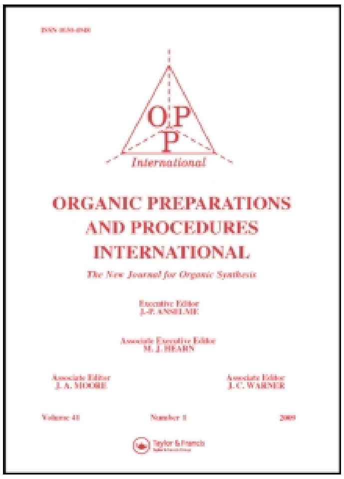

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SYNTHESIS AND REACTIONS OF FUNCTIONALIZED SILYLENOL ETHERS. A REVIEW

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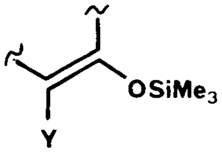
INTRODUCTION

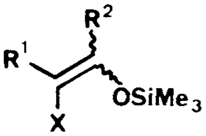
Silylenol ethers have become extremely useful intermediates for organic chemists[1-4] and their synthetic utility is growing rapidly year by year. β-Heterosubstituted silylenol ethers represent a new class of these silyl derivatives. The functionality introduced with the heteroatom gives to β-heterosubstituted silylenol ethers chemical properties which are notably different from those of their all-carbon silyl analogs. This review describes the preparations and reactions of β-heterosubstituted silylenol ethers in which the heteroatom may be a halogen, oxygen, sulfur, selenium, nitrogen or silicon.



Y = F, Cl, Br, I, OR, SR, SePh, NR_2, SiR_3

Silyl ketene acetals are not reviewed since they have been recently reviewed elsewhere.[1-4]

I. β-HALO SILYLENOL ETHERS



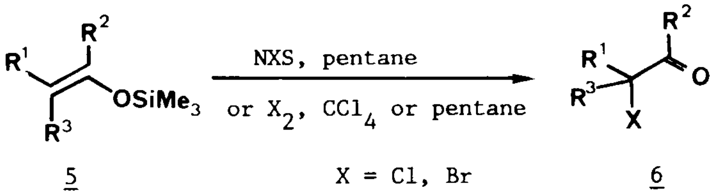
1 X = F   3 X = Br

2 X = Cl   4 X = I

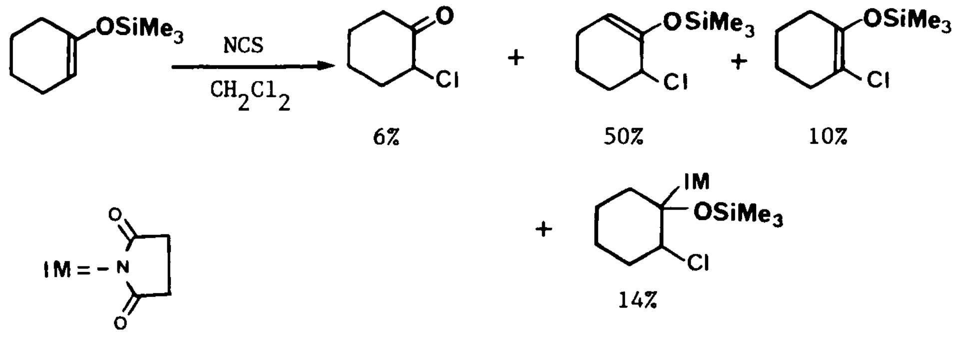
A. Synthesis

1. From Silylenol Ethers

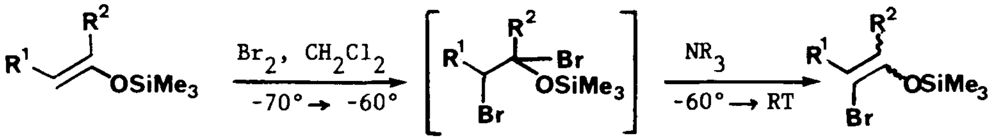
The reaction of silylenol ethers 5 with N-halosuccinimide or halogen leading to regiospecific α-halocarbonyl compounds 6 has been well known since the pioneering work of Hassner[5] and Conia.[6] At no time did these authors observe any β-halo silylenol ether.[5,7]



Recently, Chan and coworkers[8] carried out a mechanistic re-examination of the reaction of N-halosuccinimide with enol ethers and showed that at 0°C in dichloromethane the α-halo ketone was the minor product with cyclic ketones as well as with acyclic ketones, as in the following example. Under mild hydrolytic conditions, all the silyl compounds were converted to chloroketones. Thus the high yields of α-haloketones normally associated with the reaction of silylenol ethers and N-halo succinimide are almost certainly due to the hydrolytic work-up. In all the cases studied, the β-halo silylenol ethers are accompanied by three or four other products, so this method is not suitable from a synthetic perspective.

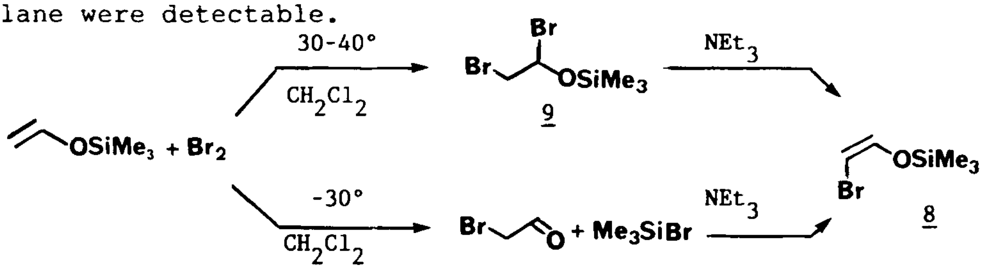


In the direct halogenation of silylenol ethers, addition of halogen to the double bond followed by spontaneous β-elimination of the volatile halotrimethylsilane was proposed as the mechanism.[5,9] Kumada et al.[10] turned to this explanation to account for the formation of β-halo silylenol ethers 3.



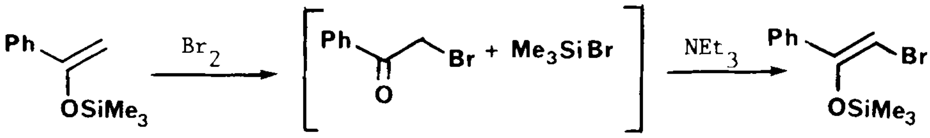
7 3

A large quantity of Z-isomer was obtained in this reaction (Z/E 90/10); silylenol ethers with bromine in the allylic position were not observed. The dibromo adduct 7 was later isolated under the same reaction conditions, except for temperature (+30°).[11,12] Voronkov et al.[12] observed that at -30° only α-bromocarbonyl compound and bromotrimethylsilane were detectable.



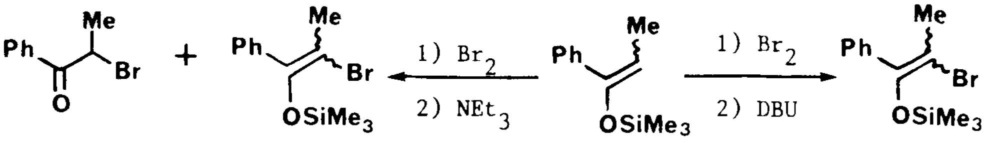
9 8

Dibromo compound 9, in the presence of a tertiary amine leads to the bromo enol ether 8.[13] Voronkov *et al.*[12] explained the previous results of Kumada[10] by a two-step reaction, namely formation of an α-bromocarbonyl compound (*via* a radical pathway at low temperature) followed by reaction in the presence of an amine (generally triethylamine) to yield a bromo silylenol ether such as 8 or 10.



10

The observations of Kumada *et al.*[10], who showed that 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) was necessary for the preparation of silylenol ether 11, were explained by the greater difficulty of enolization of the intermediate bromoketone 12. With the use of triethylamine, a mixture of silyl enol ether 11 and bromoketone 12 was obtained.



12 11 11

Nevertheless, this method is a valuable one for the preparation of β-bromo silylenol ethers in average to good yields even in the presence of a substituent-bearing double bond or an aromatic substituent.[14] (Table 1)

TABLE 1. β-Bromo Trimethylsilylenol Ethers 3 by Bromination of Silylenol Ethers[10]

R^1	R^2	Yield (%)	R^1	R^2	Yield (%)
H	H	50	Me	Ph	47
Me	H	71[a]	H	Me	48
Et	H	78	$(-CH_2-)_3$		30
H	Ph	47	$(-CH_2-)_4$		47

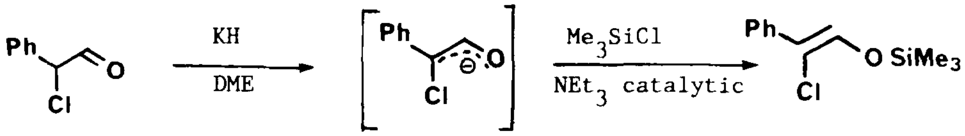
a) Z/E = 63/37

General Bromination Procedure[10]: *To a stirred solution of a* silylenol ether (100 mmol) in dichloromethane (20 mL) at low temperature (-30 or -60 °) was added bromine (1 equiv) in dichloromethane (20 mL). The addition was carried out at such *a rate that the solution always remained colorless to pale* orange. Subsequently, a tertiary amine (1.5 equiv) was added rapidly to the solution and the mixture was allowed to stand to room temperature. After evaporation of the solvent under *reduced pressure, the resulting slurry was* hydrolyzed at 0° by addition of water. The aqueous solution was extracted rapidly with petroleum ether and the extract was dried over sodium sulfate, and then distilled in vacuo to afford the *product as a colorless to pale yellow liquid.*

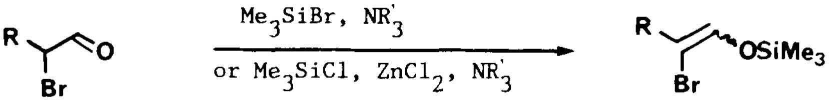
2. From α-Halocarbonyl Compounds

a. From α-Haloaldehydes

The chloro silylenol ether obtained from an aldehyde was prepared by silylation of the potassium enolate 13 of α-chlorophenylacetaldehyde 14.[15] Enol ether 15 was obtained as a single Z-isomer in high yield. β-Bromo silylenol ethers 17 can easily be prepared from α-bromoaldehydes 16 by reaction of bromotrimethylsilane in the presence of a tertiary amine.[16,17]



14 13 15



16 17

Satisfactory yields are observed with the use of bromosilane which is commercially available (Method A, Table 2) or which

TABLE 2. Preparation of β-Bromo Silylenol Ethers 17[16]

R	Method[a]	Yield[b] (%)	Ratio Z/E[c]
Me	A	50	67/33
	B	66	67/33
	C	62	63/37
Et	A	65	76/24
	B	70	76/24
	C	71	80/20
nPe	A	53	80/20
	B	55	82/18
	C	67	83/17
tBu	A	44	92/8
	B	68	93/7
	C	48	100/0

a) Method A: Me_3SiBr, NEt_3, Et_2O or C_6H_6, reflux 5-22 hrs.
Method B: Me_3SiCl, LiBr, NEt_3, MeCN, RT, 2-4hrs.
Method C: Me_3SiCl, $ZnCl_2$, NEt_3, Et_2O or C_6H_6, reflux 3-45hrs.

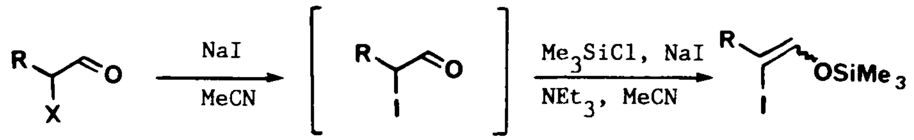
b) Distilled products.

c) Configuration determined by NOE effect or dipolar moment.

can be generated in situ from chlorotrimethylsilane and lithium bromide in acetonitrile (Method B, Table 2).[16] Chlorotrimethylsilane may also be used in the presence of $ZnCl_2$ as Lewis acid (Method C, Table 2).[18]

In all cases, almost the same mixture of Z- and E-isomers is observed for the three methods. The Z-isomer is always the major product and the percentage of this isomer increases with the bulkiness of substituent R (Table 2). Chlorotrimethylsilane without a Lewis acid catalyst or iodotrimethylsilane must be avoided because a mixture of chloro and bromo or bromo and iodo silylenol ethers is generally obtained.[16] This mixture of halo silylenol ethers can be explained by a halogen exchange on the starting α-bromoaldehyde.

