(isomer 2), 127354-08-9; (±)-**26**, 127353-92-8; (±)-**27**, 127353-93-9; (±)-**28**, 127353-94-0; (±)-**29** (isomer 1), 127353-95-1; (±)-**29** (isomer 2), 127354-09-0; (±)-**30**, 127353-96-2; (±)-**31**, 127353-97-3; (±)-**32**, 127353-98-4; **35**, 81790-10-5; (±)-**36**, 127353-99-5; (±)-**37**, 127419-76-5; (±)-**38** (isomer 1), 127354-00-1; (±)-**38** (isomer 2), 127419-77-6; (±)-**39**, 127354-01-2; (±)-**47**, 127354-02-3; **48**, 127354-03-4; **49**, 127354-04-5; (±)-**50**, 127354-05-6; (±)-**50** acid chloride, 127353-90-6; (±)-**51**, 127354-06-7; (±)-**52**, 127354-07-8; (±)-**53**, 76740-73-3; (±)-**54**, 76685-67-1; (±)-**55**, 76685-68-2; C_4H_7MgBr, 7103-09-5; (±)-Br-$(CH_2)_2CHBrCH_3$, 79390-67-3; TMSC≡CH, 1066-54-2; isobutyric anhydride, 97-72-3; methyl (±)-2-oxocyclopentanecarboxylate, 53229-93-9; methyl 2-[(trifluoromethylsulfonyl)oxy]-1-cyclopentenecarboxylate, 65832-21-5.

Supplementary Material Available: General experimental details and the preparation and characterization of all the compounds that are not contained in the Experimental Section (11 pages). Ordering information is given on any current masthead page.

Acylsilane Chemistry. Synthesis of Regio- and Stereoisomerically Defined Enol Silyl Ethers Using Acylsilanes[1]

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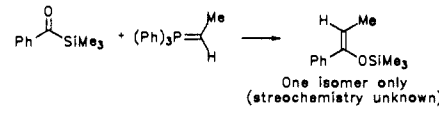
Contribution from the Samuel M. McElvain Laboratories of Organic Chemistry, Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706. *Received October 6, 1989*

Abstract: The preparation of enol silyl ethers using a carbonyl addition–Brook rearrangement–elimination sequence was studied. The key intermediate α-silyl-β-X-alkoxides could be prepared in several different ways, including the addition of organolithium or hydride reagents to α-X-acylsilanes (path a, using RM with R = alkyl, aryl, vinyl, alkynyl, silyl, stannyl, phosphinyl, and cyano), the addition of α-X-lithium reagents to acylsilanes (path b, X = phenylthio, phenylsulfonyl), or the addition of silyllithium reagents to α-X-ketones (path c, X = phenylthio, alkoxy). All of the reactions gave complete regiocontrol of silyl enol ether formation, and many gave excellent (>99%) stereocontrol as well. The selectivity of the carbonyl addition, silyl rearrangement, and elimination was studied. For path a, when the R group of RM was a poor carbanion stabilizing group the elimination of the intermediate α-silyl-β-X-alkoxides was stereospecific, and there was a large difference in rate between erythro and threo (erythro > threo). When R was a carbanion stabilizing group, such as aryl or alkynyl, the elimination process became nonstereospecific in some cases, and only small differences between threo and erythro were observed. Path b was especially effective with α-sulfonyl lithium reagents, and these reactions gave predominantly *E* enol silyl ethers (4/1 to 20/1). The addition of organolithium reagents to β-X-acylsilanes (the homologue of path a) was also briefly explored as a synthesis of siloxycyclopropanes.

Central to the utilization of the aldol condensation for the preparation of acyclic compounds with multiple asymmetric centers is the control of enolate geometry and regiochemistry. The preparation of stereoisomerically pure (or essentially pure) enol derivatives has relied on a variety of strategies.[2,3] Some are applicable to symmetric ketones or the thermodynamic enolate only. Many are not applicable to a broad range of enolate substitution patterns and geometries.

Scheme I



For symmetric ketones, where regiochemical considerations are irrelevant, reasonable stereoselectivity can be achieved by enolization under kinetic control to give *E*-enolate[2a,b] or under thermodynamic control for *Z*-enolates.[2c,d,e] The selectivity can often be augmented by the use of sterically hindered bases[2f,g] or Lewis acids.[2h] Specially designed carbonyl substrates, in which a large, removable (and sometimes chiral) group on one side of the ketone ensures the regiochemistry of the deprotonation as well as the stereochemistry of the enolate and subsequent reactions have been widely explored.[3]

Alternatively, there are several techniques in which enol silyl ethers are prepared directly by processes that do not involve enolization of carbonyl compounds. Such methods are essential for systems in which the ketone lacks regiochemically controlling substituents. Conjugate addition to enones usually gives poor stereochemical control,[4] but selectivity can be quite high when substituents on the enone cause conformational homogeneity.[5] The enolates formed by treatment of the dibromomethyllithium adducts of ketones and aldehydes with *n*-butyllithium show a significant stereochemical preference.[6] Acid-catalyzed rear-

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(2) (a) Ireland, R. E.; Mueller, R. H.; Willard, A. K. *J. Am. Chem. Soc.* **1976**, *98*, 2868. (b) Heathcock, C. H.; Buse, C. T.; Kleschick, W. A.; Pirrung, M. C.; Sohn, J. E.; Lampe, J. *J. Org. Chem.* **1980**, *45*, 1066. (c) Spears, G. W.; Caufield, C. E.; Still, W. C. *J. Org. Chem.* **1987**, *52*, 1226. (d) Beutelman, H. P.; Xie, L.; Saunders, W. H., Jr. *J. Org. Chem.* **1989**, *54*, 1703. (e) Fataftah, Z. A.; Kopka, I. E.; Rathke, M. W. *J. Am. Chem. Soc.* **1980**, *102*, 3959. (f) Masamune, S.; Ellingboe, J. W.; Choy, W. *J. Am. Chem. Soc.* **1982**, *104*, 5526. (g) Yoshifuji, M.; Nakamura, T.; Inamoto, N. *Tetrahedron* Lett. **1987**, *28*, 6325. (h) Brown, H. C.; Dar, R. K.; Bakshi, R. K.; Pandiarajan, P. K.; Singaram, B. *J. Am. Chem. Soc.* **1989**, *111*, 3441.

(3) Typically only one of a pair of isomers (usually the *Z*) is available by such techniques. (a) Corey, E. J.; Gross, A. W. *Tetrahedron Lett.* **1984**, *25*, 495. (b) Masamune, S.; Choy, W.; Kerdesky, F. A. J.; Imperiali, B. *J. Am. Chem. Soc.* **1981**, *103*, 1566. (c) Evans, D. A.; Bartroli, J.; Shih, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 2127.

(4) Barlow, A. P.; Boag, N. M.; Stone, F. G. A. *J. Organomet. Chem.* **1980**, *191*, 39. Fleming, I.; Perry, D. *Tetrahedron* **1981**, *37*, 4027.

(5) Chamberlin, A. R.; Reich, S. H. *J. Am. Chem. Soc.* **1985**, *107*, 1440.

(6) Vedejs, E.; Larson, S. D. *J. Am. Chem. Soc.* **1984**, *106*, 3030. Taguchi, H.; Yamamoto, H.; Nozaki, H. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1592.

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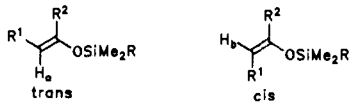
Table I. Spectroscopic Data Used for Assignment of Enol Ether Stereochemistry



no.	R^1	R^2	$\delta(H_c)$	$\delta(^{13}C_c)^a$	$\delta(H_t)$	$\delta(^{13}C_t)^a$
10a	$PhCH_2$	H	5.18	–	4.73	–
12a	$PhCH_2$	Me	4.90	17.8	4.71	–
11b	Me	Me	4.65	–	4.50	–
13a	$PhCH_2$	Et	4.80	–	4.70	–
14a	$PhCH_2$	Ph	5.25	137.1	5.45	139.0
15a	$PhCH_2$	m-$CF_3C_6H_4$	5.42	–	5.63	–
16a	$PhCH_2$	CH_2=CH	5.10	–	5.03	–
17a	$PhCH_2$	i-PrC≡C	5.35	75.6	5.15	77.7
18a	$PhCH_2$	Me_2PhSi	5.72	–	5.30	–
19a	$PhCH_2$	Me_3Sn	5.79	–	5.05	–
20c	$PhCH_2$	$(MeO)_2P(O)$	5.90	–	6.02	–
21a[b]	$PhCH_2$	CN	5.97	–	5.86	–
22a	H	$PhCH_2CH_2$	4.13	–	4.13	–
23a	Me	$PhCH_2CH_2$	4.62	–	4.52	–
24a	CH_2=CH	$PhCH_2CH_2$	5.38	34.0	–	39.0
25a	CH_2=CMe	$PhCH_2CH_2$	5.19	34.9	–	–
26a	Me_2C=CH	$PhCH_2CH_2$	5.51	33.6	5.39	38.6
27a	Me-C≡C	$PhCH_2CH_2$	4.68[c]	33.0/35.2[d]	4.68[c]	33.4/38.7[d]
28a	Ph	$PhCH_2CH_2$	5.80	34.1	5.50	39.8
29a	PhSe	$PhCH_2CH_2$	5.49	35.4	5.41	–
30a	m-$CF_3C_6H_4$	Et	5.72	30.6	5.43	–

[a] Chemical shift of first carbon of R^2 group. [b] Stereochemical assignment not verified. [c] H_c and H_t are at δ 4.96 and 4.73 in C_6D_6. [d] Assignment uncertain.

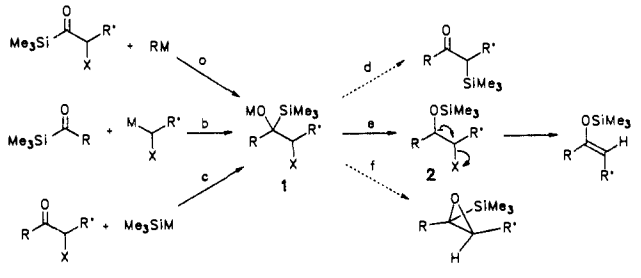
rangement of silyl epoxides[7a] and thermolysis of α-silylated ketones[7b] can proceed with high stereospecificity. The alkylation or protonation of siloxyallyllithium reagents, which can be prepared by deprotonation of allyl silyl ethers,[8] or the addition of organometallic reagents to acyl silanes,[1d,9] can proceed with excellent stereochemical control (*Z*-enolates are formed). A method which is conceptually closely related to the procedures described below is the addition of organometallic reagents to ketenes.[10] Stereochemically pure vinyllithium reagents can be oxidized to enolates or enol silyl ethers.[11]

Introduction

The many procedures outlined above, and others like it, have not completely solved the problem of preparing an arbitrary ketone enolate with both stereo- and regiocontrol. During our exploratory studies on the reaction of a variety of acylsilanes with organometallic reagents, we encountered several processes which formed enol silyl ethers with complete regiocontrol and in some cases excellent stereocontrol as well.[1a-g] Similar observations were made by other workers.[9,12] Of particular interest was an early report of Brook and co-workers that the reaction of benzoyltriphenylsilane with ethylidene Wittig reagent produced only a single stereoisomer of the enol silyl ether by a C to O silyl rearrangement (Brook rearrangement) and elimination sequence.[12a]

Generalization of this process as outlined in Scheme I seemed plausible. Since the key intermediate **1** can, in principle, be made by at least three different methods (path a, b, and c), stereochemically defined preparation of both stereoisomers seemed possible. This, coupled with their inherent complete regiospecificity, encouraged us to explore these reactions in some detail.

