride, is used for the activator, but sometimes the use of a large amount of a Lewis acid can be a drawback of the reaction. However, we have found that the regiospecific allylation reaction of acetals with allylsilane can be catalyzed very smoothly by iodotrimethylsilane (Ref. 44).

Since it is known that iodotrimethylsilane can be generated *in situ* by the reaction of allyltrimethylsilane and iodine (Ref. 3), the reaction can be effected by a catalytic amount of iodine with a slight excess amount of allyltrimethylsilane.



Typical examples are listed in Table 8.

With α,β -unsaturated acetals, only monoallylation occurred regioselectively at the acetal carbon. No diallylation product was observed. Dienylmethylsilanes as well as propargylsilane also can enter the reaction.

Although the mechanism of the reaction has not been elucidated, the results can be rationalized by the following scheme, in which the initial formation of an oxonium ion (34) takes place at low temperature. The facts found in the reaction suggest that the intermediate (34) may be subjected to the bimolecular nucleophilic displacement by the allylsilane (1). When the allylsilane is absent, 34 may be converted to 35 to give the corresponding ketone as is seen in the literature (Ref. 45).

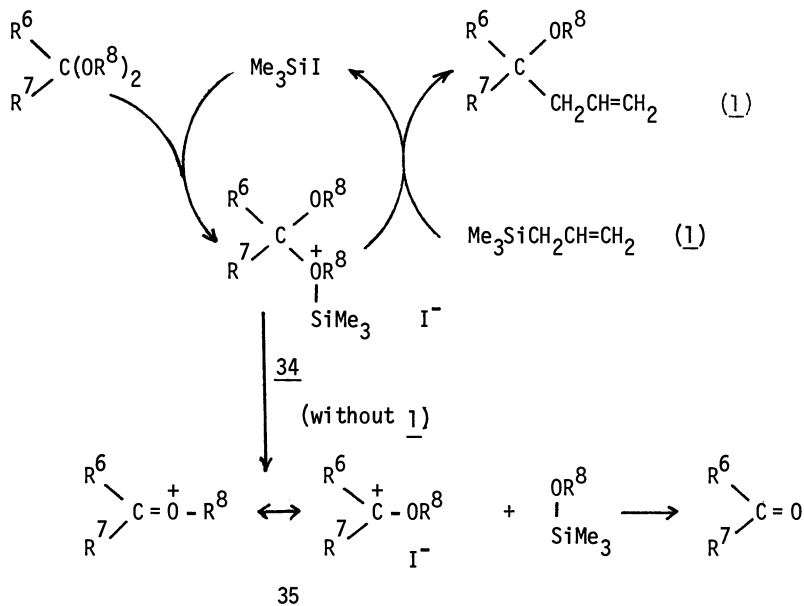
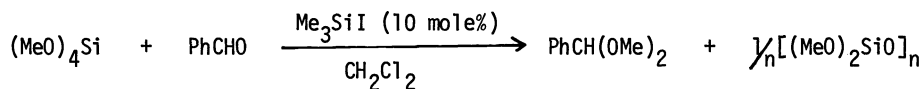


TABLE 8. Allylation of acetals with allylsilanes catalyzed by iodotrimethylsilane (10 mole %) in CH_2Cl_2 at -78° .