This exchange has been turned to good account for the preparation of β-iodo silylenol ethers 18.[19] α-Iodoaldehydes 19 have been prepared in situ from α-chloro or α-bromoaldehydes by halogen exchange with sodium iodide in acetonitrile. The subsequent reaction with iodotrimethylsilane (generated from chlorotrimethylsilane and sodium iodide in acetonitrile)[20] and triethylamine gave the iodo compounds 18 in a one-pot reaction.



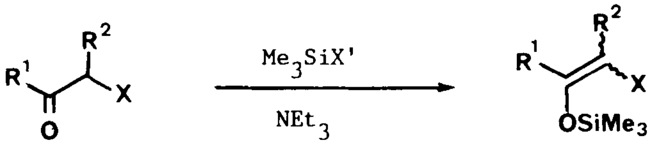
19 18

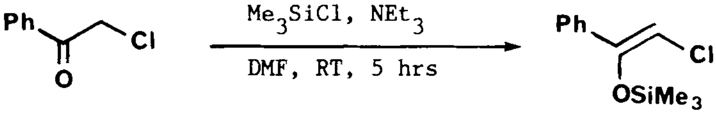
X = Cl, Br R = Me, Et, nPe $40/60 < Z/E < 80/20$

In all cases, iodo silylenol ethers 18 were a mixture of Z-and E-isomers. As previously observed for the bromo-derivatives,[16] the percentage of Z-isomer increased with the bulkiness of the R group.[19] Appreciable amounts of parent non-halogenated enol ether (separable by distillation) were obtained as by-product. Such a dehalogenation reaction has previously been observed with α-haloketones.[22,23]

b. From α-Haloketones

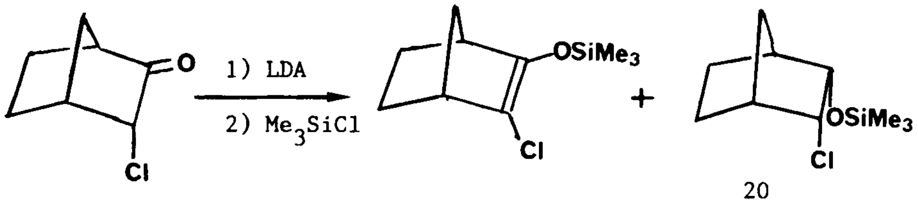
When the α-haloketones were enolizable only on the α-side, there was generally no difficulty for the preparation of the corresponding β-halo silylenol ethers which were isolated in high yields. Chlorotrimethylsilane and triethylamine were first used by House et al.[24] in DMF.





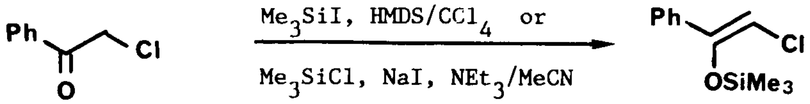
90%

Lithium enolates of chloroketones, quenched with chlorotrimethylsilane lead to β-chloro silylenol ethers[24-26] but sometimes mixed with reduction products.[25] The reduction product 20, resulting from the presence of the β-hydrogen of diisopropyl amine, may be avoided by the use of lithium hexamethyldisilazide or lithium 2,2,6,6-tetramethyl piperidide.[25]

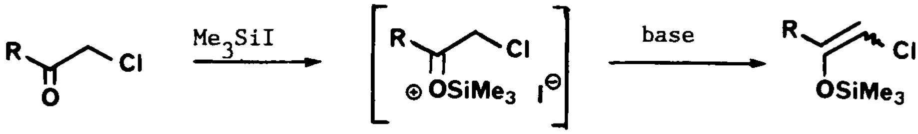


20

Iodotrimethylsilane,[27-29] more reactive than the chlorosilane, has also been successfully used. This in turn allows more hindered silyl derivatives such as t-BuMe$_2$SiCl to be used.[28,29]

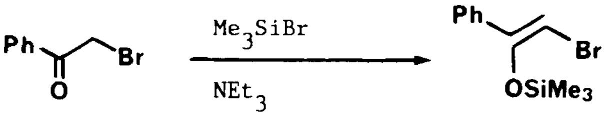


No dehalogenation occurs in any reactions; the base is obviously playing an active role in preventing dehalogenation, possibly by deprotonation of the intermediate oxonium 21.[27]



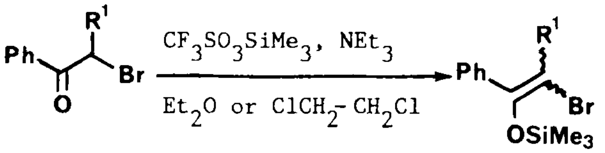
21

For the preparation of β-bromo silylenol ethers, good yields have been obtained with bromotrimethylsilane. Chloro trimethylsilane, with or without ZnCl$_2$ (in the presence of a tertiary amine) cannot be used because of the facile halogen exchange of the starting material leading (as for bromoaldehydes) to a mixture of chloro and bromo silylenol ethers[16] or to the corresponding chloroketone.[30] Trimethylsilyl triflate has also been successfully used by Simchen et al.[31] for the preparation of β-bromo silylenol ethers 22-25.



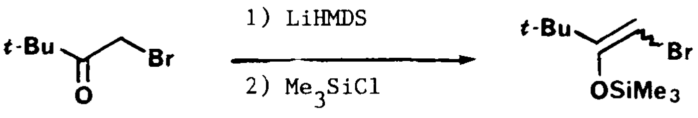
22

Solvent	Yield (%)
C_6H_6	55[16]
MeCN	77[32]



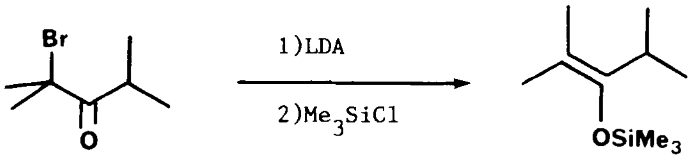
	R^1	Yield[31] (%)
22	H	83
23	Me	73
24	Et	67
25	Ph	72

The percentage of Z-isomer drops with the bulkiness of the R^1 group (100% R^1= H, 80% R^1= Me, 75% R^1= Et, 63% R^1= Ph). If a preformed lithium enolate of bromoketone is quenched with chlorotrimethylsilane the enol ether 26 is obtained.[33]



26

This process is not suitable for ketones such as 27 because in this case the non-halogenated enol ether such as 28 was obtained[34,35] instead of an enol ether with an allylic bromine.

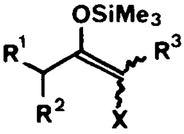


27

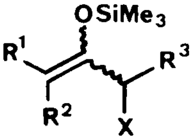
28

When possible, the use of halosilane in the presence of a base such as NEt_3, is the most convenient process for haloketones enolizable on the α-side as well as for haloaldehydes. Yields are generally high and preparation on a large scale is easy to realize.

The preparation of β-bromo silylenol ethers is more complex when α-haloketones enolizable on both the α- and α'-sides are used. Two regioisomers may be obtained, one with a vinylic halogen 29 and the second with an allylic halogen 30. All the methods described above have been used with various degrees of success in attempts to prepare one of the two isomers. None of these methods are suitable in all cases; there are always some exceptions.

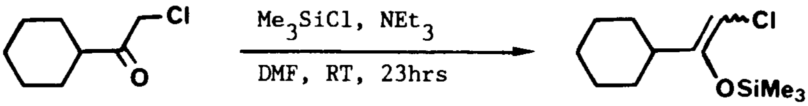


29



30

House et al.[24] were the first to isolate enol ether 31 as a single geometric isomer. But with 2-chlorocyclohexanone, a more basic amine 1,4-diazabicyclo[2.2.2] octane (DABCO) must be used to obtain the enol ether 32 in pure form. With triethylamine, the reaction was very slow and heating the reaction mixture resulted in the appearance of the regioisomer 33.[24]



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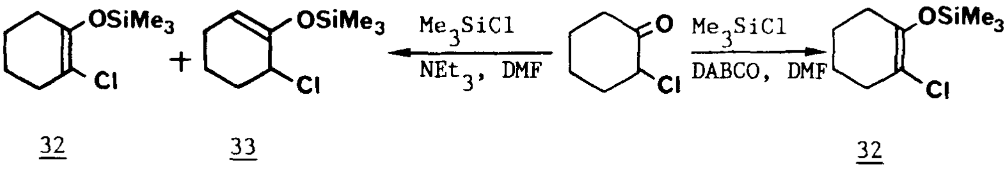
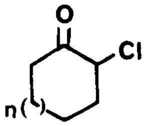
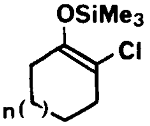
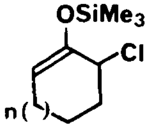
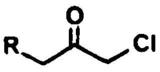
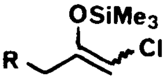
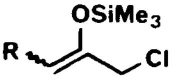


Preparation of Chloro-1-trimethylsilyloxy-2-cyclohexene 32.[24] A solution of 25.2 g (250 mmol) of 1,4-diazabicyclo[2.2.2]octane, 19.98 g (184 mmol) of chlorotrimethylsilane and 15.37 g (116 mmol) of 2-chlorocyclohexanone in 50 mL of dimethylformamide was stirred for 4 hrs. The mixture was partitioned between pentane and saturated aqueous sodium hydrogen carbonate. The organic extract was dried, concentrated and distilled. Bp 82°(4mm), yield 57%.

Miller and McKean have used iodotrimethylsilane in the presence of hexamethyldisilazane in carbon tetrachloride and generally obtained a mixture of the two regioisomers (Table 3).[27] In most cases, the major enolether is the one with an allylic halogen. Only 2-chlorocyclopentanone leads to the single regioisomer 35.(Table 3)

Preparation of chloro silylenol ethers.[27] General Procedure. To a solution of the chloroketone (2 mmol) in 5 mL of carbon tetrachloride which was cooled to -15°, was added 512 μL (2.4 mmol) of hexamethyldisilazane and 312 μL of trimethylsilyl iodide (2.2 mmol). After stirring at -15° for 0.5 h, the reaction mixture was warmed to 25° and the disappearance of the starting material monitored by IR or NMR. Upon completion, the reaction was diluted with pentane, washed with cold saturated sodium bicarbonate, 10% sodium thiosulfate, ice water and dried over sodium sulfate. Removal of the solvent yielded material which was pure enough for most purposes. The chloro trimethylsilylenol ethers could be further purified by vacuum distillation in a Kugelrohr apparatus.