Scheme II



The selection of an appropriate X group for the reactions outlined in Scheme II was governed by a number of considerations. Early in our work a report by Kuwajima and Matsumoto appeared in which an (α-chloroacyl)silane was treated with *n*-butylmagnesium halide. Hydride transfer predominates in this reaction.[13] These workers observed that the intermediate **1** (X = Cl) suffers silyl migration from C to C, giving an α-silyl aldehyde (path d, Scheme II), and not the C to O migration of path e.[14] Furthermore, the choice of a good leaving group such as halogen for X could result in epoxide formation (path f) and would also make very difficult the execution of path b of Scheme II since α-halo lithium reagents are not always easily prepared and handled.[15] Hence we selected phenylthio, phenylsulfonyl, and phenylseleno as suitable X groups for most of our experiments, although several others were tried.

Results and Discussion

Preparation of Acylsilanes. A number of effective procedures are now available for the preparation of many types of acylsilanes, including classical acyl anion routes,[1f,16] various carbonylation

(7) (a) Fleming, I.; Newton, T. W. *J. Chem. Soc., Perkin 1* **1984**, 119. (b) Matsuda, I.; Sato, S.; Hattori, M.; Izumi, Y. *Tetrahedron Lett.* **1985**, *26*, 3215.

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(11) Davis, F. A.; Lal, G. S.; Wei, J. *Tetrahedron Lett.* **1988**, *29*, 4269.

(12) (a) Brook, A. G.; Fieldhouse, S. A. *J. Organomet. Chem.* **1967**, *10*, 235. (b) Brook, A. G. *Acc. Chem. Res.* **1974**, *7*, 77. (c) Brook, A. G.; Limburg, W. W.; MacRae, D. M.; Fieldhouse, S. A. *J. Am. Chem. Soc.* **1967**, *89*, 704.

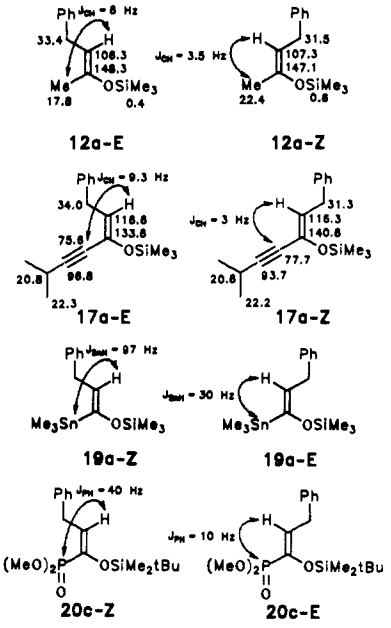
(13) Kuwajima, I.; Matsumoto, K. *Tetrahedron Lett.* **1979**, 4095.

(14) It is the nature of the leaving group that seems to control the balance between migration of silyl to O or C, since lithium reagents give similar results. The intermediate diazonium salts which result from the reaction of diazomethane with acylsilanes also suffer rearrangement to carbon.[12c]

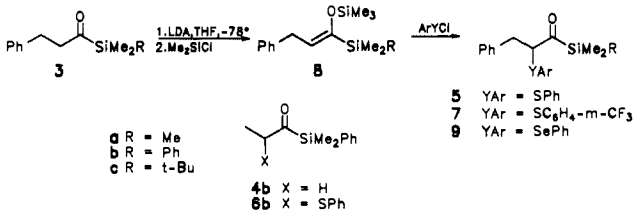
(15) Siegel, H. *Top. Curr. Chem.* **1982**, *106*, 55.

(16) (a) Brook, A. G.; Duff, J. M.; Jones, P. F.; Davis, N. R. *J. Am. Chem. Soc.* **1967**, *89*, 431. (b) Corey, E. J.; Seebach, D.; Freedman, R. *J. Am. Chem. Soc.* **1967**, *89*, 434. (c) Salzmann, T. N.; Ratcliffe, R. W.; Christensen, B. G.; Bouffard, F. A. *J. Am. Chem. Soc.* **1980**, *102*, 6161. (d) Brook, A. G.; Kucera, H. W. *J. Organomet. Chem.* **1975**, *87*, 263.

Chart I. ^{13}C Chemical Shifts and J_{CX} Values



reactions,[17] and acylations of silyl anions.[18] For the simple acylsilanes **3a–c** and **4** a modified dithiane procedure using hydrolysis with methanolic chloramine-T rather than mercury salts was employed. The [α-(phenylthio)acyl]silanes **5**, **6**, and **7** were prepared by sulfenylation of the enol silyl ether **8**, as already reported by Kuwajima.[19] The α-phenylseleno compound **9** was prepared similarly by selenenylation.[1h,20]



Determination of Enol Silyl Ether Stereochemistry. We outline here the procedures used for stereochemical assignments of enol silyl ethers. Since the *E*/*Z* nomenclature sometimes gives different descriptors for compounds with the same stereochemistry when heavy row elements are involved, we shall use cis and trans as shown in Table I to facilitate discussion of the experimental results.

1. The ^1H chemical shifts of the vinyl protons cis to the siloxy group (H_a in Table I) were usually downfield compared to the trans. Data is summarized in Table I. Notable exceptions are enol silyl ethers with a phenyl on the siloxy-bearing carbon (**14a**, **15a**), as previously observed.[2b] We have extended this generalization to substituent patterns not previously examined.

2. In several cases it was possible to equilibrate the cis and trans isomers by using TMSI/$(TMS)_2NH$. Thus treatment of the 74/26 cis/trans ratio of 1,4-diphenyl-2-(trimethylsiloxy)-1-butene **28a**, prepared by using path b of Scheme II, gave a 12/88 ratio after 60 h in $CDCl_3$. This is in accord with reported results.[2b] Since this procedure also results in regiochemical equilibration, it could not be used for many of the examples.

3. The ^{13}C chemical shift of the allylic carbon (first carbon of the R^2 group Table I) is always upfield in the isomer which has R^2 and R^1 cis). This effect is general for all types of olefins[21] and has already been clearly demonstrated for sp^3 and ipso-phenyl carbons of enol silyl ethers.[2b] It turned out to also be true for alkynyl and vinyl carbons.

4. The $^3J_{XH}$ coupling constant across the double bond in the ^{13}C NMR spectrum is usually larger for the cis isomer (trans coupling) than for the trans isomer (cis coupling). We have used J_{H-H}, J_{H-C}, J_{H-Sn}, and J_{H-P}, as shown in Chart I.

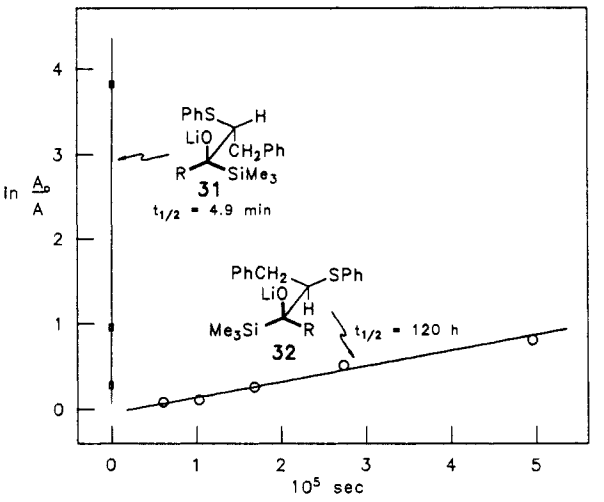
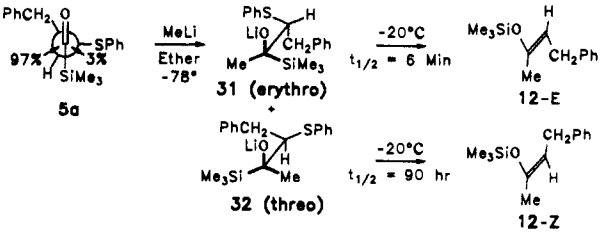
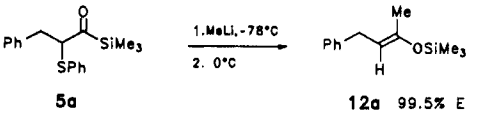


Figure 1. Rates of elimination of the lithium alkoxides prepared from erythro (**31**) and threo (**32**) silyl alcohols in ether at −20 °C.

Scheme III



Path a: Reaction of Methyllithium with (α-X-acyl)silanes. When the [α-(phenylthio)acyl]silane **5a** was allowed to react with methyllithium and the reaction mixture was warmed to 0 °C before workup, a good yield of >99.5% stereochemically pure enol ether **12a** was isolated.[22,23] This striking result prompted us to study this and a variety of similar reactions in some detail.



When the reaction mixture was quenched at −78 °C or lower, a 97/3 mixture of the two diastereomeric alcohols **31** and **32** was isolated. The isomer ratio was not changed by using either MeLi or MeLi·LiBr in ether, but the rate of addition was markedly faster for the latter (ca. 60 min at −78 °C for MeLi, complete in a few minutes with MeLi·LiBr). The discrepancy between alcohol and enol ether stereopurity was explained by the observation that the major isomer **31** underwent the silyl migration and fragmentation process much faster than the minor isomer **32**, so that it survived unchanged under conditions which caused complete reaction of

(17) Murai, S.; Ryu, I.; Iriguchi, J.; Sonoda, N. *J. Am. Chem. Soc.* **1984**, *106*, 2440. Colomer, E.; Corriu, R. J. P.; Young, J. C. *J. Chem. Soc., Chem. Commun.* **1977**, 73. Seyferth, D.; Weinstein, R. M. *J. Am. Chem. Soc.* **1982**, *104*, 5534. Seyferth, D.; Weinstein, R. M.; Wang, W.; Hui, R. C.; Archer, C. M. *Isr. J. Chem.* **1984**, *24*, 167.

(18) Capperucci, A.; Degl'Innocenti, A.; Faggi, C.; Ricci, A. *J. Org. Chem.* **1988**, *53*, 3612. Kang, J.; Lee, J. H.; Kim, K. S.; Jeong, J. U.; Pyun, C. *Tetrahedron Lett.* **1987**, *28*, 3261. Duffaut, N.; Dunogues, J.; Biran, C.; Calas, R. *J. Organomet. Chem.* **1978**, *161*, C23.

(19) Minami, N.; Abe, T.; Kuwajima, I. *J. Organomet. Chem.* **1978**, *145*, C1.

(20) Ryu, I.; Murai, S.; Niwa, I.; Sonoda, N. *Synthesis* **1977**, 874. Kita, Y.; Segawa, J.; Haruta, J.; Fuji, T.; Tamura, Y. *Tetrahedron Lett.* **1980**, *21*, 3779.

(21) Dorman, D. E.; Jautelat, M.; Roberts, J. D. *J. Org. Chem.* **1971**, *36*, 2757.

(22) Vedejs, E.; Arnost, M. J.; Eustache, J. M.; Krafft, G. A. *J. Org. Chem.* **1982**, *47*, 4384. The stereochemistry of the enol ether was not reported.

(23) This olefin synthesis is conceptually related to one on which α-X lithium reagents are added to tosylhydrazones (Vedejs, E.; Dolphin, J. M.; Stolle, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 249).