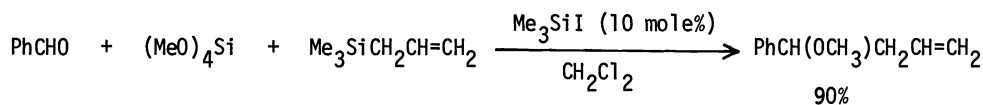
Allylsilane	Acetal	Product	(% yield)
$\text{Me}_3\text{SiCH}_2\text{CH}=\text{CH}_2$ (1)	$\text{Me}_2\text{C}(\text{OMe})_2$	$\text{Me}_2\text{C}(\text{OMe})\text{CH}_2\text{CH}=\text{CH}_2$	(83)
<u>1</u>	$\text{PhCH}(\text{OMe})_2$	$\text{PhCH}(\text{OMe})\text{CH}_2\text{CH}=\text{CH}_2$	(81)
<u>1</u>	$\text{Ph}(\text{CH}_2)_2\text{CH}(\text{OMe})_2$	$\text{Ph}(\text{CH}_2)_2\text{CH}(\text{OMe})\text{CH}_2\text{CH}=\text{CH}_2$	(95)
<u>1</u>	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{OMe})_2$	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{OMe})\text{CH}_2\text{CH}=\text{CH}_2$	(70)
<u>1</u>	$\text{PhCH}=\text{CHCH}(\text{OEt})_2$	$\text{PhCH}=\text{CHCH}(\text{OEt})\text{CH}_2\text{CH}=\text{CH}_2$	(91)
$\text{Me}_3\text{SiCH}(\text{CH}_3)\text{CH}=\text{CH}_2$	$\text{PhCH}(\text{OMe})_2$	$\text{PhCH}(\text{OMe})\text{CH}(\text{CH}_3)\text{CH}=\text{CH}_2$	(85)
<i>i</i> -Pr $\text{Me}_2\text{SiCH}_2\text{CH}=\text{CHCH}_3$	$\text{PhCH}(\text{OMe})_2$	$\text{PhCH}(\text{OMe})\text{CH}(\text{CH}_3)\text{CH}=\text{CH}_2$	(82)
$\text{Me}_3\text{SiCH}_2\text{C}(\text{CH}_3)=\text{CH}_2$	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{OMe})_2$	$(\text{CH}_3)_2\text{CHCH}_2\text{CH}(\text{OMe})\text{C}(\text{CH}_3)=\text{CH}_2$	(90)
$\text{Me}_3\text{SiCH}_2\text{CH}=\text{CHCH}=\text{CH}_2$	$\text{PhCH}(\text{OMe})_2$	$\text{PhCH}(\text{OMe})\text{CH}_2\text{CH}=\text{CHCH}=\text{CH}_2$	(88)
$\text{Me}_3\text{SiCH}_2\text{C}(\text{SiMe}_3)=\text{CH}_2$	$\text{PhCH}(\text{OMe})_2$	$\text{PhCH}(\text{OMe})\text{C}(\text{SiMe}_3)=\text{CH}_2$	(82)

The overall character of the reaction is rather similar to the recently reported reaction with trimethylsilyl trifluoromethanesulfonate (Ref. 46).

Although iodotrimethylsilane does not catalyze the reaction of allylsilane with carbonyl compounds, we have found that it can catalyze slow acetalization of carbonyl compounds with silyl ethers (Ref. 47).

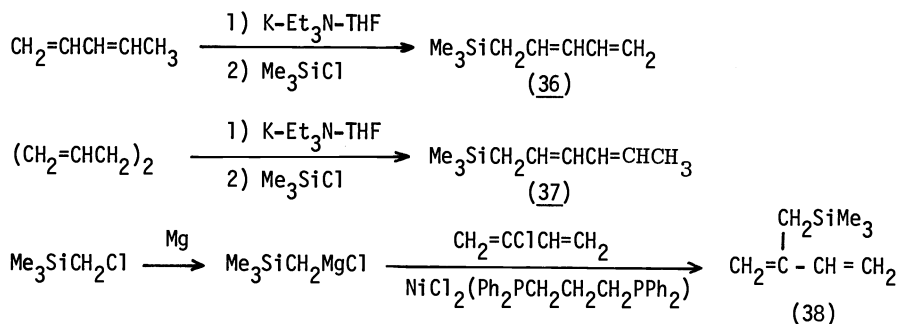


This reaction can be combined with allylation by 1 effectively. For example,

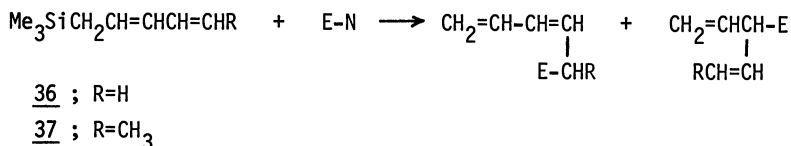


TRIMETHYLSILYLMETHYL-SUBSTITUTED DIENES

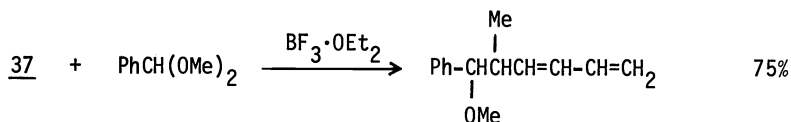
As an extension of the work on allylsilanes, we have prepared trimethylsilylmethyl substituted dienes, 36, 37 and 38, by the following reactions (Ref. 48, 49), and examined the reactions of these dienes. Seyferth and Pornet also reported the preparation and some reactions of 36 (Ref. 50).



