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SILYL KETONE CHEMISTRY

PREPARATION AND REACTIONS OF UNSATURATED SILYL KETONES[1]

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Abstract—A series of silyl ketones has been prepared by appropriate manipulation of α-silylated allenol ethers. Among the compounds prepared were alkenyl, alkynyl and acyl silyl ketones. The spectroscopic properties of representative members of these classes of compounds have been measured, and some of their chemical reactions studied. Diels–Alder cycloadditions of vinyl and alkynyl silyl ketones proceed smoothly, and can be used to prepare new types of silyl ketones. Several examples of reactions with organolithium reagents are given; the process can be an effective route to enol silyl ethers with absolute regiochemical control.

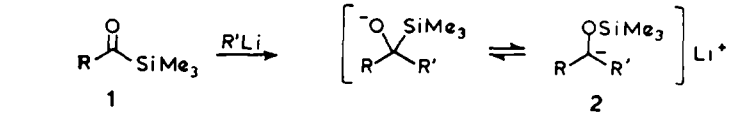
The applications of Si compounds in organic synthesis have been concentrated in four areas: (1) as protecting groups for OH, NH and CH groups; (2) as activating and directing groups during electrophilic additions to vinyl, allyl, and allenyl silanes (β-silyl cation stability); (3) in olefin-forming reactions via acid or base catalyzed elimination of silanols (Peterson olefin synthesis); (4) as easily accessible and reactive enol equivalents in the form of silyl enol ethers.

Our interest in silyl ketone (acyl silane, **1**) chemistry[1,2] and its applications to organic synthesis are based on some chemical properties of Si compounds distinct from those responsible for the applications above; i.e. the great propensity for silyl groups to undergo sigmatropic rearrangements.[3] This, coupled with the extraordinarily high bond strength of the Si–O compared to the Si–C bond makes possible the very flexible connective synthesis of α-siloxycarbanions (**2**) illustrated in eqn (1),[4] in which the exchange of a Si–C for a Si–O oxygen bond provides the driving force for the conversion of an alkoxide to a considerably more basic carbanion. This approach avoids some of the limitations associated with other methods for the preparation of such anions (e.g. metalation,[6] C–X bond reduction[7]). The siloxy anions **2** formed as in eqn (1) can be alkylated and treated with other electrophiles,[1a,2a,8a,b] or they can serve to initiate elimination reactions if suitable leaving groups are present.[1,8b,c]

The equilibrium of eqn (1) was first studied in connection with the base catalyzed rearrangement of α-silylcarbinols to siloxy compounds, which has been extensively studied by Brook *et al.*[3] Relatively little solid evidence on the thermodynamics and kinetics of the actual [1, 2] sigmatropic rearrangement step of the Brook rearrangement is available. However, the work of West and Wright[5] clearly showed that when R = Ph and R′ = H the equilibrium was on the side of the alkoxide, whereas when R = R′ = Ph the carbanion was the principal species in solution. The related 3-triethylsiloxypentadienyllithium reagent also shows only carbanion reactivity,[6b] as do other systems having anion stabilizing substituents.[6c]

Silyl ketones have other uses as synthetic reagents in addition to reactions based on eqn (1). Thermolysis leads to siloxycarbenes, which undergo interesting intra- and intermolecular reactions.[9] Either aldehydes[10] or carboxylic acids[10d,11] can be obtained by hydrolytic or oxidative cleavage of the C–Si bond. Silyl ketones can thus serve as synthetic equivalents of these functional groups. Some success with the use of silyl ketones as acyl anion equivalents has been reported, either by direct nucleophilic cleavage of the C–Si bond[10c] or the indirect pathway involving nucleophilic addition to the carbonyl, followed by [1, 2] sigmatropic rearrangement of the silyl group (eqn 1, with $R_2 = F$[12]). Full development of the synthetic applications of eqn (1), as well as the use of silyl ketones in other reactions requires general and efficient methods for their preparation.

When we began our work, no acetylenic and only two olefinic silyl ketones had been prepared.[13] Both syntheses of the silyl enones used lithiated allenyl ethers as d_1-propenone synthons, followed by hydrolytic release of the carbonyl function (eqn 2). Subsequent work by several research groups provided routes based on the alkylation and silylation of lithiated phenyl propargyl selenide,[2c] 1,3-bis(phenylseleno)propene[2b] and 1-methoxybutadienes.[14a] Successful routes based on an aldol condensation followed by Peterson olefin synthesis,[10d] the hydroboration of enynyl silanes,[14b] and on the sulfenylation of enol ethers derived from silyl ketones followed



by sulfoxide elimination were also reported.[15a] The silylation hydrolysis of dithianes, a procedure which works well for alkyl dithianes[15b] can also be used in some cases (e.g. β-styryl trimethylsilyl ketone[15c]) but suffers from difficult preparation of the unsaturated dithianes, as well as regiochemical mixtures during the silylation. Of all these procedures, the routes based on allenol ethers seemed most promising since not only d_1, but also d_2 and d_3-propenone reactivity seemed achievable. In fact, 1-hexenyl silyl ketone[10f] as well as the first allenyl silyl ketone[16] have been recently prepared from 1-silyl-1-alkoxy cumulenes.

We report here on our efforts toward the utilization of allenyl ethers for the preparation of α,β-olefinic, α,β-acetylenic, and α-keto silyl ketones (vinyl, ethynyl, and acyl silyl ketones).

RESULTS AND DISCUSSION

Preparation of allenol ethers. The procedure we have developed for the synthesis of silyl enones is illustrated by eqn (3) for the parent compounds **5a** and **5b** (throughout this paper the **a** series will refer to trimethylsilyl, TMS, the **b** series to t-butyl-dimethylsilyl, TBS). The choice of ethoxyethyl substituent for the alkoxyallene starting material **3** permits easier isolation and purification than the more commonly used but volatile and easily polymerizable methoxyallene.[17] Compound **3** was prepared by base catalyzed isomerization of ethoxyethyl protected propargyl alcohol, following the procedure of Hoff, Arens and Brandsma.[18] The metalation of **3** proceeds smoothly with n-BuLi, and high yields of the silylated allene **4a** can be obtained if good temperature control is maintained during metalation and derivatization. Successful reaction with t-butyldimethylsilyl chloride requires rather specialized conditions (Et_2O, HMPA, −85°, 15 hr) to achieve optimum yields. Both **4a** and **4b** can be stored for long periods at freezer temperature under N_2 provided a trace amount of the radical inhibitor 3-t-butyl-4-hydroxy-5-methylphenyl sulfide is present.

The silyl allenes **4** can be metalated a second time (n-BuLi/THF, −78°, 30 min) and the Li reagent treated with a variety of electrophiles (Table 1). No differences in reactivity between the TMS and TBS derivatives were encountered. Reaction occurs essentially exclusively at the γ-position, the exceptions being reaction of **4a** with n-butyl iodide and isopropyl iodide, which gives a 7/1 ratio of γ- to α-products (**4b** gave no detectable α-product).[19] To achieve good yields with less reactive electrophiles such as isopropyl iodide and n-butyl iodide it was necessary to use an excess of alkylating agent. Secondary proton transfers were encountered only when strongly acidifying substituents (e.g. PhSe) were introduced. For this reason, selenation was best carried out by a two step sequence: reaction with elemental selenium (inverse addition), followed by alkylation on Se with methyl iodide.[20] In all cases where the allene terminus has two different substituents an approximately 1/1 mixture of diastereomers (chiral center in ethoxyethyl group) was obtained.

The Li reagent from **4a** also reacts at the γ-position with carbonyl compounds, but the adducts are unstable and could not be cleanly converted to silyl enones. Apparently cyclization to dihydrofurans and furans occurs too readily.[21] This is not surprising, since the kinetic products of hydrolysis appear to be the *cis*-compounds, ideally set up for cyclization. A different d_1,d_3-propenone reagent (1,3-bisphenylselenopropene) developed in our laboratory[2b] can be used to prepare γ-hydroxyl silyl enones.

A third metalation has been carried out on several of the γ-alkylated allenes (**6a**, **6b**, **7a**, Table 1). Optimum metalation conditions were sec-BuLi/THF at −78°, 15 min. These Li reagents gave only γ-derivatization with methyl iodide and elemental Se. Some α-product (γ/α 3/2) was formed with Ph_2Se_2 as electrophile, but only with the TMS compound. If careful control of reagent stoichometry is maintained, two consecutive metalations–alkylations on compound **4** can be carried out as one pot reactions (e.g. preparation of **13b** and **14a**).

An alternate shorter approach to the β,β-disubstituted silyl enones was based on the work of Leroux and Roman.[13b] Compound **18** was prepared from 2-butyn-1-ol THP ether (**16**) by consecutive metalation–methylation (**17**) and metalation–silylation steps (eqn 4), both of which can be carried out in a one pot reaction. For reasons that are not understood, the ethoxyethyl protected butynol could not be cleanly methylated. We also found that protonation of the Li reagent from 2-butynol-O-THP gave mixtures of allene and acetylene products under conditions for which the 2-octyn-1-ol[22a] and 2-pentyn-1-ol[22b] derivatives give predominantly allenes.

Hydrolysis of silyl alkoxy allene. Most of the allenes in Table 1 have been successfully hydrolyzed to silyl enones. The best conditions we found are 2N H_2SO_4 in THF at 25° for 40 min to 4 hr. The TBS derivatives consistently hydrolyzed at a slower rate than the TMS. Results are summarized in Table 2.

The more volatile silyl ketones (e.g. **5a**) needed to be handled carefully during workup to avoid losses, otherwise most of the compounds, although more thermally sensitive

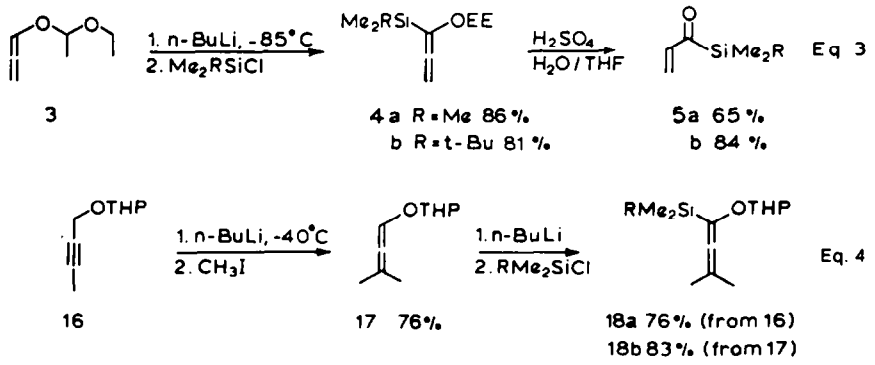
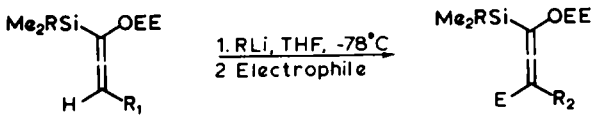


Table 1. Preparation of α-silylallenol ethers



a R = Me b. R = t-Bu

Starting Material		Reaction Conditions[a]	Product			
Cmpd. No.	R_1		No.	R_2	E	Yield
4a	H	1. n-BuLi 2. CH_3I	6a	H	CH_3	88
4b	H	1. n-BuLi 2. CH_3I	6b	H	CH_3	100
4a	H	1. n-BuLi 2. n-C_4H_9I[b]	8a	H	n-C_4H_9	93
4a	H	1. n-BuLi 2. i-C_3H_7[b]	7a	H	i-C_3H_7	94[c]
4a	H	1. n-BuLi 2.  3. Ac_2O	9a	H		d
4a	H	1. n-BuLi 2. Me_3SiCl	10a	H	$SiMe_3$	d
4a	H	1. n-BuLi 2. Ph_2Se_2[e]	11a	H	SePh	d
4a	H	1. n-BuLi 2. Se[e] 3. CH_3I	12a	H	$SeCH_3$	81
4b	H	1. n-BuLi 2. Se[e] 3. CH_3I	12b	H	$SeCH_3$	85
4b	H	1. n-BuLi 2. CH_3I 3. s-BuLi 4. CH_3I	13b	CH_3	CH_3	94
4a	H	1. n-BuLi 2. CH_3I 3. s-BuLi 4. Se[e] 5. CH_3I	14a	CH_3	$SeCH_3$	79
6a	CH_3	1. sec-BuLi 2. CH_3I	13a	CH_3	CH_3	96
6b	CH_3	1. sec-BuLi 2. Se[e] 3. CH_3	14b	CH_3	$SeCH_3$	d
7a	i-C_3H_7	1. sec-BuLi 2. Se[e] 3. CH_3I	15a	i-C_3H_7	$SeCH_3$	78

[a]These steps were carried out as one-pot reactions.
[b]Excess alkylating agent (2–3 fold) was used.
[c]Contaminated by ~ 15% of α-alkylation product.
[d]Product was not purified, but was directly carried on to silyl ketone (see Tables 2 and 3).
[e]Inverse addition.

than ordinary ketones, could be distilled or chromatographed without decomposition.