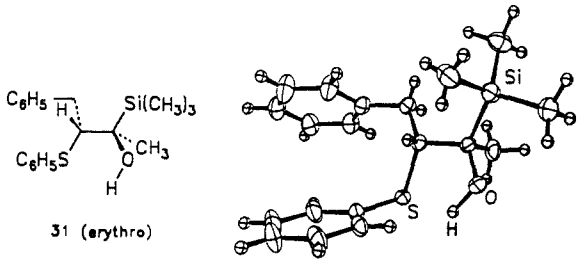
the major isomer. Above 0 °C the minor isomer **32** also fragmented, giving only the *Z*-enol ether **12a-*Z***. The reaction is thus stereospecific.[24]

We measured the rates of fragmentation of the two isomeric alkoxides in ether at −20 °C, with the results shown in Figure 1. Compound **31** reacts 1500 times as fast as **32** ($\Delta\Delta G^* = 3.7$ kcal/mol).

Careful spectroscopic studies of **31** did not allow an unambiguous assignment so the structure was determined by single-crystal X-ray diffraction. The compound has the erythro stereochemistry as shown for **31**.[1a,25] The addition to acyl silane **5a** thus occurs in the Felkin–Anh mode,[26] with phenylthio as the group anti to the attacking nucleophile. A wide variety of α-X-substituted carbonyl compounds react with nucleophiles in the same sense.[27]

With the stereochemistry of both the hydroxy silane **31** and the enol silyl ether **12a** known, the path of the reaction can be defined as shown in Scheme III. The two breaking bonds (C–S and C–Si) should be anti in the transition state, analogous to the E_2 transition state for base-catalyzed elimination of H–X groups.[28] Although the stereochemical results could also be explained by an E_1cB mechanism in which the intermediate siloxy carbanion was configurationally stable (slow pyramidal inversion), it seems improbable that such a mechanism would result in the dramatic rate difference between the two diastereomeric alkoxysilanes **31** and **32**. A concerted mechanism, in which the C to O silyl migration with development of negative charge at the carbon attached to silicon, occurs simultaneously with the cleavage of the C–S bond nicely explains both the complete stereospecificity of the fragmentation, as well as the rate effects. For the major isomer, the trimethylsilyl group must at some point be eclipsed with a hydrogen at the second carbon, whereas for the minor, unreactive isomer, it must eclipse the benzyl group. Benzyl and trimethylsilyl (*A* value 2.5[29]) are both large groups, and thus isomer **32** is expected to react with difficulty.

Like all conformations in the solid state, the one observed for **31** may be an accident of crystal packing, but it is interesting that the silyl and phenylthio groups are antiperiplanar, with a possible hydrogen bond to the sulfur. If one were to replace the OH by OLi, this structure would be identical with that which we propose for the reactive conformation in the Brook-rearrangement–elimination process which is the subject of this paper.



31 (erythro)

(24) We use the terms stereospecificity and -selectivity in their traditional physical organic sense (see House, H. O. *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972; pp 307–308 and ref 40a,b therein).

(25) For a definition see: Noyori, R.; Nishida, I.; Sakata, J. *J. Am. Chem. Soc.* **1981**, *103*, 2106, footnote 8.

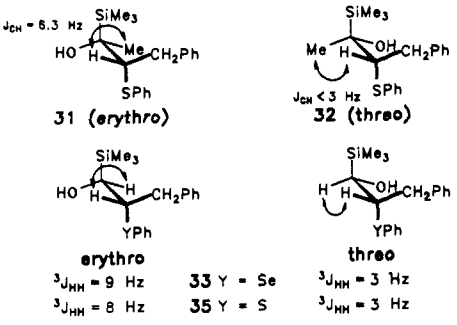
(26) Cherest, M.; Felkin, H.; Prudent, N. *Tetrahedron Lett.* **1968**, 2199. Anh, N. T.; Eisenstein, O. *Nouv. J. Chim.* **1977**, 61. Cieplak, A. S. *J. Am. Chem. Soc.* **1981**, *103*, 4540.

(27) (a) Trialkylsilyl: Hudrlik, P. F.; Kulkarni, A. K. *J. Am. Chem. Soc.* **1981**, *103*, 6251. (b) Alkoxy: Lodge, E. P.; Heathcock, C. H. *J. Am. Chem. Soc.* **1987**, *109*, 3353. (c) Alkylthio: Eliel, E. L.; Lynch, J. E. *Tetrahedron Lett.* **1981**, *22*, 2855. Shimagaki, M.; Maeda, T.; Matsuzaki, Y. *Tetrahedron Lett.* **1984**, *25*, 4775. (d) Phenylseleno: Leonard-Koppens, A. M.; Krief, A. *Tetrahedron Lett.* **1976**, 3227. (e) Phenylsulfonyl: Julia, M.; Launay, M.; Stacine, J.; Verpeax, J. *Tetrahedron Lett.* **1982**, *23*, 2465. (f) $P(O)Ph_2$: Buss, A. D.; Mason, R.; Warren, S. *Tetrahedron Lett.* **1983**, *24*, 5293. (g) Halo: Cornforth, J. W.; Cornforth, R. H.; Mathew, K. K. *J. Chem. Soc.* **1959**, 112. Takahashi, T.; Kataoka, H.; Tsuji, J. *J. Am. Chem. Soc.* **1983**, *105*, 147.

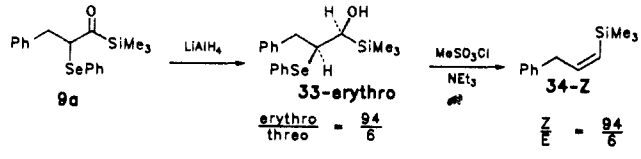
(28) Hudrlik, P. F.; Hudrlik, A. M.; Kulkarni, A. K. *J. Am. Chem. Soc.* **1985**, *107*, 4260.

(29) Kitching, W.; Olszowy, H. A.; Drew, G. M.; Adcock, W. *J. Org. Chem.* **1982**, *47*, 5153.

Chart II. $^3J_{XH}$ Coupling in β-Hydroxy Sulfides and Selenides



The isomer pair **33-*erythro*** and **33-*threo*** is the only other one for which we have convincing evidence for stereochemistry. β-Hydroxy selenides undergo a reductive elimination on treatment with dehydrating reagents, a reaction which proceeds with exclusive anti stereochemistry in simple systems.[27d,i] When a 94/6 ratio of **33-*erythro*** to **-*threo*** was treated with triethylamine–methanesulfonyl chloride, a 94/6 *Z*/*E* ratio of the vinylsilanes **34** was obtained.[30]



Anti eliminations similar to those reported here have been found in connection with Brook rearrangement of α,β-dihydroxy silanes,[28] as well in several homo-Brook rearrangements.[31]

Solid evidence on the solution structure of **31** and **32** and other α-silyl-β-thio and -seleno alcohols is not available. We have measured the $^3J_{CH}$ of both compounds, as well as $^3J_{HH}$ in the related isomer pairs **33** and **35**. The results are consistent with (but do not require) the same conformation as was seen for **31** in the crystal, with PhY and Me_3Si anti and a possible H bond to Y (Chart II).

Path a: Reaction of Other Organolithium Reagents with 2. As summarized in Table II, other alkyllithium reagents, hydride reagents, (phenyldimethylsilyl)lithium and (trimethylstannyl)-lithium show parallel behavior to that observed for methyllithium, i.e. good Felkin–Ahn selectivity during the carbonyl addition and exclusive formation of a single enol ether isomer. For the alkyllithium reagents hydride transfer products were also observed (8% for ethyllithium, 17% for *n*-butyllithium, 85% for *sec*-butyllithium and 75% for *tert*-butyllithium). These were formed with some erythro selectivity as well (7/1, 1/1, 2/1, 2/1, respectively). Early work by Brook had shown that Grignard reagents and, to a lesser extent, organolithium reagents gave substantial amounts of hydride transfer products during reactions with acyl- and benzoylsilanes, a result also observed by others.[13,32]

With R^2 groups such as phenyl and vinyl capable of modest carbanion stabilization, the rate of elimination was higher than for R = Me, ca. 1.3 times for R = vinyl, 3.3 times for R = 3-methylbutynyl, 15 times for R = phenyl, and 150 times for R = *m*-(trifluoromethyl)phenyl. The rate difference between the diastereomeric alkoxy silanes **38-*erythro*** and **38-*threo*** was much smaller (ca. 10 times, R = Ph) than observed for **31** and **32** (R = Me, 1500 times) so that both enol ethers were formed at 0 °C, but the reaction was still stereospecific.

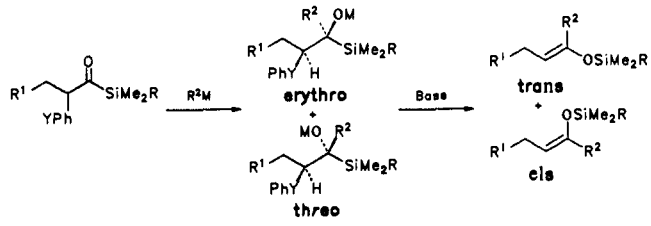
The R groups such as alkynyl and *m*-(trifluoromethyl)phenyl the stereoselectivity was good during the carbonyl addition, *but the elimination was nonstereospecific*. We believe that for these cases the elimination process has become E_1cB-like, i.e. a sequential

(30) Carey, F. A.; Toler, R. J. *J. Org. Chem.* **1976**, *41*, 1966.

(31) Yamamoto, K.; Kimura, T.; Tomo, Y. *Tetrahedron Lett.* **1984**, *25*, 2155.

(32) Brook, A. G.; Quigley, M. A.; Peddle, G. J. D.; Schwartz, N. V.; Warner, C. M. *J. Am. Chem. Soc.* **1960**, *82*, 5102.

Table II. Preparation of Enol Silyl Ethers

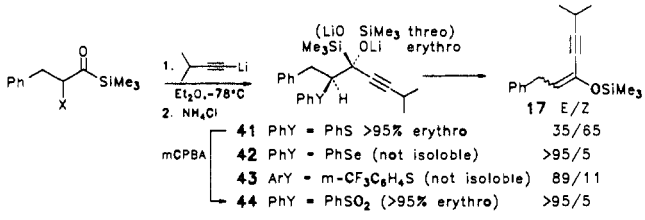


entry no.	silyl ketone	nucleophile R^2M	alcohol (M = H) no.	alcohol (M = H) erythro/threo	yield, %	silyl ether no.	silyl ether *3t/3c*[a]	yield, %[a]
1	**5a**	$LiAlH_4$	**35a**	98/2[b]	85	**10a**	>99/1	68
2	**9a**	$LiAlH_4$	**33a**	94/6	87	–	–	–
3	**6b**	MeLi	**36b**	88/12	79	**11**	98/2	40
4	**5a**	MeLi	**31a/32a**	97/3	73	**12a**	>99.5/0.5	88
5	**5b**	MeLi	–	–	–	**12b**	96/4	75
6	**5c**	MeLi	**31c/32c**	–	–	**12c**	98/2	55
7	**5a**	EtLi	**37a**	95/5[c]	54	**13a**	>99/1	74
8	**5a**	PhLi	**38a**	82/18	90	**14a**	82/18	89
9	**5a**	PhLi	**38a**	92/8[d]	88	**14a**	93/7[d]	89
10	**5a**	m-$CF_3C_6H_4Li$	**39a**	95/5[d]	65	**15a**	63/37[d]	75
11	**5a**	CH_2=CHLi	**40a**	95/5	47	**16a**	95/5	81
12	**5a**	*i*-Pr-C≡C-Li	**41a**	>95/5	32	**17a**	67/33[b]	72
13	**9a**	*i*-Pr-C≡C-Li	**42a**	*f*	*f*	**17a**	>95/5	*h*
14	**7a**	*i*-Pr-C≡C-Li	**43a**	*f*	*f*	**17a**	89/11	*i*
15	**5a**	$PhMe_2SiLi$[e]		*f*	*f*	**18a**	99/1[g]	94
16	**5a**	Me_3SnLi		*f*	*f*	**19a**	>99.5/0.5	81
17	**5c**	$(MeO)_2POLi$		*f*	*f*	**20c**	97/3	86
18	**5c**	$NC^-(n\text{-}Bu)_4N^+$		*f*	*f*	**21c**	67/33[b]	93

[a] This yield is overall from acylsilane and organolithium reagent. [b] The ratio depends on reaction conditions. [c] Reference 1a. [d] Reaction carried out at −110 °C. [e] Solvent was 1/1 ether/THF. [f] The intermediate alcohol was not isolated. [g] The product also contains 5% of (*Z*)-$PhCH_2CH$=C-($SiMe_3$)$OSiMe_2Ph$. [h] The product contains 50% of $PhCH_2CH_2C(O)SiMe_3$. [i] Accurate yield was not measured.

silyl migration to a stabilized siloxy carbanion with sufficient lifetime to undergo bond rotation followed by expulsion of benzenethiolate. The cases where R = phenyl and alkynyl are on the borderline between stereocontrolled and noncontrolled processes since small changes in R or the leaving group caused dramatic changes in the ratio of the enol ethers formed. For example, the diastereomer ratio of **39**-*erythro* to **39**-*threo* (entry 10, R = *m*-$CF_3C_6H_4$) was almost the same (at −110 °C) as for **38** (entry 9), but the enol ether ratio changed from 13/1 to 2/1. The superior carbanion stabilizing ability of the *m*-(trifluoromethyl)phenyl group of entry 10 results in a longer lived carbanion intermediate compared to phenyl.

