observing the effects of the reagent on the chemical shifts of the 6-methyl groups.

For *anti*-6-methyl-*endo*-2-bicyclo[3.1.0]hexanol (3): NMR (CCl_4) δ 0.8–2.0 (m, 7 H), 1.0 (br s, 3 H, CH_3), 3.2 (s, 1 H, OH), 4.5 (m, 1 H, CHOH).

For *syn*-6-methyl-*endo*-2-bicyclo[3.1.0]hexanol (4): NMR (CCl_4) δ 0.7–2.4 (m, 7 H), 1.2 (d, J = 7 Hz, 3 H, CH_3), 3.3 (s, 1 H, OH), 4.8 (m, 1 H, CHOH).

Reaction of Allyl Alcohol with Ethylidene Iodide. The reaction of allyl alcohol with ethylidene iodide and zinc dust–cuprous chloride in ether described in Table II was carried out in a similar manner to that described above for cyclopenten-3-ol. The stereoisomeric (2-methylcyclopropyl)methanol products obtained in a 52% distilled yield were present in a trans/cis (anti/syn) ratio of 74:26; bp 77–79 °C (76 mm) [lit.[3a] bp 134–135 °C (760 mm)].

A sample of the pure *cis*-(2-methylcyclopropyl)methanol was separated from the mixture on a 2-m 20% Carbowax 20M on 60/80-mesh non-acid-washed Chromosorb W column: NMR (CCl_4) δ −0.2 (q, 1 H, cyclopropyl), 0.5–1.2 (m, 3 H, cyclopropyl), 1.0 (d, J = 5 Hz, 3 H, CH_3), 2.3 (s, 1 H, OH), 3.3–3.7 (octet, AB portion of an ABX spin system, 2 H, CH_2OH).

A sample of pure *trans*-(2-methylcyclopropyl)methanol was obtained similarly: NMR (CCl_4) δ 0.01–1.0 (m, 4 H, cyclopropyl), 1.0 (d, J = 5 Hz, 3 H, CH_3), 3.3 (d, J = 7 Hz, 2 H, CH_2OH), 3.6 (s, 1 H, OH).

Reaction of *trans*-Crotyl Alcohol with Dibromomethane. By use of a procedure similar to that described above for cyclopenten-3-ol, the reaction of *trans*-crotyl alcohol with dibromomethane and zinc dust–cuprous chloride for 24 h gave *trans*-(2-methylcyclopropyl)methanol: 68% yield; bp 78–79 °C (78 mm); n^{30}_D 1.4265 [lit.[3a] bp 134–135 °C (760 mm); n^{25}_D 1.4291].

Reaction of Cycloocten-3-ol (6) with Ethylidene Iodide. The reaction of cycloocten-3-ol (6) with ethylidene iodide and zinc dust–cuprous chloride in ether described in Table II was carried out in a similar manner to that described above for cyclopenten-3-ol; bp 105–106 °C (10 mm). The two isomeric alcohol products were separated on a 2-m 10% diethylene glycol succinate on 60/80-mesh non-acid-washed Chromosorb W column. For *anti*-9-methyl-*exo*-2-bicyclo[6.1.0]nonanol (7): NMR (CCl_4) δ 0.2–2.2 (m, 13 H), 1.1 (d, J = 6 Hz, 3 H, CH_3), 2.3 (s, 1 H, OH), 3.2 (m, 1 H, CHOH). For *syn*-9-methyl-*exo*-2-bicyclo[6.1.0]nonanol (8): NMR (CCl_4) δ 0.5–2.1 (m, 13 H), 1.1 (br s, 3 H, CH_3), 1.2 (s, 1 H, OH), 3.5 (m, 1 H, CHOH).

Reactions of Cyclohexene, 1-Methylcyclohexene, and Methylenecyclohexane with Ethylidene Iodide. The reactions of these materials with zinc dust–cuprous chloride in ether reported in Table III were all carried out by following procedures similar to those employed for the reaction of cyclopenten-3-ol reported above. The crude reaction mixtures obtained after workup were examined by GLC on a 97-m SE-30 glass capillary column and then distilled.