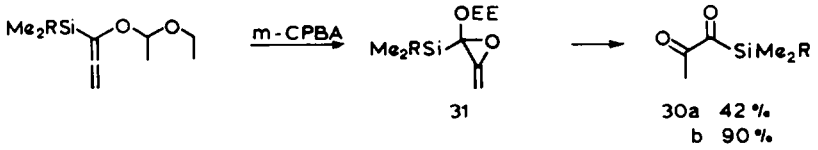
The question of *cis–trans* isomerism in the silyl enones with one β-substituted has not been carefully examined. In several cases an excess of the *cis*-isomer was observed after the hydrolysis, followed by *cis* to *trans* isomerization during distillation or storage. *Cis–trans* mixtures have been observed in previous allenol ether hydrolyses.[22a]

Halogenation and selenation of allenol ethers Treatment of allenol ethers with several electrophiles gave α-heterosubstituted silyl enones. We carried out brominations (Br_2, CH_2Cl_2), chlorinations (SO_2Cl_2 in THF) and selenations (PhSeCl in CH_2Cl_2) on several representative compounds. The reactions proceed cleanly and in good yield. It seems likely that a range of other similar electrophiles can also be used.

Oxidation of allenol ethers. When the allenol ethers **4a** and **4b** are treated with *m*-chloroperbenzoic acid under conditions similar to those used by Rubottom for enol ether oxidation,[23] they are transformed to the deep red α-dicarbonyl compounds **30**. The red color appears well after the oxidation is completed, so that an intermediate is formed, perhaps the allene oxide **31**.

Compounds **30a** and **30b** are the first acyl silyl ketones to be isolated, but carbomethoxy ketones have been prepared previously.[24]

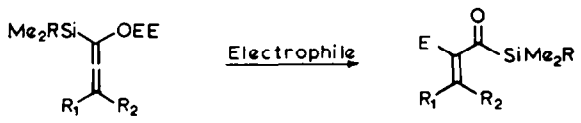
Preparation of acetylenic silyl ketones. The phenylseleno and methylseleno substituted allenol ethers were prepared with the goal of using a selenoxide [2, 3] sig-



31

30a 42 %
b 90 %

Table 2. Preparation of α,β unsaturated silyl ketones



a. R = Me b: R = t-Bu

Starting Material			Electrophile	Product		
No.	R_1	R_2		No.	E	Yield
4a	H	H	H_2SO_4	5a	H	65
			PhSeCl	19a	SePh	73
			SO_2Cl_2	20a	Cl	65
4b	H	H	H_2SO_4	5b	H	84
			SO_2Cl_2	20b	Cl	87
6b	CH_3	H	Br_2	21b	Br	71[a]
8a	n-C_4H_9	H	H_2SO_4	22a	H	70[b]
7a	i-C_3H_7	H	H_2SO_4	23a	H	52[c]
9a		H	H_2SO_4	24a	H	45[df]
10a	Me_3Si	H	H_2SO_4	25a	H	64[ef]
11a	PhSe	H	H_2SO_4	26a	H	79[fg]
12a	CH_3	CH_3	H_2SO_4	27a	H	80
			Br_2	28a	Br	83[h]
18a[i]	CH_3	CH_3	H_2SO_4	27a	H	65
13b	CH_3	CH_3	Br_2	28b	Br	81
			SO_2Cl_2	29b	Cl	91[j]
18b[k]	CH_3	CH_3	H_2SO_4	27b	H	83

[a]Only Z-isomer isolated.
[b]Predominantly E-isomer observed.
[c]Ratio of Z/E = 12/7 early in reaction.
[d]Only E-isomer observed.
[e]Ratio of Z/E = 4/1 initially, mostly E at end of reaction.
[f]Overall yield from **4a**.
[g]Only Z-isomer observed.
[h]This compound was quite unstable and was isolated in only ~80% purity.
[i]THP analog of **13a**.
[j]Unpublished result of E. Eisenhart.
[k]THP analog of **13b**.

matropic rearrangement[2c] for the introduction of an acetylenic group. In fact, oxidation of these selenides at −78° with *m*-chloroperbenzoic acid, followed by warm up gave the acetylenic silyl ketones **32**, **33** and **34** in fair yield, as summarized in Table 3. The warm up was done in the presence of ethyl vinyl ether to trap electrophilic Se compounds (e.g., methaneselenenic acid)[25] formed during the reaction. In fact, small amounts of byproduct 2,2-diethoxyethyl methyl selenide are formed together with the acetylene.

Physical properties of unsaturated silyl ketones. Table 4 summarizes some of the spectroscopic properties of the new types of silyl ketones prepared here. The ethylenic and acetylenic compounds are all bright yellow

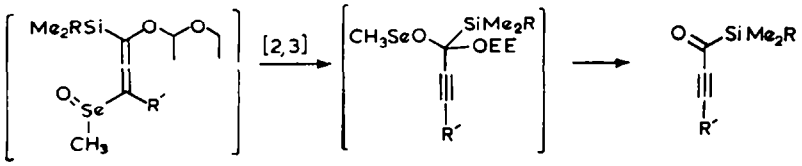
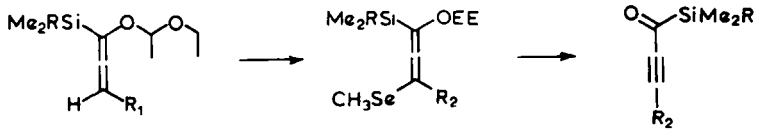


Table 3. Preparation of acetylenic silyl ketones

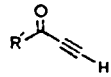


a: R = Me b: R = t-Bu

Starting Material No.	R_1	Reaction Conditions	Product No.	R_2	Yield (overall)
4b	H	1. a,b,c 2. d	32	H	48
6b	H	1. a,c,e,b,c 2. d	33	CH_3	52
7a	i-C_3H_7	1. e,b,c 2. d	34	i-C_3H_7	52

[a]n-BuLi, THF, −78°.
[b]Se°, −78°, THF, inverse addition.
[c]CH_3I, THF, −78° to 0°.
[d]M-CPBA.
[e]sec-BuLi, −78°.

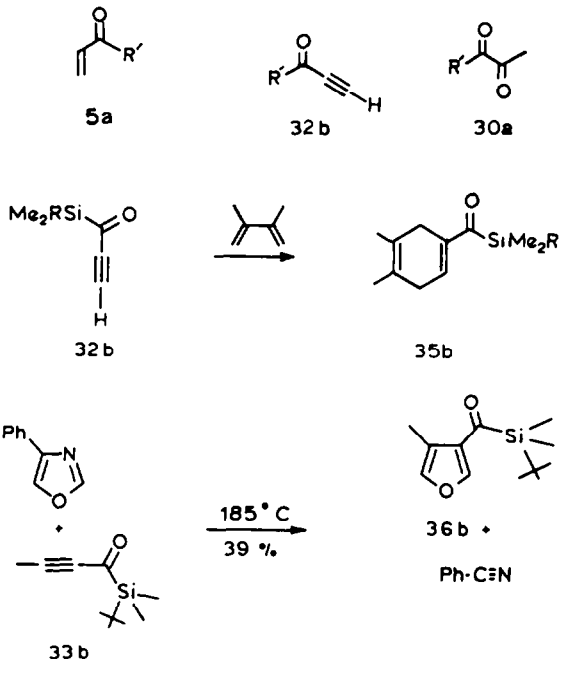
Table 4. Spectroscopic data for silyl ketones

	R′	uv/vis λmax (ε)	IR (cm^{-1})	^{13}C NMR[a]
 5a	$SiMe_3$	434(96.4),213(8630)[b]	1641,1604[c]	127.7,141.0, 236.7
	CH_3	324(24),219(3600)[d,e]	1710,1670,[f] 1610	128.6,137.5,[g] 198.1
 32b	$SiMe_2tBu$	432(148), 219(4700)[b]	2080,1605[c]	85.4,225.8
	CH_3	301(15),216(1900)[b]	2090,1688[c]	78.1,81.8, 183.6
 30a	$SiMe_3$	535(99),296(41), 285(40)[b]	1713,1658[c]	199.2,235.5
	CH_3	400-450(20),275(~15)[b,e]	1710[h]	198.0[i]

[a]Multiply bonded carbons only. See Experimental for complete ^{13}C NMR spectra.
[b]Cyclohexane.
[c]Neat.
[d]Ethanol.
[e]C.N.R. Rao, *Ultraviolet and Visible Spectroscopy*, 3rd Edn, pp. 42–48. Butterworth, London (1975).
[f]Sadtler Infrared Grating Spectra, No. 29105.
[g]G. C. Levy, G. L. Nelson, *Carbon 13 Nuclear Magnetic Resonance for Organic Chemists*, pp. 67 and 114. Wiley, New York (1972).
[h]Sadtler Infrared Grating Spectra, No. 36984.
[i]G. A. Olah, J. L. Grant and P. W. Westerman, *J. Org. Chem.* **40**, 2102 (1975).

compounds due to a shift of about 100 nm to longer wave lengths of the $n \rightarrow \pi^*$ transition compared to the analogous alkyl ketones. The π–π^* transition is relatively unaffected when methyl is replaced by trialkylsilyl. Similar effects have been observed and studied in a number of other systems.[26] The carbonyl frequencies as well as ^{13}C NMR CO chemical shifts are also displaced from their normal positions in alkyl ketones as has been found by previous workers.[26,27] In summary, the carbonyl groups of compounds **5a**, **32b** and **30a** are perturbed in a fashion well precedented by previous studies of simpler silyl ketones. The remainder of the conjugated π-system seems to be relatively unaffected by the silyl substituent.

Reactions of silyl ketones. In most of their chemical properties the silyl ketones we have studied parallel alkyl ketones. Thus, enolate and enol ether formation occurs normally,[1b,9b,10b,10d] and these derivatives can be alkyl-



ated,[1b] alkoxyalkylated,[10b] sulfenylated[15a] and halogenated,[28] and undergo aldol condensations.[10d] Cuprates and thiols add in the typical 1,4-fashion.