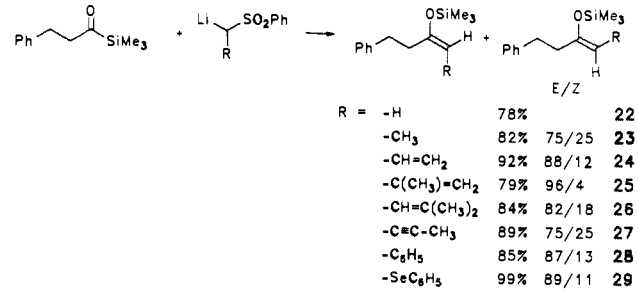
If the reaction with the lithium acetylide was carried out with use of the α-phenylseleno compound **9a**, a >95/5 trans/cis ratio of enol ethers was formed (Table II, entry **13**) compared to the 67/33 ratio formed for the sulfur compound **5a** (entry 12). The intermediate alcohol **42a** could not be isolated because addition to the acylsilane was slower than elimination. Here the use of



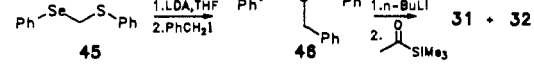
a better leaving group than PhS (i.e. PhSe) restored the stereospecificity of the elimination process. A similar result was achieved by oxidation of the hydroxy sulfide **41**-*erythro* to the sulfone **44**, which again gave exclusively the trans enol ether on treatment with lithium diisopropylamide. Finally, when the phenylthio leaving group was replaced by a [*m*-(trifluoromethyl)phenyl]thio group, the enol ether specificity again was high (entry 14), although not as high as the ratio of diastereomeric hydroxy silanes expected to be formed during the reaction.

We were also able to prepare enol silyl ethers formally derived from acyl cyanides and acyl phosphonates by addition of cyanide or lithium dialkyl phosphite to **5c**.

Scheme IV



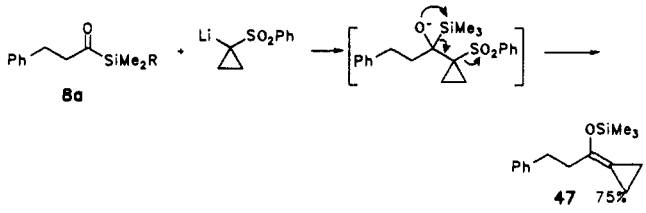
Path b: Reaction of α-X-lithium Reagents with Acylsilanes. Experiments with a number of α-X-lithium reagents (X = bromo, phenylthio, phenylsulfinyl, phenylsulfonyl, phenylseleno, phosphonyl) showed that phenylsulfonyl[33] had the most useful reactivity, and we concentrated our efforts on utilization of α-lithio sulfones for path b of Scheme I. The α-lithio sulfones were prepared by deprotonation of the sulfone with lithium diisopropylamide. The [α-(phenylthio)phenethyl]lithium was prepared by a Li/Se exchange.[11,34]



The reaction worked well in most cases tried. Scheme IV presents a summary of our results. A 1:1 mixture of THF and ether was found to be the preferred solvent. The reaction was sluggish in ether, and sometimes worked poorly in pure THF. Almost all of the enol silyl ethers could be freed from small amounts of unreacted sulfone without epimerization or hydrolysis of the enol silyl ether by quick chromatography on alumina. Exceptions were enol ethers **27a** and **30a**. If care was taken during

(33) Magnus, P. *Tetrahedron* **1977**, *33*, 2019.
(34) (a) Seebach, D.; Meyer, N.; Beck, A. K. *Liebigs Ann. Chem.* **1977**, 846. (b) Anciaux, A.; Eman, W.; Dumont, W.; Krief, A. *Tetrahedron Lett.* **1975**, 1617.

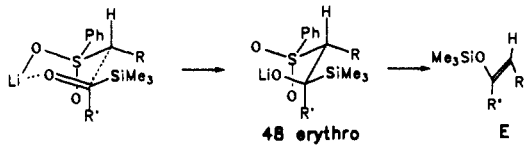
workup and purification, regiochemically pure enol silyl ethers could be isolated, even when the isomer formed was unstable with respect to the others possible, as in the case of the cyclopropyl compound **47**, which cannot be formed by enolization of phenethyl cyclopropyl ketone under either thermodynamic or kinetic control.



8a

In several cases the product enol silyl ether was cleaved during the reaction itself. For these, pure silyl ether could be obtained by silylating the enolate with triethylamine/trimethylchlorosilane before workup.

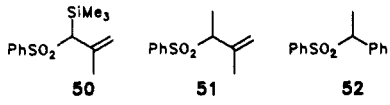
Predominantly *E* enol silyl ethers were formed in ratios ranging from 1.5/1 to 24/1. Since the detailed pathway of the reaction is not known, no precise rationale for the stereochemical preference can be given. It has been shown above that the silyl shift elimination pathway is stereospecific in cases where the leaving group is phenylthio, and one case where it is phenylsulfonyl, so it seems likely that the formation of the initial adducts control the stereochemistry of the enol silyl ether. In fact, the major enol ether formed can be traced back to a least hindered approach of the two reactants, if the transition state has lithium bridged between the oxygens of alkoxide and sulfone.[35]



48 erythro **E**

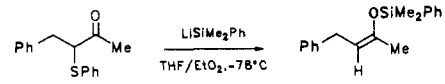
On the basis of the behavior of compounds **31** and **32**, the erythro isomer of **48** fragments much faster than the threo. It is therefore possible that the less reactive threo alkoxide sulfone adduct (precursor for the cis enol silyl ether) reversibly dissociates in at least some of the cases, and hence gives a predominance of *E* product. This was not checked.

Primary and secondary α-lithio sulfones worked well; tertiary lithium reagents were less consistent. Cyclopropyl phenyl sulfone gave good results, isopropyl and cyclobutyl sulfones gave ~50% addition to **3a**, whereas the allylic and benzylic sulfones, **49–51**, gave predominantly enolization, as shown by the isolation of the enol silyl ether **8a** when the reaction mixture was treated with trimethylchlorosilane. This problem could not be solved by conversion of the α-lithio sulfones to the corresponding zinc, magnesium, or cerium reagents.



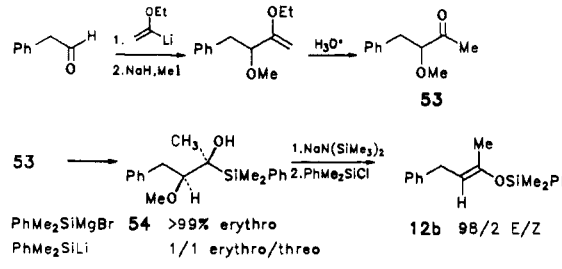
50 **51** **52**

Path c: Reaction of (Phenyldimethylsilyl)lithium with α-X-ketones. The formation of opposite diastereomers by exchanging the nucleophile and ketone substituents is well established in carbonyl additions.[36] Since very high *E*/*Z* ratios were attainable with path a, it therefore was desirable to examine the reaction of an α-phenylthio ketone with a silyllithium reagent (path c). Good stereoselectivity has been observed by Vedejs et al. in the addition of (phenyldimethylsilyl)lithium to an α-alkylthio ketone.[22] We have examined the reaction of this lithium reagent[37] with the ketone **52**, and found that a 1/99 ratio of **12b**-*E* and **12b**-*Z* was formed in 2/1 ether/THF. In pure THF some cleavage of the enol ether (presumably by the silyllithium reagent) was observed.



52 **12b** >99% Z

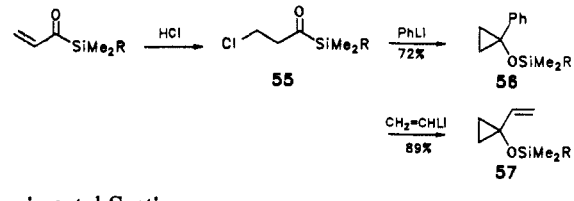
With the successful preparation of >99% isomerically pure *Z* silyl enol ether using Felkin–Ahn (Cram) selectivity in a silyllithium reaction, we next investigated the possibility that a Cram-cyclic mode of reactivity could be achieved in this system also. It has been reported that excellent chelation controlled additions are obtained when α-alkoxy carbonyl compounds[36,38] react with Grignard reagents. Accordingly, we treated **53** with (phenyldimethylsilyl)lithium and -magnesium bromide. The lithium reagent gave a 1/1 ratio of diastereomers whereas the Grignard reagent gave a single isomer (>99/1) of the expected α-silyl alcohol **54**. No fragmentation of either the magnesium



or lithium alkoxide was observed in THF even at room temperature. This contrasts with the similar α-phenylthio compound **31**, which cleaves rapidly in THF at −78 °C. The potassium (KH) and sodium ($NaN(SiMe_3)_2$) alkoxides did fragment to give enol silyl ether, which was unfortunately cleaved to enolate by the methoxide liberated. A 98/2 *E*/*Z* ratio of the phenyldimethylsilyl enol ethers could be isolated (52% yield) when the enolate was resilylated before workup.

1,3-Elimination To Give Cyclopropanes. The experiments described above have used the carbanionic center produced by a silyl shift from carbon to oxygen to initiate 1,2-elimination reaction. It is also possible to carry out 1,3-eliminations, provided that the carbanionic center bears some stabilizing groups.[1g,9] (3-Chloropropanoyl)phenyldimethylsilane (**55**) can be easily prepared by the addition of hydrogen chloride to the propenoyl silane. Treatment with phenyllithium or vinyllithium produces the silylated cyclopropanols **56** and **57** in useful yields.

The methodology described here allows the preparation of many types of enol ethers with complete regioselectivity and good to excellent stereoselectivity.