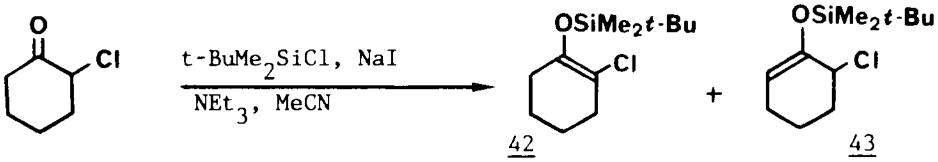
TABLE 3. Preparation of Chloro Silylenol Ethers with Me_3SiI in the Presence of HMDS in CCl_4

Ketones	Time (hrs)		Enol Ethers				Yield[a] (%)
							
	2.5	n = 1	32	57%	33	43%	94
	3	n = 0	34	0%	35	100%	85
							
	0.5	R = H	36	45%	37	55%	84
	10^b	R = nBu	38	25%	39	75%	98

a)Total yield. b)in CH_2Cl_2

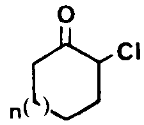
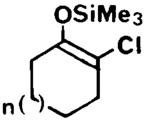
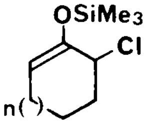
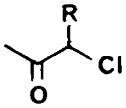
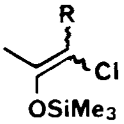
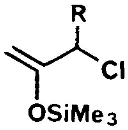
Iodotrimethylsilane (generated in situ from sodium iodide and chlorotrimethylsilane) in acetonitrile in the presence of triethylamine does not give the same results. In this case, it was the silylenol ether with a vinylic halogen which was obtained, generally uncontaminated by the regioisomer (Table 4).[28,29]

An exception is noted with 3-chloro-2-butanone which leads to the two isomeric silylenol ethers 40 and 41 in equal quantities (Table 4). This result can be explained by the increase of the steric hindrance of the double bond and the use of a more hindered silyl reagent does indeed result in a loss of the regioselectivity in this reaction.[28,29]



ratio 42/43 = 55/45

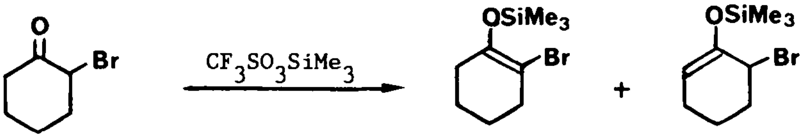
TABLE 4. Preparation of Chloro Silylenol Ethers with Me_3SiCl, NaI, in the presence of NEt_3 in Acetonitrile.

Ketones	Time (hrs)	Enol Ethers					Yield[a] (%)
							
	3	n = 1	32	95%	33	5%	87
	3	n = 0	34	95%	35	5%	55
							
	21	R = H	36	95%	37	5%	67
	3	R = Me	40	50%	41	50%	44

a)Total yield

Preparation of chloro silylenol ethers.[28] General Procedure. To a solution of chloro ketone (0.1 mol) in triethylamine (0.125 mol) was added 15.9 mL (0.125 mol) of chlorotrimethylsilane, then 18.8 g (0.125 mol) of sodium iodide in 130 mL of acetonitrile dropwise. The reaction mixture was stirred at 20°. The reaction progress was monitored by gas chromatography or thin layer chromatography (petroleum ether/ether : 50/50). Upon completion, the reaction mixture was diluted with pentane, filtered and extracted with pentane (5x50mL). The extracts were evaporated under reduced pressure and the chloro silylenol ether was distilled.

With 2-bromocyclohexanone, the use of trimethylsilyltriflate leads to the two regioisomers with a predominance for the one with bromine in the allylic position.[31]

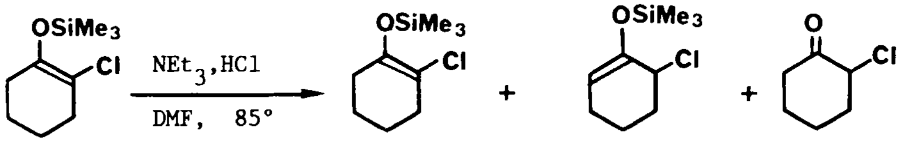


44 45

ratio 44/45 = 33/67

Preparation of bromo silylenol ethers.[31] General Procedure. To a solution of bromoketone (50 mmol) and 5.5 g (55 mmol) of triethylamine in 60 mL of dry ether or 1,2-dichloroethane was added at 0-5° 12.2 g (55 mmol) of trimethylsilyl trifluoromethanesulfonate. The reaction mixture was stirred for several hours at this temperature. The ethereal phase was separated and evaporated in dry conditions, then the crude product was distilled. In the case of 1,2-dichloroethane, the solvent was evaporated under reduced pressure and the residue was mixed with 60 mL of dry ether. Workup was completed as described above.

In House's method (Me_3SiCl,DABCO,DMF), a kinetically controlled process was proposed for the formation of the silyl enol ether 32, since this compound produced the enol ether 33 when equilibration was carried out in dimethylformamide at 85°C for 76 hrs in the presence of triethylamine hydrochloride. In this case, however, equilibration was complicated by the regeneration of considerable amounts of 2-chlorocyclohexanone.



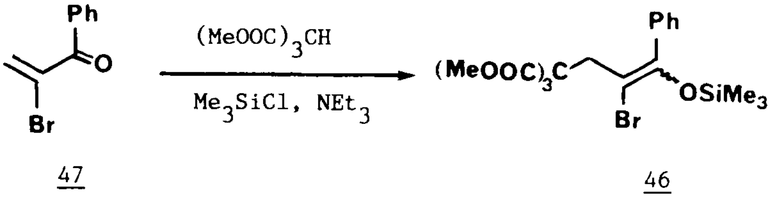
32 32 33

ratio 32/33 after equilibration = 45/55

Miller and McKean[27] have proposed that, even under mild conditions, the reaction leads to thermodynamically equilibrated products (ratio 32/33 = 57/43). The base and the solvent play a considerable role since the same silyl reagent (Me_3SiI) gives very different results with the same starting ketone (Tables 3,4). The above explanation leads to the conclusion that iodo trimethylsilane and triethylamine in acetonitrile give kinetically controlled products . However, any attempts at equilibration of enol ether 36 always lead to the corresponding chloroketone with no trace of the isomeric product 37.[36]

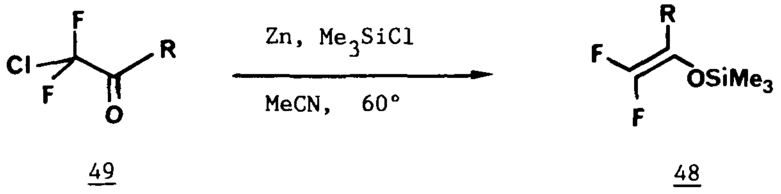
None of these methods is really a general route for the regiospecific preparation of halo silylenol ethers. The more useful methods for silylenol ethers with a vinylic halogen are those proposed by House[24] (Me_3SiCl, DABCO, DMF) and by ourselves[28] (Me_3SiCl, NaI, NEt_3, MeCN). The methods of Miller and McKean[27] (Me_3SiI, HMDS, CCl_4) and of Simchen[31] (CF_3SO_3-$SiMe_3$, NEt_3, Et_2O) are more convenient for preparing silylenol ethers with allylic halogens. For this last type of product, other efficient methods of preparation are described.[37,38]

Another procedure leading to β-bromo silylenol ether 46 used a Michael reaction of tricarbomethoxymethane on 2-bromo-1-phenyl-3-propene-1-one 47 in the presence of chlorotrimethylsilane.[30]



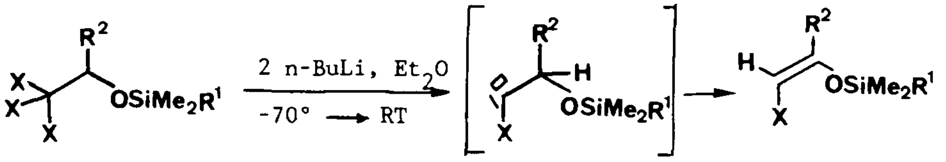
3. From Polyhalo Compounds

The only synthesis of β-fluoro silylenol ethers 48 has been described by Ishihara *et al.*[39] Chlorodifluoromethyl ketones 49 can be reduced by zinc dust to difluoromethyl ketones and the authors use this property to prepare enol ethers 48. The postulated zinc enolates, trapped by chlorotrimethylsilane in acetonitrile, lead to the corresponding silylenol ethers 48. It is noteworthy that compounds 48 cannot be prepared by the usual methods (Me_3SiCl, NEt_3 or LDA, Me_3SiCl) from difluoromethyl ketones.[39]

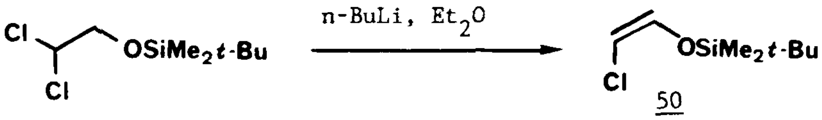


R = n-Hexyl, n-Octyl, 2-Me-n-Butyl, (35-74%)
Cyclohexyl, Benzyl, Phenyl

β-Chloro and β-bromo silylenol ethers may also be prepared from trihalosilyl ethers *via* a hydrogen migration of the intermediate carbene.[40] All the products are obtained in good yields with excellent stereochemical purity (exclusive formation of Z-isomer). β-Chloro enol ether 50 was also prepared from the corresponding dichloro silylether by dehydrohalogenation.[40]



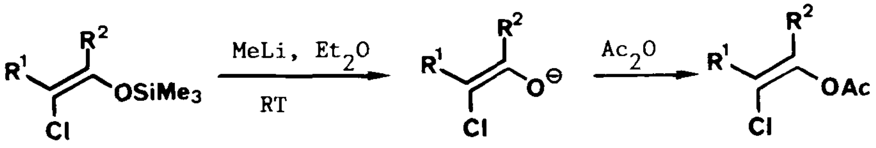
R^1 = Me, tBu X = Cl, Br R^2 = H, Me



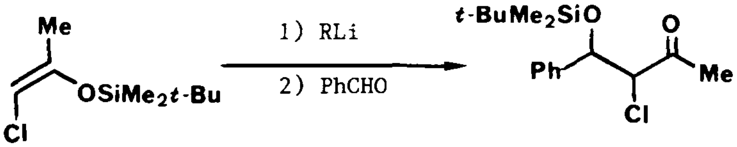
B. Reactions of β-Halo Silylenol Ethers

1. With Nucleophilic Reagents

With organolithium compounds two different reactions are observed depending on the nature of the halogen. The fundamental reaction of an alkyllithium on a silylenol ether leading to a regiospecific enolate [1-4] is also effective with β-chloro silylenol ethers.[24] These chloro enolates are very stable and can be recovered as appropriate derivatives (for example enolacetate[24]) in high yields after 24 hrs. Mukaiyama condensations provide a mixture of diastereoisomers of the protected chlorhydrin 51.[40]

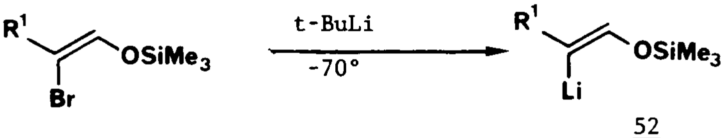


2



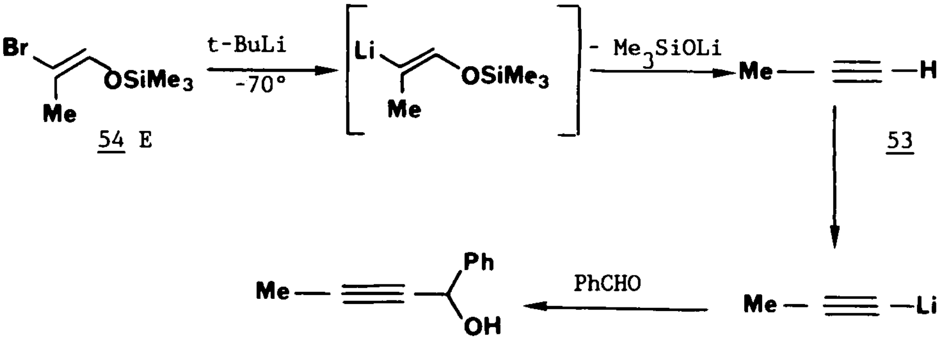
51

On the other hand, the reaction of β-bromo silylenol ethers with organolithium reagents is very different. Duhamel et al.[17,41, 42,45] have prepared a vinylic carbanion in the presence of t-butyllithium via a halogen-metal exchange.