The Diels–Alder reactivity of α,β-acetylenic and ethylenic silyl ketones is also comparable to that of the related methyl ketones, and these reactions can be used to prepare other useful unsaturated silyl enones. The acetylenic silyl ketones **32a** and **33b** react with 2,3-dimethylbutadiene and 4-phenyloxazole to give **35a** and **36b** respectively, under conditions similar to those required for other acetylenic dienophiles.[29] This route to **36b** was the only one of a number we attempted that was even moderately successful.

The cycloaddition of **19a** with 2,3-dimethylbutadiene shows an unusual effect in that a significant portion of the reverse-electron demand adduct (**38a**) is formed. It seems likely that the PhSe substituent is responsible for this unusual reactivity, since the vinyl silyl ketone **5a** gives only the normal adduct. The cycloaddition of acrolein and butadiene has been reported to give less than 0.5% of the reverse product.[30] Adduct **37a** (X = SePh) has been converted to **39a**, the conjugated isomer of dienyl silyl ketone **35a** by selenoxide syn elimination.[31]

Our principal interest in the silyl ketones whose synthesis was reported above is in the products of their reactions with organometallic reagents. Apart from a strong tendency for alkyl Grigard reagents having α-hydrogens to reduce silyl ketones by hydride donations (and, of course, the complications introduced by eqn 1),[26a,32] we have found that organometallic reagents, particularly Li reagents, usually react smoothly with silyl ketones. The rates of addition do not appear to be dramatically different than those of methyl ketones. Since all of the silyl ketones reported here are colored, the progress of orgamometallic reactions can be easily monitored.

In Table 5 are listed some representative examples of reactions in which either the silyl ketone or the lithium reagent bears an appropriately located leaving group. The siloxy carbanion intermediates suffer α-elimination to give enol silyl ethers. This process, which was first observed by Brook *et al.*[32b] with Wittig reagents and diazomethane, is of broad generality, and can be used to prepare compounds not easily available by standard techniques. Leaving groups as poor as cyanide,[33] and as good as halide have been used.

The dienol silyl ethers **40a** and **41a** are interesting

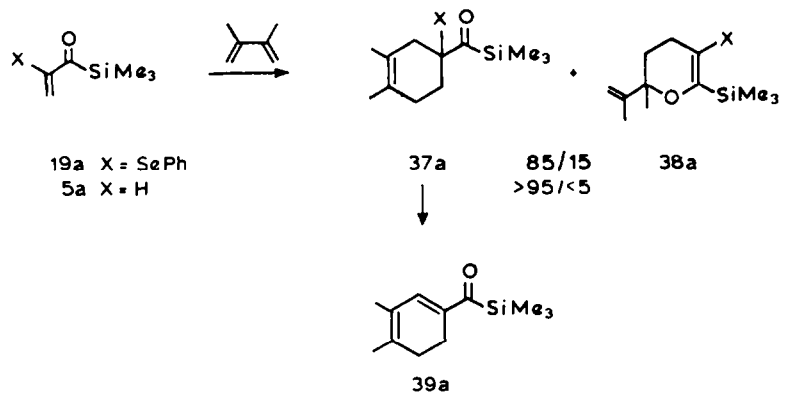
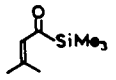
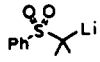
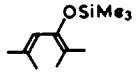
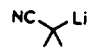
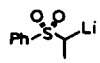
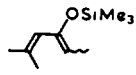
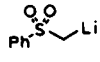
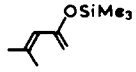
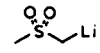
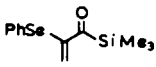
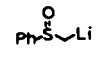
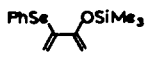
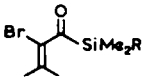
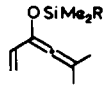
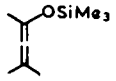


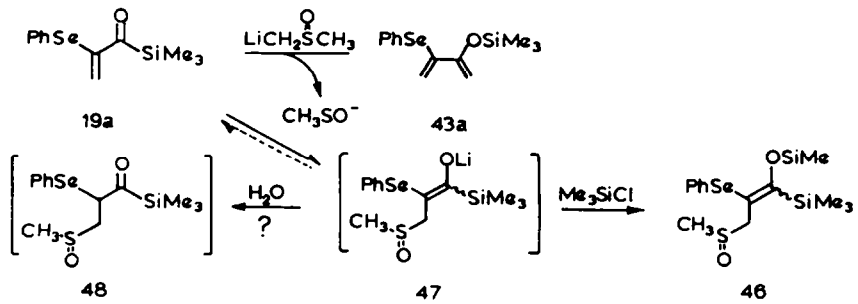
Table 5. Preparation of enol silyl ethers

SILYL KETONE	NO.	LITHIUM REAGENT	PRODUCT	NO	YIELD
	27a			40a	69
					48
				41a	78
			E/Z = 77/23		
				42a	69
					55
	19a			43a	89
	28b			44b	85
		CH_3Li		45a	73

examples in which the normal "kinetic" and "thermodynamic" enol derivatives[34] are apparently reversed. Compound **40a** and **41a** ($Z/E = 75/25$) are formed under equilibrating conditions (TMSI, HMDS), whereas the linearly conjugated dienol silyl ethers are the products obtained from the kinetic enolates (LiHMDS) of 2,5 - dimethyl - 4 - hexen - 3 - one and 5 - methyl - 4 - hexen - 3 - one.

A rather interesting side reaction was encountered during the reaction of **19a** with dimsyl lithium in THF. Under several different reaction conditions, starting enone was recovered (in addition to the diene **43a**), even though the disappearance of the strong yellow color of **19a** had signaled the completion of the reaction. Quenching at low temperature with TMSCl gave as much as 50% of a new product, tentatively identified from its NMR spectrum (AB quartet at δ 3.70, J = 13 Hz; singlets at 2.80, 0.256, 0.42) as compound **46**. It was too unstable to be isolated in pure form. This compound is apparently formed by conjugate addition of methanesulfenate anion to starting enone, followed by O-silylation. Hydrolysis of either the enolate **47** or silyl ether **46** leads to starting enone. The ketone **48** was not detected, and may not be an intermediate in the transformation of **46** and **47** back to **19a**. The occurrence of this side reaction is probably due to several factors, including the low solubility of dimsyl lithium which allows sulfenate anion to compete successfully for enone. The Li reagent from phenyl methyl sulfoxide gave no such side reaction. In this case, and in the reaction of dimsyllithium–LiBr (also only slightly soluble in the reaction medium) with the β,β-dimethyl enone **27a**, the formation of diene[35] is complete in < 10 min at −78° (THF).

Table 5 includes two examples (**44b** and **45a**) of the preparation of siloxy allenes using α-halo silyl enones. These compounds cannot normally be prepared by enolization of carbonyl compounds.[36] A more complete discussion of the syntheses and chemistry of allenol silyl ethers is deferred to a future detailed publication on the subject.



Summary. The potential of allenol ethers as d_1, d_2 and d_3 (twice) propenone reagents for the preparation of vinyl silyl ketones having α,β,β-substitution has been examined, and a number of new silyl enones were prepared using this reagent. The first preparations of silyl ynones and silyl 1,2-diones have also been accomplished. Several reactions of silyl enones illustrating their potential for regiospecific synthesis of silyl enol and allenol ethers are presented.

EXPERIMENTAL

NMR spectra were obtained on a Jeol MH-100, FX-60, or FX-200, IBM WP-200, or a Bruker WH-270 spectrometer. Unless otherwise stated, MH-100 spectra were measured in CCl_4, WP-200 and WH-270 spectra were taken in $CDCl_3$ with reference to $CHCl_3$ (δ 7.23) or CH_2Cl_2 (δ 5.32). The $CDCl_3$ triplet (δ 77.0) was used as a reference for ^{13}C spectra, all of which were measured in $CDCl_3$. IR spectra were taken of neat liquids between salt plates and were recorded on a Beckman Acculab 7 spectrophotometer. An AEI-MS-902 spectrometer was used to obtain mass spectra. Elemental analyses were performed by Galbraith or Spang Microanalytical laboratories.

Starting materials were commercially available, with the exception of diphenyl diselenide,[37] benzeneselenenyl chloride,[37] ethoxyethyl propargyl ether,[18] and lithium diisopropylamide (LDA),[31] which were prepared following lit. procedures. Diisopropylamine and pyridine were distilled from KOH and stored over 4A molecular sieves. Diethyl ether and THF were freshly distilled from sodium benzophenone ketyl. Solns of LDA, n-BuLi, s-BuLi and t-BuLi were titrated using n-propanol with 1,10-phenanthroline as indicator. All reactions involving organolithium reagents were carried out under an atmosphere of dry N_2, in glassware which had been dried at 110° for at least 2 hr. The radical inhibitor used was 3-t-butyl-4-hydroxy-5-methylphenyl sulfide.

The standard workup for allenol ethers and enol ethers consisted of pouring the mixture into sat $NaHCO_3$ aq and ether/pentane (1 : 1), then washing the organic phase with H_2O and brine. The organic phase was poured through Na_2SO_4, dried over K_2CO_3 and concentrated on a rotary evaporator. The allenol and enol ethers are very sensitive to water and air, and were best stored over radical inhibitor under an atmosphere of N_2 in a freezer.

The standard workup for silyl enones involved dilution of the acidic reaction medium with water, and extracting the brightly colored enone from the aqueous with pentane. The combined organic fractions were washed with 3 portions of H_2O and 1 portion of brine, then poured through Na_2SO_4 and concentrated by rotary evaporation. Silyl enones are light and temp sensitive. They were stored over radical inhibitor in a freezer.

1-(1-Ethoxyethoxy)-1-trimethylsilyl-1,2-propadiene (**4a**). A Morton flask, containing 100 mg of radical inhibitor and 100 mL of THF, was equipped with a mechanical stirred and cooled to −90°. After introducing **3** (14.4 mL, 12.8 g, 100 mmol), n-BuLi (1.56 M, 67 mL, 104 mmol) was added slowly to the flask via cannula. One min after the addition was completed, Me_3SiCl was added slowly. The mixture was stirred for 20 min at −90°, then allowed to warm to room temp. Addition of Et_3N (10 mL) followed by standard workup gave a yellow liquid. Distillation (13 mm, 72–75°), gave 17.23 g (86% yield) of **4a** as a colorless liquid. NMR: δ 0.10 (ss, 9H), 1.11, 1.21 (t, J = 7 Hz, d, J = 5 Hz, 6H), 3.12–3.76 (m, 2H), 4.78, 4.92 (q, J = 5 Hz, apparent d, 3H). ^{13}C NMR: δ 2.5, 15.0, 20.2, 62.5, 83.9, 100.0, 126.8, 201.9, IR: 3037, 2990, 2905, 1929, 1448, 1390, 1350, 1262, 1227, 1155, 1090, 850, 767, 708, 636 cm^{-1}. (Found: C, 59.82; H, 10.15. Calc. for $C_{10}H_{20}O_2Si$: C, 59.95; H, 10.06%).