Experimental Section

General Experimental. NMR spectra (^1H) were obtained on a JEOL MH-100, IBM WP-200, WP-270, or a Bruker WH-270. Carbon NMR (^{13}C) spectra were obtained on a JEOL FX-60 or FX-200. Unless otherwise stated, 200- and 270-MHz ^1H spectra were taken in $CDCl_3$ with reference to TMS, $CHCl_3$ (δ 7.23), CH_2Cl_2 (5.32) or acetone (2.05). Carbon NMR were taken in $CDCl_3$ with $CDCl_3$ (δ 76.9) as reference or in acetone-d_6 with the methyl carbon (δ 29.7) as reference. IR spectra were taken of neat liquids between salt plates or as solutions in CCl_4 or $CDCl_3$ (0.1-mm solution cells) and were recorded on a Beckman Acculab 7 or Beckman IR 4230 spectrophotometer. An AEI MS902 or Kratos MS80 were used to obtain mass spectra.

Starting materials were commercially available, with the exception of PhSeSePh,[1j] PhSeCl,[1j] $PhMe_2SiLi$,[39] $PhSSO_2Ph$,[40] (m-$CF_3C_6H_4S)_2$,[1h]

(35) (a) Burford, C.; Cooke, F.; Roy, G.; Magnus, P. *Tetrahedron* **1977**, *51*, 4521. (b) In the solid state, metalated sulfones have lithium on oxygen: Boche, G. *Angew. Chem.* **1989**, *101*, 286. Gais, H.-J.; Vollhardt, J.; Hellman, G.; Paulus, H.; Lindner, H. J. *Tetrahedron Lett.* **1988**, *29*, 1259.

(36) Cram, D. J.; Kopecky, K. R. *J. Am. Chem. Soc.* **1959**, *81*, 2748.

(37) (Trimethylsilyl)lithium would be preferred, but is not easily available in ether or THF solution (Still, W. C. *J. Org. Chem.* **1976**, *41*, 3063).

(38) Still, W. C.; McDonald, J. H., III *Tetrahedron Lett.* **1980**, 1031.

Me_3SnLi,[41] $MgBr_2$,[42] $PhCH_2I$,[43] LDA,[1h] 1-(1-ethoxyethoxy)-1-(dimethylphenylsilyl)-1,2-propadiene,[18] and cyclopropyl phenyl sulfone,[44] which were made according to literature procedures. Other phenyl sulfones (methyl, ethyl, allyl, methallyl, prenyl, but-2-ynyl, benzyl, and phenylselenomethyl) were prepared by reaction of sodium benzenesulfinate with the appropriate halide or mesylate in DMF or ethanol.[45] *n*-Butyllithium was used as a 1.5–2 M solution in hexane.

Diisopropylamine was distilled from KOH and stored over 4A molecular sieves. Diethyl ether (Et_2O) and tetrahydrofuran (THF) were freshly distilled from sodium benzophenone ketyl. Solutions of LDA, *n*-BuLi, *s*-BuLi, *t*-BuLi, Me_3SnLi, and $PhMe_2SiLi$ were titrated with 1-propanol with 1,10-phenanthroline as indicator. All reactions involving organolithium reagents were carried out under an atmosphere of dry nitrogen, in glassware which had been dried at 110 °C for at least 2 h.

The temperatures reported for Kugelrohr distillations were the bath temperatures.

Normal workup consisted of pouring the reaction mixture into saturated $NaHCO_3$ solution and ether/pentane (1/1), then washing the organic phase with distilled water and brine. Reaction mixtures containing PhSH or MCPBA were washed with NaOH after the water wash. The organic phase was poured through Na_2SO_4, dried over K_2CO_3, and concentrated on a rotary evaporator. The silyl enol ethers are sensitive to moisture and were best stored in a freezer.

Phenyldimethyl(3-phenylpropanoyl)silane (3b). To a solution of 16.72 g (74.6 mmol) of the dithiane prepared from 3-phenylpropanal in 150 mL of THF at −25 °C was added 78.4 mmol of *n*-BuLi over 15 min. The mixture was stirred at 0 °C for 100 min. $PhMe_2SiCl$ (82 mmol, 13.9 g, 13.5 mL) was added over 10 min, followed by stirring at 0 °C for 2 h. Normal workup gave 26.9 g of clean crude silylated dithiane (100%): NMR (270 MHz, $CDCl_3$) δ 0.75 (s, 6 H), 2.9–3.1 (m, 2 H), 2.3–2.55 (m, 4 H), 2.6–2.8 (m, 2 H), 2.9–3.1 (m, 2 H), 7.0–7.8 (m, 10 H); IR 3150, 2940, 1600, 1500, 1430, 1250, 1120, 840, 700 cm^{-1}; MS (M^+) calcd for $C_{20}H_{26}S_2Si$ 358.1247, found 358.1241.

To this material, dissolved in 180 mL of MeOH and 45 mL of water at 0 °C, was added 104 g (370 mmol) of Chloramine-T over 5 min. The solution was stirred at 0 °C for 0.5 h and 25 °C for 1 h. $NaHCO_3$ (aqueous) was added (150 mL), and the aqueous layer was washed five times with 50 mL of Et_2O/hexane. Normal workup and Kugelrohr distillation (90 °C/0.02 mm) gave 16.04 g of **3b** (81% yield): NMR (200 MHz, $CDCl_3$) δ 0.52 (s, 6 H), 2.7–3.0 (m, 4 H), 7.0–7.6 (m, 5 H); IR 3020, 2960, 1650, 1430, 1250, 1110, 900, 800 cm^{-1}; MS (M^+) calcd for $C_{17}H_{20}OSi$ 268.1278, found 268.1283.

***tert*-Butyldimethyl(3-phenylpropanoyl)silane (3c).** To 4.48 g (20 mmol) of the dithiane prepared from 3-phenylpropanal in 100 mL of THF at 0 °C was added 21 mmol of *n*-BuLi over 10 min. After 30 min 3.32 g (22 mmol) of *tert*-butyldimethylsilyl chloride in 10 mL of THF was added, followed by 3.49 mL (20 mmol) of HMPA. The mixture was stirred 18 h at 0 °C. Normal workup including three water washes gave 6.3 g of silylated dithiane (94% crude). A small sample was purified by TLC for NMR, IR, and MS: NMR (200 MHz, $CDCl_3$) δ 0.35 (s, 6 H), 1.15 (s, 9 H), 2.05 (m, 2 H), 2.45 (dt, J = 15, 4 Hz, 2 H), 2.65 (m, 2 H), 3.10 (ddd, J = 15, 13, 4 Hz, 2 H), 7.2–7.4 (m, 5 H); IR 3020, 2920, 2850, 1600, 1460, 1250, 820, 700 cm^{-1}; MS (M^+) calcd for $C_{18}H_{30}S_2Si$ 338.1551, found 338.1558.

To a mixture of 5.56 g of the above dithiane (16.5 mmol not completely dissolved) in 80 mL of MeOH and 20 mL of H_2O at 0 °C was added 23.3 g (83 mmol) of Chloramine-T over 5 min. The solution was warmed to 25 °C for 1.5 h, then washed four times with 20 mL of Et_2O. Normal workup of the combined organic layers and flash chromatography (7% Et_2O/hexane) gave 1.62 g (41%) of **3c**. Recrystallization from hexane at −20 °C gave white crystals: mp 41 °C; NMR (200 MHz, $CDCl_3$) δ 0.20 (s, 6 H), 0.95 (s, 9 H), 2.90 (m, 4 H), 7.1–7.4 (m, 5 H); IR 2960, 2860, 1640, 1470, 1250, 820 cm^{-1}; MS (M^+) calcd for $C_{15}H_{24}OSi$ 248.1590, found 248.1598.

1-(Trimethylsilyl)-3-phenyl-1-(trimethylsiloxy)-1-propene (8).[46] To a solution of 14.4 mL (10.40 g, 103 mmol) of diisopropylamine in 125 mL of THF at −78 °C was added 102 mmol of *n*-BuLi over 10 min. The solution was warmed to 0 °C for 15 min, then cooled to −78 °C. To this solution was added 21.6 mL (20.6 g, 100 mmol) of **3a** over 10 min, and stirring was continued at −78 °C for 20 min. Me_3SiCl (11.3 g, 13.2 mL, 104 mmol) was added over 5 min, and stirring was continued at −78 °C for 5 min and at 25 °C for 5 min. Normal workup and Kugelrohr distillation (60 °C, 0.005 mm) gave 25.2 g of **8** (90%, E/Z = 84/16). *E* isomer: NMR (200 MHz, $CDCl_3$) δ 0.10 (s, 9 H), 0.21 (s, 9 H), 3.43 (d, J = 7 Hz, 2 H), 5.20 (t, J = 7 Hz, 1 H), 7.1–7.4 (m, 5 H); IR 3020, 2980, 2950, 1610, 1495, 1450, 1250, 1130, 850 cm^{-1}. *Z* isomer: NMR (partial) (200 MHz, $CDCl_3$, CH_2Cl_2) δ 0.17 (s, $SiMe_3$), 0.20 (s, $OSiMe_3$), 3.29 (d, J = 7 Hz, $PhCH_2$), 5.61 (t, J = 7 Hz, C=C*H*), 7.1–7.4 (Ar*H*).

Phenyldimethyl[2-(phenylthio)-3-phenylpropanoyl]silane (5a).[19] To 43.5 g of *N*-chlorosuccinimide (5.81 g) in 40 mL of CH_2Cl_2 in a flask with a reflux condenser was added dropwise 4.43 mL of PhSH (4.74 g, 43 mmol) until initiation (refluxing and orange color). The solution was cooled to 0 °C and addition was completed over 5 min, followed by stirring at 25 °C for 30 min. The solution was cooled to −78 °C and 11.8 g (43 mmol) of **8** was added. The solution was warmed to 25 °C for 5 min and 6.02 mL (4.35 g, 43 mmol) of Et_3N was added. Standard workup including a NaOH wash gave 12.72 g of **5a** (94%): mp 48 °C; NMR (200 MHz, $CDCl_3$) δ 0.20 (s, 9 H), 2.95 (dd, J = 14, 7.5 Hz, 1 H), 4.20 (dd, J = 7.5, 7 Hz 1 H), 7.1–7.5 (m, 10 H); IR 3060, 3020, 2950, 1640, 1500, 1485, 1460, 1440, 1250, 800 cm^{-1}; MS (M^+) calcd for $C_{18}H_{22}OSSi$ 314.1161, found 314.1158.

***tert*-Butyldimethyl[2-(phenylthio)-3-phenylpropanoyl]silane (5c).** To a solution of 5.25 mmol of LDA in 5 mL of THF at −78 °C was added 1.24 g (5 mmol) of **3c** in 10 mL of THF over 2 min. Inverse addition to a solution of 1.38 g (5.5 mmol) of $PhSSO_2Ph$ in 10 mL of THF at 0 °C was followed by warming to 25 °C for 5 min. Normal workup including a NaOH wash gave 1.46 g (82% crude) of **5c**. The product was recrystallized from hexane: NMR (200 MHz, $CDCl_3$) δ 0.20 (s, 3 H), 0.22 (s, 3 H), 0.77 (s, 9 H), 2.90 (dd, J = 14, 5.5 Hz, 1 H), 3.24 (dd, J = 14, 9 Hz, 1 H), 4.20 (dd, J = 9, 5.5 Hz, 1 H), 7.1–7.4 (m, 10 H); IR 3060, 2950, 2850, 1640, 1470, 1440, 1250, 1030, 840, 700 cm^{-1}; MS (M^+) calcd for $C_{21}H_{28}OSSi$ 356.1623, found 356.1630. Anal. Calcd: C, 70.73; H, 7.91. Found: C, 70.86; H, 8.00.

