pyranyloxy)dodecanoic acid, 1.381 g (3.15 mmol) of GPC·$CdCl_2$, 0.854 g (7.0 mmol) of 4-(dimethylamino)pyridine, and 1.648 g (8.0 mmol) of dicyclohexylcarbodiimide was suspended in 15 mL of dry dichloromethane and stirred under nitrogen in the dark for 40 h. After removal of solvent in vacuo, the residue was dissolved in 50 mL of $CH_3OH/H_2O$ (95/5, v/v) and stirred in the presence of 8.0 g of AG MP-50 (23 °C, 2 h) to allow for complete deprotection of the hydroxyl groups (monitored by thin-layer chromatography).[11] The resin was then removed by filtration and the solution concentrated under reduced pressure. The crude product (2.75 g), obtained after drying [12 h, 23 °C (0.05 mm)], was then subjected to chromatographic purification by using a 30-g (4 × 4 cm) silica gel column, eluting with solvents A and C, to yield 0.990 g (48%) of **2**: $R_f$ 0.25 (solvent C); IR (KBr) $\nu_{OH}$ 3390, $\nu_{C=O}$ 1728, $\nu_{N(CH_3)_3}$ 967, 1055, 1090 $cm^{-1}$; $^1H$ NMR ($CD_3OD$) $\delta$ 1.30–1.65 (br s, 36 H, $CH_2$), 2.32 (t, 4 H, $CH_2C{=}O$), 3.22 (s, 9 H, $N(CH_3)_3$), 3.52 (t, 4 H, $CH_2O$), 3.60–4.55 (m, 8 H, $CH_2O$, $N(CH_2)$), 4.85 (s, 2 H, OH), 5.2 (m, 1 H, CH).

**Lipoic Acid Anhydride.**[12] A mixture of lipoic acid (1.03 g, 5.0 mmol) and dicyclohexylcarbodiimide (0.65 g, 3.0 mmol) was stirred in 15 mL of dry methylene chloride for 20 h at room temperature under a nitrogen atmosphere. The product mixture was filtered in order to remove the urea which had formed. Examination of the filtrate by IR revealed the presence of lipoic acid anhydride (1735 and 1805 $cm^{-1}$) and the absence of the parent carboxylic acid ($\nu_{C=O}$ 1701 $cm^{-1}$). This solution was used directly in the synthesis of **1** described below.

**1,2-Bis[12-(lipoyloxy)dodecanoyl]-*sn*-glycero-3-phosphocholine (1).** 1,2-Bis(12-hydroxydodecanoyl)-*sn*-glycero-3-phosphocholine (0.04 g, 0.06 mmol) was added to 2.0 mL of a 0.15 M solution of lipoic acid containing 16 mg (0.13 mmol) of 4-(dimethylamino)pyridine. After the mixture was stirred for 6 h under nitrogen at room temperature, thin-layer chromatography (silica, solvent C) indicated complete conversion to **1**. The product mixture was then filtered and concentrated under reduced pressure. The residue was dissolved in 5 mL of solvent B and passed through a 1.2 × 1.5 cm AG MP-50 cation-exchange column in order to remove 4-(dimethylamino)pyridine. The filtrate was concentrated under reduced pressure, dissolved in a minimum volume of absolute ethanol, and then concentrated again. Chromatographic purification of the residue on a silica gel column (0.9 × 6 cm), eluting first with solvent A and then with solvent C (compound **1** elutes on silica as a single yellow band), afforded, after drying [10 h, 22 °C (0.05 mm)], 0.055 g (90%) of **1** as a yellow solid: $R_f$ 0.45 (solvent C); IR (KBr) $\nu_{C=O}$ 1732, $\nu_{N(CH_3)_3}$ 970, 1050, 1090 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 1.25 (s 28 H, $CH_2$), 1.40–2.05 (m, 20 H, lipoic-$CH_2$, $CH_2CH_2O$, $CH_2CH_2CO_2$), 2.3 (t, 8 H, $CH_2C{=}O$), 2.20–2.65 (m, 4 H, $CH_2$–lipoic ring), 3.15 (t, 4 H, $CH_2SS$), 3.40 (s, 9 H, $N(CH_3)_3$), 3.55 (m, 2 H, CHSS), 4.08 (t, 4 H, $CH_2OC{=}O$), 3.80–4.6 (m, 8 H, $CH_2O$, $NCH_2$), 5.20 (m, 1 H, $CH(CH_2O)$). Anal. Calcd for $C_{48}H_{88}O_{12}NPS_4$: C, 55.95; H, 8.61; N, 1.36; P, 3.01; S, 12.44. Found: C, 53.85; H, 8.58; N, 1.19; P, 3.01; S, 11.99.

Upon drying, a small and unavoidable percentage (less than 10%) of lipid **1** becomes polymerized on the walls of the glass flask. For storage purposes, the lipid should be dissolved in dichloromethane (0.017 M), filtered (0.2-$\mu$m FG Millipore filter), and kept at 0 °C in the dark.

**Polymerized Vesicle Formation.** Typically, 1 mL of a 0.017 M dichloromethane solution of **1** was concentrated under a stream of nitrogen and dried under vacuum [0.5 h, 23 °C (0.05 mm)]. The lipid was then dissolved in 0.85 mL of absolute ethanol. An aliquot of this solution (90 $\mu$L, 1.8 $\mu$mol) was then rapidly injected into 0.75 mL of a 10 mM borate buffer (140 mM NaCl, 2 mM $NaN_3$, pH 8.5) by using a 100-$\mu$L Hamilton syringe (22 S gauge). The dispersion was incubated at 30 °C for 30 min under a nitrogen atmosphere, with brief vortex mixing. Polymerization was carried out by injecting an aqueous solution of DTT (17 $\mu$L of a 0.01 M solution) directly into the dispersion. To ensure complete polymerization, samples were normally allowed to stand at room temperature for 16 h.

**Acknowledgment.** We are grateful to Dr. Kazuo Yamaguchi (Tokyo Institute of Technology) for valuable discussions.

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# Silyl Ketone Chemistry.[1] Preparation and Reactions of Silyl Allenol Ethers. Diels–Alder Reactions of Siloxy Vinylallenes Leading to Sesquiterpenes[2]

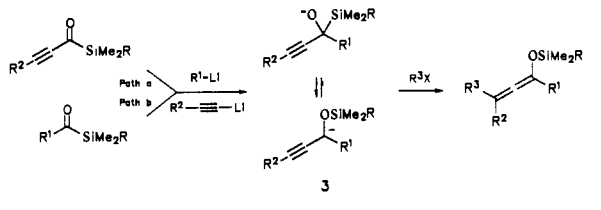
**Hans J. Reich,* Eric K. Eisenhart, Richard E. Olson, and Martha J. Kelly**

*Contribution from the S. M. McElvain Laboratories of Organic Chemistry, Department of Chemistry, University of Wisconsin, Madison, Wisconsin 53706.* *Received April 28, 1986*

**Abstract:** Allenol silyl ethers **1** with various substitution patterns were prepared. The allene functionality was introduced either by the alkylation of siloxypropargyllithium reagents **3** (Scheme I) or the $\beta$-elimination of 2-halo-1-siloxyallyllithium reagents **4** (Scheme II). In each case the lithium reagent was formed by a [1,2]-sigmatropic rearrangement of a suitable $\alpha$-silyl alkoxide, which in turn was prepared by addition of alkynyl, vinyl, or other lithium reagents to silyl ketones. The allenol silyl ether **22a** could be halogenated, selenenylated, and cleaved to the lithium allenolate **24**. This vinylic enolate reacts with aldehydes to give aldol products. Vinylallenol ethers **27b** and **28b** were easily prepared by the above methods. Intramolecular Diels–Alder reactions of **27b** and **28b** were key steps in the synthesis of dehydrofukinone (**31**) and selina-4(14),7(11)-dien-8-one (**32**).

Enol silyl ethers are widely used as enol and enolate equivalents both for the purpose of performing chemical reactions and for the masking of carbonyl groups.[3] This is because enol silyl ethers participate in many useful reactions and are in general more easily

**Scheme I**

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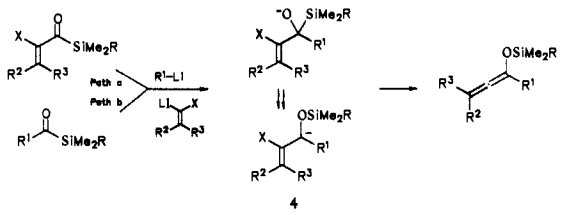
**Scheme II**



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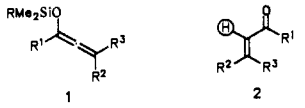
prepared than other enolate equivalents such as alkyl enol ethers or enol acetates. Allenol silyl ethers **1** are a class of silyl ethers



1 2

with largely unexplored synthetic potential.[4] They are not available by the usual procedures such as enolization–silylation of carbonyl compounds, since only in exceptional situations is it possible to cause enolization of the $\alpha$-vinyl proton of $\alpha,\beta$-unsaturated ketones **2**.[5] More general approaches to allenolates include the metal–halogen or metal–tin exchange reaction of $\alpha$-X-$\alpha,\beta$-unsaturated carbonyl compounds[6] and the conjugate addition of organocopper reagents to acetylenic carbonyl compounds,[4a,7]

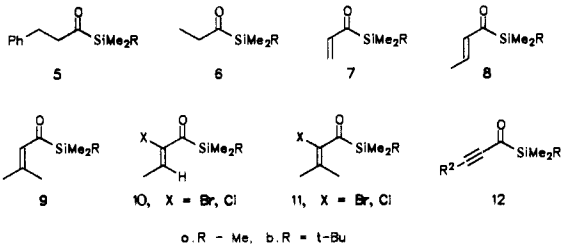
The work of Ahrens and Brandsma as well as others[8] on the deprotonation of propargyl and allenyl ethers has provided a number of alkoxy allenyl/propargyllithium reagents which are seeing increasing use in synthesis,[1d,9] However, the same procedures are not, in general, useful for the preparation of silyl allenol ethers.

In the course of our studies of the synthetic applications of silyl ketones we discovered that a variety of allenol silyl ethers can be prepared as outlined in Schemes I and II by taking advantage of the Brook rearrangement[10] of silyl substituted alkynyl alkoxides **3**. The resulting propargyl/allenyl anions[1b] can react with electrophiles to give allenes (Scheme I),[4b,11] Alternatively, if an $\alpha$-halovinyl $\alpha$-silyl alkoxide **4** is prepared, its Brook rearrangement will also produce an allene, in this case by an elimination[4c,12] rather than an alkylation process (Scheme II).[13] Variations of the process in Scheme II in which the leaving group is not $\alpha$ but rather $\gamma$ have also been examined but not in much detail.[4b,14]

The discussion which follows is divided into five parts: (1) preparation of silyl ketones and other starting materials; (2) preparation of allenol ethers according to Scheme I and (3) Scheme II; (4) reactions of allenol silyl ethers with electrophiles; (5) application of the method of Scheme II in the synthesis of eremophilane and eudesmane sesquiterpenes using vinyl siloxyallenes as Diels–Alder dienes.

## Results and Discussion

**Preparation of Silyl Ketones.** The starting materials needed for this work were prepared as follows, The alkyl silyl ketones **5** and **6** were available by using the dithiane method, employing a chloramine-T/methanol[17] rather than the usual mercury salt hydrolysis.[15,16] The silyl enones **7–11** and the silyl ynone **12** were

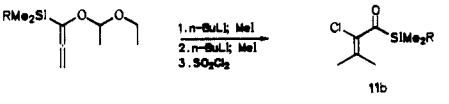


5 6 7 8

9 10, X = Br, Cl 11, X = Br, Cl 12

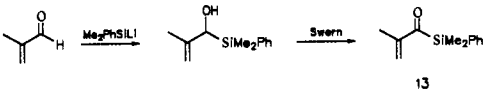
a, R = Me, b, R = t-Bu

prepared by using our procedures based on alkoxyallene chemistry,[1d] first applied to the synthesis of silyl enones by Leroux and Mantione.[8b] The enone **13** was not available in this way but was



11b

prepared as shown. Throughout this paper the **a** series of compounds will refer to trimethylsilyl (R = $CH_3$), the **b** series to *tert*-butyldimethylsilyl (R = *tert*-$C_4H_9$).