The reaction 36 with acetal and aldehyde proceeds very smoothly to afford the corresponding pentadienylation products selectively in good yield, but the reaction with acid chloride takes place at the γ -carbon of 36 in a considerable extent (Ref. 48).



In order to examine whether the reaction occurred in a regioselective manner with concomitant rearrangement of the pentadienyl group, 37 was employed as a diagnostic reagent in the reaction. The reaction gave the product in which the new carbon-carbon linkage occurred specifically at the ϵ -carbon of 37. Therefore, transposition of the diene/methyl group occurs just as the case of the allyl group.



The isoprenyltrimethylsilane (38) is a quite versatile reagent to introduce an isoprenyl group to an electrophilic carbon. The following is a simple synthesis of ipsenol and ipsdienol, two principal components of the aggregation pheromone of *Ips paraconfusus* Lanier (male bark beetle boring in Ponderosa Pine).

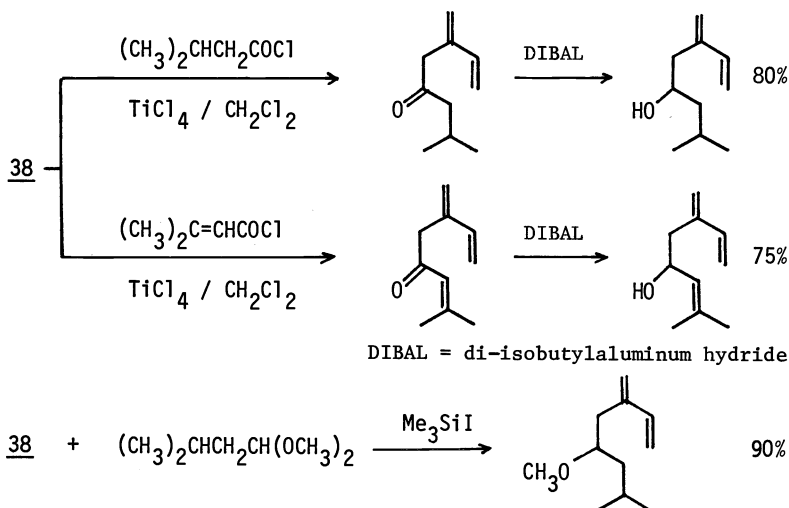
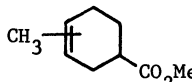
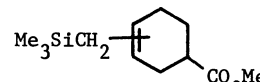
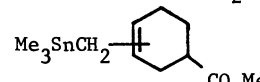
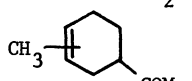
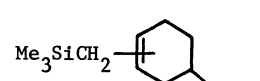
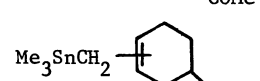
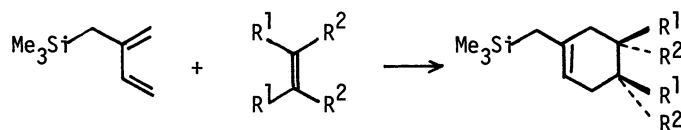


TABLE 9. Regioselectivity in the Diels-Alder reaction of 1,3-dienes with unsymmetrical dienophiles

Dienophile	Diene	Product	<i>para/meta</i>
CH ₂ =CHCO ₂ Me	<u>40</u>		70 / 30
	<u>38</u>		84 / 16
	<u>39</u>		91 / 9
CH ₂ =CHCOMe	<u>40</u>		71 / 29
	<u>38</u>		83 / 17
	<u>39</u>		92 / 8

As a diene, 38 can enter the Diels-Alder reaction (Ref. 51).



Interestingly, 38 and its tin analogue (39) undergo the Diels-Alder reaction with unsymmetrical dienophiles in a more regioselective fashion than isoprene.

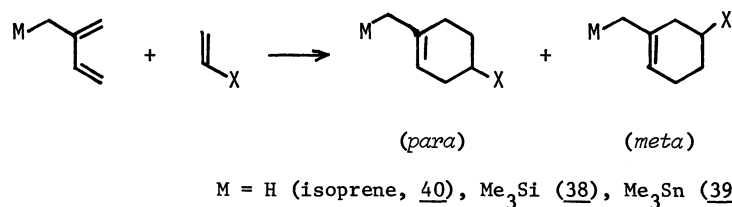


Table 9 lists the results.