52

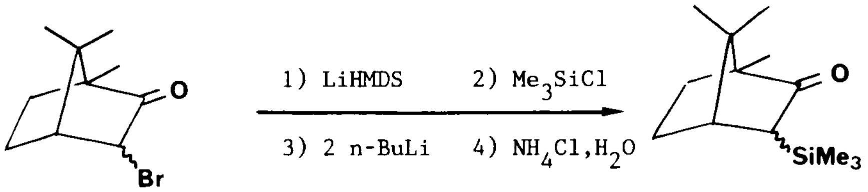
These authors have shown the importance of the geometry of the double bond: a Z-isomer yields anion 52 which is stable at low temperature (16 hrs at -70°). On the other hand an E-isomer rapidly gives an acetylenic compound such as 53 which can be metallated as shown by the reaction of the acetylide with benzaldehyde. Moreover, when a mixture of Z-and E-isomers of the silyl derivative 54 (Z/E = 65/35) was treated with a quantity of t-butyllithium equal to the E-isomer, the E-isomer reacted with the lithium reagent giving propyne 53 while the Z-isomer did not react at all.



Under related conditions, an O to C migration of the silyl group has been reported[33] to afford α-silyl ketones 55-57. Such a rearrangement was previously proposed from silylenol ethers of phenylselenoketones[43] (See II,B).

55 R= t-Bu

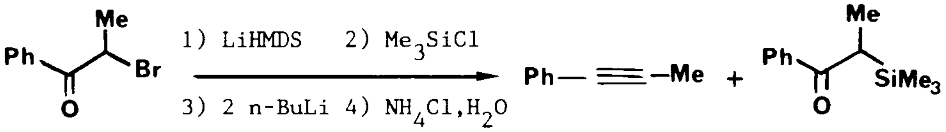
56 R= Ph



58

57

With α-bromopropiophenone 59, the major product was the acetylenic compound 60 accompanied by a little silylketone 61.



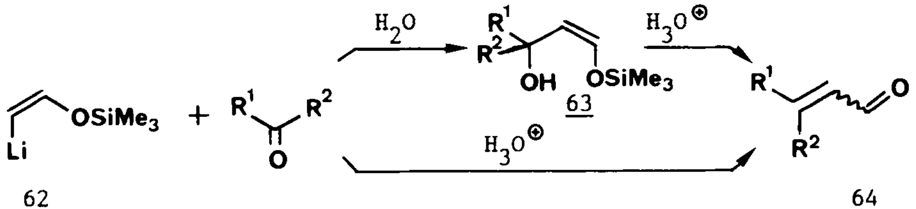
59

60 (83%)

61 (6%)

The presence of acetylenic derivative 60 was accounted for by a Peterson olefination. It also seems possible to explain the formation of this compound 60 by a trans-elimination of trimethylsilyloxylithium from the vinylic anion. Generally a methyl substituent, such as in ketone 59, increases the amount of E-isomer[31] which, even at -70°, leads to an acetylenic derivative.[17] Thus the O to C migration of the silyl group seems to be limited to bromomethyl ketones or to secondary α-bromoketones when the formation of the corresponding acetylene compound is not possible, as in ketone 58.

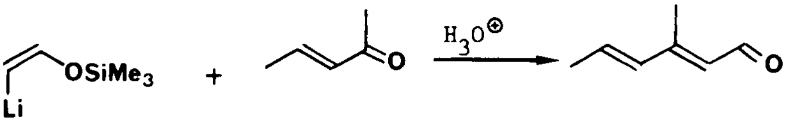
The vinylic anion 62 produced from the Z-isomer was able to react at -70° with carbonyl compounds leading to β-hydroxy silylenol ether 63, the precursor of α,β-unsaturated carbonyl compounds 64. Compounds 63 and 64 may be obtained in high and sometimes quantitative yields depending on the hydrolysis conditions.[17,41,42,44-46]



62

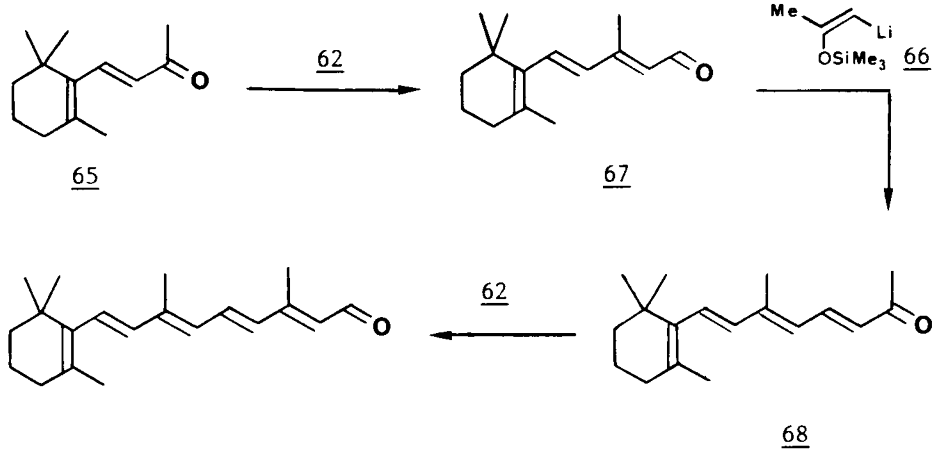
64

Taking into consideration the very high yields observed and the easy access to the starting β-bromo silylenol ether, this reaction seems to be the most valuable method for a one-step vinylogation of carbonyl compounds. The same type of reaction has also been obtained with unsaturated carbonyl compounds[44,45] where only the 1,2-addition was observed.

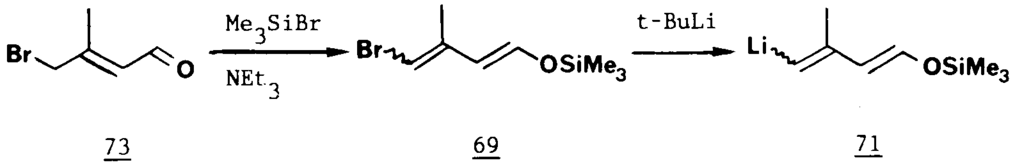


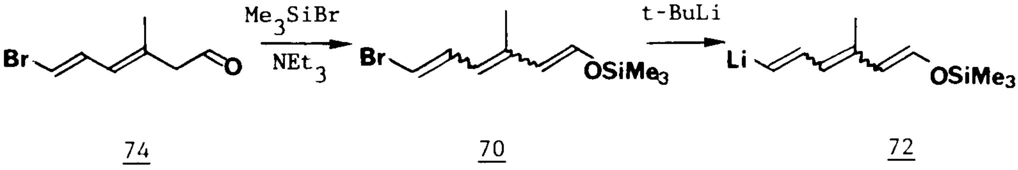
62

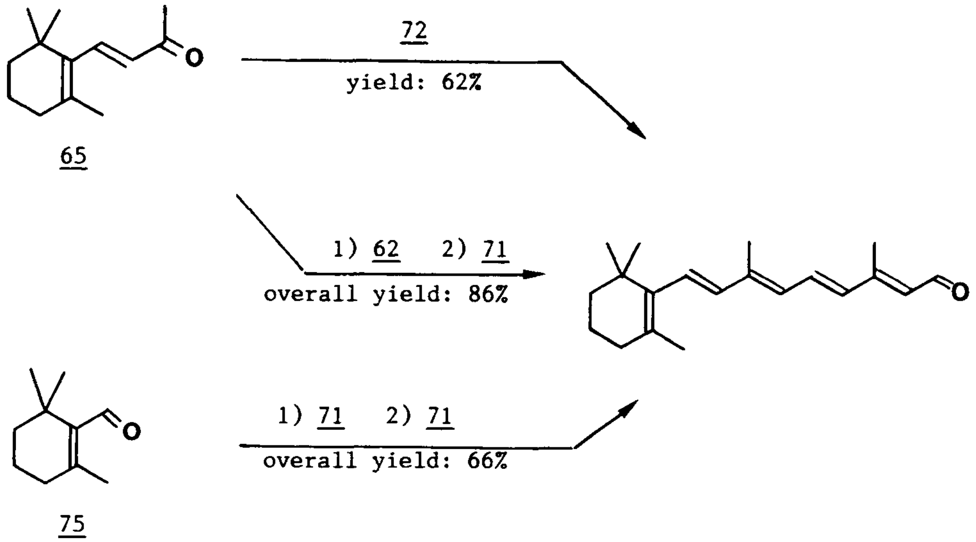
Using this synthetic route, a very short iterative synthesis of retinal has been reported from β-ionone 65. Two vinylic anionic reagents 62 and 66 (the synthetic equivalents of the α-anion of acetaldehyde and acetone respectively) were used, leading to enealdehyde 67, enone 68 and finally to retinal in 48% overall yield.[44,45] In all these reactions β-bromo silylenol ethers can be regarded as α-aldo or α-keto anion precursors.



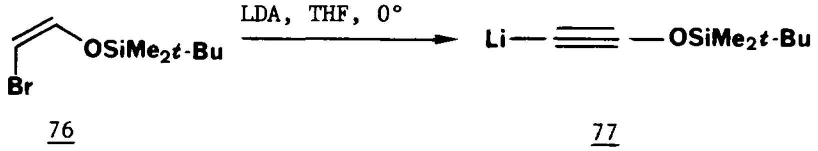
It is noteworthy that vinylogs of β-bromo silylenol ethers 69 and 70 and the corresponding anionic species 71 and 72 can also be produced from the corresponding bromoaldehydes 73 and 74.[44] Combinations of these anionic reagents have also been used in a short synthesis of retinal from β-ionone 65 or cyclocitral 75.[44]

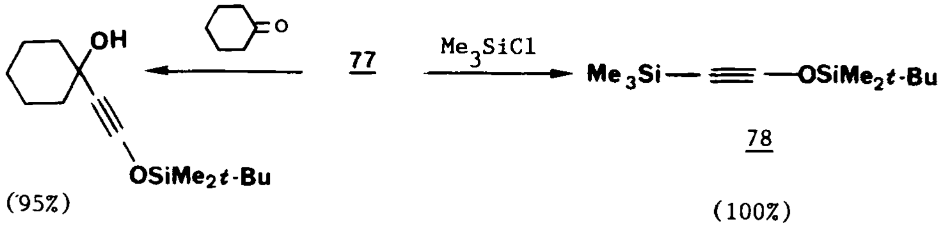




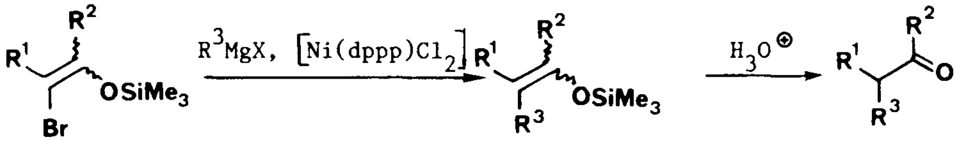


Dehydrohalogenation of β-bromo silylenol ether 76 with lithium diisopropylamide readily gave access to acetylide 77[40] which gives the silyl compounds 78 with chlorotrimethylsilane or undergoes condensation with cyclohexanone.[40]





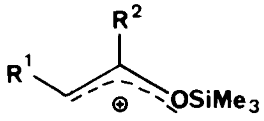
In the presence of nickel-phosphines, as catalysts, β-bromo silylenol ethers 3 coupled with Grignard reagents to produce alkylated or arylated silylenol ethers 5 or the corresponding carbonyl compounds 79 after acidification.[47]



3 5 79

dppp = $Ph_2P(-CH_2-)_3PPh_2$

In this reaction silylenol ethers 3 may be regarded as the enolonium equivalent 80 in the reaction with the nucleophilic moiety $R_3^{\ominus}$ of the Grignard reagent.