13

**Preparation of Siloxyallenes by Alkylation of Siloxyallenyllithium Reagents (Scheme I).** A number of siloxyallenes (see Table I) were synthesized according to Scheme I in good yields. The reaction worked best with reactive electrophiles such as primary alkyl iodides and dimethyl disulfide. Intramolecular alkylation could also be effected by using this procedure to prepare three- and five-membered rings, When less reactive electrophiles were used, increasing amounts of byproducts were observed. A principal side reaction was the 1,4 O to C silyl shift analogous to that described for siloxyallyllithium reagents by Still[18] and others.[19]

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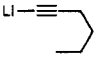
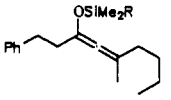
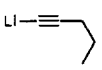
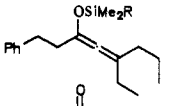
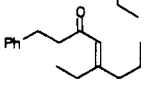
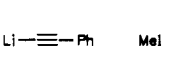
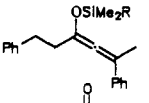
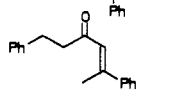
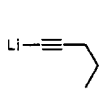
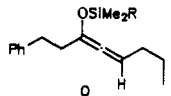
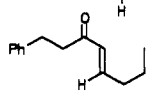
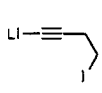
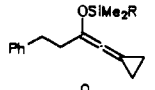
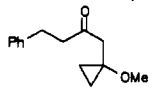
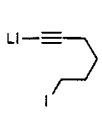
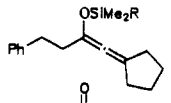
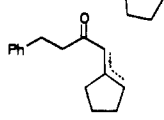
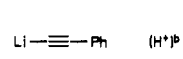
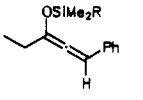
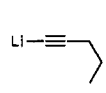
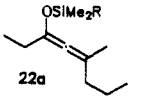
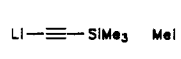
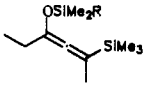
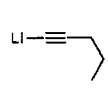
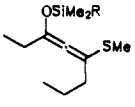
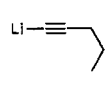
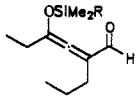
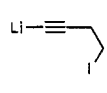
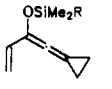
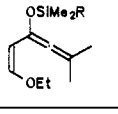
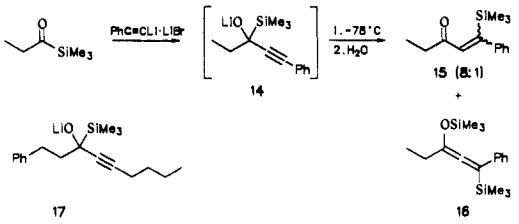
**Table I.** Preparation of Silyl Allenol Ethers Using Scheme I

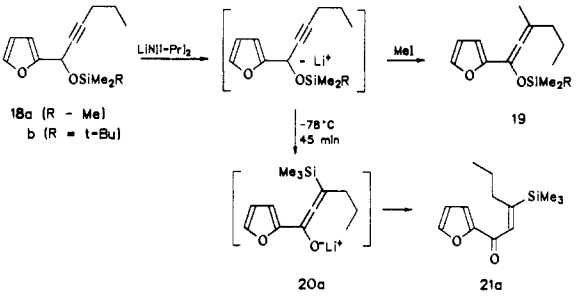
| No. | Silyl Ketone | Lithium Reagent | Electrophile | Product | Yield (%) |
|---|---|---|---|---|---|
| 1 | 5a |  | MeI |  | 83 |
| 2 | 5a |  | EtI |  | a |
| | | | |  | 55 |
| 3 | 5a |  | MeI |  | a |
| | | | |  | 61 |
| 4 | 5a |  | $(H^+)^{b,c}$ |  | 92[b] |
| | | | |  | 63[c] |
| 5 | 5a |  | |  | 92 |
| | | | |  | 61 |
| 6 | 5a |  | |  | a |
| | | | |  | 62 |
| 7 | 6a |  | $(H^+)^b$ |  | 73 |
| 8 | 6a |  | MeI |  22a | 76 |
| 9 | 6a |  | MeI |  | 67 |
| 10 | 6a |  | $Me_2S_2$ |  | 73 |
| 11 | 6a |  | DMF |  | 36 |
| 12 | 7b |  | |  | 38 |
| 13 | 12b |  | MeI |  | 77 |

[a] This product was isolated and characterized spectroscopically but was not purified. It was converted to enone by hydrolysis (HCl/methanol). [b] This allenol ether was formed by using isopropyl alcohol as proton source. [c] The reaction leading to this enone was carried out by using excess 1-pentyne as proton source.

For example, alkoxide **14**, prepared by the addition of lithium



phenylacetylide/lithium bromide to propionylsilane, underwent rearrangement at −78 °C to give, after workup, varying amounts of enone **15**. Interestingly, small amounts of the allenol ether **16** were also isolated.[20] The alkoxide **17**, presumably in equilibrium with a smaller concentration of carbanion compared to **14**, was recovered unchanged after 30 min at 0 °C. As is the case for siloxyallyllithium reagents, steric bulk at silicon slows the 1,4 O to C shift. Metalation of **18a** at −78 °C followed by treatment with methyl iodide for 45 min gave enone **21a**. In contrast, the *tert*-butyldimethylsilyl analogue **18b**, when subjected to similar conditions, gave clean formation of **19b**.



When hard electrophiles such as proton sources or trimethylsilyl chloride were used, derivatizations usually occurred on oxygen to give α-silyl carbinols or their silyl ethers. C-protonation could be achieved by allowing equilibration of the α-silyl alkoxide by using excess acetylene or isopropanol as proton source (Brook rearrangement) prior to workup (Table I, entries 4 and 7).[4b]

The process of Scheme I is a delicate one because of a potential side reaction: the new lithium reagent formed by silyl shift may react with the starting silyl ketone. Although we have not isolated pure products which demonstrably arose from such a sequence, it proved productive in designing reaction conditions to assume that this was a principal side reaction. The optimum conditions for preparation of unconjugated siloxy allenes **1** ($R_1$ to $R_3$ alkyl) involve addition of silyl ketone to a solution of the lithium acetylide in *ether*, followed by addition of the electrophile in THF solution. *The presence of a full equivalent of lithium halide is essential in some cases* and beneficial in all, so the lithium acetylide should be prepared by deprotonation of acetylene with $CH_3Li$–LiBr complex.[21] In the absence of lithium halide, only mixtures of oligomeric products and none of the allenol silyl ether were seen with several systems (e.g., Table I, entry 1). This effect is not clearly understood, but the lithium halide probably exerts an influence on the rate and equilibrium of the C to O silyl rearrangement and thus reaction of silyl ketone with product lithium reagent and may also reduce the extent of enolization suffered by the silyl ketone.[22]

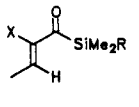
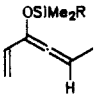
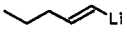
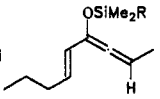
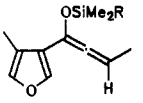
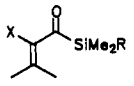
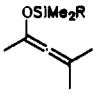
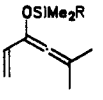
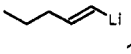
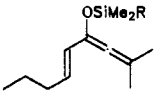
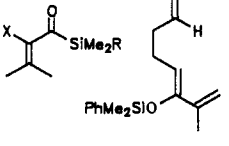
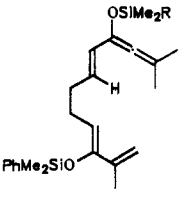
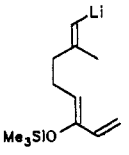
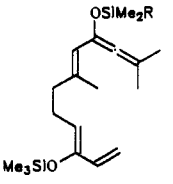
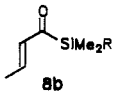
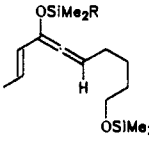
When the intermediate siloxy substituted lithium reagent **3** bears two carbanion stabilizing groups ($R^1$ = vinyl or phenyl), the technique described above (e.g., reaction of lithium acetylide with a silyl enone) could sometimes be executed effectively only if the electrophile (e.g., $CH_3I$) was present during the addition step, i.e., slow addition of silyl ketone to a cold solution containing

(20) The formation of allenol ether **16** indicates that the mechanism of the 1,4 O to C silyl shift may be intermolecular.

(21) The presence of LiBr is also necessary to achieve clean deprotonation of α-silyl propargylic alcohols.[4b]

(22) Van Rijn, P. E.; Mommers, S.; Visser, R. G.; Verkruijsse, H. D.; Brandsma, L. *Synthesis* **1981**, 459.

**Table II.** Preparation of Silyl Allenol Ethers Using Scheme II

| Entry No. | Silyl Enone | Lithium Reagent | Product | Yield (%) |
|---|---|---|---|---|
| 1 |  10b, X = Br |  |  | 72 |
| 2 | 10b, X = Cl |  |  | 82 |
| 3 | 10b, X = Br |  |  | 87 |
| 4 |  11a, X = Br | MeLi |  | 73 |
| 5 | 11b, X = Cl | | | 82 |
| 6 | 11a, X = Br |  |  | 88 |
| 7 | 11b, X = Br | | | 85 |
| 8 | 11b, X = Cl |  |  | 88 |
| 9 |  11b, X = Cl | |  35b | >51[a] |
| 10 |  11b, X = Cl | |  38b | >51[a] |
| 11 |  8b |  |  | 62[b] |

[a] These reactions were part of the total syntheses described below. [b] The reaction of silyl enone with 2-lithiodihydropyran was followed by trimethylsilyl chloride quench.

lithium acetylide and methyl iodide. Better results were achieved from the reaction of a vinyllithium with a silyl ynone (path a, Scheme I) than reaction of alkynyllithium with a silyl enone (path b). Apparently the more reactive vinyllithium is better than alkynyllithium in competing with product anions for the silyl ketone. The difficulties encountered during alkylations of anions

**Table III.** Electrophilic Substitution of Siloxyallenes

22a 23

| electrophile condtns, (°C) | yield (%) |
|---|---|
| $SO_2Cl_2$, Py −78 | 64, X = Cl |
| $Br_2CCl_4$/THF/Py −78 | 63, X = Br |
| NBS, $CH_2Cl_2$/Py 0 | 46, X = Br |
| $I_2$, $CCl_4/CHCl_3$/Py 0 | 74, X = I |
| PhSeCl, $CH_2Cl_2$/Py 0 | 73, X = SePh |

with extended conjugation probably resulted from a relatively high equilibrium ratio of carbanion to oxyanion.[23] For such systems the methods of Scheme II are preferred.

**Preparation of Siloxyallenes by Fragmentation of β-X Siloxy Carbanions (Scheme II).** Table II lists a series of siloxyallenes which have been prepared by the addition of lithium reagents to α-halovinyl silyl ketones. The process appears to be more general than the one outlined in Scheme I and less sensitive to solvent and other experimental parameters.

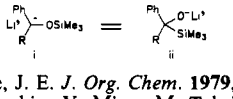
Thus alkyl, vinyl, and aryllithiums worked effectively in the α-halo silyl enone version of the reaction, and few problems occurred by using even fairly complex vinyllithium reagents. These allenol silyl ethers did not survive normal chromatography on silica gel, although some purification could be achieved by quick passage through silica gel deactivated with bis(trimethylsilyl)acetamide. For the lower molecular weight examples distillation could be carried out if the sample was carefully dried. It is therefore a valuable feature of these reactions that the crude products after mild aqueous workup were usually pure enough for further use. The usefulness of the process is enhanced by the ease with which the precursor α-halo silyl enones can be prepared from propargyl alcohols,[1c,d]

The only clearcut failures we encountered were for α-halo silyl enones having no β-substitutents (e.g., 2-chloro-1-(*tert*-butyldimethylsilyl)-2-propen-1-one) for which conjugate addition became a major side reaction with several vinyllithium reagents.

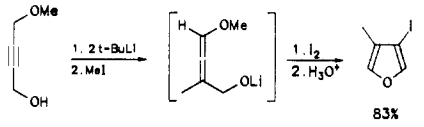
Efforts to prepare siloxyallenes by several variations of path b and Scheme II, in which the leaving group is placed on the lithium reagent, have been much less successful. This is in part due to the poor availability of suitable α-substituted vinyllithium reagents (e.g., α-halo vinyllithiums). Several attempts with α-sulfonyl-,[24] α-sulfinyl-,[25] α-(phenylthio)-,[26,1f] and α-(phenylseleno)-[1f] vinyllithium reagents did not lead to clean reactions, although fair yields of the expected enol silyl ether were formed in the reaction of 1-lithio-1-(phenylsulfonyl)-2-methylpropene[24] with **9a**.[1g] Another reasonably successful example was provided by the reaction of α-lithiodihydropyran with **8b** (Table II, entry 11).

The 2-lithiodihydropyran needed for Table II, entry 11 was prepared by Li/Sn exchange[1h] of 2-(trimethylstannyl)dihydropyran. Successful reaction could not be achieved by using directly the lithium reagent prepared by metalation of dihydropyran probably because of the deleterious effect of THF on the silyl ketone reaction.[27] The iodide used as precursor for the 3-lithio-4-methylfuran used in Table II, entry 3 was prepared as shown below, by using a modification of a furan synthesis reported by Schlosser.[1j,28]

(23) It is known that the equilibrium i ⇄ ii lies to the right for R = H and to the left for R = Ph.[11]



(24) Eisch, J. J.; Galle, J. E. *J. Org. Chem.* **1979**, *44*, 3277, 3279.
(25) Okamura, H.; Mitsuhira, Y.; Miura, M.; Takei, H. *Chem. Lett.* **1978**, 517. Posner, G. H.; Tang, P.-W.; Mallamo, J. P. *Tetrahedron Lett.* **1978**, 3995.
(26) Harirchian, B.; Magnus, P. *J. Chem. Soc., Chem. Commun.* **1977**, 522.
(27) Boeckman, R. K., Jr.; Bruza, K. J. *Tetrahedron* **1981**, *37*, 3997.