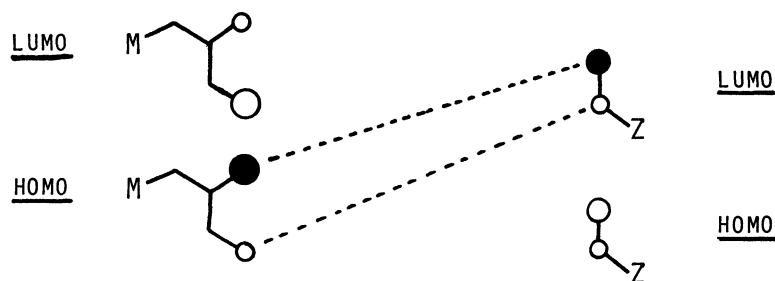
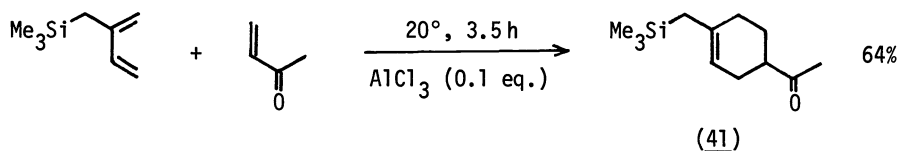


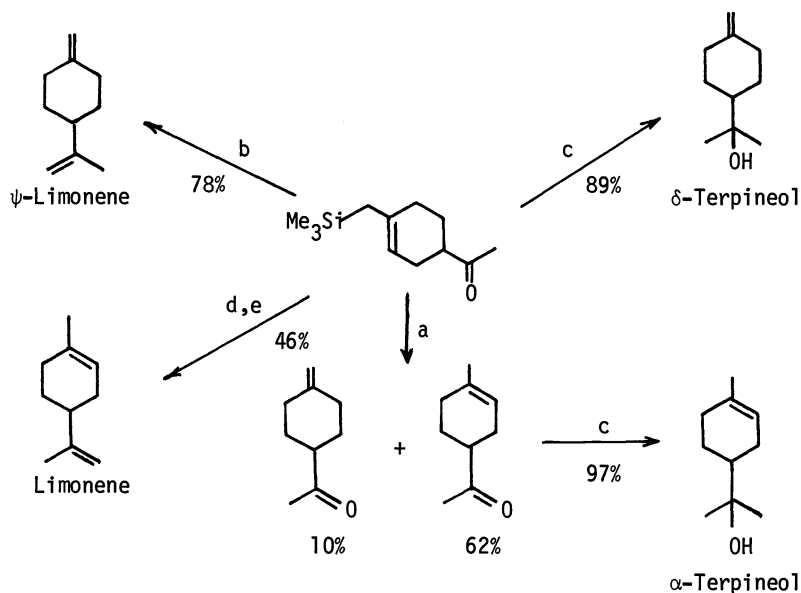
Fig. 1 Frontier orbitals for Diels-Alder reaction between a 2-electron-releasing group-substituted diene and an electron-withdrawing group-substituted olefin

These results may be explained in terms of the HOMO-LUMO interaction in the Diels-Alder reaction (Ref. 52). The extensive $\sigma(M-C)-\pi$ conjugation for 38 and 39 raises the HOMO of the dienes with increasing coefficients of atomic orbitals at the 1-position of the HOMO (Fig. 1). Higher *para/meta* ratio of 39 than 38 is thus reasonable because of the stronger $\sigma-\pi$ conjugation effect exerted by the Sn-C than the Si-C bond.

The regioselectivity in the Diels-Alder reaction of 38 can be improved dramatically by adding a small amount of aluminum trichloride. Aluminum trichloride can complex with dienophiles such as acrolein and methyl vinyl ketone and thus can lower the LUMO level of the dienophile.