Trimethyl[2-(phenylseleno)-3-phenylpropanoyl]silane (9a). To a solution of 0.72 g (2.5 mmol) of **8** in 1 mL of CH_2Cl_2 at −78 °C was added a solution of 0.58 g (3 mmol) of benzeneselenenyl chloride in 1 mL of CH_2Cl_2. After 5 min the solution was warmed to 25 °C. Normal workup, TLC (5% Et_2O/pentane, R_f = 0.4), and recrystallization from pentane gave 0.63 g (70%) of **9a**: mp 50–51 °C; NMR (200 MHz, $CDCl_3$) δ 0.18 (s, 9 H), 2.95 (dd, J = 14, 7 Hz, 1 H), 3.30 (dd, J = 14, 9 Hz, 1 H), 4.25 (dd, J = 9, 7 Hz, 1 H), 7.1–7.5 (m, 10 H); IR (CCl_4) 3060, 3020, 2950, 1625, 1495, 1475, 1455, 1245, 840 cm^{-1}; MS (M^+) calcd for $C_{18}H_{22}OSeSi$ 362.0599, found 362.0605. Anal. Calcd: C, 59.82; H, 6.14. Found: C, 59.93; H, 6.16.

1-(Trimethylsilyl)-2-(phenylseleno)-3-phenyl-1-propanol (33a, Table II, Entry 2). To a solution of 0.36 g (1.0 mmol) of **9** in 5 mL of Et_2O at −78 °C was added a solution of $LiAlH_4$ (1.0 mmol) in 4 mL of Et_2O over 5 min. After 30 min at −78 °C the reaction was quenched with dilute NH_4Cl/THF. Normal workup and TLC (20% EtOAc/hexane, R_f = 0.7) gave 0.316 g (87%) of **33** (erythro/threo = 94/6). Erythro (*RR/SS*): NMR (200 MHz, $CDCl_3$) δ 0.22 (s, 9 H), 2.60 (br s, 1 H), 2.72 (dd, J = 14.5, 9.5 Hz, 1 H), 3.20 (dd, J = 14.5, 5 Hz, 1 H), 3.25 (d, J = 9 Hz, 1 H), 3.55 (ddd, J = 9.5, 9, 5 Hz, 1 H), 7.15–7.45 (m, 10 H); IR 3420, 3060, 3030, 2950, 1710, 1580, 1495, 1480, 1455, 1440, 1250, 850, 740, 690 cm^{-1}; MS (no M^+). threo *RS/SR*: NMR (partial) (200 MHz, $CDCl_3$) δ 0.19 (s, $SiMe_3$), 2.96 (dd, J = 15, 12 Hz, PhC*H*), 3.20 (dd, J = 15, 3.5 Hz, PhC*H*), 3.40 (d, J = 2.5 Hz, C*H*OH), 3.85 (ddd, J = 12, 3.5, 2.5 Hz, PhSeC*H*), 7.15–7.45 (m, Ar*H*).

cis*-1-(Trimethylsilyl)-3-phenyl-1-propene[30] (34).** To a solution of 109 mg (0.3 mmol) of **33** (erythro/threo = 94/6) in 2 mL of CH_2Cl_2 at 0 °C was added Et_3N (1.5 mmol, 152 mg, 0.21 mL) and methanesulfonyl chloride (0.9 mmol, 103 mg, 0.07 mL). The reaction was stirred for 30 min at 25 °C. Normal workup and Kugelrohr distillation (50 °C/0.1 mm) gave 0.023 g (40%) of **34** as a 94/6 mixture of Z/E isomers. **34-*Z: NMR (200 MHz, $CDCl_3$) δ 0.29 (s, 9 H), 3.60 (d, J = 7 Hz, 2 H), 5.71 (dt, J = 14, 1 Hz, 1 H), 6.50 (dt, J = 14, 7 Hz, 1 H), 7.20–7.50 (m, 5 H); IR 3020, 2960, 2900, 1600, 1495, 1455, 1250, 865, 845, 705 cm^{-1}; MS (M^+) calcd for $C_{12}H_{18}Si$ 190.1173, found 190.1177. **34-*E***: NMR (partial, in above mixture): δ 0.18 (s, $SiMe_3$), 5.80 (dt, J = 18, 1 Hz, SiC*H*=C), 6.25 (dt, J = 18, 6 Hz, CC*H*=C), 7.20–7.50 (m, Ar*H*).

***erythro*-1-Phenyl-2-(phenylthio)-3-(trimethylsilyl)-3-butanol (31,** Table II, Entry 4). To 6.6 mmol of MeLi·LiBr in 12 mL of Et_2O at −78 °C in a long-neck flask was added 1.88 g (6 mmol) of **5a**. After stirring for 3 min, 6 mL of 1 M NH_4OAc in MeOH was added. Normal workup (erythro/threo = 97/3) and recrystallization from pentane gave 1.28 g (65%) of *erythro*-(*RR/SS*)-**31**: mp 50–51 °C; NMR (200 MHz, $CDCl_3$,

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CH_2Cl_2) δ 0.28 (s, 9 H), 1.30 (s, 3 H), 2.65 (dd, J = 13.5, 12 Hz, 1 H), 2.88 (s, 1 H), 3.20 (dd, J = 14, 2.5 Hz, 1 H), 3.38 (dd, J = 12.5, 2.5 Hz, 1 H), 6.8–7.4 (m, 10 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ −2.5, 20.5 (qd, J = 125, 6.3 Hz), 40.1 (t), 66.7 (d), 69.1 (s), 126.3, 128.1, 128.3, 129.4, 131.7, 136.8, 139.1; IR 3440, 3050, 3020, 2940, 1575, 1490, 1475, 1450, 1435, 1300, 1245, 855, 830 cm^{-1}; MS (M^+) calcd for $C_{19}H_{26}OSSi$ 330.1467, found, 330.1472. Anal. Calcd: C, 69.04; H, 7.93; Found: C, 69.40; H, 8.08.

(*E*)-3-(Trimethylsiloxy)-1-phenyl-2-butene (12a, Table II, Entry 4).[47] To a solution of 3.14 g (10 mmol) of **5a** in 30 mL of Et_2O at −78 °C was added by cannula a cold solution of 10.5 mmol of MeLi·LiBr in 20 mL of Et_2O. The solution was stirred at −78 °C for 10 min and at 0 °C for 20 min. Normal workup and Kugelrohr distillation (40 °C, 0.02 mm) gave 1.93 g of **12a** (88%, *E*/*Z* >99.5/0.5). *E* isomer: NMR (200 MHz, $CDCl_3$) δ 0.25 (s, 9 H), 1.87 (s, 3 H), 3.36 (d, J = 7 Hz, 2 H), 4.90 (t, J = 7 Hz, 1 H), 7.1–7.4 (m, 5 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 0.4 (q), 17.8 (qd, J = 126, 7 Hz), 33.4 (t), 106.3 (d), 125.4 (d), 127.7 (d), 127.9 (d), 141.5 (s), 148.6 (s); IR 3010, 2940, 2900, 1720, 1665, 1600, 1490, 1450, 1250, 1150, 1000, 850 cm^{-1}; MS (M^+) calcd for $C_{13}H_{20}OSi$ 220.1278, found 220.1283. *Z* isomer (made by elimination of **32**: NMR (200 MHz, $CDCl_3$ δ 0.27 (s, 9 H), 1.87 (s, 3 H), 3.42 (d, J = 7 Hz, 2 H), 4.75 (t, J = 7 Hz, 1 H), 7.1–7.4 (m, 5 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 0.6 (q), 22.4 (qd, J = 126, 3.5 Hz), 31.5 (t), 107.3 (d), 125.4 (d), 128.0 (d), 128.1 (d), 142.0 (s), 147.1 (s).

1,3-Diphenyl-1-(trimethylsilyl)-2-(phenylthio)-1-propanol (38, Table II, Entry 9). To a solution of 2.20 mmol of *t*-BuLi in 4 mL of Et_2O at −78 °C was added 0.188 g (0.126 mL, 1.20 mmol) of PhBr. The solution was stirred for 10 min at −78 °C and cooled to −110 °C, and 0.314 g (1.0 mmol) of **5a** in 4 mL of Et_2O was added. Stirring was continued at −110 °C for 2 min, followed by addition of NH_4OAc in MeOH. Normal workup gave 0.34 g of **38** (88%, erythro/threo = 92/8). The yield by comparison with an NMR standard was 90%. Recrystallization was done in pentane, mp 64–66 °C. Erythro (*RR*/*SS*): NMR (200 MHz, $CDCl_3$) δ 0.10 (s, 9 H), 2.74 (s, 1 H), 2.88 (dd, J = 14, 11 Hz, 1 H), 3.19 (dd, J = 14, 2.5 Hz, 1 H), 3.96 (dd, J = 11, 2.5 Hz, 1 H), 6.9–7.4 (m, 15 H); IR 3060, 3020, 2920, 1600, 1580, 1495, 1480, 1455, 1440, 1250, 845, 745 cm^{-1}. Anal. Calcd for $C_{24}H_{28}OSSi$: C, 73.42; H, 7.19. Found: C, 73.66; H, 7.24.

Threo: NMR (partial) (200 MHz, $CDCl_3$) δ 0.12 (s, $SiMe_3$), 2.99 (dd, J = 14, 12 Hz, PhSC*H*), 3.52 (dd, J = 14, 2.5 Hz, PhC*H*), 4.00 (dd, J = 12, 2.5 Hz, PhC*H*), 6.9–7.4 (m, Ar*H*).

(*E*)-1,3-Diphenyl-1-(trimethylsiloxy)-1-propene (14, Table II, Entries 8 and 9). To a solution of 1.1 mmol of PhLi in 5 mL of Et_2O at −78 °C was added 0.31 g (1 mmol) of **5a** in 4 mL of Et_2O. After 10 min, the solution was warmed to 0 °C for 30 min. Normal workup and Kugelrohr distillation (110 °C, 0.03 mm) gave 0.25 g of **14** (89%, *E*/*Z* = 82/18). **14**-*E*: NMR (200 MHz, $CDCl_3$) δ 0.18 (s, 9 H), 3.48 (d, J = 8 Hz, 2 H), 5.25 (t, J = 8 Hz, 1 H), 7.1–7.6 (m, 10 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ 0.6 (q), 33.8 (t), 108.7 (d), 125.6 (d), 126.8 (d), 127.6 (d), 128.0 (d), 137.1 (s), 141.3 (s), 150.3 (s); IR 3010, 2950, 2920, 1750, 1650, 1495, 1450, 1250, 1080, 1030, 840 cm^{-1}; MS (M^+) calcd for $C_{18}H_{22}OSi$ 282.1434, found 282.1440. Anal. Calcd: C, 76.54; H, 7.85. Found: C, 76.41; H, 7.86.

14-*Z* (prepared by silylation of ketone): NMR (200 MHz, $CDCl_3$) δ 0.18 (s, 9 H), 3.59 (d, J = 7 Hz, 1 H), 5.45 (t, J = 7 Hz, 1 H), 7.1–7.6 (m, 10 H); ^{13}C NMR (50 MHz, $CDCl_3$) δ −0.6 (q), 32.3 (t), 109.7 (d), 125.5 (d), 125.7 (d), 127.5 (d), 127.9 (d), 128.28 (d), 128.31 (d), 138.9 (s), 141.4 (s), 149.8 (s).

A similar experiment, except that the addition of PhLi was done at −110 °C gave an 89% yield of **14** (*E*/*Z* = 93/7).