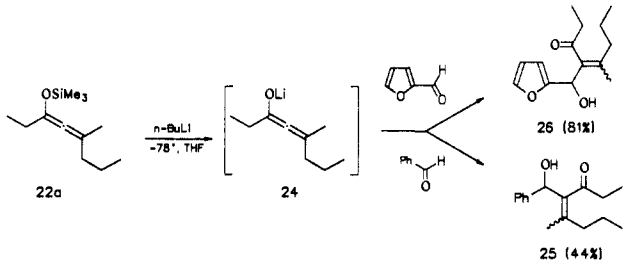



**Reactions of Siloxyallenes with Electrophiles.** Silyl allenol ethers behave in the expected fashion toward electrophilic halogenating or selenenylating agents, giving $\alpha$-halo or $\alpha$-seleno enones **23** (Table III), usually as a mixture of cis/trans isomers. Our attempts to carry out $TiCl_4/Ti(OiPr)_4$ catalyzed aldol condensations by using **22** and benzaldehyde were not successful, There have been a small number of reactions of this type reported involving alkoxyalkylation[4b] or phenylthioalkylation[4a] of allenol silyl ethers.

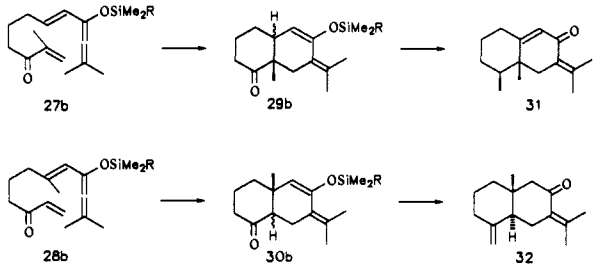
Somewhat more successful were attempts to convert allenol silyl ethers to lithium allenolates, in analogy with the much used cleavage of enol silyl ethers to lithium enolates.[29] The preparation of *lithium* allenolates (which are chemically distinct from copper allenolates in that copper appears to be bonded to carbon whereas the lithium enolate has allenolate character[30]) derived from enones has been much less frequently reported[4a,4f,5a] than those derived from $\alpha,\beta$-unsaturated esters, acids, and amides.[5b,6,7]

We have examined the cleavage of a typical siloxyallene **22a** and found that complete reaction can be achieved in THF at −78 °C (90 min) by using *n*-BuLi or in DME at 0 °C in 30 min by using MeLi·LiBr. The allenolate **24** formed showed bands in the infrared at 1960 $cm^{-1}$, similar to bands at 1900–1930 $cm^{-1}$ observed by Klein for a series of allenolates.[30]

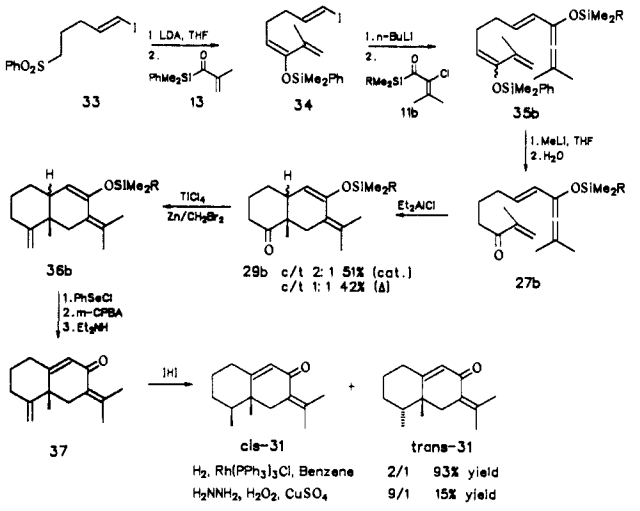
Trapping of a lithium allenolate with furfural and benzaldehyde to give **25** and **26** was accomplished. However, other electrophiles tried (MeI, $Me_2S_2$) gave poor results. Proton transfer appeared to be a side reaction. Thus, the direct vinylic enolate process does not seem to be superior to the many indirect processes involving $\beta$-amino, $\beta$-thio, or $\beta$-seleno enolate derivatives.[31]



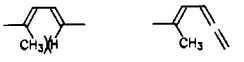

**Intramolecular Diels–Alder Reactions of Siloxy Vinylallenes.** The ease with which siloxy allenes could be prepared by using silyl ketone chemistry encouraged us to attempt some applications in more complicated systems. We chose to examine the preparation and Diels–Alder cyclization of two isomeric siloxy vinylallenes (**27b** and **28b**).[32] These systems were selected because




**Scheme III**




their Diels–Alder cyclization products **29b** and **30b** had suitable methyl substitution patterns for conversion to the sesquiterpenes **31** (dehydrofukinone)[33] and **32** (selina-4(14),7(11)-dien-8-one).[34] They were also suitable substrates for study of a key feature which should distinguish vinylallene cycloadditions from simple diene counterparts, i.e., that the dramatic reactivity differences which one finds in cis and trans substituted dienes[35] should be attenuated




in cis substituted vinylallenes, where the steric interaction which prevents attainment of the s-cis conformation is expected to be much diminished, Unfortunately, it is also to be anticipated that such a system would be subject to extremely facile 1,5-hydrogen shifts, processes which have been productively used in polyene synthesis by Okamura and co-workers.[36]

The synthesis of the eremophilane sesquiterpene **31** and its precursor **27b** is detailed in Scheme III. The enol silyl ether functions were introduced by two consecutive silyl ketone reactions. In the first one, the lithium reagent prepared from sulfone **33** was treated with 2-methyl-1-(phenyldimethylsilyl)-2-propen-1-one (**13**) to form **34**. We chose the method of Scheme II for introduction of the allenol silyl ether grouping because of the easy availability of the starting enone, and because this method had proven to be superior to Scheme I for vinylallene preparations. The vinyl iodide **34** was converted to the vinyllithium by metal–halogen exchange with use of *n*-butyllithium and allowed to react with $\alpha$-chloro silyl enone **11b** to form the vinylallene **35b**. Selective cleavage of the phenyldimethylsilyl dienol ether in the presence of the *tert*-butyldimethylsilyl allenol ether to form **27b** was achieved by treatment with methyllithium in THF at −78 °C. Enone **27b** (like its precursor **35b**) was not stable enough for effective chromatographic purification but was subjected directly to Diels–Alder cyclization. Both Lewis acid catalysis ($Et_2AlCl$, −78 to 0 °C) and thermal conditions (75 °C, $C_6H_6$, 3 h) gave good yields for the three-step sequence **34** to **29b**.

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(33) Previous syntheses of **31**: (a) Torii, S.; Inokuchi, T.; Yamafuji, T. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 2640. (b) Hagiwara, H.; Uda, H.; Kodama, T. *J. Chem. Soc., Perkin Trans. 1* **1980**, 963. (c) Ohasi, M. *J. Chem. Soc., Chem. Commun.* **1969**, 893.
(34) Previous syntheses of **32**: (a) Torii, S.; Inokuchi, T. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2642. (b) Tsankova, E. T.; Ognyanov, I. V.; Orahovats, A. S. *Chem. Ind. (London)* **1980**, 87.
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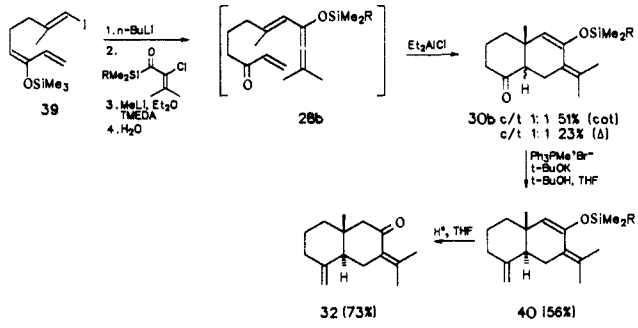
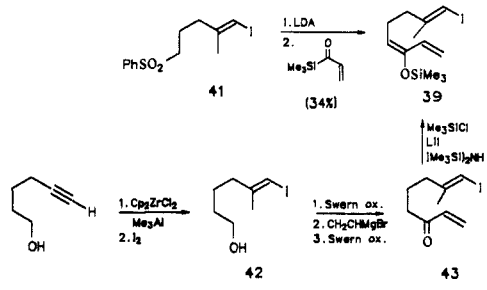
**Scheme IV**



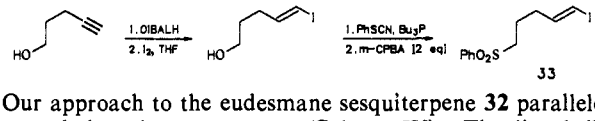
**Scheme V**



The assignment of cis stereochemistry to the major isomer of **29b** was made by the method of Williamson, Howell, and Spencer[37] which utilizes differences of long range couplings to angular methyl groups in *cis*- and *trans*-decalins. The catalyzed cycloaddition thus shows a small preference for the endo transition state. Similar selectivity has been reported for a Diels–Alder cyclization of a nonallenic diene with a related substitution pattern.[38]

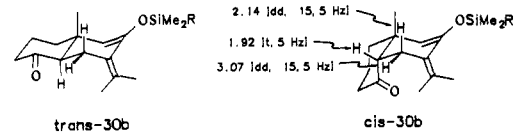
The conversion of **29b** to dehydrofukinone (*cis*-**31**) required the introduction of the characteristic cis vicinal dimethyl substituents common to many eremophilanes. Methylenation of **29b** using the procedure of Takai, Hotta, Oshima, and Nozaki[39] (Wittig reaction failed) followed by selenation–selenoxide elimination[11] gave **37**. Hydrogenation of the exo methylene group with Wilkinson's catalyst gave good yields, but the cis/trans selectivity was only 2:1. Conversely, on reduction with diimide the cis/trans ratio was improved to 9:1, but the yield was poor. Attempted reductions of **36b** also did not solve the stereochemical problems (almost complete trans selectivity).[40] Pure (±)-dehydrofukinone was prepared by separation of the 2:1 mixture. Spectral properties were identical with literature values.[33a]

The starting vinyl iodide **33** needed for Scheme III was prepared in a straightforward fashion from pentyn-5-ol.



Our approach to the eudesmane sesquiterpene **32** paralleled that used above in most respects (Scheme IV). The dienol silyl ether **39** was prepared from **41** in about 34% yield by the silyl ketone reaction used to prepare **34** (extensive Michael polymerization occurred). Similar results were obtained by using the analogous $\alpha$-lithio sulfoxide and nitrile. Hence **39** was prepared by an alternative sequence (Scheme V). The E vinyl iodide function was in each case prepared by Negishi carbometalation[41] of either 5-pentynyl phenyl sulfide or 6-hexynol. The Diels–Alder cyclization of **28b** ($Et_2AlCl$, −78 to 0 °C) proceeded in good yield (51% over the three steps **39** to **30b**) in spite of the steric problem presented by the cis methyl group. The stereochemical ratio is 1:1. The thermal reaction also gives a 1:1 ratio but proceeds in much lower yield, presumably the result of competing 1,5-hydrogen shifts,[36] as indicated by the appearance of numerous new resonances in the vinyl region of the $^1H$ NMR spectrum.

Stereochemical assignments of the two isomers of **30b** were again made by using the angular methyl line width method.[37] Confirmation of the assignment was obtained by careful analysis of the NMR spectrum of a partially deuterated ($CH_3ONa$, $CD_3OD$) sample of *cis*-**30b**. The three signals at 1.92, 2.14, and



3.07 δ could be identified as shown. The appearance of the 1.92 δ signal as a triplet with a 5-Hz coupling proves the cis decalin structure, since this proton would not have equal couplings in the trans isomer. Conversion of **30b** to the sesquiterpene **32** was accomplished by Wittig reaction under equilibrating conditions which resulted in conversion of only *trans*-**30** to olefin (*cis*-**30** was enolized and mostly recovered unchanged on workup) followed by hydrolysis of the enol silyl ether.

**Summary.** The preparation of a variety of allenol silyl ethers using silyl ketones as precursors has been achieved. Successful use of this chemistry in key steps of two sesquiterpene syntheses **31** and **32** illustrate the applicability to complex systems.

## Experimental Section

**General Methods.** Solutions of 1 M lithium diisopropylamide (LDA) in THF–hexane were prepared as in ref 1i and titrated against *n*-propanol with phenanthroline as indicator. All reactions involving organolithium reagents were conducted under an atmosphere of dry nitrogen by using apparatus dried at 110 °C for at least 2 h. "Flash" chromatography refers to the method described by Still et al.[42] A number of alkoxy and siloxy allenes as well as silyl enones were prone to polymerize, so a few crystals of an inhibitor were added to many reaction mixtures. The radical inhibitor used was 3-*tert*-butyl-4-hydroxy-5-methylphenyl sulfide.