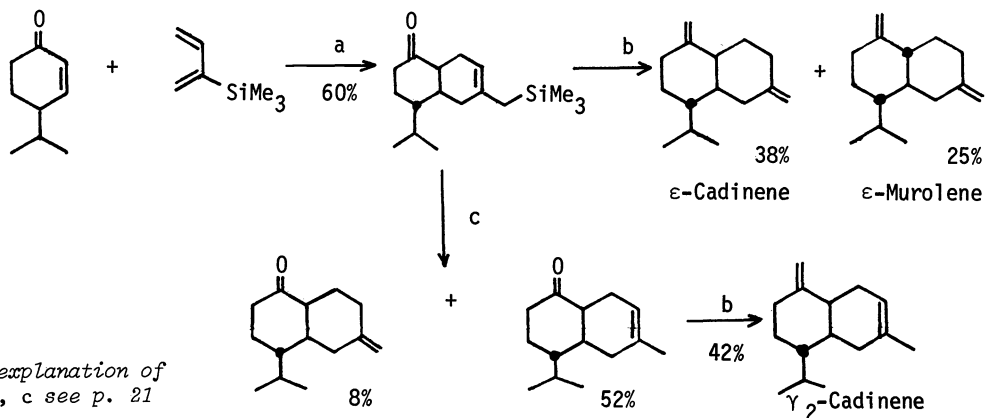


The Diels-Alder adduct (41) was obtained in 100% regioselectivity (Ref. 29). The product itself is an allylsilane and can be used for terpene synthesis. For example,

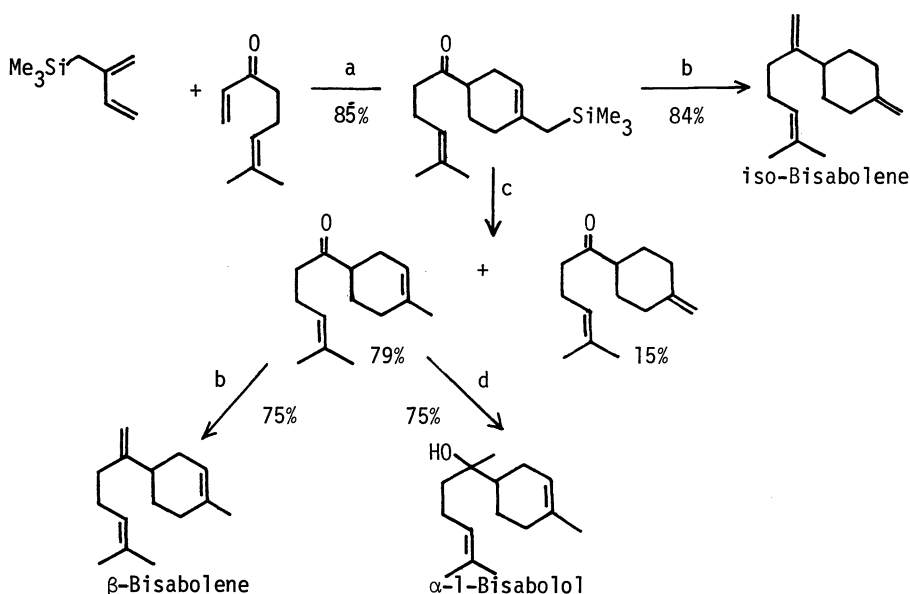


^aKF/DMSO, 120°, 12h. ^b1) Me₃SiCH₂MgCl/Et₂O, 35°, 2h. 2) MeCOCl-MeOH, 0°, 15min.
^c1) MeMgBr/Et₂O, 35°, 2h. 2) HCl-MeOH, rt, 20min. ^dMe₃SiCH₂MgCl/Et₂O, 35°, 2h.
^eCsF/DMSO, 130°, 3h.

Further applications to terpene syntheses are illustrated below.



^aAlCl₃ (0.1 equiv.)/CHCl₃, 60°, 13h. ^{b1})Me₃SiCH₂MgCl/Et₂O, 35°, 11h. 2)HCl-MeOH, 65°, 3h. ^cCsF/DMSO, 100°, 1h.



^aAlCl₃ (0.1 equiv.)/CH₂Cl₂, 30°, 16h. ^{b1})Me₃SiCH₂MgCl/Et₂O, 35°, 3h. 2)HCl-MeOH, 65°, 3h. ^cCsF/DMSO, 100°, 1h. ^dMeMgBr/Et₂O, 35°, 3h.

CONCLUSION

The reaction of allylsilanes with carbon electrophiles is very much versatile in the carbon-carbon bond formation. Regiospecificity, high reactivity, and stability of the reagent are the most important features of the reaction. A variety of allylsilanes has been prepared already, but if more general method of preparing functionalized allylsilanes could be developed, the reaction of allylsilanes would be a really useful method in organic synthesis. We have been working actively in this field.

Although it is only a few years that the use of allylsilane in organic syntheses has been studied extensively, there are many applications of the reaction. We can anticipate that the chemistry of allylsilanes will bring more fruitful results into the organic synthesis in near future.

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