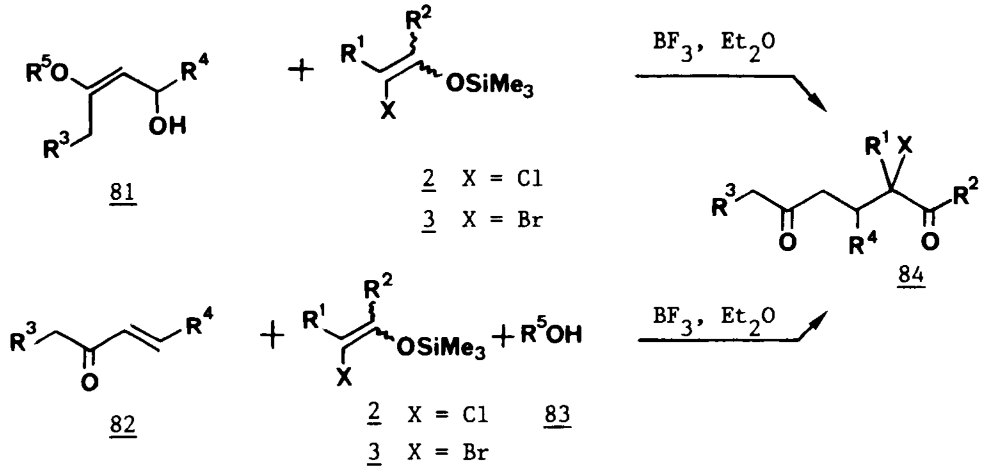


80

A noteworthy feature of these reactions, involving the nucleophilic reagents, is that the reaction of alkyllithium reagents with β-bromo silylenol ethers is equivalent to the exchange with the substrates of "$Br^{\oplus}$ " groups while reactions with LDA and Grignard reagents are equivalent to the exchange of "$Br^{\ominus}$ " groups.

2) With Electrophilic Reagents

Like silylenol ethers, β-halosilylenol ethers can also give electrophilic reactions. In the presence of a Lewis acid as catalyst, silylenol ethers 2 or 3 react with hemiacetal vinylogs 81 or with a mixture of enone 82 and hydroxy compounds 83 to yield α-halo δ-dicarbonyl compounds 84.[29,48,49]



81

2 X = Cl
3 X = Br

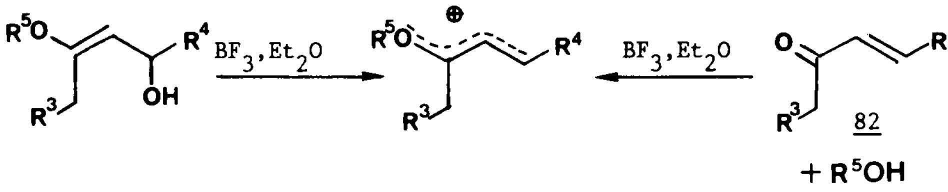
84

82

2 X = Cl
3 X = Br

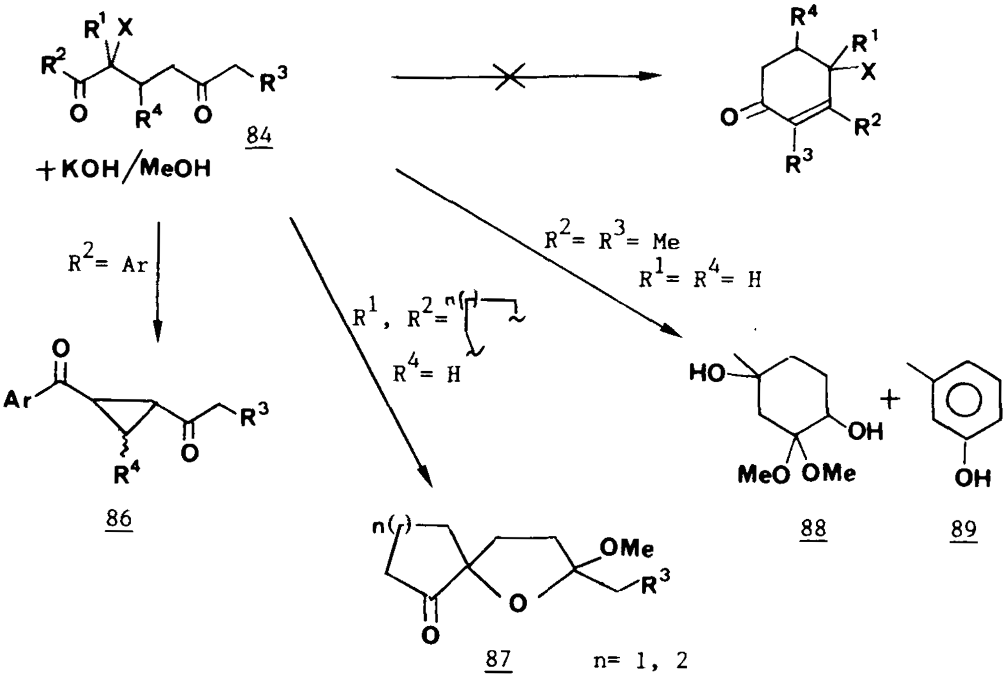
83

Hydroxy compounds 83 may be primary or secondary alcohols. The proposed mechanism supposes an intermediate delocalized oxonium 85 generated from hemiacetal vinylogs 81 or from the mixture of 82 and 83. This reaction is the only general preparative method for compounds 84.



81 85 82 83

On basic treatment, δ-dicarbonyl compounds 84 do not give the corresponding cyclohexenones, but instead yield cyclopropanes 86, spiroheterocycles 87 or ketal 88 and phenol 89 depending on the nature of the R^2 group.[29]



The properties of β-bromo silylenol ethers make them useful intermediates which can be regarded as precursors of synthetic equivalents of α-keto or α-aldo anions[17,40-42,44-46] or α-keto cations.[47] β-Chloro silylenol ethers can generate anions regiospecifically when in reaction with alkyllithiums.[24] All these enol ethers can also yield halogenated 1,5-dicarbonyl compounds on reaction with electrophilic species 85.[29,48,49]

II. β-ALKOXY, β-ALKYLTHIO AND β-PHENYL SELENO SILYLENOL ETHERS

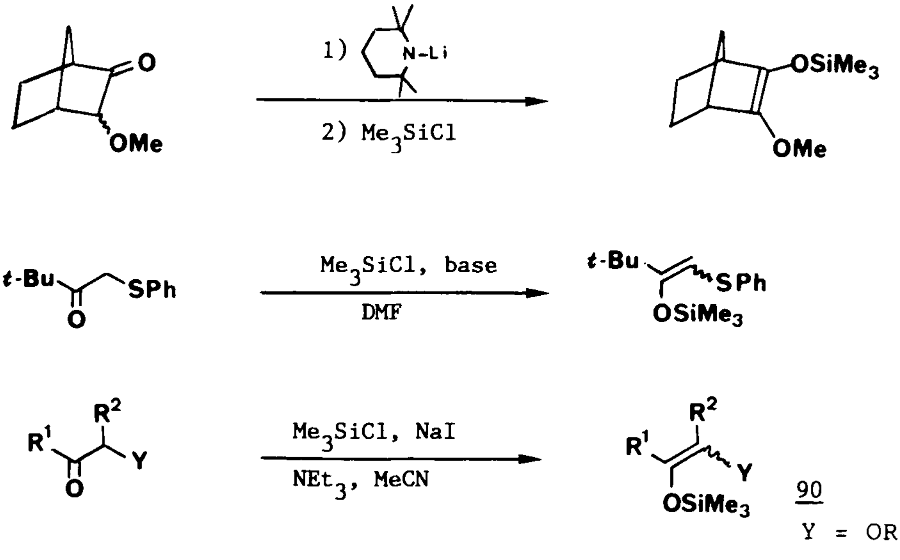
A. Synthesis

1. From α-Heterosubstituted Aldehydes and Ketones Enolizable only on the α-Side

Y = OR , SR

90

As previously observed with the halogenated analogs, enol ethers 90 are generally easy to prepare. Two methods have been described. The first involves quenching a preformed lithium enolate with chlorotrimethylsilane.[25] Lithium diisopropylamide must be avoided because of its tendency to give a reduction reaction. The second uses the reaction of a halosilane with the carbonyl compounds in dimethylformamide[50] or in acetonitrile[49,51] in the presence of a base.



90

Y = OR, SR

Preparation of methoxy silylenol ethers.[49,51] General Procedure. To a cooled solution (5-10°) of 12.6 g (0.125 mol) of triethylamine, 13.56 g (0.125 mol) of chlorotrimethyl silane and 18.75 g (0.125 mol) of sodium iodide in 130 mL of acetonitrile was added dropwise under nitrogen 0.1 mol of α-methoxyaldehyde. After 15 min at this temperature the reaction mixture was allowed to warm to room temperature, while stirring, for 20 h. The reaction mixture was diluted with 30 mL of pentane, filtered and extracted with pentane (5x30 mL). The extract was evaporated under reduced pressure and the methoxy silylenol ether was distilled.

The results of the second method are summarized in Table 5.[49,51]

TABLE 5. Preparation[a] of β-Alkoxy and β-Alkylthio Silylenol Ethers 90[49,51]

R^1	R^2	Y	Yield (%)	Isomer Ratio
H	Ph	OMe	70	70/30
H	nPe	OMe	67	55/45
H	Ph	SEt	60	70/30
H	Ph	StBu	68	60/40
H	nPe	SEt	60	80/20
H	Et	SEt	60	75/25
H	Et	SPh	92	Z[b]
Ph	H	OMe	70	100/0
Ph	Ph	OMe	55	90/10
Ph	H	SEt	70	100/0
Ph	Ph	SEt	90	60/40
tBu	H	SEt	60	E[b]

a) Me_3SiCl, NaI, NEt_3, MeCN. b) Geometry was determined by NOE effect.

This method[49,51] generally leads to a mixture of the two geometric isomers except for the derivatives of substituted acetophenone or pinacolone.

2. Synthesis from α-Substituted Ketones Enolizable on the α-and α'-Sides

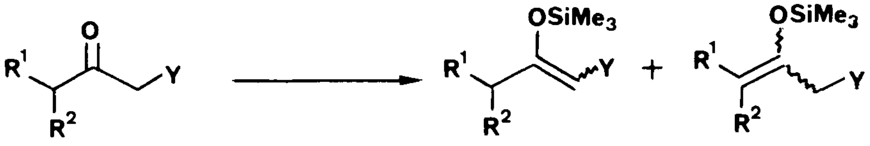
The reaction methods described in section I are used for acyclic and cyclic ketones:

a) Reaction of a preformed enolate with chlorotrimethylsilane (or t-butyl dimethylchlorosilane).[49,51,52]

b) Reaction of a ketone with chlorotrimethylsilane, a base in dimethylformamide[50] or in dichloromethane.[52]

c) Reaction of a ketone with iodotrimethylsilane (generated in situ from chlorotrimethylsilane and sodium iodide) and triethylamine in acetonitrile.[49,51]

The regioisomers with vinylic heteroatom (92 or 97) and allylic heteroatom (93 or 98) can be obtained. The ratio 92/93 or 97/98 is highly dependent on whether the structure of the starting ketone is acyclic or cyclic. The results for acyclic ketones are shown in Table 6.

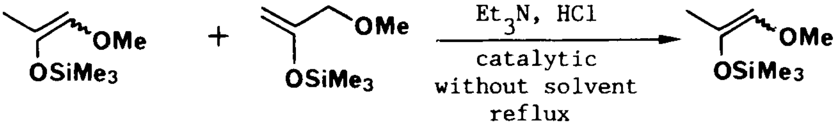


91 92 93

Method A leads to enol ethers 92 with one of the geometric isomers as the sole product or as the major isomer, the E-isomer for the enol ethers prepared from heterosubstituted acetone ($R^1 = R^2 = H$) and the Z isomer for the others. The geometry of the double bond is very dependent on the bulkiness of the R^1 and R^2 substituents.

Methoxyketones always give a mixture of the two regioisomers in almost the same quantity by method C. In contrast, the sulfur compounds lead to the enol ethers 92 by methods B and C as by method A but with a change in the geometry of the double bond.