**Standard Enol and Allenol Silyl Ether Workup (Illustrated for 0.5 mmol).** The reaction mixture was partitioned between stirred, cold 7% aqueous $NaHCO_3$ (20 mL) and $Et_2O$–pentane (1:1, 30 mL). The aqueous layer was extracted with a second portion (20 mL) of $Et_2O$–pentane, and the combined organic extracts were washed with brine, dried ($Na_2SO_4$, then $K_2CO_3$), and evaporated.

**Standard Hydrolysis for Silyl Allenol Ether (Illustrated for 0.5 mmol).** To a solution of silyl ether in 3 mL of MeOH at 0 °C was added 1 drop of concentrated HCl. The solution was stirred 2–4 h, quenched with 5 mL of 7% aqueous $NaHCO_3$, concentrated, and then extracted with 2 × 20 mL of $Et_2O$–pentane (1:1, v/v). The organic extracts were washed with brine, dried ($Na_2SO_4$), and evaporated.

**1-(Trimethylsilyl)-1-propanone (6a).** To a round-bottom flask was added 18 mL (250 mmol) of propionaldehyde, 25.1 mL (250 mmol) of 1,3-propanedithiol, and 1.9 g (10 mmol) of *p*-toluenesulfonic acid. Chloroform (250 mL) was added, and the solution was heated to reflux with a heavier than water distillation apparatus. After 3.5 h the solution was cooled and poured into a separatory funnel. The organic layer was washed with 5% NaOH (2 × 100 mL), $H_2O$ (1 × 200 mL), and brine. The organic phase was filtered through $Na_2SO_4$ and evaporated. Kugelrohr distillation at 76 °C and 0.4 mm gave 35.3 g of the protected aldehyde.

The above material was dissolved in 200 mL of THF and cooled to 0 °C. Over 45 min, from a pressure equilizing funnel, *n*-BuLi (173 mL, 260 mmol, 1.5 M in hexane) was added. The solution turned deep yellow-orange. After 2 h 35 mL (275 mmol) of $Me_4SiCl$ was added by syringe to quench. The contents were transferred to a separatory funnel and extracted with $H_2O$ (1 × 100 mL). The aqueous layer was extracted with 1:2 ether/pentane (3 × 100 mL), and the organic layers were combined. The combined layers were washed with brine, dried over $Na_2SO_4$, filtered, and evaporated.

The sample from above was placed in a flask containing 600 mL of methanol and 150 mL of $H_2O$. The flask was cooled to 0 °C, and 350 g (1.25 mol) of chloramine-T was added in portions over 45 min. After an additional 30 min the ice bath was removed, and the solution was

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(38) Unpublished result of Taber, D. F.; Gunn, B. P. cited in Ciganek, E. *Org. React.* **1984**, *32*, 1.
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(42) Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

stirred at room temperature for 45 min. The solution was poured into a separatory funnel containing water (100 mL). The mixture was extracted with 1:1 ether/pentane (7 × 200 mL). The organic layers were combined and extracted with water and with brine. The layer was dried over $Na_2SO_4$, filtered through $Na_2SO_4$, dried over $K_2CO_3$, and filtered. The solvent was removed by distillation through a vigreux column at atmospheric pressure. The residue was then distilled at aspirator pressure. The band distilling at 55–65 °C was collected to yield 19.9 g (61% yield from propionaldehyde) of **6a**.[43]

**3-Phenyl-1-(trimethylsilyl)-1-propanone (5a).** To a solution of 5.6 g (25 mmol) of the dithiane prepared from 3-phenylpropionaldehyde in 40 mL of THF at −78 °C was added 17 mL (27.5 mmol, 1.61 M in hexane) of *n*-BuLi. After 5 min the flash was placed in an ice bath and stirred 2 h. The anion was quenched with a centrifuged mixture of 6.3 mL (50 mmol) of $Me_4SiCl$ and triethylamine (6 mL, 42 mmol). The reaction was stirred for $4^1/_2$ h as the flask was brought to room temperature. The entire mixture was then poured into a separatory funnel containing saturated $NH_4Cl$ (100 mL). The layers were separated and saved. The aqueous phase was extracted with 1:1 ether/pentane (3 × 75 mL), and the organic layers were combined. The combined organic phases were washed with brine, dried over $Na_2SO_4$, filtered, and evaporated.

The sample from above was dissolved in 120 mL of methanol, and then 30 mL of water added. Chloramine-T (28 g, 100 mmol) was added, and the mixture was stirred at 0 °C for 1 h. The solution was then warmed to room temperature for 30 min. The solution was poured into a separatory funnel containing saturated $NH_4Cl$. The mixture was extracted with 1:1 ether/pentane (9 × 75 mL). The organic layers were combined, washed with brine, dried through $Na_2SO_4$, and evaporated. The residual oil was passed through silica gel in a 60-mL fritted glass funnel by using 200 mL of 10% ether/pentane. The eluant was collected and evaporated. The remaining material was Kugelrohr distilled to yield 7.32 g (84% yield from dithiane) of **5a**:[44] $^1$H NMR ($CDCl_3$, 200 MHz) $\delta$ 1.23 (s, 9 H), 2.80–3.04 (m, 4 H), 7.13–7.37 (m, 5 H); IR 2960, 1650, 1510, 1465, 1265, 850, 760, 710 cm$^{-1}$.

**1-(*tert*-Butyldimethylsilyl)-2-chloro-3-methyl-2-buten-1-one (11b, X = Cl).** In a 25-mL, round-bottom flask was placed 10 mL $CH_2Cl_2$, followed by addition of 3.2 mL (10.0 mmol) of 1-(*tert*-butyldimethylsilyl)-1-(1-ethoxyethoxy)-3-methyl-1,2-butadiene.[1d] The flask was cooled to −78 °C, and 0.88 mL (11.0 mmol) of $SO_2Cl_2$ was added by syringe over 5 min. After an additional 5 min the flask was brought to room temperature, and the solution was poured into a separatory funnel containing water. The layers were mixed and separated. The organic layer was saved, washed with water (3 × 10 mL), washed with brine (1 × 10 mL), dried by passage through a cone of $Na_2SO_4$, and evaporated. The resulting bright yellow liquid was Kugelrohr distilled at 40–60 °C and 0.1 mm to give 2.25 g (97% yield) of yellow silyl ketone **11b**: $^1$H NMR ($CDCl_3$, 100 MHz) $\delta$ 0.15 (s, 6 H), 0.87 (s, 9 H), 1.83 (s, 6 H); IR 2960, 2930, 2860, 1640, 1610, 1475, 1380, 1265, 1150, 1050, 920, 855, 795, 695 cm$^{-1}$; $^{13}$C NMR ($CDCl_3$, 15 MHz) $\delta$ −5.1, 17.3, 21.2, 22.6, 25.8, 26.8, 27.9, 130.7, 135.3, 202.7; MS, M$^+$ calcd for $C_{11}H_{15}ClOSi$, found 232.1045 [$^{35}$Cl peak], found 232.1050. Anal. Calcd for $C_{11}H_{15}ClOSi$: C, 56.75; H, 9.09. Found: C, 56.52; H, 9.08.

**2-Methyl-1-(phenyldimethylsilyl)-2-propen-1-ol.** To a round-bottom flask containing 160 mL (74 mmol, 0.46 M in THF) of (phenyldimethylsilyl)lithium[45] was added 250 mL of ether, and the solution was cooled to −78 °C. Methacrolein (6.1 mL, 74 mmol) was added as a −78 °C solution in 50 mL of ether over 2.5 h. The solution was stirred at −78 °C after the addition was complete and then poured into a stirred solution of methanol/water/ammonium chloride to quench the reaction. The mixture was transferred to a separatory funnel, and the layers were separated. The organic layer was washed with brine (1 × 75 mL), dried ($Na_2SO_4$), and evaporated. The sample was then fractionally distilled collecting the fraction boiling from 77–87 °C at 0.05 mm. This produced 10.87 g (71% yield) of silyl carbinol: $^1$H NMR ($CDCl_3$, 200 MHz) $\delta$ 0.33, 0.38 (2 s, 6 H), 1.55 (s, 3 H), 4.07 (s, 1 H), 4.77 (s, 2 H), 7.3–7.61 (m, 5 H); IR 3420, 3060, 2960, 2910, 1690, 1640, 1430, 1380, 1250, 1115, 885, 840, 790, 740, 705 cm$^{-1}$; MS, M$^+$ calcd for $C_{12}H_{18}OSi$ 206.1122, found 206.1056.

**2-Methyl-1-(phenyldimethylsilyl)-2-propen-1-one (13).** To a 100-mL, three-necked flask, equipped with an overhead mechanical stirrer, was added 40 mL of $CH_2Cl_2$ and 2.9 mL (33.0 mmol) of oxalyl chloride. The flask was placed in a −55 °C cold bath, and 4.7 mL (66.0 mmol) of $Me_2SO$ was added via cannula as a solution in 10 mL of $CH_2Cl_2$ (CAUTION: vigorous gas evolution). After 20 min 6.25 g (30.0 mmol) of 2-methyl-1-(phenyldimethylsilyl)-2-propen-1-ol as a solution in 10 mL of $CH_2Cl_2$ was added to the solution via cannula. This was stirred at −55 °C for 20 min, and then 17.0 mL (120.0 mmol) of $NEt_3$ was added by syringe.

The solution turned yellow, and a solid precipitated. The flask was brought to room temperature and left stirring for 1 h. The mixture was then transferred to a separatory funnel and washed with cold 2 N HCl (1 × 20 mL). The organic layer was washed with saturated $NaHCO_3$ (1 × 15 mL), washed with brine (1 × 10 mL), dried ($Na_2SO_4$), and evaporated. The resulting yellow liquid was purified by flash chromatography by using 5% ether/hexane. The yellow bands were collected. Evaporation gave 5.04 g (83% yield) of yellow silyl ketone **13**: $^1$H NMR ($CDCl_3$, 200 MHz) $\delta$ 0.56 (s, 6 H), 1.73 (s, 3 H), 5.86 (s, 1 H), 5.98 (s, 1 H), 7.3–7.6 (m, 5 H); IR 3080, 2970, 2930, 1620, 1440, 1315, 1265, 1125, 1055, 950, 850, 840, 805, 750, 720 cm$^{-1}$; $^{13}$C NMR ($CDCl_3$, 15 MHz) $\delta$ −2.5, 15.6, 127.9, 128.5, 129.3, 133.5, 136.1, 149.4, 199.5; MS, M$^+$ calcd for $C_{12}H_{16}OSi$ 204.0966, found 204.0971. Anal. Calcd for $C_{12}H_{16}OSi$: C, 70.53; H, 7.89. Found: C, 70.28; H, 7.97.

**5-Methyl-1-phenyl-3-((trimethylsilyl)oxy)-3,4-nonadiene (Table I, Entry 1).** To a solution of 2.3 mL (1.8 g, 22 mmol) of 1-hexyne in 40 mL of THF at −78 °C was added 10.5 mL of a 2.0 M solution of MeLi·LiBr (21 mmol) over 10 min, followed, in 15 min, by a solution of 4.3 mL (4.1 g, 20 mmol) of 3-phenyl-1-(trimethylsilyl)-1-propanone (**5a**) in 5 mL of THF, added over 15 min. After 10 min, 1.5 mL (3.4 g, 24 mmol) of methyl iodide was added, and the solution was warmed to 0 °C, stirred 35 min, then evaporated to $\sim^1/_2$ of the original volume, and partitioned between cold 1:1 $Et_2O$–pentane (50 mL) and 7% $NaHCO_3$ (50 mL). The aqueous layer was extracted with two 20-mL portions of $Et_2O$–pentane, and the combined organic extracts were washed with brine, dried ($Na_2SO_4$, then $K_2CO_3$), and evaporated. A small amount of radical inhibitor was added, and the crude product was distilled (Kugelrohr, 105 °C, 0.2 mm) to give 5.04 g (83%) of 5-methyl-1-phenyl-3-((trimethylsilyl)oxy)-3,4-nonadiene: $^1$H NMR ($CDCl_3$, 270 MHz) $\delta$ 0.24 (s, 9 H), 0.98 (br t, $J$ = 7 Hz, 3 H), 1.41 (m, 2 H), 1.72 (s, 3 H), 2.01 (m, 2 H), 2.50 (approx t, $J \sim$ 8 Hz, 2 H), 2.82 (approx t, $J \sim$ 8 Hz, 2 H), 7.30 (m, 5 H); $^{13}$C NMR ($CDCl_3$, 15 MHz) $\delta$ 0.11, 14.0, 21.0, 22.6, 30.0, 33.0, 35.7, 36.2, 110.2, 124.3, 125.4, 127.9, 128.2, 141.9, 190.1; IR 2915, 1958, 1454, 1251, 1195, 1162, 995, 846, 752, 700 cm$^{-1}$; MS, M$^+$ calcd for $C_{19}H_{30}OSi$: 302.2066, found 302.2055. Anal. Calcd for $C_{19}H_{30}OSi$: C, 75.41; H, 10.01. Found: C, 75.33; H, 10.16.