1-t-Butyl-dimethylsilyl-1-(1-ethoxyethoxy)-1,2-propadiene (**4b**). A soln of **3** (14.4 mL, 12.8 g, 100 mmol) and 150 mg of radical inhibitor in approximately 300 mL ether was placed in a 1 L Morton flask equipped with a mechanical stirrer. The soln was cooled to −85°. n-BuLi (1.58 M, 67 mL, 106 mmol) was added dropwise by cannula over a period of 70 min. After addition was complete, the soln was stirred at −85° for 15 min. A soln of TBSCl (16.28 g, 108 mmol) in approximately 40 mL ether was added, then a soln of HMPA (20 mL, 18.0 g, 110 mmol) in 40 mL ether was added. The mixture was stirred at −85° overnight. Et_3N (15 mL) was added, and a standard allenol ether workup was performed. Distillation (0.4 mm, 55–60°) gave 19.70 g (81%) of **4b**. NMR: δ 0.09 (apparent d, 6H), 0.94 (s, 9H), 1.20, 1.30 (t, J = 7 Hz, d, J = 5 Hz, 6H), 3.25–3.85 (m, 2H), 4.86 (q, J = 5 Hz, 1H), 5.00 (apparent d, 2H), IR: 2977, 2938, 2855, 1919, 1388, 1381, 1250, 1218, 1080, 863, 839, 780, 675 cm^{-1}. MS: M^+ 242.1707 (Calc. 242.17027).

1-t-Butyldimethylsilyl-1-(1-ethoxyethoxy)-1,2-butadiene (**6b**). A soln of **4b** (7.10 mL, 6.09 g, 25 mmol) and radical inhibitor (25 Mg), in 50 mL THF was cooled to −78° and treated with n-BuLi (1.5 M, 17.5 mL, 26.3 mmol). After 40 min, MeI (1.71 mL, 3.90 g, 27.5 mmol) was added. The mixture was stirred at −78° for 0.5 hr, then subjected to a standard allenol ether workup. Kugelrohr distillation (0.4 mm, 50–60°) gave an 100% yield (6.48 g) of **6b**. NMR: δ −0.01, 0.01 (apparent d, 6H), 0.89 (s, 9H), 1.02, 1.22 (t, J = 7 Hz, d, J = 5 Hz, 6H), 1.68 (d, J = 8 Hz, 2H), 3.17–3.82 (m, 2H), 4.85 (q, J = 5 Hz, 1H), 5.37 (apparent pentet, J = 7 Hz, 1H). IR: 2953, 2925, 2855, 1923, 1472, 1462, 1380, 1249, 1198, 1080, 835, 672 cm^{-1}. MS: M^+ 256.1858 (Calc. 256.18592).

1-(1-Ethoxyethoxy)-1-trimethylsilyl-1,2-butadiene (**6a**). Compound **4a** (20 mmol) was metalated and methylated as for **4b** above to give an 88% yield of **6a**, a colorless liquid. NMR: δ 0.01 (s, 9H), 1.05, 1.14 (t, J = 7 Hz, d, J = 5 Hz, 6H), 1.62 (d, J = 6 Hz, 3H), 3.04–3.66 (m, 2H), 4.74 (q, J = 5 Hz, 1H), 5.27 (pentet, J = 6 Hz, 1H). IR: 2978, 2898, 1926, 1450, 1365, 1252, 1204, 1155, 1090, 870, 850 cm^{-1}. MS: M^+ 214.1387 (Calc. 214.13897).

1-Trimethylsilyl-1-(1-ethoxyethoxy)-4-methyl-1,2-pentadiene (**7a**). A soln of **4a** (11.4 mL, 10.0 g, 50 mmol) and radical inhibitor (50 mg) in 75 mL THF was cooled to −78° and treated with n-BuLi (34 mL, 1.54 M, 52 mmol). After 25 min excess isopropyl iodide (15.0 mL, 150 mmol) was added, then the mixture was placed in a 0° bath, stirred for 40 min, and worked up (standard allenol ether workup). Kugelrohr distillation (5.6 mm, 80–95°) provided 11.34 g (94% yield) of **7a** which was contaminated by ~15% of the α-alkylated material (3-(1-ethoxyethoxy)-4-methyl-3-trimethylsilyl-1-pentyne). The two diastereomeric α-alkylated compounds, which could be separated from **7a** by preparative glc (10 ft SE 30 column, 150°), had NMR resonances for the acetylenic protons at δ 2.69 and 2.71. Spectral data for **7a**: NMR δ 0.06 (s, 9H), 0.95 (d, J = 7 Hz, 6H), 1.14, 1.15 (2t, J = 7 Hz, 3H), 1.26, 1.28 (2d, J = 5 Hz, 3H), 2.15–2.36 (m, 1H), 3.28–3.48 (m, 1H), 3.57–3.80 (m, 1H), 4.88, 4.90 (2q, J = 5 Hz, 1H), 5.43, 5.49 (2d, J = 5 Hz, 1H). IR: 2960, 2870, 1933, 1470, 1455, 1258, 1097, 854 cm^{-1}. MS: M^+ 242.1702 (Calc. 242.17027).

1-(1-Ethoxyethoxy)-1-trimethylsilyl-3-methylseleno-1,2-butadiene (**14a**). A soln of **4a** (0.457 mL, 0.400 g, 2.0 mmol) in approximately 2 mL THF was cooled to −78° and deprotonated with n-BuLi (1.4 M, 1.49 mL, 2.08 mmol). After 15 min, MeI (0.13 mL, 2.09 mmol) was added, and the mixture was stirred at −78° for 0.5 hr, then warmed to room temp for a few min. The soln was cooled again to −78° and treated with s-BuLi (1.25 M, 1.69 mL, 2.11 mmol). After 15 min, the anion soln was transferred by a Teflon cannula to a rapidly stirring suspension of grey powdered Se in 8 mL THF at −78°. This was stirred for 50 min at −78°, warmed briefly to 0° (3 min), then quenched with MeI (0.138 mL, 2.2 mmol). The mixture was stirred at room temp for 0.5 hr, then poured into a separatory funnel containing ether/pentane (1 : 1) and sat $NaHCO_3$ aq, the organic phase was washed twice more with sat $NaHCO_3$ aq, and with brine, then poured through Na_2SO_4, dried over K_2CO_3, and rotary evaporated. A 79% yield (0.483 g) of **14a** was obtained after Kugelrohr distillation (0.1 mm, 50–70°), as a mixture of diastereomers. NMR (270 MHz, $CDCl_3$): δ 0.081, 0.085 (s, s, 9H), 1.15, 1.16 (t, t, J = 7.1, 7.0 Hz, 3H), 1.25, 1.26 (d, d, J = 5.1, 5.1 Hz, 3H), 1.93, 1.96 (s, s, 3H), 2.02, 2.02 (s, s, 3H), 3.29–3.45 (m, 1H), 3.57–3.74 (m, 1H), 4.86, 4.90 (q, q, J = 5.1, 5.1 Hz, 1H). IR: 2970, 2925, 1908, 1380, 1256, 1070(b), 860(b) cm^{-1}. MS: M^+ 308.0710 (Calc. 308.07114).

1-(1-Ethoxyethoxy)-3-methylseleno-1-t-butyldimethylsilyl-1,2-propadiene (**12b**). A soln of **4a** (0.283 mL, 0.242 g,

1.0 mmol) was metalated as for the preparation of **6b**, and the anion soln was selenated as in the procedure above. Kugelrohr distillation (0.15 mm, 70–90°) gave 0.284 g (85%) of **12b**. NMR: δ 0.10 (apparent t, 6H), 0.98 (S, 9H), 1.19 (t, J = 7 Hz, 3H), 1.30 (d, d, J = 5 Hz, 5 Hz, 3H), 3.21–3.86 (m, 2H), 4.77–4.95 (m, 1H), 6.16, 6.24 (s, s, 1H). IR: 2940, 2920, 2847, 1898, 1468, 1458, 1070(b), 840(b) cm^{-1}.

1 - *t* - *Butyldimethylsilyl* - 1 - (1 - *ethoxyethoxy*) - 3 - *methyl* - 1,2 - *butadiene* (**13b**). n-BuLi (1.4 M, 7.5 mL, 10.5 mmol) was added to a cooled (−78°) soln of **4b** (2.82 mL, 2.42 g, 10 mmol) and 10 mg of radical inhibitor in THF (20 mL). After 30 min the anion was quenched with MeI (0.672 mL, 10.8 mmol), and the mixture was stirred at −78° for 1 hr. s-BuLi (1.25 M, 8.8 mL, 11.0 mmol) was added and the anion was quenched after 15 min with MeI (0.710 mL, 11.4 mmol). After 1 hr at −78° 5 mL of Et_3N was added, and the mixture was subjected to a standard allenol ether workup. Kugelrohr distillation (0.25 mm, 45–70°) gave 2.55 g (94% yield) of **13b**, a colorless liquid. NMR: δ −0.09, −0.06 (apparent d, 6H), 0.84 (s, 9H), 1.07, 1.16 (t, J = 7 Hz, d, J = 5 Hz, 6H), 1.68 (s, 6H), 3.15–3.76 (m, 2H), 4.79 (q, J = 5 Hz, 1H). IR: 2990, 2855, 1935, 1480, 1470, 1388, 1256, 875, 855, 815, 785, 682 cm^{-1}. MS: M^+ 270.2009 (Calc. 270.20157).

1 - (1 - *Ethoxyethoxy*) - 1 - *trimethylsilyl* - 3 - *methyl* - 1,2 - *butadiene* (**13a**). NMR: δ 0.05 (s, 9H), 1.10, 1.19 (t, J = 7 Hz, d, J = 5 Hz, 6H), 1.72 (s, 6H), 3.1–3.7 (m, 2H), 4.75 (q, J = 5 Hz, 1H). IR: 2980, 2904, 1934, 1454, 1387, 1258, 1160, 1075, 885, 855 cm^{-1}. MS: M^+ 228.1545 (Calc. 228.15462).

1 - (2 - *Tetrahydropyranoxy*) - 3 - *methyl* - 1,2 - *butadiene* (**17**). To a soln of **16** (6.16 g, 6.1 mL, 40 mmol) in 50 mL THF at −40° under N_2 was added 28 mL n-BuLi (1.5 M in hexane, 42 mmol). After 10 min at −40°, 6.25 g MeI (2.74 mL, 44 mmol) was added, then the soln was warmed to 25° for 10 min. The mixture was diluted with 1 : 1 ether/pentane, washed with H_2O and brine, dried with Na_2SO_4, and the solvent evaporated. Kugelrohr distillation (60°, 0.2 mm) yielded 5.09 g of **17** (76% yield). NMR: δ 1.10–1.80 (m, 6H), 1.80 (d, J = 2 Hz, 6H), 3.40–4.05 (m, 2H), 5.15 (m, 1H), 6.38 (heptet, J = 2 Hz, 7H). IR: 2950, 2880, 1965, 1460, 1370, 1210, 1150 cm^{-1}. MS: M^+ 168.1149 (Calc. 168.1146).

1 - *t* - *Butyldimethylsilyl* - 1 - (2 - *tetrahydropyranoxy*) - 3 - *methyl* - 1,2 - *butadiene* (**18b**). To a soln of 4.2 g of **17** (4.39 mL, 25 mmol) in 40 mL THF was added 17.1 mL of a 1.5 M soln of n-BuLi in hexane (25.6 mmol) at −78°. After 5 min a soln of 3.96 g t-butyldimethylsilyl chloride (26.3 mmol) in 5 mL THF was added, followed by addition of a soln of 4.48 g of HMPA (4.35 mL, 25 mmol) in 5 mL THF. After 2 hr a few drops of Et_3N were added and the mixture was diluted with 1 : 1 ether/pentane and worked up. Kugelrohr distillation (70°, 0.15 mm) gave 5.82 g of **18b** (83% yield). NMR: δ 0.15 (s, 6H), 0.77 (s, 9H), 1.30–1.60 (m, 6H), 1.60 (s, 6H), 3.30–3.80 (m, 2H), 4.85 (br s, 1H). IR: 2940, 2860, 1940, 1250, 1150, 1100, 1050 cm^{-1}. MS: M^+ 282.2016 (Calc. 282.2007).