It is noteworthy that the mixture of enol ethers 94 and 95 from methoxyacetone, (94/95 = 55/45) placed in isomerization conditions leads to the pure enol ether 94 in 2 hrs.[36]



94 95 94

(78%)

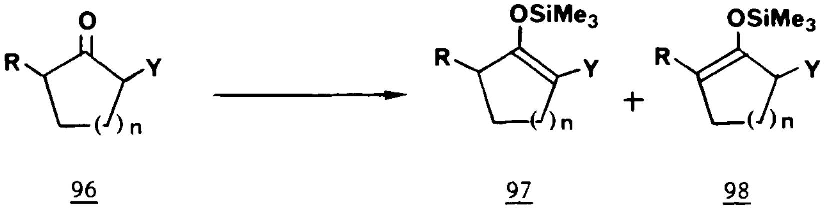
Ratio Z/E = 25/75

TABLE 6. Preparation of Enol Ethers 92 and 93 from Acyclic Ketones 91

R^1	R^2	Y	Method[a]	Total Yield (%)	Ratio 92/93	92 Ratio Z/E[c]	Ref.
H	H	OMe	A	80	100/0	0/100	49
H	H	OMe	C	60	55/45	15/85	49
Me	Me	OMe	A	80	100/0	100/0	49
Me	Me	OMe	C	60	55/45	100/0	49
Me	Et	OMe	A	80	100/0	95/5	49
H	H	SMe	A	b	100/0	20/80	52
H	H	SMe	B	b	100/0	83/17	52
H	H	SEt	A	75	100/0	0/100	51
H	H	SEt	C	b	100/0	65/35	51
H	H	SPh	B	b	100/0	b	50

a) Method A: LDA, Me_3SiCl; Method B: Me_3SiCl, base, DMF or CH_2Cl_2; Method C: Me_3SiCl, NaI, NEt_3, MeCN. b) Not given. c) Geometry was determined by NOE effect.

With cyclic ketones, results are dramatically dependent on the ring size, the method used and the nature of the heteroatom. The results are summarized in Table 7. The low yield (entry 1) obtained in the cyclobutyl series is not typical. With the cyclopentane ring, method A leads to enol ether 97 as the sole or preponderant product (entries 2,3), but method C yields enol ether 98. With the cyclohexane ring, results are more complex. With selenium and oxygen as the heteroatoms, method A leads selectively (entries 6,11) or specifically (entries 10,12) to the enol ether 97, but with an alkylthio group the ratio 97/98 is reversed (entry 8). Method C (entries 7,9) changes the preceding ratio yielding preferentially enol ether 98 with a methoxy group and enol ether 97 with an alkylthio group. The solvent also plays a major role in the isomer ratio observed (entries 2,3 and 5,6).



While the choice of a methodology for the preparation of β-heterosubstituted silylenol ethers 92 from acyclic ketones is easy, there is some difficulty in choosing a procedure for silylenol ethers 97 from cyclic ketones. Silylenol ethers 93 or 98 bearing the substituent Y (Y = OR, SR) in the allylic position (uncontaminated by the regioisomer) are never obtained, except for the silylenol ether of 2-methylthiocyclopentanone with method C (Table 7).

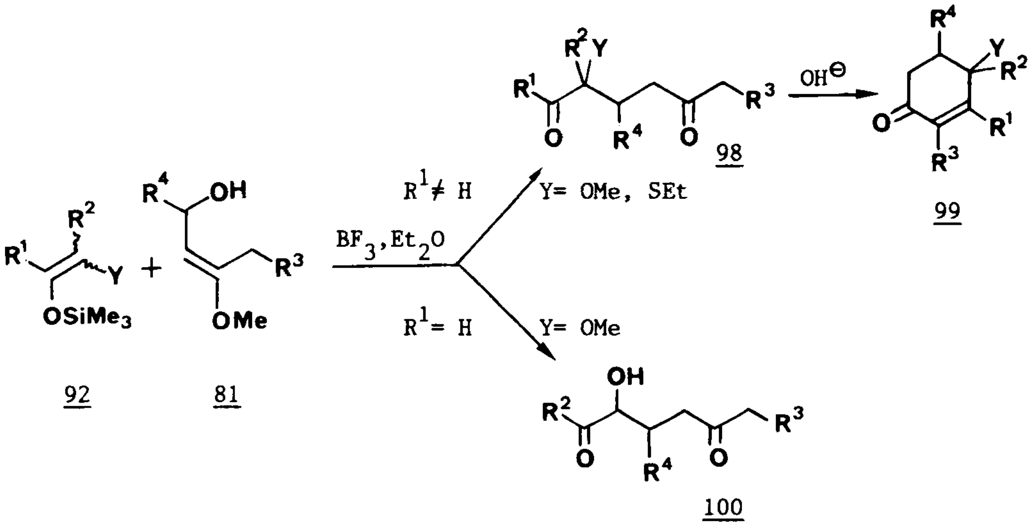
TABLE 7. Preparation of Enol Ethers of Cyclic Ketones <u>96</u>

Entry	n	R	Method[a]	Y	solvent (°C)	Total Yield (%)	Ratio <u>97</u>/<u>98</u>	Ref.
1	0	H	A	OMe	Et_2O (-78)	20	100/0	25
2	1	H	A	OMe	Et_2O (-78)	74	30/70	25
3	1	H	A	SEt	THF (-78)	70	5/95	51
4	1	H	C	SEt	MeCN (RT)	60	95/5	51
5	2	H	A	OMe	Et_2O (-78)	80	15/5	25
6	2	H	A	OMe	THF (-78)	75	75/25	49
7	2	H	C	OMe	MeCN (RT)	62	45/55	49
8	2	H	A	SEt	THF (-78)	82	45/55	51
9	2	H	C	SEt	MeCN (RT)	82	70/30	51
10	2	H	A[b]	SePh[c]	THF/HMPA (0)	82	100/0	43
11	2	H	A[b]	SePh	THF/HMPA (-78)	d	80/20	43
12	2	Me	A[b]	SePh	THF/HMPA (-78)	87	100/0	43

a) See Table 6. b) <u>t</u>-Bu(Me)$_2$SiCl. c) Some other β-phenylseleno silylenol ethers were prepared.[43] No yield and no preparation method were given. d) Not given.

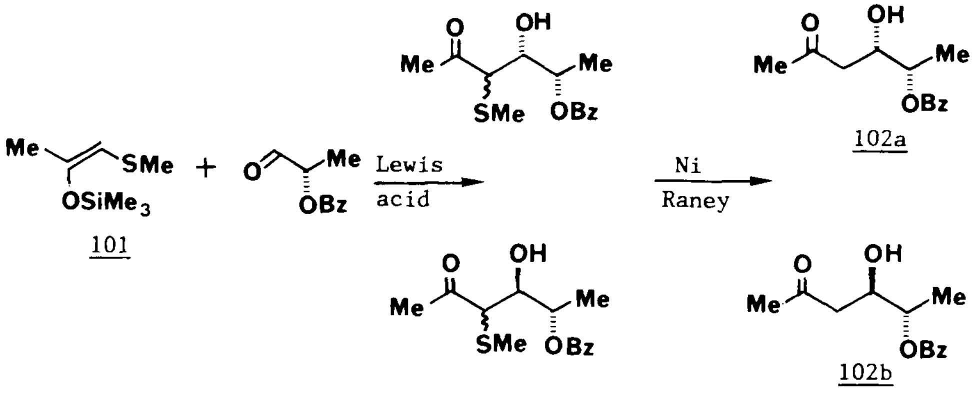
B. Reactions

Silylenol ethers <u>92</u> or <u>97</u> (Y = OR, SR) have been used for Lewis acid mediated reactions with hemiacetals vinylogs <u>81</u>. In all cases, 1,5-dicarbonyl compounds are obtained.[49,51]

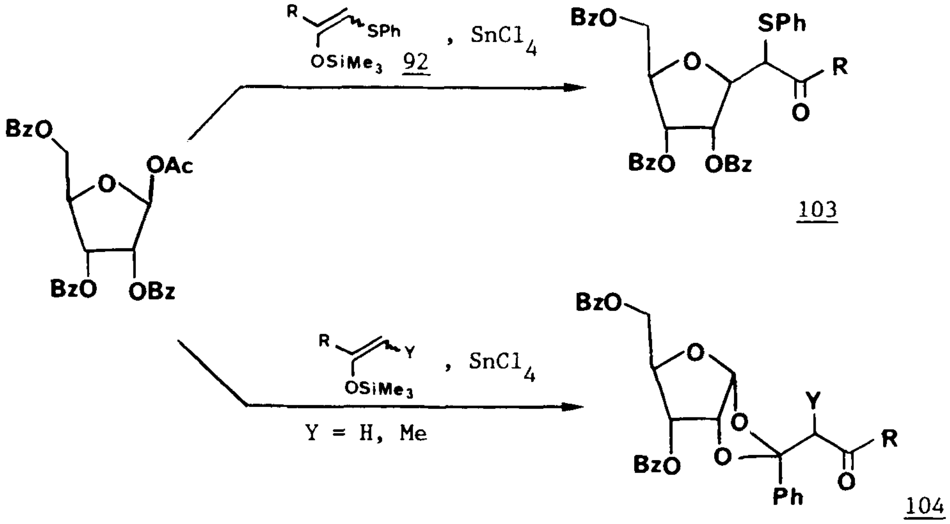


When $R^1 \neq H$ (silylenol ethers of ketones), a regiospecific reaction of the cation 85 is observed on the carbon bearing the methoxy or ethylthio group, leading to 1,5-diketones 98 which can be in turn cyclized in basic medium to cyclohexenone 99.[49,51] The same reaction is observed with silylenol ethers 97 of cyclic ketones. But when the substituent R^1 is H (silylenol ethers from aldehydes), reaction of the cation 85 takes place on the less hindered carbon bearing the trimethylsiloxy group leading to 2-hydroxy-1,5-diketones 100.[49,51]

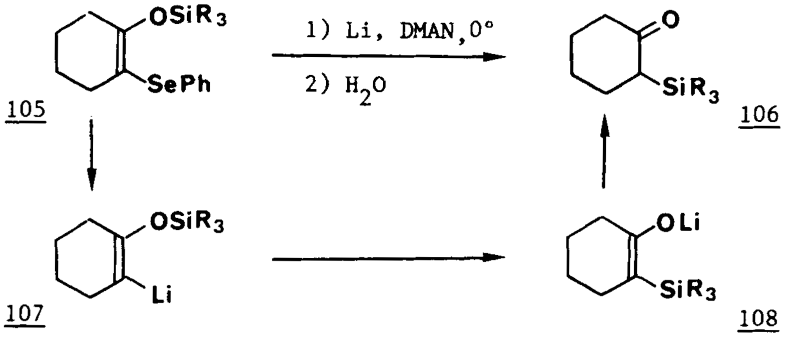
In aldol reactions, Uenishi *et al.*[52] used the silylenol ether 101 and proposed a stereocontrolled synthesis of β,γ-dihydroxyketone derivatives 102a,b. Pure syn-diol 102a (102a/102b = 99/1) may be so obtained in the presence of $MgBr_2$.



Kuwajima et al.[50] have shown that phenylthio silylenol ethers 92 react selectively at C[1] of 2,3,5-tribenzoyl-D-ribofuranosyl acetate yielding compound 103 whereas their all-carbon equivalent gave the product 104.



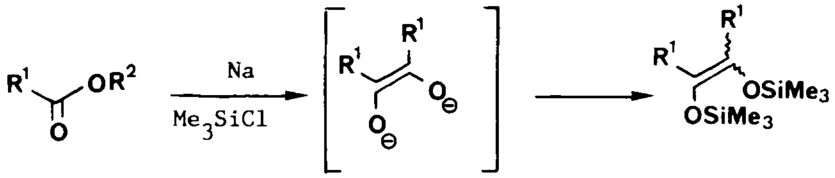
In the presence of lithium and dimethylaminonaphthalene (DMAN) phenylseleno silylenol ethers such as 105, yielded silylketones such as 106 after aqueous work-up.[43] The authors explained this result via a vinylic anion 107, which underwent an O to C migration of the silyl group to lead to an enolate 108. With cyclic enol ethers, yields are good and there are no by-products other than diphenyldiselenide. With phenylseleno silylenol ethers from acyclic ketones, however, acetylenic compounds are formed as by-products. These acetylenic compounds resulting from the elimination of silyloxylithium, may be produced, as for bromo silylenol ethers,[17] from the E-isomer.