**1-Phenyl-4-octen-3-one (Table I, Entry 4).** To a solution of 0.296 mL (204 mg, 3.00 mmol) of 1-pentyne in 1.5 mL of THF at 0 °C was added 1.0 mL of a 1.0 M solution of MeLi·LiBr (1.0 mmol). After 40 min, the solution was cooled to −78 °C, and 0.216 mL (206 mg, 1.00 mmol) of 3-phenyl-1-trimethylsilyl-1-propanone (**5a**) was added, dropwise. The solution was warmed to 0 °C, stirred for 30 min, then worked up, and hydrolyzed directly, following the standard procedures. Purification by preparative TLC (5% $Et_2O$–pentane) gave 128 mg (63%) of 1-phenyl-4-octen-3-one: $^1$H NMR ($CCl_4$, 100 MHz) $\delta$ 1.00 (t, $J$ = 7 Hz, 3 H), 1.56 (sextet, $J$ = 7 Hz, 2 H), 2.23 (q, $J$ = 7 Hz, 2 H), 2.74–3.12 (m, 4 H), 6.12 (br d, $J$ = 16 Hz, 1 H), 6.86 (dt, $J$ = 16 Hz, 1 H), 7.30 (br s, 5 H); IR 2950, 1695, 1671 (s), 1637, 1496, 1451, 1185, 978, 750, 704 cm$^{-1}$; MS, M$^+$ calcd for $C_{14}H_{18}O$ 202.1358, found 202.1357.

**1-Phenyl-3-((trimethylsilyl)oxy)-3,4-octadiene (Table I, Entry 4).** To a solution of 0.051 mL (35 mg, 0.52 mmol) of 1-pentyne in 1.5 mL of THF at −78 °C was added 0.52 mL of a 1.0 M solution of MeLi·LiBr (0.52 mmol). After 10 min, 0.108 mL (103 mg, 0.500 mL) of 3-phenyl-1-(trimethylsilyl)-1-propanone (**5a**) was added, followed by 10 min by 0.061 mL (48 mg, 0.80 mmol) of isopropyl alcohol. The solution was warmed to 0 °C, stirred 30 min, and then worked up, following the standard procedure. The crude product was purified by Kugelrohr distillation (90 °C, 0.15 mm) to give 126 mg (92%) of 1-phenyl-3-((trimethylsilyl)oxy)-3,4-octadiene, contaminated with ~20% of the enones resulting from hydrolysis: $^1$H NMR ($CDCl_3$, 270 MHz) $\delta$ 0.27 (s, 9 H), 1.00 (t, $J$ = 7 Hz, 3 H), 1.48 (sextet, $J$ = 7 Hz, 2 H), 2.04 (qd, $J$ = 7, 2 Hz, 2 H), 2.51 (, 2 H), 2.84 (t, $J$ = 8 Hz, 2 H), 5.60 (tt, $J$ = 6.5, 2.8 Hz, 1 H), 7.29 (m, 5 H); $^{13}$C NMR ($CDCl_3$, 15 MHz) $\delta$ 0.2, 13.9, 22.0, 32.9, 33.4, 36.1, 101.9, 125.5, 125.8, 127.9, 128.3, 141.7, 194.5; IR 2955, 1957, 1498, 1455, 1255, 1196, 1175, 855, 754, 701 cm$^{-1}$; MS, M$^+$ calcd for $C_{17}H_{26}OSi$ 274.1753, found 274.1754.

**1-Cyclopropylidene-4-phenyl-2-((trimethylsilyl)oxy)-1-butene and 1-(1-Methoxycyclopropyl)-4-phenyl-2-butanone (Table I, Entry 5).** To a −78 °C solution of 0.54 mL (0.97 g, 5.4 mmol) of homopropargyl iodide in 10 mL of THF was added 2.7 mL of a 1.91 M solution of MeLi·LiBr (5.2 mmol). After 10 min, a solution of 1.08 mL (1.03 g, 5.00 mmol) of 3-phenyl-1-(trimethylsilyl)-1-propanone (**5a**) in 2 mL of THF was added. The solution was stirred at −78 °C for 15 min and at 0 °C for 40 min and then worked up following the standard procedure except the

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aqueous layer was extracted with an additional portion of $Et_2O$/pentane, 1:1. Kugelrohr distillation (100 °C, 0.4 mm) of the crude product gave 1.03 g (80%) of 1-cyclopropylidene-4-phenyl-2-((trimethylsilyl)oxy)-1-butene: $^1H$ NMR ($CCl_4$, 100 MHz) $\delta$ 0.24 (s, 9 H), 1.42 (br s, 4 H), 2.48–2.7 (m, 2 H), 2.80–3.02 (m, 2 H), 7.30 (br s, 5 H); IR 3020, 2945, 2010, 1945, 1605, 1490, 1250, 1205, 1170, 1060, 845, 750, 700 $cm^{-1}$; MS, $M^+$ calcd for $C_{16}H_{22}OSi$ 258.1440, found 258.1436. Anal. Calcd for $C_{16}H_{22}OSi$: C, 74.34; H, 8.60. Found: C, 74.28; H, 8.75.

A portion of the allenol ether (94 mg, 0.36 mmol) was hydrolyzed by using the standard procedure, which gave 69 mg (87%) of 4-phenyl-1-(1-methoxycyclopropyl)-2-butanone after preparative TLC (5% $Et_2O$–pentane, $R_f$ 0.07): $^1H$ NMR ($CCl_4$, 100 MHz) $\delta$ 0.50–0.72 (m, 2 H), 0.78–1.00 (m, 2 H), 2.58 (s, 2 H), 2.92 (s, 4 H), 3.26 (s, 3 H), 7.24 (br s, 5 H); IR 3040, 2940, 1710, 1583, 1458, 1069, 843, 749, 700 $cm^{-1}$; MS, $M^+$ calcd for $C_{14}H_{19}O_2$ 218.1292, found 218.1294.

**5-Methyl-3-((trimethylsilyl)oxy)-3,4-octadiene (Table I, Entry 8).** To a stirred solution of 0.31 mL (0.21 g, 3.1 mmol) of 1-pentyne in 5 mL of THF at −78 °C was added 3.2 mL of 1,0 M MeLi·LiBr (3.2 mmol). After 20 min, 0.47 mL (0.39 g, 3.0 mmol) of 1-(trimethylsilyl)-1-propanone (**6a**) was added dropwise. A white precipitate formed. After 10 min, 0.25 mL (0.57 g, 4.0 mmol) of methyl iodide was added, and the flask was warmed to 0 °C and stirred for 30 min. After standard workup, distillation of the residue (Kugelrohr, 80 °C, 20 mm) gave 0.484 g (76%) of 5-methyl-3-((trimethylsilyl)oxy)-3,4-octadiene as a clear, mobile liquid: $^1H$ NMR ($CDCl_3$, 100 MHz) $\delta$ 0.08 (s, 9 H), 0.94 (t, $J$ = 7 Hz, 3 H), 1.44 (br sextet, $J$ = 7 Hz, 2 H), 1.67 (s, 3 H), 1.84–2.0 (m, including a quartet, $J$ = 7 Hz, at 1.98 $\delta$, 4 H); IR 2978, 1958, 1458, 1260, 1196, 1170, 880, 760 $cm^{-1}$; MS, $M^+$ calcd for $C_{12}H_{24}OSi$ 212.1597, 212.1579.

**5-(Methylthio)-3-((trimethylsilyl)oxy)-3,4-octadiene (Table I, Entry 10).** To a −78 °C solution of 0.051 mL (35 mg, 0.52 mmol) of 1-pentyne in 1 mL of THF was added 0.52 mL of 1.0 M MeLi·LiBr (0.52 mmol). After 10 min, 0.078 mL (65 mg, 0.500 mmol) of 1-(trimethylsilyl)-1-propanone (**6a**) was added, followed in 10 min by 0.054 mL (57 mg, 0.60 mmol) of dimethyl disulfide. The flask was placed in an 0 °C bath, stirred 30 min, and then worked up following the standard procedure. Kugelrohr distillation (100 °C, 20 mm) of the crude product gave 89 mg (73%) of 5-(methylthio)-3-((trimethylsilyl)oxy)-3,4-octadiene: $^1H$ NMR ($CDCl_3$, 100 MHz) $\delta$ 0.10 (s, 9 H), 0.96 (t, $J$ = 7 Hz), 1.00 (t, $J$ = 7 Hz, total 6 H), 1.62 (br sextet, $J$ = 7 Hz, 2 H), 2.12 (s), 2.22 (q, $J$ = 7 Hz, total 5 H); $^{13}C$ NMR ($CDCl_3$, 15 MHz) $\delta$ 0.1, 11.4, 13.9, 15.3, 22.0, 28.4, 37.8, 114.4, 134.8, 183.4; IR 2955, 1935, 1560, 1249, 1190, 1168, 970, 870, 845, 760 $cm^{-1}$; MS, $M^+$ calcd for $C_{12}H_{24}OSSi$ 244.1318, found 244.1318. Anal. Calcd for $C_{12}H_{24}OSSi$: C, 58.94; H, 9.91. Found: C, 59.10; H, 10.12.

**1-Ethoxy-3-(*tert*-butyldimethylsiloxy)-5-methyl-*cis*-1,3,4-hexatriene (Table I, Entry 13).** *cis*-1-Bromo-2-ethoxyethylene (0.063 mL, 0.088 g, 0.58 mmol) was added to a solution of *t*-BuLi (0.63 mL, 1.74 M, 1.1 mmol) and radical inhibitor (~1 mg) in 5 mL of $Et_2O$ at −78 °C. After 1 h, 1-(*tert*-butyldimethylsilyl)but-2-yn-1-one (**12b**, R = $CH_3$, 0.100 mL, 0.5 mmol)[1d] was added. The reaction mixture was stirred at −78 °C for 15 min, and then MeI was added (0.040 mL, 0.64 mmol). Slowly, 4 mL of THF was added by cannula to the flask. After 15 min at −78 °C the cold bath was removed, and the reaction mixture was allowed to warm to room temperature. A few drops of $NEt_3$ were added, and then the contents of the flask were poured into a separatory funnel containing ether/pentane (1:1) and $NaHCO_3$. The organic phase was washed with $H_2O$ and brine, poured through $Na_2SO_4$, and dried over $K_2CO_3$. The solution was rotary evaporated and then put on a pump to remove solvent residues. An NMR yield of 77% of 1-ethoxy-3-(*tert*-butyldimethylsiloxy)-5-methyl-1-*cis*-3,4-hexatriene, the only compound observed in the 270 MHz NMR, was obtained by integration relative to a measured amount of trichloroethylene: NMR ($CDCl_3$, 270 MHz) $\delta$ 0.07 (s, 6 H), 0.89 (s, 9 H), 1.21 (t, $J$ = 7.0 Hz, 3 H), 1.72 (s, 6 H), 3.77 (q, $J$ = 7.0 Hz, 2 H), 4.55 (d, $J$ = 6.7 Hz, 1 H), 5.91 (d, $J$ = 6.8 Hz, 1 H); IR 2918, 2847, 1943, 1646, 1472, 1460, 1105, 840, 783 $cm^{-1}$; MS, $M^+$ calcd for $C_{15}H_{28}O_2Si$ 268.1859, found 268.1860.

**3-(*tert*-Butyldimethylsiloxy)-1,3,4-hexatriene (Table II, Entry 1).** Excess vinyl bromide (0.740 mL, 10 mmol) was added to *t*-BuLi (7.2 mL, 1.4 M, 10 mmol)[46] and radical inhibitor (1–2 mg) in 20 mL of ether at −78 °C. After 25 min at −78 °C, a solution of 1-(*tert*-butyldimethylsilyl)-2-bromobut-2-en-1-one[1d] (**10b**, X = Br, 1.05 g, 4 mmol) in 5 mL of ether was transferred by cannula to the vinyllithium solution. The reaction mixture was stirred at −78 °C for 20 min, then a few drops of $NEt_3$ were added, and the solution was poured into a separatory funnel containing ether/hexane (1:1) and saturated $NaHCO_3$. The organic phase was washed with $H_2O$ and brine, poured through $Na_2SO_4$, and dried over $K_2CO_3$. Kugelrohr distillation (0.2 mm, 26–60 °C) gave 0.610 g (72% yield) of 3-(*tert*-butyldimethylsiloxy)-1,3,4-hexatriene, a pale yellow liquid; $^1H$ NMR ($CDCl_3$, 270 MHz) $\delta$ 0.10 (s, 6 H), 0.93 (s, 9 H), 1.72 (d, $J$ = 7.0 Hz, 3 H), 4.99 (dt, $J$ = 10.3, 1.8 Hz, 1 H), 5.41 (dt, $J$ = 16.9, 1.8 Hz, 1 H), 5.64 (br q, $J$ = 7.0 Hz, 1 H), 6.08 (dd, $J$ = 16.9, 10.6 Hz, 1 H); IR 2967, 2865, 1937, 1620, 1484, 1474, 1255, 1060 $cm^{-1}$; MS, $M^+$ calcd for $C_{12}H_{22}OSi$ 210.1434, found 210.1441.