***erythro*-6-Methyl-3-(trimethylsilyl)-2-(phenylthio)-1-phenyl-4-heptyn-3-ol (41**, Table II, Entry 12). To a solution of 238 mg (3.5 mmol) of 3-methyl-1-butyne in 3 mL of Et_2O at 0 °C was added 3 mmol of MeLi (low halide). The mixture was stirred for 20 min and then cooled to −78 °C, and a solution of 310 mg (1 mmol) of **5a** in 4 mL of Et_2O was added. After 2 h at −78 °C the reaction was quenched with NH_4Cl/H_2O/THF. Normal workup and TLC (20% EtOAc/hexane, R_f = 0.7) gave 122 mg of **41** (32%, erythro/threo > 99/1). Erythro (*RR*/*SS*): NMR (200 MHz, $CDCl_3$) δ 0.39 (s, 9 H), 1.31 (d, J = 7 Hz, 6 H), 2.74 (heptet, J = 7 Hz, 1 H), 2.92 (dd, J = 14, 12.5 Hz, 1 H), 3.25 (dd, J = 14, 2.5 Hz, 1 H), 3.47 (dd, J = 12.5, 2.5 Hz, 1 H), 3.60 (br s, 1 H), 6.9–7.4 (m, 10 H); IR 3450, 3020, 2960, 2200, 1580, 1470, 1440, 1250, 850, 700 cm^{-1}; MS (M^+) calcd for $C_{23}H_{30}OSSi$ 382.1788, found 382.1792.

1-Phenyl-3-(trimethylsiloxy)-6-methylhept-2-en-4-yne (17, Table II, Entry 12). To a solution of 102 mg of 3-methyl-1-butyne (5.0 mmol, 0.51 mL) in 5 mL of Et_2O at 0 °C was added 4.4 mmol of MeLi·LiBr in 2.30 mL of Et_2O. After 20 min the mixture was cooled to −78 °C, and a solution of **5a** (4.0 mmol, 1.26 g) in 10 mL of Et_2O was added by cannula. Stirring at −78 °C for 5 min and at 0 °C for 20 min followed by aqueous workup and Kugelrohr distillation (55 °C/0.06 mm) gave 0.78 g (72%) of **17** as a 67/33 mixture of *E*/*Z* isomers. **17**-*E* isomer: NMR (200 MHz, $CDCl_3$) δ 0.23 (s, 9 H), 1.22 (d, J = 7 Hz, 6 H), 2.70 (heptet, J = 7 Hz, 1 H), 3.48 (d, J = 8 Hz, 2 H), 5.35 (t, J = 8 Hz, 1 H), 7.10–7.40 (m, 5 H); ^{13}C NMR (50 MHz, $(CD_3)_2CO$) δ −0.1 (q), 20.8 (d), 22.3 (q), 34.0 (t), 75.6 (dd, J = 9.3, 3.5 Hz), 98.8 (heptet, J = 5 Hz), 116.8 (d), 126.0 (d), 128.2 (d), 128.3 (d), 133.8 (s), 140.9 (s); IR 3020, 2940, 2210, 1635, 1490, 1450, 1250, 1000, 850 cm^{-1}; MS (M^+) calcd for $C_{17}H_{24}OSi$ 272.1597, found 272.1596.

17-*Z*: NMR (partial) (200 MHz, $CDCl_3$) δ 0.27 (s, 9 H), 1.17 (d, J = 7 Hz, 6 H), 2.70 (heptet, J = 7 Hz, 1 H), 3.42 (d, J = 8 Hz, 2 H), 5.15 (t, J = 8 Hz, 1 H), 7.10–7.40 (m, 5 H); ^{13}C NMR (50 MHz, $(CD_3)_2CO$) δ 0.1 (q), 20.6 (d), 22.2 (q), 31.3 (t), 77.7 (dd, J = 4, 3 Hz), 93.7 (heptet, J = 5 Hz), 116.3 (d), 125.8 (d), 128.2 (d), 128.3 (d), 132.6 (s), 140.8 (s).

(*Z*)-3-Phenyl-1-(trimethylstannyl)-1-(trimethylsiloxy)-1-propene (19, Table II, Entry 16). To a solution of 0.157 g (0.5 mmol) of **5a** in 1 mL of THF at −78 °C was added Me_3SnLi[41] (0.55 mmol) in 1.4 mL of THF. After 5 min the solution was warmed to 0 °C and stirred 1 h. Normal workup and Kugelrohr distillation (75 °C/0.02 mm) gave **19** (81%, *Z*/*E* > 99.5/0.5). **19**-*Z*: NMR (200 MHz, $CDCl_3$) δ 0.25 (s, 9 H), 0.32 (s, 9 H, J_{Sn-H} = 54 Hz), 3.40 (d, J = 8 Hz, 2 H, J_{Sn-H} = 10 Hz), 5.79 (t, J = 8 Hz, 1 H, J_{Sn-H} = 97 Hz), 7.2–7.5 (m, 5 H); IR 3010, 2960, 2900, 1610, 1500, 1120, 850, 750 cm^{-1}; MS (M^+) calcd for $C_{15}H_{26}OSiSn$ 368.0774, found 368.0774.

19-*E* (prepared as mixture with **19**-*Z* by isomerization of **19**-*Z* with acid): NMR (partial) δ 3.52 (d, J = 8 Hz, PhCH_2), 5.05 (t, J = 8 Hz, C=C*H*, J_{Sn-H} = 30 Hz).

Dimethyl (*E*)-[3-Phenyl-1-(*tert*-butyldimethylsiloxy)-1-propenyl]-phosphonate (20, Table II, Entry 17). To a solution of 0.058 g (0.53 mmol) of dimethyl phosphite in 1 mL of Et_2O at −78 °C was added 0.55 mmol of LDA in 0.55 mL of THF. After 5 min, 0.178 g (0.5 mmol) of **5c** in 2 mL of Et_2O was added, and the solution was stirred for 5 min at −78 °C and 5 min at −50 °C. Normal workup and Kugelrohr distillation (100 °C, 0.01 mm) gave 0.149 g of **20** (84% yield, *Z*/*E* = 97/3). **20**-*Z*: NMR (200 MHz, $CDCl_3$) δ 0.17 (s, 6 H), 0.92 (s, 9 H), 3.78 (d, J = 12 Hz, 6 H), 3.90 (dd, J = 8, 2.5 Hz, 2 H), 5.90 (dt, J = 40, 8 Hz, 1 H), 7.1–7.4 (m, 5 H); IR 3020, 2950, 2850, 1620, 1470, 1250, 1050, 850 cm^{-1}; MS (M^+) calcd for $C_{17}H_{29}O_4PSi$ 356.1573, found 356.1567. Anal. Calcd: C, 57.28; H, 8.20. Found: C, 57.63; H, 8.28.

20-*E*: NMR (partial, 200 MHz, $CDCl_3$): δ 6.02 (dt, J = 10, 8 Hz, C=C*H*).

2-(*tert*-Butyldimethylsiloxy)-4-phenyl-2-butenenitrile (21, Table II, Entry 18). To a solution of 0.182 g (0.68 mmol) of Bu_4NCN in 2 mL of $CDCl_3$ at −65 °C was added a solution of 0.178 g (0.5 mmol) of **5c** (0.178 g, 0.173 mL) in 1 mL of $CDCl_3$. After 5 min at −65 °C and 5 min at 0 °C, 0.142 g (1 mmol) of MeI was added, and the solution was warmed to 25 °C for 5 min. The solvent was evaporated, and the residue was extracted with pentane. Kugelrohr distillation (80 °C/0.01 mm) of the filtrate gave 0.127 g of **21** (93% yield, *E*/*Z* = 67/33). **21**-*E*: NMR (200 MHz, $CDCl_3$): δ 0.25 (s, 6 H), 0.95 (s, 9 H), 3.69 (d, J = 8.5 Hz, 2 H), 5.97 (t, J = 8.5 Hz, 1 H), 7.1–7.4 (m, 5 H); IR 3020, 2950, 2920, 2850, 2210, 1700, 1660, 1470, 1250, 840, 780 cm^{-1}; MS (M^+) calcd for $C_{16}H_{23}NOSi$ 273.1550, found 273.1543. Anal. Calcd: C, 70.28; H, 8.48. Found: C, 70.01; H, 8.59.

21-*Z*: NMR (partial, 200 MHz, $CDCl_3$): δ 0.32 (s, $SiMe_2$), 1.01 (s, CMe_3), 3.73 (d, J = 7.5 Hz, PhCH_2), 5.86 (t, J = 7.5 Hz, C=C*H*), 7.1–7.4 (m, Ar*H*).

(Phenylseleno)methyl Phenyl Sulfide (45).[34b] To a solution of 15.6 g (50 mmol) of PhSeSePh in 250 mL of dry EtOH in a flask equipped with a reflux condenser was added 4.71 g (124 mmol) of $NaBH_4$ over 15 min. $PhSCH_2Cl$ (100 mmol, 15.9 g, 13.5 mL) was added, and the solution was stirred for 1.5 h. $ClCH_2CO_2H$ (10 mmol, 1.0 g) was added and stirring was continued for 30 min. Normal workup and Kugelrohr distillation (100 °C/0.05 mm) gave 25.4 g (91% yield) of **45**: NMR (100 MHz, CCl_4) δ 4.10 (s, 2 H, J_{Se-H} = 14 Hz), 7.0–7.5 (m, 5 H); IR 3050, 1570, 1470, 1430, 1020, 730, 690 cm^{-1}; MS (M^+) calcd for $C_{13}H_{12}SSe$ 279.9822, found 279.9825.

1-(Phenylseleno)-1-(phenylthio)-2-phenylethane (46). To a solution of 2.79 g (10 mmol) of **46** in 20 mL of THF at −78 °C was added 10.25 mmol of LDA in 8 mL of THF. After 45 min a solution of 2.29 g (10.5 mmol) of $PhCH_2I$ in 5 mL of THF was added. The mixture was then warmed to 25 °C for 5 min, and 2 mL of NH_4OH was added to react with any remaining $PhCH_2I$. The product was diluted with ether/hexane, washed with $Na_2S_2O_3$, HCl, NaOH, H_2O, and NaCl, and dried, and the solvent was evaporated to give 3.37 g (91%) of **46** (contaminated with 6% of **45**): NMR (100 MHz, CCl_4) 3.15 (d, J = 7 Hz, 2 H), 4.45 (t,

(47) Nakamura, E.; Murofushi, T.; Shimizu, M.; Kuwajima, I. *J. Am. Chem. Soc.* **1976**, *98*, 2346.

J = 7 Hz, 1 H), 7.0–7.5 (m, 15 H); IR 3040, 3010, 1580, 1475, 1445, 1025, 740, 690 cm^{-1}; MS (M^+) calcd for $C_{20}H_{18}SSe$ 370.0290, found 370.0293.

***threo*-1-Phenyl-2-(phenylthio)-3-(trimethylsilyl)-3-butanol (12a, Path b).** To a solution of 0.55 mmol of *n*-BuLi in 4 mL of THF at −78 °C was added a solution of 0.184 g (0.5 mmol) of **46** over 4 min. After 10 min, 0.60 mmol of trimethylacetylsilane (0.70 g, 0.85 mL) was added slowly, and the solution was stirred for 20 min at −78 °C. If NH_4Cl was added at this point, normal workup and TLC purification (25% EtOAc/hexane, R_f = 0.53) gave **12a**-*E* (20%) and the hydroxy silane **32** (28% yield). NMR (200 MHz, $CDCl_3$) δ 0.24 (s, 9 H), 1.43 (s, 3 H, 2.08 (broad s, 1 H), 2.83 (dd, J = 14, 12 Hz, 1 H), 3.35 (dd, J = 14, 3 Hz, 1 H), 3.40 (dd, J = 12, 3 Hz, 1 H), 6.9–7.4 (m, 10 H); ^{13}C NMR (50 MHz, $CDCl_3$, decoupled INEPT, no quaternary carbons) δ −2.0 (q), 23.8 (q, J = 125 Hz, $^3J_{C-H}$ < 3 Hz), 39.1 (t), 66.1 (d), 126.1 (d), 126.2 (d), 128.1 (d), 128.4 (d), 129.5 (d), 130.8 (d); MS (M^+) calcd for $C_{19}H_{26}OSSi$ 330.1467, found 330.1472.