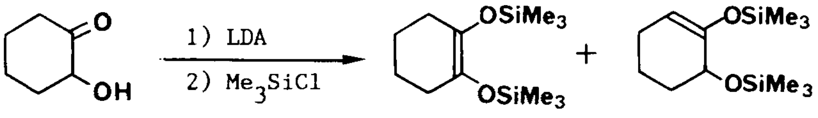
III. SILYLENEDIOL ETHERS

A. Synthesis

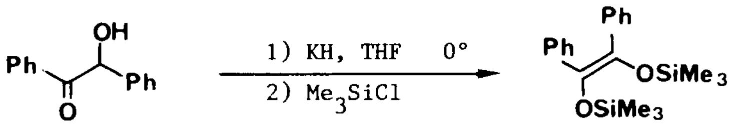
These compounds may be prepared by the acyloin condensation in the presence of chlorotrimethylsilane as previously described in two excellent reviews.[53,54] In these reactions the intermediacy of enediolate 110 is generally accepted. However Wilson *et al.*[55] have shown that adipoin reacts with lithium diisopropylamide at -78° with chlorotrimethylsilane to yield the silylenediol ethers 111 and 112. Under these conditions silylenediol ether 112 is the major product (ratio 111/112 = 15/85). However, adipoin in the presence of chlorotrimethylsilane and triethylamine in refluxing dimethylformamide leads to compound 111 as the major product (ratio 111/112 = 67/33). The acyloin condensation gives a 89/11 ratio for compounds 111/112. Quite pure enol ether 113-Z has been prepared from benzoin 114.[56]



110 109



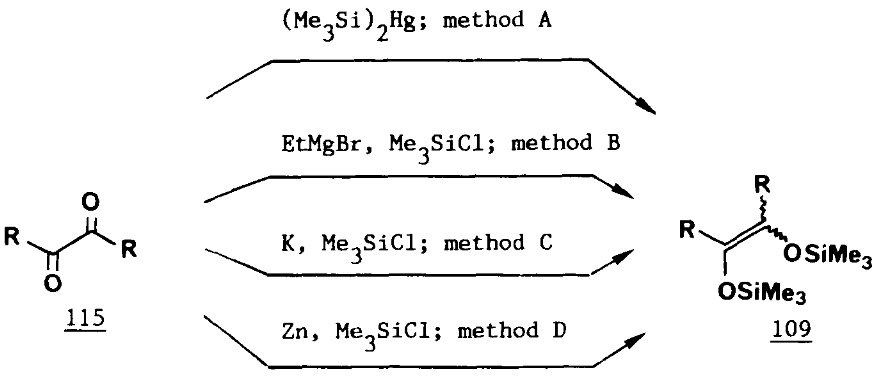
111 112



114 113-Z

Ratio 113-Z/113-E = 95/5

These enol ethers can also be prepared from diketones 115 by treatment with bis(trimethylsilyl)mercury,[57] by reduction with ethylmagnesium bromide[58] or potassium[59] followed by trapping of the enolate with chlorotrimethylsilane. These enol ethers may be more easily obtained by stirring a mixture of diketone 115, zinc powder and chlorotrimethylsilane in ether at room temperature.[60]



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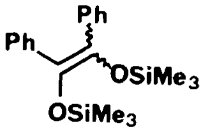


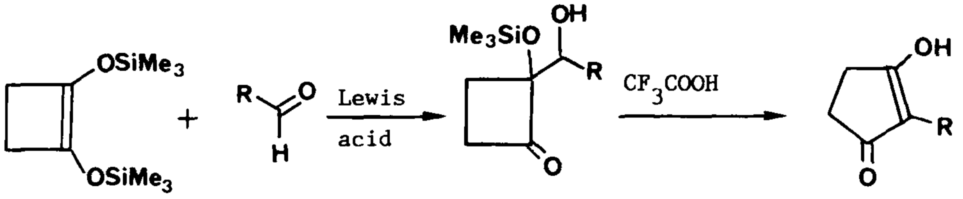
113

Method	A	B	C	D
Yield (%)	75		88	75
Z/E Ratio	0/100	57/23	90/10	94/6

The last two methods[59,60] lead to silylenediol ethers 113 in good yields with the Z-isomer predominating.

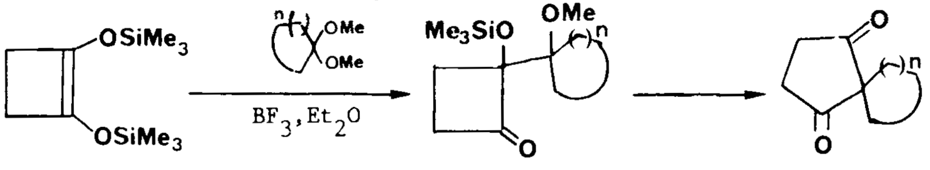
B. Reactions

This part describes the use of silylenediol ethers 109 in reactions not previously reviewed.[53,54] The aldol reaction is the most useful one, especially with the bis-silylated succinoid 117 leading to cyclopentanedione after treatment with trifluoroacetic acid.[61,62]



117

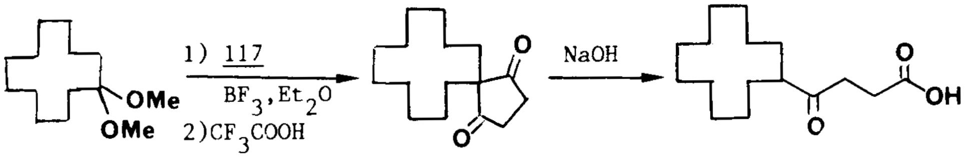
Ketals may also be used in the presence of boron trifluoride etherate as the Lewis acid.[61,62] Spirocompounds 118 may be so obtained with ketals of cyclic ketones.[61]



117

118

1,3-Diketone 119 undergoes cleavage thus affording a useful sequence for the synthesis of ketocarboxylic acids 120.[63] The aldol reaction product 121 can also be treated with a Grignard reagent and then oxidized by lead tetraacetate to 1,4-diketones 122.[64] Thioketals may also be used in this type of reaction.[65] Silylenediol ethers 123 were also used for the preparation of fused polycyclic compounds via cyclopropanation.[66]



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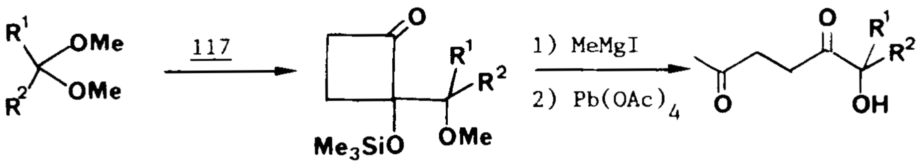
120



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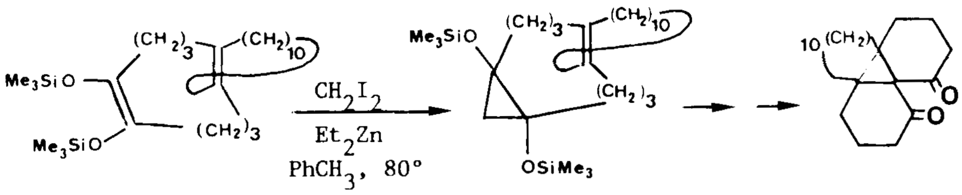
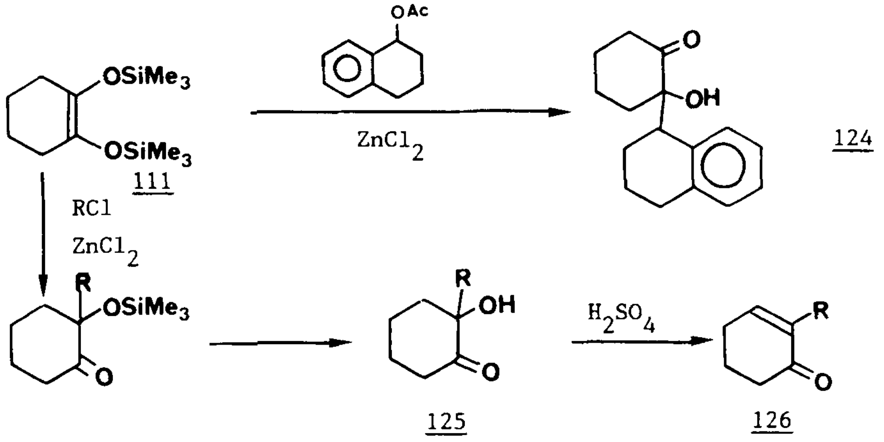


123

The reaction of silyl ethers 111 with secondary or tertiary acetates or halides leads to hydroxyketones 124,125 or enone 126.[67,68] The use of silylenediol ethers 109 in the synthesis of spirovetivone has also been reported.[69]



IV. β-AMINO SILYLENOL ETHERS

A. Synthesis from α-Amino or α-Amidoketones

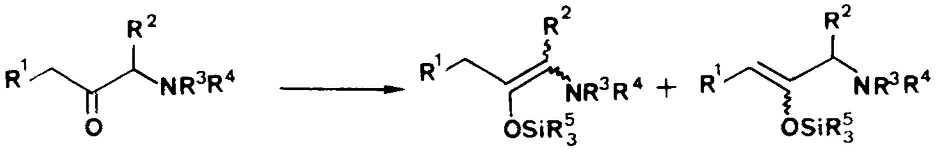
Four major routes have been used to produce amino silylenol ethers:

Method A: lithium diisopropylamide, chlorotriethylsilane in THF at -78°C.[70]

Method B: lithium hexamethyl disilazane, chlorotriethylsilane in THF (-78°C RT).[70]

Method C: chlorotriethylsilane, triethylamine in dimethylformamide at 80°C (48hrs).[70]

Method D: iodotrimethylsilane (generated in situ from chlorotrimethylsilane and sodium iodide), triethylamine in acetonitrile at room temperature.[71,72]


128 129

<u>Preparation of amino silylenol ethers. General Procedure</u>

<u>Method A</u> (with lithium diisopropylamide)[70] : a solution of n-butyl lithium in hexane (1.4 mmol) was concentrated under a nitrogen stream. This concentrate was cooled to 0° and charged with 7 mL of THF and 0.19 mL of diisopropylamine. The solution was stirred at 0° for 10 min and cooled to -78°. A solution of ketone (1.0-1.2 mmol)in 3 mL of THF was added dropwise over 5 min. The reaction was stirred for 30 min and then quenched with 1.7 mmol of chlorotrialkylsilane. The resulting mixture was stirred for 10 min, warmed rapidly to room temperature and concentrated on a rotary evaporator. The residue was partitioned between 10% aqueous sodium carbonate and hexane. The aqueous layer was separated and washed with equal volume of hexane (x2). The combined organic phases were evaporated and distilled.

<u>Method B</u> (with lithium hexamethyldisilazide)[70] : a solution of 1.4 mmol of lithium hexamethyldisilazide in 7 mL of THF was prepared and cooled to -78° as described above. To this solution was added a solution of 1.6 mmol of ketone in 3 mL of THF over 5 min. The resulting solution was stirred at -78° for 30 min and at 0° for 30 min and then quenched. Workup was completed as described for Method A.

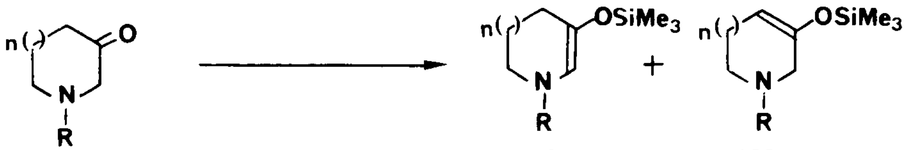
The ratio <u>128</u>/<u>129</u> depends on two factors, first the method used and on the structure of the starting ketone.

With acyclic compounds, the ratio <u>128</u>/<u>129</u> and the ratio <u>128</u>-Z/<u>128</u>-E increase from Method A to Method C (Table 8). However, Method D yields almost pure enol ether <u>129</u>. With 2-dimethylamino cyclohexanone, Methods A to C yield enol ether <u>129</u> but Method D leads to a mixture of the two isomers (Table 8, entries 5-11). The results observed with Method D in the case of 2-amino cyclohexanone show the importance of the amino group since the replacement of the dimethylamino group by diethylamino morpholino or piperidino group reverses the ratio 128/129 (Table 8, entries 8-11).