1 - (2 - *Tetrahydropyranoxy*) - 1 - *trimethylsilyl* - 3 - *methyl* - 1,2 - *butadiene* (**18a**). To a soln of 3.58 g of **16** (3.81 mL, 25 mmol) in 40 mL THF was added 1.4 M n-BuLi (18.2 mL, 25.5 mmol) in hexane at −40°. After 15 min 3.69 g MeI was added (1.62 mL, 26 mmol). After 15 min more the mixture was cooled to −78° and n-BuLi in hexane (18.2 mL, 25.5 mmol) was added. After 5 min, 2.82 g TMSCl (3.30 mL, 26 mmol) was added and stirred for 10 min at −78°, then warmed to 25°. A few drops of Et_3N were added to prevent hydrolysis. Workup and Kugelrohr distillation (50°, 0.2 mm) gave 4.58 g (76%) of **18a**. NMR: δ 0.02 (s, 9H), 1.2–1.7 (m, s, 12H), 3.20–3.82 (m, 2H), 4.84 (m, 1H). IR: 2960, 2875, 1935, 1445, 1360, 1250, 1120 cm^{-1}. MS: M^+ 240.1546 (Calc. 240.1539).

1 - *Trimethylsilyl* - 2 - *propen* - 1 - *one* (**5a**). Allenol ether **4a** (2.3 mL, 2.0 g, 10 mmol) was added to 1.25 mL 2 N H_2SO_4 in 10 mL THF in a flask wrapped with foil to exclude light. The pale yellow color began to deepen immediately. The soln was stirred at room temp for 40 min, then subjected to the standard enone workup. Care was taken (a bleed was inserted in the aspirator line of the roto-vap) in the rotary evaporation of this volatile compound.Kugelrohr distillation (50 mm, 40–60°) gave 828 mg (65% yield) of **5a**, a brilliant yellow liquid. NMR: δ 0.08 (s, 9H), 5.76, 5.88 (dd, J = 10, 2 Hz, dd, J = 18, 2 Hz, 2H), 6.28 (dd, J = 18, 10 Hz, 1H). ^{13}C NMR (FX-200, completely decoupled and off-resonance decoupled): δ −2.5 (q), 127.7 (t), 141.0 (d), 236.7 (s). IR: 2961, 2899, 1641, 1604, 1582, 1256, 850, 760, 709 cm^{-1}. MS: M^+ 128.0656 (Calc. 128.06577). UV (cyclohexane): $\lambda_{max}(\epsilon)$: 434 (96.4), 213 (8630).

1 - *t* - *Butyldimethylsilyl* - 2 - *propen* - 1 - *one* (**5b**). Compound **4b** was hydrolyzed by the same procedure used for **4a**, except that reaction was continued for 4 hr to give an 84% of the bright yellow **5b**. NMR: δ −0.04 (s, 6H), 0.72 (s, 9H), 5.57 (dd, J = 11, 2 Hz, 1H), 5.84 (dd, J = 18, 2 Hz, 1H), 6.46 (dd, J = 18, 11 Hz, 1H), IR: 2955, 2930, 2860, .1642, 1603, 1563, 1447, 1470, 1257, 845, 832, 785, 680 cm^{-1}. (Found: C, 63.33; H, 10.74. Calc. for $C_9H_{18}OSi$: C, 63.47; H, 10.65%).

2 - *Phenylseleno* - 1 - *trimethylsilyl* - 2 - *propen* - 1 - *one* (**19a**).[2c] A soln of **4a** (0.228 mL, 200 mg, 1.0 mmol) in 1 mL CH_2Cl_2 under N_2 was cooled to −78°. A soln of PhSeCl (192 mg, 1.0 mmol) in 1 mL CH_2Cl_2 was added by cannula. After 5 min at −78°, the mixture was poured into ether/pentane (1 : 1), washed with sat $NaHCO_3$ aq, H_2O, sat NaCl aq, poured through Na_2SO_4, and evaporated. Purification by preparative tlc (ether/pentane, 1 : 19, R_f = 0.4) resulted in a 73% yield (207 mg) of the bright yellow, crystalline **19a**. NMR: δ 0.40 (s, 9H), 5.63 (d, J = 2 Hz, 1H), 6.44 (d, J = 2 Hz, 1H), 7.22–7.39 (m, 3H), 7.46–7.62 (m, 2H). MS: M^+ 284.0123 (Calc. 284.01359).

1 - *Trimethylsilyl* - 2 - *chloroprop* - 2 - *en* - 1 - *one* (**20a**). Compound **4a** (3.20 mL, 2.81 g, 14 mmol) was dissolved in 14 mL THF, cooled to −78° under N_2, and treated with sulfuryl chloride (1.18 mL, 1.98 g, 14.7 mmol). After 6 min, 3 mL THF/H_2O (9 : 1) was added. The mixture was poured into ether/pentane (1 : 1) and 10% $NaHSO_3$. The organic phase was washed with H_2O and brine, poured through Na_2SO_4 and rotary evaporated. Kugelrohr distillation (20 mm, 40–60°) gave 1.47 g (65% yield) of bright yellow **20a**. NMR: δ 0.35 (s, 9H), 6.13 (AB quartet, J_{AB} = 1.5 Hz, 2H). IR: 2987, 2905, 1635, 1260, 1198, 850(b) cm^{-1}. MS: M^+ 162.0267 (Calc. 162.02679).

1 - *t* - *Butyldimethylsilyl* - 2 - *bromobut* - 2 - *en* - 1 - *one* (**21b**). A soln of **6b** (0.740 mL, 0.642 g, 2.5 mmol) in 7.5 mL CH_2Cl_2 was cooled to −78°. A 2.0 M soln of Br_2 in CCl_4 (1.25 mL, 2.5 mmol) was added. After 5 min the mixture was poured into a separatory funnel containing ether/pentane (1 : 1) and 10% $NaHSO_3$. The organic phase was washed with water and brine, and poured through Na_2SO_4. Preparative tlc (ether/pentane 3 : 97, R_f = 0.3 after 2 elutions) gave 0.465 g (71% yield) of **21b** as bright yellow needles. NMR: δ 0.28 (s, 6H), 0.96 (s, 9H), 2.11 (d, J = 6.5 Hz, 3H), 7.07 (q, J = 6.5 Hz, 1H). IR (CCl_4): 2955, 2925, 2855, 1633, 1602, 1473, 1468, 1255 cm^{-1}. (Recrystallization from pentane, mp 74–74.5°): (Found: C, 45.55; H, 7.21%. Calc. for $C_{10}H_{19}BrOSi$: C, 45.63; H, 7.27%). UV (cyclohexane): $\lambda_{max}(\epsilon)$ 416 (126), 398 (128), 251 (7000).

Z and E 1 - *Trimethylsilyl* - 4 - *methyl* - 2 - *penten* - 1 - *one* (**23a**). To a soln of **7a** (1.46 g, 6.0 mmol) and radical inhibitor (6 mg) in 6 mL THF was added 1.5 mL 2 N H_2SO_4. The mixture was stirred at RT for 40 min then worked up (standard enone workup). The NMR spectrum of the unpurified enone showed a *Z* : *E* ratio of 12 : 7. Purification by flash chromatography gave 0.29 g (28%) of *Z*-**23a** (faster moving fraction) and 0.24 g (23%) of *E*-**23a** (slower moving fraction). *Z*-**23a**: NMR: δ 0.12 (s, 9H), 0.91 (d, J = 6.5 Hz, 6H), 3.10–3.35 (m, 1H), 5.57 (dd, J = 11, 10 Hz, 1H), 6.38 (d, J = 11 Hz, 1H). IR: 2955, 1685, 1625, 1565, 1240, 840 cm^{-1}. *E*-**23a**: NMR: δ 0.18 (s, 9H), 1.03 (d, J = 7 Hz, 6H), 2.28–2.55 (m, 1H), 6.10 (dd, J = 16, 1 Hz, 1H), 6.65 (dd, J = 16, 7 Hz, 1H). IR: 2965, 1640, 1595, 1255, 850(b) cm^{-1}. MS (mixture of isomers, *E* predominant: M^+ 170.1123 (Calc. 170.11273). (Found: C, 63.39; H, 10.66. Calc. for $C_9H_{18}OSi$: C, 63.47; H, 10.65%).

Z and E 1,3 - *Bis* - *trimethylsilyl* - 2 - *propen* - 1 - *one* (**25a**).[38] Metalation of **4a** (5 mmol) as described for the preparation of **6b** was followed by addition of TMSCl (0.700 mL, 5.5 mmol) at −78°. After 5 min, the soln was allowed to warm to room temp, Et_3N was added, and a standard allenol ether workup was performed. NMR of **10a**: δ 0.10 (s, 18H), 1.10, 1.21 (t, J = 7 Hz, d, J = 5 Hz, 6H), 3.19–3.72 (m, 2H), 4.47 (q, J = 5 Hz, 1H), 5.37 (apparent d, 1H).

The product, a pale yellow liquid, was dissolved in 5 mL THF. The flask was wrapped with foil, and 0.625 mL 2 N H_2SO_4 was

added. The mixture was stirred at room temp for 45 min, then worked up (standard enone workup). Kugelrohr distillation (13 mm, 65–70°) gave a 64% yield (0.640 g) of predominantly (*E*) **25a**. NMR: δ 0.15 (s, 9H), 0.22 (s, 9H), 6.37 (d, J = 19 Hz, 1H), 6.74 (d, J = 19 Hz, 1H). The IR and MS spectral data given is for a 4 : 1 (*Z* : *E*) mixture of geometrical isomers. IR: 2960, 2900, 2090, 1635, 1609, 1263, 860 cm^{-1}. MS: M^- 200.1053 (Calc. 200.10531).

(Z)-3-*Phenylseleno*-1-*trimethylsilyl*-2-*propen*-1-*one* (**26a**). A two bulb flask was employed for this reaction. The compound **4a** (0.228 mL, 200 mg, 1.0 mmol) was deprotonated with n-BuLi (1.45 M, 0.71 mL, 1.03 mmol) for 20 min, then the anion soln was slowly poured at −78° into a soln of PhSeSePh (0.312 g, 1.0 mmol) in 1 mL THF. After 1 min at −78° normal workup (under a CO_2 atmosphere, dry ice was added to the separatory funnel to prevent the oxidation of $PhSe^-$ to PhSeSePh) gave **11a** which was used without further purification. The NMR revealed some starting material (less than 10%) present in the allenol ether. NMR: δ 0.13 (s, 9H), 1.08–1.34 (m, 6H), 3.10–3.86 (m, 2H), 4.66–5.00 (m, 1H), 6.25 (apparent d, 1H), 7.14–7.70 (m, approx. 6H). IR: 3070, 2972, 1900, 1575, 1537, 1379, 1250, 850, 739, 691 cm^{-1}. MS: M^+ 356.0694 (Calc. 356.07114).