**3-(1-(*tert*-Butyldimethyldimethylsiloxy)-1,2-propadienyl)-4-methylfuran (Table II, Entry 3).** A solution of *t*-BuLi (2.57 mL, 1.71 M, 4.4 mmol) and radical inhibitor (1–2 mg) in 20 mL of ether was cooled to −78 °C. 3-Iodo-4-methylfuran[1j] (0.262 mL, 0.459 g, 2.4 mmol) was added, the metal–halogen exhange was allowed to proceed for $^1/_2$ h, and then a solution of 1-(*tert*-butyldimethylsilyl)-2-bromobut-2-en-1-one[1d] (**10b**, X = Br, 0.527 g, 2.0 mmol) in approximately 5 mL of ether was added by cannula. The reaction mixture was stirred at −78 °C for 1 h, then a few drops of $NEt_3$ were added, and the solution was poured into a separatory funnel containing ether/pentane (1:1) and saturated $NaHCO_3$. The organic phase was washed with $H_2O$ and brine, poured through $Na_2SO_4$, dried over $K_2CO_3$, and rotary evaporated. An 87% yield (0.459 g) of 3-(1-*tert*-butyldimethylsiloxy)-1,2-propadienyl)-4-methylfuran, a pale yellow liquid, was obtained after Kugelrohr distillation (0.3 mm, 60–80 °C): $^1H$ NMR ($CDCl_3$, 100 MHz) $\delta$ 0.26 (s, 6 H), 1.05 (s, 9 H), 1.95 (d, $J$ = 7 Hz, 3 H), 2.02 (br s, 3 H), 5.84 (q, $J$ = 7 Hz, 1 H), 7.12 (m, 1 H), 7.40 (br s, 1 H); IR 2970, 2870, 1960, 1610, 1480, 1405, 1380, 1315, 1270, 1235, 1220, 800, 695; MS, $M^+$ calcd for $C_{15}H_{24}O_2Si$ 264.1539, found 264.1517.

**1-(*tert*-Buthyldimethylsiloxy)-4-methyl-2,3-pentadiene (Table II, Entry 5).** A flask containing 1.5 mL (2.0 mmol, 1.36 M in ether) of MeLi·LiBr in 4 mL of ether was cooled to −78 °C, and 0.42 mL (2.0 mmol) of chloro ketone **11b** in 4 mL of ether was added over 1 min. After 10 min the flask was warmed to 0 °C, and $NEt_3$ added to prevent hydrolysis. The solution was poured into a separatory funnel containing saturated $NaHCO_3$. The two layers were mixed and separated. The organic phase was washed with brine, dried by passage through a cone of $Na_2SO_4$, and evaporated. The resulting liquid was purified by Kugelrohr distillation at 5 mm and 40–60 °C gave 0.346 g (82% yield) of colorless allene: $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 0.07 (s, 6 H), 0.88 (s, 9 H), 1.68 (s, 6 H), 1.79 (s, 3 H); IR 2950, 2920, 2850, 1955, 1460, 1360, 1245, 1190, 1070, 1005, 905, 830, 770 $cm^{-1}$; MS $M^+$ calcd for $C_{12}H_{24}OSi$ 212.1590, found 212.1586.

**(5*E*)-2-Methyl-4-(*tert*-butyldimethylsiloxy)-2,3,5-nonatriene (Table II, Entry 8).** To a flask containing 3 mL of ether at −78 °C was added 0.61 mL (1.0 mmol, 1.65 M in hexane) of *n*-BuLi. This was followed by rapid addition of 0.13 mL (1.0 mmol) of (*E*)-1-iodo-1-pentene via cannula as a solution in 2 mL of ether. The solution was stirred at −78 °C for 20 min, and then 0.21 mL (1.0 mmol) of the silyl ketone **11b**, X = Cl, was added by syringe. After 1 h at −78 °C the solution was warmed to 0 °C over 10 min, and several milliliters of $NEt_3$ were added to prevent hydrolysis. Saturated $NaHCO_3$ was poured into the flask, and then the mixture was transferred to a separatory funnel containing 50% ether/hexane (10 mL). The organic layer was washed with brine (1 × 10 mL), dried ($Na_2SO_4$), and evaporated. The resulting oily liquid was carefully chromatographed on the chromatotron under the following conditions. A dry 2-mm plate was preeluted with a 1% bis(trimethylsilyl)acetamide/pentane solution (volume of eluant about 75 mL). The solvent was then switched to a solution composed of pentane, ether, and $NEt_3$ (several drops, approximately 10, of BSA were added) in a ratio of 90:5:5, respectively (all solvents used were dried prior to use). The plate was washed with about 100 mL of this new mixture, and the sample was introduced. Collecting the first band gave after evaporation of the solvent 0.235 g (88% yield) of triene: $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 0.10 (s, 6 H), 0.84–0.98 (t with s, $J$ = 7 Hz, 12 H), 1.42 (hextet, $J$ = 7.2 Hz, 2 H), 1.76 (s, 6 H), 2.06 (q, $J$ = 7 Hz, 2 H), 6.73 (d, $J$ = 14.5 Hz, 1 H), 6.87 (dt, $J$ = 15, 7 Hz, 1 H); IR 2975, 2940, 2915, 2875, 1960, 1495, 1480, 1465, 1410, 1380, 1275, 1255, 1200, 1080, 980, 855, 805, 715 $cm^{-1}$. MS, $M^+$ calcd for $C_{16}H_{30}OSi$ 266.2058, found 266.2065.

**4-Iodo-5-methyl-4-octen-3-one (Table III, 23, X = I).** To a 0 °C solution of 0.127 mL (106 mg, 0.500 mmol) of 5-methyl-3-(trimethylsiloxy)-3,4-octadiene (**22a**) and 0.040 mL (40 mg, 0.50 mmol) of pyridine in 1 mL of $CCl_4$ was added a solution of 127 mg (0.500 mmol) of $I_2$ in 8 mL of $CHCl_3$. After 10 min, the solution was worked up following the standard procedure, adding a wash (of the organic layer) with 10% $Na_2S_2O_3$ (prior to brine wash) and neglecting the $K_2CO_3$ drying. Purification of the crude product by preparative TLC (5% $Et_2O$–pentane) gave **23**, X = I as two bands: $R_f$ 0.57, 57 mg (35%); $^1H$ NMR ($CCl_4$, 100 MHz) $\delta$ 0.94, 1.12 (two t, $J$ = 7, 7 Hz, total 6 H), 1.32 (br sextet, $J$ ~ 7 Hz, 2 H), 2.02 (s, 3 H), 2.25 (approx t, $J$ = 8 Hz, 2 H), 2.81 (q, $J$ = 7 Hz, 2 H); IR 2960, 1690, 1622, 1460, 1380, 1343, 1160, 1105, 1061, 990, 868 $cm^{-1}$; MS, $M^+$ calcd for $C_9H_{15}IO$ 266.0168, found 266.0163. $F_f$ 0.47, 53 mg (40%); $^1H$ NMR ($CCl_4$, 100 MHz) $\delta$ 1.04, 1.12 (two overlapping t, $J$ = 8, 7 Hz, total 6 H), 1.56 (br sextet, $J$ ~

(46) Procedure of Neumann, H.; Seebach, D. *Chem. Ber.* **1978**, *111*, 2785.

8 Hz, 2 H), 1.94 (s, 3 H), 2.30 (approx q, $J \sim 8$ Hz, 2 H), 2.82 (q, $J = 7$ Hz, 2 H); IR 2955, 1687, 1629, 1460, 1378, 1340, 1158, 1100, 1050, 865 $cm^{-1}$; MS, $M^+$ calcd for $C_9H_{15}IO$ 266.0168, found 266.0171.

**4-((2-Furyl)hydroxymethyl)-5-methyl-4-octen-3-one (26).** To a 0 °C solution of 0.10 mL (85 mg, 0.40 mmol) of 5-methyl-3-(trimethylsiloxy)-3,4-octadiene (**22a**) in 1 mL of THF at 0 °C was added 0.29 mL of 1.53 M *n*-BuLi (0.44 mmol). After 10 min, the solution was cooled to −78 °C, and a solution of 0.033 mL (38 mg, 0.50 mmol) of furfural in 0.5 mL of THF was added, followed in 5 min by 0.5 mL of saturated aqueous methanolic $NH_4Cl$. The mixture was worked up following the standard procedure, and the residue was purified by preparative TLC (30% EtOAc/hexane, $R_f$ 0.16) to give **26** (82 mg, 87%) as a mixture of isomers: $^1H$ NMR ($CDCl_3$, 270 MHz) $\delta$ 0.94 (m, 6 H), 1.48 (m, 2 H), 1.77 (approx t, $J \sim 1$ Hz, 3 H), 2.00 (br t, $J \sim 8$ Hz), 2.15 (t, $J = 8$ Hz, total 2 H), 2.45 (br m, 2 H), 3.60 (br s, 1 H), 5.64 (br s, 1 H), 6.26, 6.32 (two m, total 2 H), 7.35 (br s, 1 H), a triplet at 4.65 ppm ($J \sim 7$ Hz) was tentatively assigned to the isomeric hydroxyenone resulting from Cannizzaro reaction (approximately 10% of mixture); IR 3420, 2960, 1690, 1460, 1380, 1148, 1014, 742 $cm^{-1}$; MS, $M^+$ calcd for $C_{14}H_{20}O_3$ 236.1407, found 236.1412.

**(*E*)-1-Iodo-1-penten-5-ol.** To a −20 °C solution of 600 mL (600 mmol, 1 M in hexane) of DIBAL-H was slowly added 18.8 mL (200 mmol) of 4-pentyn-1-ol by syringe over 30 min. After gas evolution had subsided, the nitrogen inlet/bypass line was removed, and the solution was stirred for 14 h. The hexane solvent was removed under vacuum, and the mixture was redissolved in 200 mL of THF. The flask was cooled to −78 °C and 161.0 g (240 mmol) of $I_2$ in 300 mL of THF was added via cannula. After stirring for 20 min at −78 °C, the mixture was brought to room temperature. After 10 min the solution was poured into a beaker containing ice and 2 N HCl (75 mL). More 2 N HCl (100 mL) was added slowly (CAUTION: rapid addition of HCl causes the solution to boil), and after the aluminum salts had been dissolved, the mixture was transferred to a separatory funnel. The two phases were separated and both were saved. The aqueous layer was extracted with ether/hexane (2 × 100 mL), and the organic layers were combined. The combined organic layers were extracted with 2 N HCl (1 × 75 mL), saturated $NaHCO_3$ (1 × 75 mL), and brine (1 × 50 mL). The organic phase was then dried ($Na_2SO_4$) and evaporated. Fractional distillation of the resulting liquid, collecting the fraction with a boiling point of 75–85 °C at 0.7 mm, gave 22.87 g (54% yield) of liquid product: $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 1.56 (m, 2 H), 2.07 (q, $J = 7$ Hz, 2 H), 2.93 (s, 1 H), 3.52 (t, $J = 6.5$ Hz, 2 H), 5.97 (d, $J = 14.5$ Hz, 1 H), 6.45 (dt, $J = 14.5, 7$ Hz, 1 H); IR 3320 (br), 2920, 2860, 1605, 1450, 1430, 1220, 1205, 1060, 945, 910, 660 $cm^{-1}$; $^{13}C$ NMR ($CDCl_3$, 15 MHz) $\delta$ 31.3, 32.2, 61.7, 74.8, 145.7; MS, $M^+$ calcd for $C_5H_9IO$ 211.9698, found 211.9700.

**(*E*)-1-Iodo-5-(phenylthio)-1-pentene.** To a round-bottom flask was added 35 mL of $CH_2Cl_2$ and 1.06 g (5.0 mmol) of (*E*)-1-iodo-1-penten-5-ol. The flask was placed in an ice bath, and 0.80 mL (7.0 mmol) of PhSCN was added. Slowly over the next 10 min, 1.74 (7.0 mmol) of tributylphosphine was syringed into the solution. The mixture was left at 0 °C for 10 additional min and then brought to room temperature. After 1 h the solution was poured into a separatory funnel and extracted with 3 N NaOH (1 × 15 mL). The organic layer was collected, washed with water (1 × 15 mL), washed with brine (1 × 15 mL), dried ($Na_2SO_4$), and evaporated. The sample was passed through a column of silica gel by using 30% ether/hexane as eluant. The first band was collected. The solvent was evaporated, and the remaining liquid was Kugelrohr distilled at 0.03 mm and 100–115 °C to give 1.27 g (84% yield) of sulfide: $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 1.75 (m, 2 H), 2.21 (dq, $J = 1, 7$ Hz, 2 H), 2.92 (t, $J = 7$ Hz, 2 H), 6.03 (dt, $J = 14.5$, 1 Hz, 1 H), 6.49 (dt, $J = 14.5, 7$ Hz, 1 H), 7.12–7.4 (m, 5 H); IR 3040, 2920, 2860, 1605, 1585, 1480, 1440, 1220, 1095, 1030, 950, 740, 690 $cm^{-1}$; MS, $M^+$ calcd for $C_{11}H_{13}IS$ 303.9782, found 303.9783.