TABLE 8. Preparation of Silylenol Ethers 128 and 129[70-72]

entry	R^1	R^2	NR^3R^4	R^5	Method	Ratio 128/129	Ratio 128-Z/128-E
1	H	H	NMe_2	Me	D	5/95	
2	H	H	NMePh	Et	A	25/75	2/98
3					B	70/30	10/90
4					C	95/5	50/50
5	$(-CH_2-)_3$		NMe_2	Et	A	2/98	
6					B	2/98	
7					C	98/2	
8				Me	D	40/60	
9			NEt_2	Me	D	70/30	
10					D	70/30	
11					D	70/30	
12	Me	H	$NPhCO_2Et$	Et	A	82/18	20/80
13					B	1/99	2/98
14					C	10/90	75/25
15	$(-CH_2-)_3$		$NPhCO_2Me$	Et	A	33/66	
16					B	2/98	

The results for heterocyclic compounds 130 are summarized below[70] :

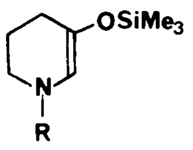


130 131 132

		R = Et n = 1	R = Bz n =0
Method A	131/132	17/83	30/70
Method B	131/132	2/98	5/95
Method C	131/132	86/14	decomposition

Methods A and B yielded compounds 132 as major or quite pure products. Method C reversed the ratio 131/132. Products obtained by Method B under the conditions of Method C afforded a product ratio approaching those of Method C. A longer reaction time leads to substantial decomposition and the authors were unable to achieve complete equilibration. Enolization of the ketones under kinetic conditions (Method A) affords products qualitatively similar to their all-carbon analogs and as a result the alkyl substituted nitrogen has little effect on kinetic acidity. Under equilibrating conditions (Method B) enolization occurs towards nitrogen in the acyclic ketone but away from nitrogen in the others. Method C provided mainly enol ethers conjugated with nitrogen. Method D is close to Method C except for the reaction temperature and when comparison is possible the two methods reverse the ratio 128/129. Method D, therefore, could be taken as leading to kinetically controlled products.

If the alkyl substituent is replaced by an electron-withdrawing group (carbethoxy or trifluoroacetyl group) the ratio of enol ether bearing vinylic nitrogen increased with the electronegativity of the nitrogen moiety (Table 8 and results below for heterocyclic compounds).[70]



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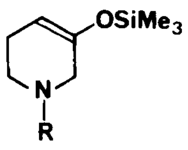


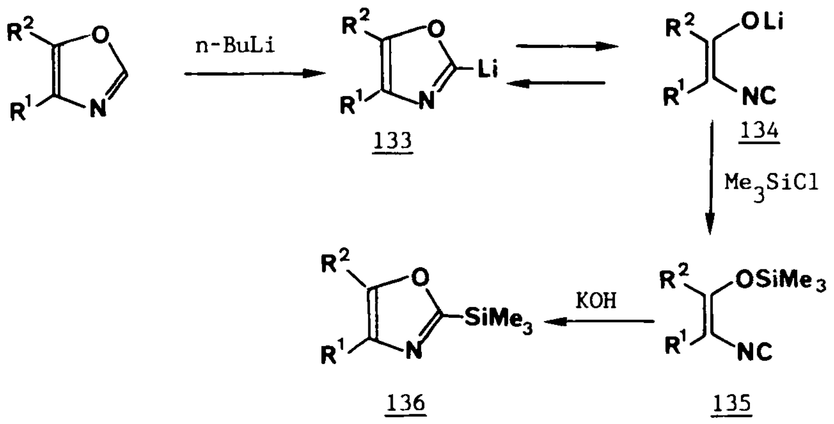
132

	ratio 131/132		
method	A	B	C
R = Et	17/83	2/98	86/14
R = CO_2Et	77/23	75/25	95/5
R = $COCF_3$	80/20	98/2	

These silylenol ethers can, as usual, be transformed by methyllithium in enolate species and then alkylated regiospecifically.[70]

B. Synthesis of Isocyano Silylenol Ethers

Lithiation of isoxazole produced an equilibrium mixture of C anion 133 and the open-chain isomer 134. The isocyanate enolate can be trapped by chlorotrimethylsilane leading to β-isocyano silyl enol ethers 135 in pure Z form.[73,74] These enol ethers are cyclized to trimethylisoxazole 136 in the presence of potassium hydroxide at 100-105°.



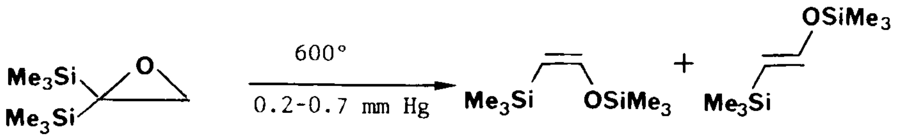
V. β-TRIMETHYLSILYL SILYLENOL ETHERS

A. Synthesis

These compounds may be produced by pyrolytic rearrangement of epoxysilanes or by silylating a vinylic anion or α-ketodianions.

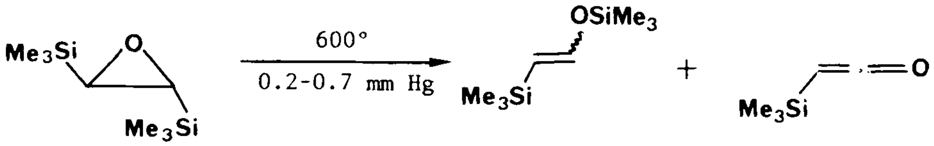
1. From Epoxysilanes[75]

By flash vacuum pyrolysis, epoxysilane may be rearranged to silylenol ethers and this rearrangement is facilitated by the presence of the trimethylsilyl group. With bis trimethylsilyl epoxide 137, the two isomeric trimethylsilyl silylenol ethers 138-Z and 138-E were obtained in 67% yield (ratio Z/E = 71/29).



137 138Z 138E

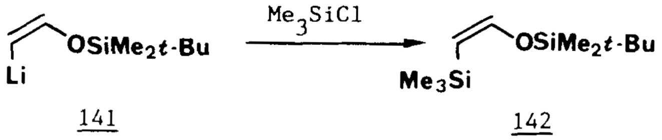
Silyl derivatives 138 were formally derived from trimethylsilyl acetaldehyde. The isomeric epoxide 139 yielded the same enol ethers but with a different ratio (138-Z/138-E = 25/75), accompanied by the trimethylsilylketene 140.



139 138 (Z+E) 140

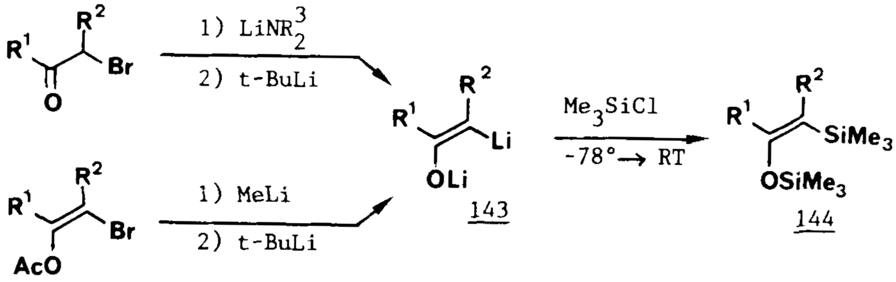
2. From a Silyloxy Vinylic Anion[76]

The vinylic anion 141 may be used for the preparation of β-silyl silylenol ether 142.

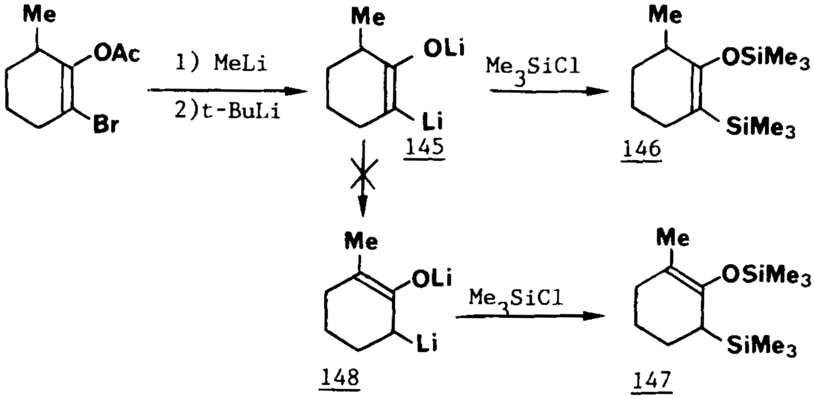


3. From α-Keto Dianions[77]

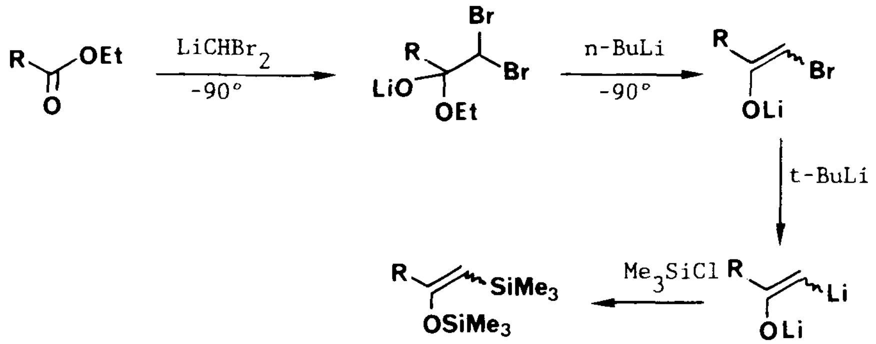
Kowalski *et al.* have prepared enol ethers 144[77] in order to study α-keto dianions 143, generated from primary and secondary bromoketones or from α-bromoenolacetates.



There was no rearrangement of the dianion 145 produced, as depicted in the scheme below. The single ether 146 was obtained in good yield and little or none of the regioisomer 147 expected from α,α'-dianion 148 was present.

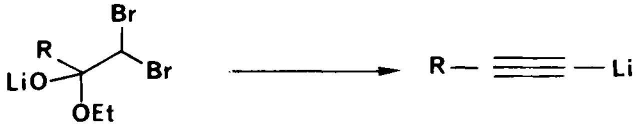


Dianions 149 and the corresponding silylenol ethers 150 were also prepared from esters in the sequence depicted below[78]:



R = Ph 150 149

This process cannot be used when the R group is a secondary hydrocarbon moiety; in this case much of the starting material was converted to alkynoate anion 151 upon sequential treatment with lithiodibromomethane and then butyl lithium.[78]

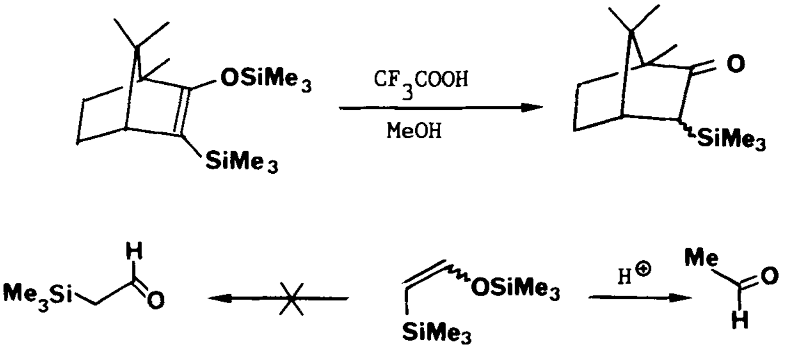


151

R = cyclohexenyl

B. Reactions

The sole reaction described was the acidic hydrolysis of these compounds leading to α-silylketone.[77] Surprisingly, enol ethers 138-Z and 138-E did not yield trimethylsilylacetaldehyde but only acetaldehyde. Attempts to isolate the 2,4-dinitrophenylhydrazone of the silylacetaldehyde always failed and only the 2,4-dinitrophenylhydrazone of acetaldehyde was observed.[75]



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