The selenenylated compound **11a** was hydrolyzed as for the preparation of **5a** (50 min). Rotary evaporation yielded 253 mg of an orange liquid, essentially pure *Z*-isomer. The enone was purified by preparative tlc (ether/pentane 1 : 19). At R_f 0.71, 225 mg of *Z*-**26a** (79% yield) was obtained. NMR (270 MHz, benzene-d_6, reference benzene at 7.15 ppm): δ 0.07 (s, 9H), 7.12 (m, 3H), 7.14 (d, (superimposed on another small doublet), J = 8.8 Hz, 1H), 7.37 (m, 2H), 7.54 (d, J = 8.8 H, 1H). IR: 3065, 2975, 2910, 1610, 1593, 1490, 1453, 1265, 1084, 897, 855, 755, 728, 710, 647 cm^{-1}. MS: M^+ 284.0126 (Calc. 284.01359).

The band at R_f 0.5 yielded 15 mg (0.5% from **4a**) of a yellow liquid which contained the *E*-isomer of the enone contaminated with the *Z*-enone and another unidentified impurity. The NMR of the *E*-isomer (benzene-d_6) contained a doublet at δ 6.65 (J = 15.8 Hz) and a doublet at δ 8.04 (J = 15.8 Hz).

3-*Methyl*-1-*trimethylsilyl*-2-*buten*-1-*one* (**27a**). The compound **13a** (2.8 mL, 2.3 g, 10 mmol) was added to 1.25 mL 2 N H_2SO_4 in 10 mL THF. A yellow color began to appear immediately. In order to exclude light, the flask was wrapped with foil. After 1 hr at room temp, the mixture was subjected to the standard enone workup, and **27a**, a bright yellow liquid which distilled at 40–50° (Kugelrohr, 15 mm), was obtained in 80% yield (1.25 g).[14] NMR (270 MHz): δ 0.14 (s, 9H), 1.83 (d, J = 0.9 Hz, 3H), (d, J = 0.7 Hz, 3H), 6.51 (m, 1H). IR: 2960, 2905, 1643, 1588, 1446, 1384, 1257, 1100, 1025, 840, 800, 755 cm^{-1}. MS: M^+ 156.0971 (Calc. 156.09707).

3-*Methyl*-1-*t*-*butyldimethylsilyl*-2-*buten*-1-*one* (**27b**). Hydrolysis of **18b** (20 mmol) was carried out as for the preparation of **27a** (3 hr at room temp). Kugelrohr distillation (30°, 0.2 mm) gave 3.30 g of **27b** (83%): NMR ($CDCl_3$): δ 0.15 (s, 6H), 0.95 (s, 9H), 1.80 (br s, 3H), 2.00 (br s, 3H), 6.45 (m, 1H). IR: 2960, 2940, 2860, 1640, 1580, 1250, 850 cm^{-1}. MS: M^+ 198.1439 (Calc. 198.1434).

2-*Bromo*-3-*methyl*-1-*trimethylsilyl*-2-*buten*-1-*one* (**28a**). Prepared as described for **21b**. NMR: δ 0.31 (s, 9H), 1.85, 2.00 (s, s, 6H), IR: 2958, 2914, 1624, 1577, 1448, 1250, 1237, 1030, 887, 884 cm^{-1}. MS: M^+ 234.0074 (Calc. 234.0076).

2-*Bromo*-3-*methyl*-*t*-*butyldimethylsilyl*-2-*buten*-1-*one* (**28b**). Procedure as for **21b**. Preparative tlc (ether/pentane 3 : 97, R_f 0.5 after 2 elutions) gave an 81% yield (784 mg) of the bright yellow liquid α-bromo enone **28b**. NMR: δ 0.21 (s, 6H), 0.91 (s, 9H), 1.80 (s, 3H), 1.89 (s, 3H). IR: 2940, 2890, 2855, 1633, 1476, 1468, 1264, 1246, 1033, 845, 785, 685 cm^{-1}. MS: M^+ 276.0545 (Calc. 276.05452).

1-*Trimethylsilyl*-1,2-*propanedione* (**30a**).[23] A slurry of *m*-CPBA (85% pure, 4.39 g, 21.6 mmol) in 250 mL pentane was cooled to −10° (ice/salt bath), **4a** (4.6 mL, 4.0 g, 20 mmol) was added slowly, and the mixture was stirred at −10° for 15 min, then at room temp for 45 min. The pentane soln was filtered into a separatory funnel, washed with water (two portions), and sat NaCl aq, then poured through Na_2SO_4. The pentane was removed by distillation through a Vigreux column. Distillation (33 mm, 53°) yielded a reddish purple liquid (1.217 g, 42% yield). NMR ($CDCl_3$): δ 0.13 (s, 9H), 2.03 (s, 3H). IR: 2970, 2815, 1713, 1658, 1430, 1363, 1266, 870–840, 772, 718 cm^{-1}. MS: M^+ 144.0607 (Calc. 144.06072). ^{13}C NMR: δ −2.9, 21.5, 199.2, 235.5. UV (cyclohexane): $\lambda_{max}(\epsilon)$ 535 (99), 296 (41), 285 (40) nm. (Found: C, 49.74; H, 8.22. Calc. for $C_6H_{12}O_2Si$, C, 49.96; H, 8.39%).

1-*t*-*Butyldimethylsilyl*-1,2-*propanedione* (**30b**). A soln of compound **4b** (0.282 mL, 242 mg, 1.0 mmol) in 2 mL CH_2Cl_2 under dry N_2 was cooled to −78°. *m*-CPBA (216 mg, 85% pure, 1.04 mmol) was added. After 20 min at −78°, during which time the soln remained colorless, the flask was placed in a 0° bath, and wrapped with foil to exclude light. Color began to develop almost immediately. After 45 min at 0°, the soln was poured into ether/pentane (50 : 50), washed with 3 portions water and one of sat NaCl aq, poured through Na_2SO_4, and rotary-evaporated. Kugelrohr distillation (15 mm, 45–80°) provided a 90% yield (167 mg) of reddish-purple **30b**. NMR: δ 0.28 (s, 6H), 0.99 (s, 9H), 2.12 (s, 3H). ^{13}C NMR (FX-200, off-resonance decoupled): δ −6.6 (q), 16.7 (s), 20.8 (q), 26.4 (q), 199.8 (s), 236.4 (s). IR: 2930, 2877, 2834, 1711, 1646, 1604, 1472, 1360, 1260, 850 cm^{-1}. MS: M^+ 186.1072 (Calc. 186.10767).

1-(*t*-*Butyldimethylsilyl*)-2-*propyn*-1-*one* (**32b**). The selenated ether **12b** was prepared on a 25 mmol scale from **4b** (7.06 mL, 6.06 g), according to the procedure above. The crude product (8.35 g, ~100%) was dissolved in 50 mL CH_2Cl_2 and cooled to −78°. *m*-CPBA (5.33 g, 85% pure, 26 mmol) was added, and the mixture was stirred at −78° for 40 min. Ethyl vinyl ether (17 mL, 12.8 g, 178 mmol) was added, and the flask was placed in a 0° bath for 40 min. The CH_2Cl_2 was diluted with pentane, washed with 3 portions H_2O and 1 of brine, dried over $MgSO_4$ and rotary evaporated. A Kugelrohr distillation with a vacuum pump was used to collect all volatile products. In order to remove volatile Se-containing impurities, the product was dissolved in 50 mL CH_2Cl_2, cooled to −78° and treated with *m*-CPBA (1.42 g, 85% pure, 7 mmol). After 35 min, 14 mmol ethyl vinyl ether (1.34 mL) was added, and the soln was warmed to 0°, then worked up as described above. Kugelrohr distillation (12 mm, 60–80°) gave 2.0 g (48% overall) of **32b**. NMR: δ 0.25 (s, 6H), 0.98 (s, 9H), 3.79 (s, 1H). ^{13}C NMR (FX-60): δ −7.6, 16.8, 26.3, 85.4, 225.8 (the acetylenic carbons were not resolved). IR: 3255, 2965, 2937, 2862, 2080, 1605, 1470, 1392, 1368, 1267, 1010, 850, 830, 817, 790, 688 cm^{-1}. MS: M^+ 168.0971 (Calc. 168.09707). (Found: C, 64.34; H, 9.47. Calc. for $C_9H_{16}OSi$: C, 64.23%; H, 9.58%).

1-(*t*-*Butyldimethylsilyl*)-2-*butyn*-1-*one* (**33b**). The procedure used to prepare **14a** was employed for the synthesis of **14b** from **4b** (3 mmol). NMR (270 MHz, $CDCl_3$): δ −0.05, −0.04, 0.00, 0.01, (4s, 6H), 0.90, 0.91 (2s, 9H), 1.11 (t, J = 7 Hz, 3H), 1.20, 1.21 (2d, J = 5H, 3H), 3.28–3.45 (m, 1H), 3.54–3.76 (m, 1H), 4.87, 4.90 (2q, J = 5 Hz, 1H). IR: 2980, 2910, 2840, 1904, 1467, 1456, 1377, 1253, 1070(b), 840(b). MS: M^+ 350.1180 (Calc. 350.11809).

A soln of **14b** and 1–2 mg of radical inhibitor in 6 mL CH_2Cl_2 was cooled to −78°. *m*-CPBA (0.650 g, ~85% pure, 3.2 mmol) was added, and the mixture was stirred at −78° for 40 min. Ethyl vinyl ether (1.91 mL, 1.44 g, 20 mmol) was added, then the flask was placed in a 0° for 30 min. The solvent was diluted with 25 mL pentane and washed 3 times with water, washed with brine, poured through Na_2SO_4, dried over K_2CO_3 and rotary evaporated. Kugelrohr distillation (15 mm, 80–115°) gave a yellow liquid which was purified by preparative tlc (Et_2O: pentane 4 : 96, R_f = 0.47 after 2 elutions) to give a 52% yield (0.284 g) of **33b**. NMR: δ 0.10 (s, 6H), 0.87 (s, 9H), 2.05 (s, 3H). ^{13}C NMR: δ −7.5, 4.3, 16.7, 26.3, 85.0, 98.2, 225.7. IR: 2960, 2870, 2290 (w), 2200 (s), 1731, 1605, 1480, 1476, 1260, 1155, 850, 795, 692 cm^{-1}. MS: M^+ 182.1128 (Calc. 182.11272). UV (cyclohexane): $\lambda_{max}(\epsilon)$ 420 (170), 227 (7450). ((Found: C, 65.82; H, 9.89. Calc. for $C_{10}H_{18}OSi$: C, 65.87; H, 9.95%).

1-*Trimethylsilyl*-4-*methyl*-2-*pentyn*-1-*one* (**34a**). A soln of **7a** (4.26 mL, 3.64 g, 15 mmol) and radical inhibitor (15 mg) in 20 mL THF was metalated with s-BuLi (1.23 M, 12.7 mL, 15.6 mmol) at −78° (25 min), then selenated as described for the preparation of **14a**. Kugelrohr distillation gave 4.36 g (87% yield) of **15a**. NMR (200 MHz, $CDCl_3$): δ 0.10 (s, 9H), 1.05, 1.08 (2d, J = 7 Hz, 6H), 1.12, 1.13 (2t, J = 7 Hz, 3H), 1.20, 1.25 (2d, J =

5 Hz, 3H), 1.90, 1.93 (2s, 3H), 2.20–2.40 (m, 1H), 3.20–3.45 (m, 1H), 3.55–3.80 (m, 1H), 4.87, 4.90 (2q, J = 5 Hz). IR: 2930, 2897, 2870, 1920, 1470, 1455, 1262, 1070(b), 850(b), MS: M^+ 336.1025 (Calc. 336.10244). (Found: C, 64.18; H, 9.68. Calc. for $C_9H_{16}OSi$: C, 64.23; H, 9.58%).