If 6 mL of THF was added and the reaction mixture was warmed to 25 °C for 45 min, then normal workup gave a 52% yield of **12a** (*E*/*Z* = 62/38).

Reaction of α-Lithio Sulfones with Acylsilanes. Illustrative Procedure. 1,1-Cyclopropylidene-3-phenyl-1-(trimethylsiloxy)propane (47). In a 25-mL round-bottom flask 182 mg (1 mmol) of cyclopropyl phenyl sulfone was dissolved in 3 mL of THF/ether (1:1) and cooled to −78 °C. To the colorless mixture 0.603 mL of *n*-BuLi (1.05 mmol, 1.75 N in hexane) was slowly added. After 5 min 206 mg (1 mmol) of trimethyl(3-phenylpropanoyl)silane (**3a**) dissolved in 2 mL of THF/ether (1:1) (precooled) was transferred to the reaction flask via cannula. Stirring for 5 min at −78 °C and for additional 10 min at 0 °C produced a white precipitate. The mixture was poured into 7 mL of saturated aqueous NH_4Cl, and 10 mL of ether/pentane (1:1) was added. The organic layer was extracted with H_2O and dried over Na_2SO_4. Evaporation of solvent gave 230 mg of crude product (containing 11% sulfone). This could be purified by fast chromatography (N_2 pressure) through 4.5 g of nonactivated Al_2O_3 (additional 6% H_2O was added) using pentane as eluent. **47** (185 mg, 75%) was obtained: ^1H NMR (200 MHz, $CDCl_3$) δ 0.18 (s, 9 H), 1.00 (t, J = 5.5 Hz, 2 H), 1.10 (t, J = 5.9 Hz, 2 H), 2.49 (t, J = 7.9 Hz, 2 H), 2.82 (t, J = 7.9 Hz, 2 H), 7.08–7.32 (m, 5 H); ^{13}C NMR (decoupled) δ 0.8, 3.1, 5.6, 33.2, 37.9, 94.3, 125.3, 127.7, 128.0, 141.4, 141.7; IR (neat) 2960, 1780, 1615, 1260, 860, 705 cm^{-1}; MS (M^+) calcd for $C_{15}H_{22}SiO$ 246.1439, found 246.1439. Anal. Calcd: C, 73.1; H, 9.02. Found C, 72.96; H, 9.09.

6-Phenyl-4-(trimethylsiloxy)-1,3-hexadiene (24a). Allyl phenyl sulfone was used to produce **24a** in a 92% yield, E:Z = 88:12 (by GC). *E* isomer: ^1H NMR (270 MHz) δ 0.23 (s, 9 H), 2.49 (m, 2 H), 2.78 (m, 2 H), 4.75 (dd, J = 10.7 Hz, 2 Hz, 1 H), 4.92 (dd, J = 17 Hz, 2 Hz, 1 H), 5.38 (d, J = 10.7 Hz, 1 H), 6.35 (dt, J = 10.7 Hz, 17 Hz, 1 H), 7.10–7.36 (m, 5 H); ^{13}C NMR (decoupled): δ 0.7, 33.6, 34.0, 110.1, 111.5, 125.7, 128.2, 132.3, 141.4, 154.6 (one peak not observed). *Z* isomer: ^1H NMR (partial) δ 2.28–2.41 (m, 2 H), 6.55 (dt, J = 17.2, 10.4, ^1H); ^{13}C NMR (partial) δ 1.0, 33.1, 39.0, 110.6, 112.0, 131.3; IR 2930, 1638, 1580, 1485, 1242, 1210, 975, 688 cm^{-1}; MS (M^+) calcd for $C_{15}H_{22}SiO$ 246.1439, found 246.1439. Anal. Calcd: 73.10; H, 9.02. Found: C, 72.91; H, 9.09.

(*Z*)-1-Phenyl-3-(phenyldimethylsiloxy)-2-butene (12b, Path c). To a solution of 0.128 g (0.5 mmol) of **52** in 5 mL of Et_2O at −78 °C was added 0.55 mmol of $PhMe_2SiLi$ in 1 mL of THF. Stirring was continued for 5 min at −78 °C and 30 min at 0 °C. Normal workup and Kugelrohr distillation (80 °C/0.01 mm) gave 0.108 g (77% yield, *Z*/*E* > 99/1) of **12b**. *Z* isomer: NMR (200 MHz, $CDCl_3$) δ 0.5 (s, 6 H), 1.80 (d, J = 1 Hz, 3 H), 3.40 (d, J = 7 Hz, 2 H), 4.68 (td, J = 7, 1 Hz, 1 H), 7.1–7.6 (m, 10 H); IR 3060, 3020, 2950, 1680, 1425, 1250, 1100, 825, 690 cm^{-1}; MS (M^+) calcd for $C_{18}H_{22}OSi$ 282.1434, found 282.1440.

***erythro*-1-Phenyl-2-methoxy-3-(phenyldimethylsilyl)-3-butanol Using (Phenyldimethylsilyl)magnesium Bromide (54).** To a solution of 0.7 mmol of $MgBr_2$ in 3 mL of THF at 0 °C was added 0.6 mmol of $PhMe_2SiLi$ in 1 mL of THF. To this was added 0.071 g (0.4 mmol) of **53** and the solution was stirred for 30 min at 0 °C. NH_4Cl (aqueous) was added, and the product was extracted three times with Et_2O/hexane and dried, and the solvent was evaporated. TLC (15% EtOAc/hexane, R_f = 0.5) gave 0.075 g of **54** (60% yield, erythro/threo > 98/2).

54-*erythro*: NMR (270 MHz, $CDCl_3$) δ 0.45 (d, J = 3 Hz, 6 H), 1.22 (s, 3 H), 2.12 (broad s, 1 H), 2.55 (dd, J = 14, 9 Hz, 1 H), 2.78 (dd, J = 14, 2.5 Hz, 1 H), 2.95 (s, 3 H), 3.37 (dd, J = 9, 2.5 Hz, 1 H), 7.0–7.7 (m, 10 H); IR 3490, 2950, 1430, 1250, 1100, 700 cm^{-1}; MS (fragment, M^+ − MeOH, no M^+) calcd for $C_{18}H_{22}OSi$ 282.1434, found 282.1443.

54-*threo*: NMR (partial) δ 0.42 (d, J = 3 Hz, Si*Me*$_2$), 1.27 (s, C*Me*), 2.63 (dd, J = 14, 9 Hz, PhC*H*), 2.83 (dd, J = 14, 3 Hz, PhC*H*), 2.97 (s, O*Me*), 3.33 (dd, J = 9, 3 Hz, MeOC*H*), 7.0–7.7 (m, Ar*H*).

1-Phenyl-2-methoxy-3-(phenyldimethylsilyl)-3-butanol Using (Phenyldimethylsilyl)lithium (54). To a solution of 0.041 g (0.23 mmol) of **50** in 2 mL of Et_2O at −78 °C was added 0.26 mmol of $PhMe_2SiLi$ in 0.5 mL of THF. After 5 min at −78 °C the reaction was quenched with NH_4Cl. Normal workup and TLC (15% EtOAc/hexane, R_f = 0.55) gave 0.039 g (54% yield) erythro/threo = 55/45) of **54**.

(*E*)-1-Phenyl-3-(phenyldimethylsiloxy)-2-butene (12b). To a solution of 0.157 g (0.5 mmol) of **54**-*erythro* in 4 mL of THF was added 1.0 mmol of $(Me_3Si)_2NNa$ in 1.7 mL of THF at −78 °C. After 5 min, 0.17 g (1.0 mmol) of $PhMe_2SiCl$ was added, and the solution was warmed to 0 °C for 10 min. Normal workup and Kugelrohr distillation (80 °C/0.005 mm) gave 0.082 g of **12b** (58% yield, *E*/*Z* = 98/2).

Phenyldimethyl(3-chloropropanoyl)silane (55). To a solution of 2.13 g (8.1 mmol) of 1-(1-ethoxyethoxy)-1-(dimethylphenylsilyl)-1,2-propadiene[1c] in 15 mL of THF at −78 °C was added 0.839 mL (1.3 equiv, 10.6 mmol) of concentrated HCl. The solution was stirred for 2 min at −78 °C and was warmed to room temperature over 20 min, and THF, water, and excess HCl were removed under vacuum (0.3 mm). The product was used without further purification. Attempted purification by chromatography or distillation led to various ratios of the product to the enone. Crude yield 1.81 g (98.6%): ^1H NMR (200 MHz, $CDCl_3$) 0.50 (s, 6 H), 3.0 (t, J = 6.5 Hz, 2 H), 3.6 (t, J = 6.5 Hz, 2 H), 7.3–7.6 (m, 5 H); ^{13}C NMR (50 MHz, $CDCl_3$) −5.0, 37, 50, 123, 125, 128, 242; IR 3030, 2950, 2900, 1650, 1430, 1250, 1115, 840, 820, 790, 740, 700 cm^{-1}.

1-(Dimethylphenylsiloxy)-1-ethenylcyclopropane (57). To a solution of 0.260 mL (3.6 mmol) of vinyl bromide in 10 mL of diethyl ether at −78 °C was slowly added 3.75 mL (5.68 mmol) of *tert*-butyllithium. The mixture was stirred for 15 min, and a solution of 0.635 g of the crude phenyldimethyl(3-chloropropanoyl)silane (**55**, 2.84 mmol) in 5 mL of diethyl ether was added via cannula to the vinyllithium solution. After 5 min at −78 °C, the solution was warmed to room temperature and poured into 20 mL of H_2O and extracted three times with 15-mL portions of 1:1 ether/pentane. The organic extracts were washed once with 10 mL of water and 10 mL of brine, dried over Na_2SO_4, and concentrated. Kugelrohr distillation at 80 °C at 0.3 mmHg (bath temperature) gave 0.552 g of **57** (2.53 mmol, 89% from 1-(1-ethoxyethoxy)-1-(dimethylphenylsilyl)-1,2-propadiene): ^1H NMR (200 MHz, $CDCl_3$) 0.40 (s, 6 H), 0.64–1.04 (m, 4 H), 5.00 (dd, J = 10.4, 2.0, 1 H), 5.2 (dd, J = 17.0, 2.0, 1 H), 5.6 (dd, J = 17.0, 10.5, 1 H), 7.30–7.60 (m, 5 H); ^{13}C NMR (50 MHz, $CDCl_3$) 0, 16, 111, 128, 130, 133, 143; IR (neat) 3075, 3015, 2960, 1650, 1460, 1440, 1420, 1320, 1305, 1260, 1230, 1125, 1050, 1020, 940, 920, 890, 860, 840, 800, 740, 710 cm^{-1}. MS calcd for $C_{13}H_{18}OSi$ 218.1122; found 218.1122.

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Supplementary Material Available: Summary of crystallographic data for compound **31** and experimental details for **4b**, **5b**, **6b**, **7a**, **17**, **18**, **52**, **22a**, **23a**, **25a**, **26a**, **28a**, **29a**, **30a**, **53**, **56** and for entries 1, 3, 6, 7, 10, 11, 13, 15 in Table II (16 pages). Ordering information is given on any current masthead page.