**(*E*)-1-Iodo-5-(phenylsulfonyl)-1-pentene (33).** To a 100-mL, three-necked flask, equipped with an overhead mechanical stirrer and a pressure equalizing funnel, was added 4.61 g (15.0 mmol) of (*E*)-1-iodo-5-(phenylthio)-1-pentene and 30 mL of $CH_2Cl_2$. The flask was immersed in a cold bath at −35 °C and 6.9 g (34 mmol, 85% pure by weight) of MCPBA in 60 mL of $CH_2Cl_2$ was added dropwise to the sulfide over a 30-min period. The mixture, which now contained a white solid, was stirred for 2 h at −35 °C and then warmed to 0 °C. The reaction mixture was poured into a separatory funnel containing 3 N NaOH (15 mL). The organic layer was washed with additional 3 N NaOH (2 × 15 mL), and then the combined NaOH washings were extracted with $CH_2Cl_2$ (1 × 25 mL). The organic layers were combined, washed with water (1 × 20 mL), washed with brine (1 × 25 mL), dried ($Na_2SO_4$), and evaporated. The resulting orange oil was dissolved in methanol and cooled to cause crystallization. The white crystals were recrystallized from methanol to yield 3.74 g (73% yield) of sulfone **33**: mp 44.5–46 °C; $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 1.80 (m, 2 H), 2.14 (q, $J = 7$ Hz, 2 H), 3.06 (t, $J = 8$ Hz, 2 H), 6.03 (d, $J = 14.5$ Hz, 1 H), 6.36 (dt, $J = 14.5, 7$ Hz, 1 H), 7.5–8.0 (m, 5 H); IR (KBr) 2920, 2890, 1610, 1580, 1470, 1440, 1400, 1310, 1285, 1220, 1190, 1140, 1075, 940, 785, 745, 730, 685 $cm^{-1}$; $^{13}C$ NMR ($CDCl_3$, 15 MHz) $\delta$ 21.5, 34.1, 55.1, 76.3, 127.5, 128.9, 133.3, 139.1, 143.5; MS, $M^+$ calcd for $C_{11}H_{13}IO_2S$ 335.9680, found 335.9684. Anal. Calcd for $C_{11}H_{13}IO_2S$: C, 39.30; H, 3.90. Found: C, 39.24; H, 3.77.

**(*E*)-1-Iodo-7-methyl-6-(phenyldimethylsiloxy)-1,5,7-octatriene (34).** To a 100-mL, round-bottom flask was added 2.35 g (7.0 mmol) of sulfone **33** and 50 mL of THF. The flask was placed in a −78 °C cold bath, and 6.7 mL (7.0 mmol, 1.04 M in THF/hexane) of lithium diisopropylamide was syringed in. The solution was left at −78 °C for 20 min, and then 1.4 mL (7.1 mmol) of silyl ketone **13** as a solution in 25 mL of THF was added via cannula. The solution was kept at −78 °C for 1 h and then brought to 0 °C. Several milliliters of $NEt_3$ were added to prevent hydrolysis and then saturated $NaHCO_3$ to quench the reaction. The organic layer was washed with brine (1 × 10 mL), dried ($Na_2SO_4$), and evaporated. The remaining yellow oil was rapidly passed through a 1 in. × 3 in. column of silica gel by using pentane as eluant. Evaporation of the pentane gave a 2.19 g (79% yield) of enol silyl ether **34** free from impurities as a 75:25 mixture of isomers: $^1H$ NMR of both isomers ($CDCl_3$, 200 MHz) $\delta$ 0.45 (s, 6 H), 1.86 (s, 3 H), 1.91–2.08 (m, 2 H), 2.09–2.21 (m, 2 H), 4.67 (t, $J = 7$ Hz), 4.89 (s), 5.09 (t, $J = 1.5$ Hz), 5.19 (s, all four previous peaks, 3 H), 5.90 (dt, $J = 14.5$, 1.0 Hz, 1 H), 5.41 (dt, $J = 14.5, 7$ Hz, 1 H), 7.35–7.68 (m, 5 H); IR 2955, 2915, 1645, 1610, 1435, 1225, 1140, 1120, 945, 865, 830, 785, 735, 700 $cm^{-1}$; MS, $M^+$ calcd for $C_{17}H_{23}IOSi$ 398.0559, found 398.0564.

**6-(*tert*-Butyldimethylsiloxy)-8a-methyl-7-(1-methylethylidene)-3,4,4a,7,8,8a-hexadhydro-1(2*H*)-naphthalenone (29b).** To a flask containing 5 mL of ether at −78 °C was added 0.61 mL (1.0 mmol, 1.65 M in hexane) of *n*-BuLi. This was followed by rapid addition of 0.32 mL (1.0 mmol) of vinyl iodide **34** via cannula as a solution in 3 mL of ether. The solution was allowed to stir for 20 min, and then 0.21 mL (1.0 mmol) of silyl ketone **11b**, X = Cl, was added. After 1 h the mixture was warmed to −20 °C, several milliliters of $NEt_3$ were added to prevent hydrolysis, and saturated $NaHCO_3$ was added to quench the reaction. The mixture was transferred to a separatory funnel, and the organic layer was washed with brine (1 × 10 mL), dried ($Na_2SO_4$), and evaporated. The resulting oily liquid was placed under vacuum (0.1 mmHg) to remove any residual volatile impurities.

The crude mixture from above was dissolved in 10 mL of THF and cooled to −78 °C. To the solution was added 0.71 mL (1.2 mmol, 1.69 M in ether) of methyllithium. After 15 min, the flask was immersed in an ice bath for 15 min and poured into 10 mL of a stirred methanol/water/$NH_4Cl$ solution. The organic layer was washed with brine (1 × 10 mL), dried ($Na_2SO_4$), and evaporated. The oily liquid obtained was placed under vacuum (0.1 mmHg) to remove volatile impurities.

The oil from above was dissolved in 40 mL of $CH_2Cl_2$ and cooled to −78 °C. Diethylaluminum chloride (1.2 mmol, 25% by weight in toluene) was added causing an immediate color change to deep red. The solution was left at −78 °C for 5 min, and then the flask was placed in an ice bath for 1 h. Several milliliters of $NEt_3$ was added, to prevent hydrolysis, and saturated $NaHCO_3$ was added to quench the reaction. The mixture was poured into a separatory funnel, and the layers were separated. The aqueous phase was extracted with $CH_2Cl_2$ (3 × 15 mL), and the organic layers were combined. The organic layer was dried ($Na_2SO_4$) and evaporated. Preparative TLC on a chromatotron with 10% ether/pentane, collecting the second band to elute, gave 0.170 g (51% yield from **34**) of cyclic ketone **29b** as a 2:1 mixture of isomers: $^1H$ NMR of both isomers ($CDCl_3$, 270 MHz) $\delta$ 0.10, 0.12, 0.15 (3 s, 6 H), 0.8–2.8 (m, 27 H including singlets at 0.90, 0.92, 1.73, 1.76, 1.98, 2.03), 4.56, 4.68 (2 d, $J = 2$ Hz, $J = 3.5$ Hz, 1 H); IR 2940, 2920, 2850, 1705, 1605, 1460, 1370, 1255, 1195, 1180, 1120, 885, 840, 780 $cm^{-1}$; MS, $M^+$ calcd for $C_{21}H_{34}O_2Si$ 334.2319, found 334.2328.

Careful examination of the angular methyl singlets at $\delta$ 0.90 (major) and $\delta$ 0.92 (minor) showed peak widths at half height of 1.5 and 2.2 Hz, compared to $Me_4Si$ 1.3 Hz. The major isomer thus has cis ring fusion.

**2-(*tert*-Butyldimethylsiloxy)-4a-methyl-3-(1-methylethylidene)-5-methylene-3,4,4a,5,6,7,8,8a-octahydronaphthalene (36b).** To a round-bottom flask was added 7 mL of THF and 0.601 g (9.2 mmol) of zinc dust. The flask was placed in a −40 °C bath while 0.22 mL (3.1 mmol) of $CH_2Br_2$ was syringed in. $TiCl_4$ (0.24 mL, 2.2 mmol) was very slowly (CAUTION: very vigorous reaction) added over a 10-min period. The solution was stirred for 10 min and then placed in a 5 °C bath for 3 days. The entire solution was transferred via cannula to a flask containing a room temperature solution of 0.174 g (0.52 mmol) of ketone **29b** in 15 mL of $CH_2Cl_2$. The mixture was stirred at room temperature for 45 min, several milliliters of $NEt_3$ were added to prevent hydrolysis, and saturated $NaHCO_3$ was added. The organic layer was washed with brine (1 × 15

mL), dried ($Na_2SO_4$), and evaporated. The remaining liquid was purified by preparative TLC on a chromatotron with 10% ether/pentane; the first band to elute was collected. This gave 0.162 g (94% yield) of olefin **36b** as a 2:1 mixture of isomers after evaporation of the solvent: $^1H$ NMR of both isomers ($CDCl_3$, 200 MHz) $\delta$ 0.10, 0.15 (2 s, 6 H), 0.89, 0.95, 1.10 (3 s, 12 H), 1.18–2.65 (m, 15 H), 4.52–4.72 (m, 3 H); IR 2920, 2840, 1640, 1605, 1460, 1445, 1370, 1250, 1200, 1190, 1120, 1060, 890, 840, 790 $cm^{-1}$; MS, $M^+$ calcd for $C_{21}H_{36}OSi$ 332.2526, found 332.2553.

**4a-Methyl-3-(1-methylethylidene)-5-methylene-1-(phenylseleno)-1,4,4a,5,6,7,8,8a-octahydro-2(3*H*)-naphthalenone.** To a round-bottom flask was added 0.362 g (1.1 mmol) of enol silyl ether **36b**. The silyl ether was dissolved in 25 mL of $CH_2Cl_2$, 0.11 mL (1.3 mmol) of pyridine were added, and the flask was placed in a −78 °C cold bath. Slowly added to this solution was 0.214 g (1.12 mmol) of benzeneselenenyl chloride[47] as a −78 °C solution in 10 mL of $CH_2Cl_2$. The total time of addition was 25 min. After the addition was complete, the mixture was left at −78 °C for 5 min and poured into a separatory funnel containing saturated $NaHCO_3$ (20 mL). The organic layer was extracted with brine (1 × 10 mL), dried ($Na_2SO_4$), and evaporated. The remaining yellow liquid was purified by preparative TLC on a chromatotron by using 20% ether/pentane; the second band to elute was collected. Evaporation gave 0.339 g (83% yield) of seleno ketone as a mixture of isomers: $^1H$ NMR of all isomers ($CDCl_3$, 200 MHz) $\delta$ 0.98, 1.21 (2 s, 3 H), 1.51–2.82 (m, 15 H), 2.30, 2.48 (2 d, $J$ = 9.5, 6 Hz, 1 H), 4.52, 4.67, 4.73, 4.79 (4 s, 2 H), 7.22–7.64 (m, 5 H); IR ($CCl_4$) 3085, 3055, 2925, 2860, 1685, 1645, 1620, 1590, 1485, 1450, 1380, 1295, 1225, 1125, 1075, 1035, 910 $cm^{-1}$; MS, $M^+$ calcd for $C_{21}H_{26}OSe$ 374.1142, found 374.1137.

**4a-Methyl-3-(1-methylethylidene)-5-methylene-4,4a,5,6,7,8-hexahydro-2(3*H*)-naphthalenone (37).** The seleno ketone prepared above (0.339 g, 0.91 mmol) was dissolved in 10 mL of $CH_2Cl_2$ and cooled to −78 °C, and 0.181 g (1.05 mmol, 85% by weight) of MCPBA was added as a solution in 10 mL of $CH_2Cl_2$. The solution was left at −78 °C for 1 h during which time a white solid formed. Diethylamine (0.23 mL, 2.2 mmol) was syringed in causing the solid to dissolve. After 45 min the flask was gradually warmed to room temperature over 45 min. The solution was then poured into a separatory funnel containing saturated $NaHCO_3$ (10 mL). The organic layer was washed with brine (1 × 10 mL), dried ($Na_2SO_4$), and evaporated. The yellow liquid was purified by preparative TLC on a chromatotron by using 20% ether/pentane; the second band to elute was collected. Evaporation of the solvent gave 0.189 g (96% yield) of white solid **37** which could be recrystallized from pentane: mp 69.8–70.8 °C; $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 1.21 (s, 3 H), 1.30–1.57 (m, 1 H), 1.80–2.00 (m with s, 4 H), 2.09 (s, 3 H), 2.21–2.60 (m, 5 H), 2.89 (d, $J$ = 13.5 Hz, 1 H), 4.77 (s, 1 H), 4.80 (s, 1 H), 5.70 (d, $J$ = 2 Hz, 1 H); IR ($CCl_4$) 2930, 2860, 1675, 1635, 1305, 1235, 1100, 900 $cm^{-1}$; $^{13}C$ NMR ($CDCl_3$, 15 MHz) $\delta$ 22.3, 22.7, 24.7, 26,9, 32.3, 32.9, 39.6, 44.0, 107.4, 126.3, 127.9, 142.9, 153.9, 166,2, 190.7; MS, $M^+$ calcd for $C_{15}H_{20}O$ 216.1509, found 216.1542.