A soln of **15a** (4.20 g, 12.5 mmol) and 13 mg of radical inhibitor in 13 mL CH_2Cl_2 was cooled to −78° and treated with *m*-CPBA (2.70 g, ~85% pure, 13.3 mmol). After 1 hr, ethyl vinyl ether (8 mL, 84 mmol) was added, and the mixture was warmed to 0° for 45 min, then diluted with hexane and filtered. The organic phase was washed with 3 portions H_2O, brine, then poured through Na_2SO_4 and rotary evaporated. Flash chromatography (ether/hexane 5 : 95) gave 1.26 g (60% yield) of **34a**. NMR: δ 0.25 (s, 9H), 1.25 (d, J = 7 Hz, 6H), 2.77 (septet, J = 7 Hz, 1H). IR: 2970, 2190, 2170, 1599, 1254, 850 cm^{-1}. MS: M^+ 168.0970 (Calc. 168.09707).

4,5 - *Dimethyl* - 1,4 - *cyclohexadienyl* - *t* - *butyldimethylsilyl ketone* (**35b**). 2,3-Dimethyl butadiene (0.500 mL, 4.4 mmol) was added to an NMR tube containing **32b** (0.192 mL, 0.168 g, 1.0 mmol) and 1–2 mg of radical inhibitor. The tube was flushed briefly with N_2 then sealed and heated at 90–92° for 3.75 hr. The tube was cooled, then broken open, and the excess 2,3-dimethylbutadiene was removed on a rotary evaporator. Preparative tlc (ether : hexane 2.5 : 97.5, R_f = 0.32) gave 0.200 g (80%) of the Diels–Alder adduct, a yellow solid, m.p. 64–66°. NMR (270 MHz): δ 0.225 (s, 6H), 0.88 (s, 9H), 1.63 (bs, 6H), 2.62–2.64 (m, 2H), 2.67–2.87 (m, 2H), 6.77 (bs, 1H). IR (CCl_4, soln): 2940, 2915, 2843, 1645, 1580, 1467, 1459, 1247 cm^{-1}. MS: M^+ 250.1753 (Calc. 250.17532). (Found: C, 71.86; H, 10.54. Calc. for $C_{15}H_{26}OSi$: C, 71.93; H, 10.46%).

(4 - *Methyl* - 3 - *furoyl*)*t* - *butyldimethylsilane* (**36b**). In a thick walled pyrex tube was placed 0.995 mL (5.0 mmol) of **33b**, 6.4 mL (50 mmol) 4-phenyloxazole[29a] and 18 mg (0.05 mmol) of radical inhibitor. The mixture was degassed (6 freeze-thaw cycles), sealed under vacuum and placed in an 182° oil bath for 4.5 hr. Workup of these dark mixtures was problematic, since the removal of excess 4-phenyloxazole by distillation[29a] was unsuccessful. Most of the oxazole was separated by flash chromatography (10% EtOAc–hexane). The remaining material was distilled (Kugelrohr, 100°, 0.2 mm). Tlc (5% Et_2O–pentane) gave 0.025 g (3%) of starting **33b** and 0.418 g (37%) of **36b**. NMR: δ 0.26 (s, 6H), 0.92 (s, 9H), 2.14 (s, 3H), 7.10 (broad s, 1H), 7.88 (broad s, 1H), IR (CCl_4): 2940, 2850, 1598, 1526, 1466, 1255, 1146, 1054, 881, 687 cm^{-1}. MS: M^+ 224.1232 (Calc. 224.12333).

3,4 - *Dimethyl* - 1 - *phenylseleno* - 3 - *cyclohexenyl trimethylsilyl ketone* (**37a**, X = SePh). A small water cooled sublimation apparatus was charged with 284 mg (1.00 mmol) of **19a**, 0.8 mL (7 mmol) 2,3-dimethyl-1,3-butadiene and about 2 mg of polymerization inhibitor. The sublimator was covered with foil and placed in a 76° oil bath for 4 hr. After cooling, the contents were rinsed into a flask and evaporated. Purification by preparative tlc (10% ether–pentane) gave 2 products. R_f = 0.55, 290 mg (79%) of **37a**, as an oil which crystallized in the freezer. NMR (CCl_4): δ 0.37 (s, 9H), 1.70 (bs, 6H), 1.60–2.24 (m), 2.28–2.64 (m), total 6H, 7.20–7.36 (m, 5H). IR: 3060, 2960, 1620, 1445, 1255, 850, 749, 700 cm^{-1}. MS: M^+ 366.0919 (Calc. 366.09105). R_f = 0.89, 56 mg (15%) of the alternative Diels–Alder adduct **38a**. NMR: δ 0.29 (s, 9H), 1.45 (s, 6H), 1.86 (bs, 3H), 1.68–3.12 (m, 2H), 3.20–3.36 (m, 2H), 5.0 (bs, 2H, at 270 MHz ($CDCl_3$) this pattern resolved into two peaks at 4.94 and 4.90 each broadened by further coupling, the latter, more so), 7.16–7.44 (m, 5H). IR: 3070, 2955, 2930, 1580, 1480, 1252, 1090, 845, 740, 697 cm^{-1}. MS: M^+ 366.0919 (Calc. 366.09105).

1 - (3,4 - *Dimethyl* - 1,3 - *cyclohexadienyl*) *trimethylsilyl ketone* (**39a**). To a soln of 290 mg (0.79 mmol) of **37a** (X = SePh) in 2 mL CH_2Cl_2 at −78° was added 160 mg (0.80 mmol, 85%) *m*-CPBA in 2 mL CH_2Cl_2. The soln was stirred 15 min at −78°, warmed to 0°, stirred 25 min, poured into CH_2Cl_2, washed with 7% $NaHCO_3$ aq and sat NaCl aq, dried (Na_2SO_4) and evaporated. Purification by preparative tlc (10% ether–pentane, R_f = 0.31) gave 104 mg (63% yield) of **39a**, 82% pure. NMR: δ 0.28 (s, 9H), 1.85 (bs, 6H), 2.00–2.52 (m, 4H), 6.77 (bs, 1H). IR: 3020, 2950, 1775, 1550, 1250, 1110, 845, 790, 690 cm^{-1}. MS: M^+ 208.1280 (Calc. 208.12838).

3,4 - *Dimethyl* - 3 - *cyclohexenyl trimethylsilyl ketone* (**37a**, X = H). Excess 2,3-dimethylbutadiene (0.452 mL, 4.0 mmol) was added to **5a** (0.22 mL, 1.5 mmol) and radical inhibitor (1–2 mg) in an NMR tube. The tube was sealed and heated at 40° for 37 hr. The product was purified by preparative tlc (ether/pentane 5 : 95, R_f = 0.37, only band observed other than baseline) to give 265 mg (84% yield) of the pale yellow liquid Diels–Alder adduct. NMR (270 MHz): δ 0.11 (s, 9H), 1.18–1.40 (m, 1H), 1.49, 1.51 (s, s, 6H), 1.64–2.08 (m, 5H), 2.75–2.93 (m, 1H). IR: 2960, 2900, 2825, 1650, 1450, 1436, 1250, 885–820, 760, 702, 623 cm^{-1}. MS: M^+ 210.1441 (Calc. 210.14402). (Found: C, 68.24; H, 10.48. Calc. for $C_{12}H_{22}OSi$: C, 68.51; H, 10.54%).

1,5 - *Dimethyl* - 3 - *trimethylsiloxy* - 2,4 - *hexadiene* (**40a**). A soln of phenyl isopropyl sulfone (0.080 mL, 93 mg, 0.50 mmol) in 1 mL THF was cooled to −78°, and treated with LDA (1.08 M, 0.48 mL, 0.52 mmol). After 15 min, **27a** (0.091 mL, 78 mg, 0.50 mmol) was added. The bright yellow color faded almost immediately. The reaction was stirred at −78° for 10 min, 0° for 20 min and worked up (standard enol ether workup). Kugelrohr distillation (15 mm, 40–60°) provided 70 mg (71% yield) of **40a**. NMR (270 MHz): δ 0.07 (s, 9H), 1.48 (s, 3H), 1.59, 1.61 (d, J = 1.1 Hz, d, J = 1.1 Hz, 6H), 1.71 (d, J = 1.3 Hz, 3H), 5.53 (m, 1H). IR: 2959, 2906, 2844, 1671, 1652, 1449, 1252, 1200, 1145, 970, 885, 845 cm^{-1}.

This compound was also prepared using α-lithio isobutyronitrile (LDA, −78°). Reaction with **27a** was carried out at 0° for 20 min.

5 - *Methyl* - 3 - *trimethylsiloxy* - 2,4 - *hexadiene* **41a**. To a soln of phenyl ethyl sulfone (0.173 g, 1.02 mmol) in 2 mL THF at −78°, was added LDA (1.10 M, 1.00 mL, 1.10 mmol). After 15 min, **27a** (0.184 mL, 0.156 g, 1.00 mmol) was added. The bright yellow color faded immediately. The reaction was stirred at −78° for 10 min, 0° for 20 min and worked up (standard enol ether workup). Kugelrohr distillation (15 imm, 60°) provided 0.144 g (78% yield) of **41a** (ratio *E*/*Z* = 77/23) NMR (200 Mz, $CDCl_3$, $CHCl_3$) δ 0.13 (s, 9H), 1.50, 1.59 (d, J = 7 Hz, 3H), 1.73, 1.70 (s, 3H), 1.77, 1.79 (s, 3H), 4.77, 4.62 (q, J = 7 Hz, 1H), 5.61, 5.50 (s, 1H). IR: 2960, 2920, 1655, 1450, 1380, 1250, 1100, 850 cm^{-1}. MS (M^+) Calc. 184.1278; Found: 184.1283.

2 - *Trimethylsiloxy* - 4 - *methyl* - 1,3 - *pentadiene* (**42a**). A cooled (−78°) soln of phenyl methyl sulfone (0.237 g, 1.52 mmol) in 3 mL THF was treated with LDA (1.03 M, 1.5 mL, 1.55 mmol). After 25 min **27a** (0.273 mL, 0.234 g, 1.5 mmol) was added, and the mixture was stirred at −78° for 15 min. A few drops of Et_3N were added. Standard workup, followed by Kugelrohr distillation gave 0.177 g (69%) of **41a**.[39] NMR: δ 0.27 (s, approx. 9H), 1.78, 1.90 (s, s, 6H), 4.05, 4.13 (s, s, 2H), 5.47 (m, 1H). IR: 3110, 2952, 2905, 1668, 1631, 1596, 1353, 1318, 1270, 1050, 870 cm^{-1}. MS: M^+ 170.1128 (Calc. 170.11272).

2 - *Phenylseleno* - 3 - *trimethylsiloxy* - 1,3 - *butadiene* (**43a**). To a cooled (−78°) soln of 91 mg (0.65 mmol) methyl phenyl sulfoxide in 5 mL THF was added 0.62 mL of a 1 M soln of LDA (0.62 mmol). After 10 min, a cold soln (−78°) of 170 mg (0.60 mmol) of **19a** in 4 mL THF was added by cannula. After stirring 2.5 hr; the mixture was worked up. Anisole (65 μL, 0.60 mmol) was added as an NMR standard. The yield (by integration) was 89%. NMR: δ (no anisole present) 0.27 (s, 9H), 4.51 (bs, 1H), 5.12 (bs, 1H), 5.47 (bs, 1H), 6.25 (bs, 1H), 7.24–7.40 (m, 3H), 7.44–7.64 (m, 2H). IR: 3060, 2960, 1680, 1615, 1575, 1481, 1443, 1286, 1257, 1117, 1029, 1020, 883, 853, 740, 698 cm^{-1}. MS: M^+ 298.0285 (Calc. 298.02845).