**4a,5-Dimethyl-3-(1-methylethylidene)-4,4a,5,6,7,8-hexahydro-2-(3*H*)-naphthalenone (Dehydrofukinone) (*cis*-31).** To a round-bottom flask containing 0.210 g (0.97 mmol) of enone **37** was added 0.148 g (0.16 mmol) of $(Ph_3P)_3RhCl$ and 15 mL of benzene. The flask was attached to an atmospheric hydrogenation apparatus and hydrogenated for 8 h. The mixture was then passed through a 1 in. × 6 in. silica gel column by using 100 mL of 10% ether/pentane. The solvent was evaporated, and the resulting oil was purified by preparative TLC on a chromatotron; the first band to elute was collected. Evaporation gave 0.197 g (93% yield) of a 2:1 mixture of *cis*- and *trans*-*31*. The two isomers were separated by HPLC by using 2% ethyl acetate/hexane (flow rate = 4 mL/min, retention times = 8 min, trans; 9 min, cis). Dehydrofukinone (*cis*-**31**):[33a] $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 0.87–0.93 (m with s, 6 H), 1.28–2.32, 1.76, 2.01 (m with 2 s, 14 H), 2.80 (d, $J$ = 13 Hz, 1 H), 5.66 (s, 1 H); IR 2945, 2885, 1675, 1640, 1470, 1450, 1385, 1305, 1235, 1210, 1120, 1050, 900, 865, 655 $cm^{-1}$; $^{13}C$ NMR ($CDCl_3$, 15 MHz) $\delta$ 15.5, 16.1, 22.1, 22.6, 26.6, 30.6, 32.5, 41.0, 41.8, 42.5, 125.9, 127.9, 141.7, 168.0, 191.5; MS, $M^+$ calcd for $C_{15}H_{22}O$ 218.1665, found 218.1671.

*Trans*-**31**: $^1H$ NMR ($CDCl_3$, 200 MHz) $\delta$ 0.90 (d, $J$ = 8 Hz, 3 H), 1.15 (s, 3 H), 2.32–2.36, 1.77, 2.03 (m with 2 s, 14 H), 2.50 (d, $J$ = 14 Hz, 1 H), 5.77 (d, $J$ = 2 Hz, 1 H); $^{13}C$ NMR ($CDCl_3$, 15 MHz) $\delta$ 16.5, 20.9, 22.3, 22.7, 24.3, 28.8, 31.1, 38.7, 39.6, 42.1, 128.0, 128.7, 141.8, 166.7, 191.4.

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**Registry No.** **5a**, 61157-31-1; **6a**, 30608-90-3; **7b**, 80594-32-7; **8b**, 83578-67-0; **10b** (X = Br), 86486-64-8; **10b** (X = Cl), 104376-41-2; **11a** (X = Br), 80594-37-2; **11b** (X = Cl), 86486-68-2; **12b** ($R^2$ = $CH_3$), 80594-40-7; **13**, 93782-78-6; **14**, 104376-40-1; (*E*)-**15**, 104376-26-3; (*Z*)-**15**, 104376-27-4; **16**, 104376-28-5; **18a**, 104376-29-6; **18b**, 104376-30-9; **19a**, 104376-32-1; **19b**, 104376-31-0; (*E*)-**23** (X = Cl), 104376-18-3; (*E*)-**23** (X = Br), 104393-19-3; (*E*)-**23** (X = I), 104376-19-4; (*E*)-**23** (Y = SePh), 104376-20-7; (*Z*)-**23** (X = Cl), 104376-21-8; (*Z*)-**23** (X = Br), 104376-22-9; (*Z*)-**23** (X = SePh), 104376-23-0; (*Z*)-**23** (X = I), 104376-47-8; (*E*)-**25**, 104376-33-2; (*Z*)-**25**, 104376-34-3; (*E*)-**26**, 104376-42-3; (*Z*)-**26**, 104376-43-4; **28b**, 93782-87-7; *cis*-**29b**, 93782-82-2; *trans*-**29b**, 93782-83-3; *cis*-**30b**, 93782-88-8; *trans*-**30b**, 93782-89-9; *cis*-**31**, 93861-15-5; *trans*-**31**, 93861-16-6; **32**, 72656-93-0; **33**, 93782-77-5; **34**, 104376-44-5; **35b**, 93782-80-0; *cis*-**36b**, 104376-45-6; *trans*-**36b**, 104376-46-7; **37**, 93782-84-4; **38b**, 104376-16-1; **39** (isomer 1), 104376-38-7; **39** (isomer 2), 104376-39-8; **40**, 93782-90-2; **42**, 93782-92-4; **43**, 104376-37-6; **43**-ol, 104376-36-5; $LiC{\equiv}C(CH_2)_3CH_3$, 17689-03-1; $LiC{\equiv}C(CH_2)_2CH_3$, 18643-50-0; $LiC{\equiv}CPh$, 4440-01-1; $LiC{\equiv}C(CH_2)_2I$, 104375-93-1; $LiC{\equiv}C(CH_2)_4I$, 104375-94-2; $LiC{\equiv}CSi(CH_3)_3$, 54655-07-1; (*Z*)-LiCH=CHOEt, 64724-28-3; LiCH=$CH_2$, 917-57-7; (*E*)-LiCH=$CH(CH_2)_2CH_3$, 76814-24-9; (*E*)-LiCH=$CHCH_2$, 104375-96-4; (*E*,*E*)-LiCH=$C(CH_3)CH_2CH_2CH=C(CH=CH_2)OSiMe_3$, 104375-97-5; $CH_3(CH_2)_3C(CH_3)=C=C(CH_2CH_2Ph)OSiMe_3$, 73341-04-5; $(CH_3CH_2)_2C=C=C(CH_2CH_2Ph)(OSiMe_3)$, 104375-98-6; (*E*)-$PhCH_2CH_2COCH=C(CH_2CH_3)CH_2CH_2CH_3$, 104375-99-7; $PhCH_2CH_2C(Si(CH_3)_3)=C=C(Ph)CH_3$, 104375-00-3; Ph-$(CH_2)_2COCH=C(CH_3)Ph$, 90729-70-7; $Ph(CH_2)_2C(OSiMe_3)=C=CH(CH_2)_2CH_3$, 73341-06-7; (*E*)-$PhCH_2CH_2COCH=CH(CH_2)_2CH_3$, 104376-01-4; $Ph(CH_2)_2C(OSi(CH_3)_3)=C=\overbrace{CCH_2CH_2}$, 104376-02-5; $Ph(CH_2)_2COCH_2(CH_3O)\overbrace{CCH_2CH_2}$, 104376-03-6; $Ph(CH_2)_2C(OSiMe_3)=C=\overbrace{CCH_2CH_2CH_2CH_2}$, 104376-04-7; Ph-$(CH_2)_2COCH=\overbrace{C(CH_2)_3CH_2}$, 104376-05-8; $CH_3CH_2C(OSiMe_3)=C=CHPh$, 104376-07-0; $CH_3CH_2C(OSiMe_3)=C=C(CH_3)CH_2CH_2CH_3$, 104376-08-1; $CH_3CH_2C(OSiMe_3)=C=C(CH_3)SiMe_3$, 104376-09-2; $CH_3CH_2C(OSiMe_3)=C=C(SMe)CH_2CH_2CH_3$, 104393-16-0; $CH_3CH_2C(OSiMe_3)=C=C(CHO)CH_2CH_2CH_3$, 104376-10-5; $CH_2=CHC(OSiMe_2Bu\text{-}t)=C=\overbrace{CCH_2CH_2}$, 104393-17-1; $(CH_3)_2C=C=C(OSiMe_2Bu\text{-}t)CH=CHOEt$, 80612-22-2; $CH_2=CHC(OSiMe_2Bu\text{-}t)=C=CHCH_3$, 104376-11-6; (*E*)-$CH_3CH_2CH_2CH=CHC(OSiMe_2Bu\text{-}t)=C=CHCH_3$, 104376-12-7; $Me_3SiOC(CH_3)=C=C(CH_3)_2$, 86486-78-4; (*t*-$BuMe_2SiO)C(CH_3)=C=C(CH_3)_2$, 104376-14-9; $CH_2=CHC(OSiMe_3)=C=C(CH_3)_2$, 104376-15-0; $CH_2=CHC(OSiMe_2Bu\text{-}t)=C=C(CH_3)_2$, 80612-21-1; $CH_3(CH_2)_2CH=CHC(OSiMe_2Bu\text{-}t)=C=C(CH_3)_2$, 104393-18-2; (*E*)-$CH_3CH=CHC(OSiMe_3)=C=CH(CH_2)_4OSiMe_3$, 104376-17-2; $CH_3CH_2CH_2CH=CHB(OH)_2$, 104376-24-1; (*E*)-$CH_3CH_2CH_2CH=CHI$, 66703-03-5; $(CH_3)_2C=CBrCOSiMe_2Bu\text{-}t$, 80594-38-3; (*E*)-$CH_2=C(CH_3)CO(CH_2)_3CH=CHC(OSiMe_2Bu\text{-}t)=C=C(CH_3)_2$, 93782-81-1; (*Z*)-$PhCH_2CH_2COCH=C(CH_2CH_3)CH_2CH_2CH_3$, 104376-50-3; (*Z*)-$PhCH_2CH_2COCH=C(CH_3)Ph$, 90729-71-8; (*Z*,*E*)-LiCH=$C(CH_3)CH_2CH_2CH=C(CH=CH_2)OSiMe_3$, 104376-52-5; $(Z,E)$-$(CH_3)_2C=C=C(OSiMe_2Bu\text{-}t)CH=C(CH_3)CH_2CH_2CH=C(OSiMe_3)CH=CH_2$, 104376-53-6; MeI, 74-88-4; EtI, 75-03-6; $Me_2S_2$, 624-92-0; PhCHO, 100-52-7; propionaldehyde, 123-38-6; methacrolein, 78-85-3; methyllithium, 917-54-4; 1-pentyne, 627-19-0; 5-hexyn-1-ol, 928-90-5; furfural, 98-01-1; 4-pentyn-1-ol, 5390-04-5; dihydropyran, 110-87-2; DMF, 68-12-2; 2-ethyl-1,3-dithiolane, 6008-80-6; 2-ethyl-2-trimethylsilyl-1,3-dithiolane, 104375-90-8; 2-phenethyl-1,3-dithiolane, 14505-46-5; 2-phenethyl-2-trimethylsilyl-1,3-dithiolane, 104375-91-9; 1-(*tert*-butyldimethylsilyl)-1-(1-ethoxyethyloxy)-3-methyl-1,2-butadiene, 86486-56-8; 2-methyl-1-(phenyldimethylsilyl)-2-pyren-1-ol, 104375-92-0; 2-methyl-3-lithiofuran, 104375-95-3; 5-lithio-3,4-dihydro-2*H*-pyran, 72081-15-3; 4-phenyl-1-cyclopentenyl-2-butanone, 104376-06-9; 3-methyl-4-[(*tert*-butyldimethylsilyl)-1,2-butadienyl]oxirane, 104376-13-8; 6-trimethylstannyl-3,4-dihydro-2*H*-pyran, 104376-25-2; (*E*)-6-iodo-5-methylhex-5-enal, 104376-35-4; (*E*)-1-iodo-1-penten-5-ol, 93782-93-5; (*E*)-1-iodo-5-(phenylthiol-1-pentene)-4a-methyl-3-(1-methylethylidene)-5-methylene-1-(phenylseleno)-1,4,4a,5,6,7,8,8a-octahydro-2(3*H*)-naphthalene, 104376-49-0; 1,5-diphenyl-3-methoxy-3-trimethylsilyl-1-pentyne, 104376-51-4.

**Supplementary Material Available:** Experimental details for the compounds **14–21**, **25**; Table I, entries 2, 3, 6, 7, 9, 11, and 12; Table II, entries 2, 6, 7, and 11; and Table III, entries X = Cl, Br, and SePh; also the synthesis of **32** (compounds **28b**, **30b**, **32**, **38b**, **39**, **40**, **41**, **42**, **43**) (20 pages). Ordering information can be found on any current masthead page.

(47) Reich, H. J.; Cohen, M. L.; Clark, P. S. *Org. Synth.* **1979**, *59*, 141.