3 - *t* - *Butyldimethylsiloxy* - 5 - *methyl* - 1,3,4 - *hexatriene* (**44b**). Vinyl bromide (0.192 mL, 2.6 mmol) was added to t-BuLi (1.71 M, 2.6 mL, 4.4 mmol) and radical inhibitor (1–2 mg) in 20 mL Et_2O cooled to −78°. After 0.5 hr, **28b** (0.486 mL, 0.555 g, 2.0 mmol) was added to the vinyllithium soln. The bright yellow color of the enone disappeared within 5 min. The mixture was stirred at −78° for 1/2 hr then warmed to room temp over approximately 20 min. A few drops of Et_3N were added, then the soln was diluted with 20 mL pentane, and a standard workup was performed. After Kugelrohr distillation 0.380 g (85%) of **44b** was obtained. NMR ($CDCl_3$): δ 0.06 (s, 6H), 0.88 (s, 9H), 1.72 (s, 6H), 4.97 (dd, J = 10, 2 Hz, 1H), 5.39 (dd, J = 17, 2 Hz, 1H), 6.07 (dd, J = 17, 10 Hz, 1H). IR: 3100, 2950, 1951, 1621, 1482, 1471, 1374, 1240, 1060 cm^{-1}. MS: M^+ 224.1596 (Calc. 224.15967).

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REFERENCES

[1]Some of these results were reported in preliminary communications: [a]H. J. Reich and M. J. Kelly, *J. Am. Chem. Soc.* **104**, 1119 (1982); [b]H. J. Reich, J. J. Rusek and R. E. Olson, *Ibid.* **101**, 2225 (1979).

[2a]H. J. Reich, R. E. Olson and M. C. Clark, *Ibid.* **102**, 1423 (1980); [b]H. J. Reich, M. C. Clark and W. W. Willis, Jr., *J. Org. Chem.* **47**, 1618 (1982); [c]H. J. Reich, S. K. Shah, P. M. Gold and R. E. Oslon, *J. Am. Chem. Soc.* **103**, 3112 (1981).

[3a]A. G. Brook, *Acc. Chem. Res.* **7**, 77 (1974); [b]A. G. Brook and A. R. Bassindale, *Rearrangements in Ground and Excited States* (Edited by P. deMayo), Vol. 2, pp. 149–221. Academic Press, New York (1980).

[4]The equilibrium between siloxy carbanion and silyl alkoxide (Eq. 1 with R = Ph, R′ = H) was carefully studied by Wright and West.[5] This included methylations at C and O.

[5]A. Wright and R. West, *J. Am. Chem. Soc.* **96**, 3214 (1974).

[6a]W. C. Still and T. L. Macdonald, *Ibid.* **96**, 5561 (1974); [b]W. Oppolzer, R. L. Snowden and D. P. Simmons, *Helv. Chim. Acta* **64**, 2002 (1981); W. Oppolzer, R. L. Snowden and P. H. Briner, *Ibid.* **64**, 2022 (1981); [c]A. Hosomi, H. Hashimoto, H. Sakurai, *J. Organomet. Chem.* **175**, C1 (1979); P. W. K. Lau and T. H. Chan, *Ibid.* **179**, C24 (1979); D. A. Evans, J. M. Takacs and K. M. Hurst, *J. Am. Chem. Soc.* **101**, 371 (1979); M. Sekine, M. Nakajima, A. Kume, A. Hashizume and T. Hata, *Bull. Chem. Soc. Japn.* **55**, 224 (1982); S. Hünig and M. Öller, *Chem. Ber.* **113**, 3803 (1980).

[7]T. Cohen and J. R. Matz, *J. Am. Chem. Soc.* **102**, 6900 (1980).

[8a]I. Kuwajima and M. Kato, *Chem. Commun.* 708 (1979); I. Kuwajima, M. Kato and A. Mori, *Tetrahedron Letters* 2745 (1980); [b]I. Kuwajima and M. Kato, *Ibid.* 623 (1980); [c]I. Kuwajima, K. Atsumi, T. Tanaka and T. Inoue, *Chem. Lett.* 1239 (1979).

[9a]A. R. Bassindale, A. G. Brook and J. Harris, *J. Organomet. Chem.* **90**, C6 (1975); W. Ando and A. Sekiguchi, *Ibid.* **133**, 219 (1977); [b]P. J. Stang and D. P. Fox, *J. Org. Chem.* **42**, 1667 (1977).

[10a]A. G. Brook, *J. Am. Chem. Soc.* **79**, 4373 (1957); [b]T. Sato, M. Arai and I. Kuwajima, *Ibid.* **99**, 5827 (1977); [c]D. Schinzer and C. H. Heathcock, *Tetrahedron Letters* 1881 (1981); [d]J. A. Miller and G. Zweifel, *J. Am. Chem. Soc.* **103**, 6217 (1981); [e]J. Dunogues, M. Bolourtchian, R. Calas, N. Duffaut and J. P. Picard, *J. Organomet. Chem.* **43**, 157 (1972); [f]J.-C. Clinet and G. Linstrumelle, *Tetrahedron Letters* 3987 (1980).

[11]G. Zweifel and S. J. Backlund, *J. Am. Chem. Soc.* **99**, 3184 (1977).

[12]A. Degl'Innocenti, S. Pike, D. R. M. Walton, G. Seconi, A. Ricci and M. Fiorenza, *Chem. Commun.* 1201 (1980).

[13a]R. Mantione and Y. Leroux, *Tetrahedron Letters* 593 (1971); *J. Organomet. Chem.* **31**, 5 (1971); [b]Y. Leroux and C. Roman, *Tetrahedron Letters* 2585 (1973).

[14a]J. A. Soderquist and A. Hassner, *J. Am. Chem. Soc.* **102**, 1577 (1980); [b]A. Hassner and J. A. Soderquist, *J. Organomet. Chem.* **131**, C1 (1977).

[15a]N. Minami, T. Abe and I. Kuwajima, *Ibid.* **145**, C1 (1978); [b]A. G. Brook, J. M. Duff, P. F. Jones and N. R. Davis, *J. Am. Chem. Soc.* **89**, 431 (1967); E. J. Corey, D. Seebach and R. Freedman, *Ibid.* **89**, 434 (1967); [c]J. J. Rusek, unpublished results.

[16]R. G. Visser, L. Brandsma and H. J. T. Bos, *Tetrahedron Letters* 2827 (1981).

[17]Methoxyallene has been used for the synthesis of silyl enones.[10f] For other recent synthetic applications see: D. Gange, P. Magnus, *J. Am. Chem. Soc.* **100**, 7746 (1978); N. Miyaura, T. Yoshinari, M. Itoh and A. Suzuki, *Tetrahedron Letters* 537 (1980); J. M. Oostveen, H. Westmijze and P. Vermeer, *J. Org. Chem.* **45**, 1158 (1980).

[18]S. Hoff, L. Brandsma and J. F. Arens, *Recl. Trav. Chim. Pays-Bas* **87**, 916 (1968).

[19]Increased amounts of substitution α to O with more hindered alkyl halides has also been observed for siloxyallithium,[6a] and 3-siloxypentadienyllithium.[6b]

[20]For other examples of this technique for introducing alkylseleno groups see: L. Brandsma, H. Wijers and J. F. Arens, *Recl. Trav. Chim. Pays-Bas* **81**, 583 (1962); D. Liotta, G. Zima, C. Barnum and M. Saindane, *Tetrahedron Letters* 3643 (1980); M. Mikolajczyk, S. Grzejszczak and K. Korbacz, *Ibid.* 3097 (1981).

[21]M. Stähle and M. Schlosser, *Angew. Chem.* Int. Ed. Engl. **18**, 875 (1979); P. Pappalardo, E. Ehlinger and P. Magnus, *Tetrahedron Letters* 309 (1982).

[22a]E. J. Corey and S. Terashima, *Ibid.* 1815 (1972); [b]R. M. Waters, D. J. Voaden, A. Shani and J. Klug, *Org. Prep. Proc. Int.* **10**, 1 (1978).

[23]G. Rubottom and J. M. Gruber, *J. Org. Chem.* **43**, 1599 (1978).

[24]A. Sekiguchi, Y. Kabe and W. Ando, *Tetrahedron Letters* 871 (1979).

[25]H. J. Reich, S. Wollowitz, J. E. Trend, F. Chow and D. F. Wendelborn, *J. Org. Chem.* **43**, 1697 (1978).

[26a]A. G. Brook, M. A. Quigley, G. J. D. Peddle, N. V. Schwartz and C. M. Warner, *J. Am. Chem. Soc.* **82**, 5102 (1960); [b]F. Agolini, S. Klemenko, I. G. Csizmadia and K. Yates, *Spectrochim. Acta* **24A**, 169 (1968); [c]H. Bock, H. Alt and H. Seidl, *J. Am. Chem. Soc.* **91**, 355 (1969); B. G. Ramsey, A. G. Brook, A. R. Bassindale and H. Bock, *J. Organomet. Chem.* **74**, C41 (1974).

[27]E. M. Dexheimer, G. R. Buell and C. LeCroix, *Spectroscopy Lett.* **11**, 751 (1978).

[28]T. Sato, T. Abe and I. Kuwajima, *Tetrahedron Letters* 259 (1978).

[29a]J. Hutton, B. Potts and P. F. Southern, *Synthetic Commun.* **9**, 789 (1979); [b]M. F. Ansell, M. P. L. Caton and P. C. North, *Tetrahedron Letters* 1727 (1981); H. Konig, F. Graf and V. Weberndorfer, *Liebigs Ann.* 668 (1981); S. R. Ohlsen and S. Turner, *J. Chem. Soc.* (C), 1632 (1971).

[30]J.-P. Schirmann, G. Bonnard and F. Weiss, *Bull. Soc. Chim. Fr.* 3326 (1968).

[31]H. J. Reich, J. M. Renga and I. L. Reich, *J. Am. Chem. Soc.* **97**, 5434 (1975).

[32a]A. G. Brook and J. D. Pascoe, *Ibid.* **93**, 6224 (1971); R. J. P. Corriu and J. P. Masse, *J. Organometal. Chem.* **22**, 321 (1970); [b]A. G. Brook, W. W. Limburg, D. M. MacRae and S. A. Fieldhouse, *J. Am. Chem. Soc.* **89**, 704 (1967); A. G. Brook and S. A. Fieldhouse, *J. Organomet. Chem.* **10**, 235 (1967).

[33]The reaction of aldehyde tosylhydrazones with α-lithio nitriles to give olefins is a related reaction in which cyanide functions as a leaving group. E. Vedejs, J. M. Dolphin and W. T. Stolle, *J. Am. Chem. Soc.* **101**, 249 (1979).

[34]R. A. Lee, C. McAndrews, K. M. Patel and W. Reusch, *Tetrahedron Letters* 965 (1973).

[35]For a synthesis of related sulfur compounds see: B. M. Trost and A. J. Bridges, *J. Am. Chem. Soc.* **98**, 5017 (1976).

[36]The Cu enolates can be obtained by conjugate addition to α,β-acetylenic ketones: J. Klein and R. Levene, *J. Chem. Soc.* Perkin II, 1971 (1973).

[37]H. J. Reich, M. L. Cohen and P. S. Clark, *Org. Synth.* **59**, 141 (1979).

[38]This compound has recently been prepared by a different route: K. J. H. Kruithof, G. W. Klumpp, *Tetrahedron Letters* 3101 (1982).

[39]I. Paterson, *Ibid.* 1519 (1979).