For the cyclohexene reaction, the scale and yield were so small that no materials could be obtained by distillation. However, GLC examination revealed that approximately a 5% yield of a mixture of *syn*- and *anti*-7-methylbicyclo[4.1.0]heptanes[3a] had been obtained.

For the 1-methylcyclohexene reaction, a 13% distilled yield of a mixture of isomeric 1,7-dimethylbicyclo[4.1.0]heptanes was obtained; bp 60–75 °C (70 mm). No attempt was made to determine the product stereochemistries. A precise mass spectrometric molecular weight was determined: calcd for C_9H_{16} m/e 124.1253, found m/e 124.1255.

For the methylenecyclohexane reaction, a 31% distilled yield of cyclopropyl product was obtained as one isomer: bp 70–78 °C (77 mm); NMR (CCl_4) δ −0.2 (t, 1 H, cyclopropyl), 0.2–0.7 (m, 2 H, cyclopropyl), 0.7–2.2 (m, 10 H), 1.0 (d, J = 6 Hz, 3 H, CH_3). A precise molecular weight was determined by mass spectrometry: calcd for C_9H_{16} m/e 124.1253, found m/e 124.1246.

Acknowledgment. We acknowledge support for this work in part by a Faculty Research Grant to E.C.F. from the Committee on Research of the University of California, Davis, and in part by an Earl C. Anthony Grant to G.B.

Registry No. 1, 3212-60-0; 2, 822-58-2; 3, 80865-50-5; 4, 80865-51-6; 5, 107-18-6; 6, 3212-75-7; 7, 62929-18-4; 8, 62861-98-7; ethylidene iodide, 594-02-5; *cis*-(2-methylcycloproply)methanol, 21003-35-0; *trans*-(2-methylcyclopropyl)methanol, 21003-36-1; *trans*-crotyl alcohol, 504-61-0; dibromomethane, 74-95-3; cyclohexene, 110-83-8; 1-methylcyclohexene, 591-49-1; methylenecyclohexane, 1192-37-6; *syn*-7-methylbicyclo[4.1.0]heptane, 14135-43-4; *anti*-7-methylbicyclo[4.1.0]heptane, 14222-39-0; 1,7-dimethylbicyclo[4.1.0]heptane, 80924-08-9; 1-methylspiro[2.5]octane, 41417-81-6; methylene iodide, 75-11-6; zinc, 7440-66-6; cuprous chloride, 7758-89-6.

Selenium-Stabilized Carbanions.[1] Synthesis of Enals and Silyl Enones Using 1,3-Bis(phenylseleno)propene

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The utility of 1,3-bis(phenylseleno)propene (4) as a propenone synthon having n_3 (1) or n_1 and n_3 (3) reactivity has been examined. Deprotonation of 4 with lithium diisopropylamide in THF at −78 °C proceeds to give a lithium reagent which reacts smoothly with alkyl halides (isopentyl bromide, 2-bromobutane), epoxides (propylene oxide, cyclohexene oxide), carbonyl compounds (isobutyraldehyde, acetone, 4-*tert*-butylcyclohexanone, 3-pentanone), and trimethylsilyl chloride. The products are smoothly converted to 3-substituted propenal derivatives in 71–88% yield by oxidation with 4 equiv of hydrogen peroxide in dichloromethane. The reaction product with acetone has also been converted to 1-(phenylseleno)-4-methyl-1,3-pentadiene by reductive elimination of the groups PhSeOH. Deprotonation of 3-(trimethylsilyl)-1,3-bis(phenylseleno)propene with lithium diethylamide gives a reagent which can be alkylated (2-bromopropane, 2-bromobutane, 2-methyl-1-bromopropane) and hydroxyalkylated (acetone) with good regioselectivity. Oxidation of these products (7) with peracetic acid gives 3-substituted 1-(trimethylsilyl)propenones (8, vinyl silyl ketones). The anions prepared from 4 and 6 show exceptional nucleophilicity compared to other synthetically equivalent reagents, and the unmasking of the propenone moiety can be accomplished under unusually mild conditions.

A number of reagents for umpolung of the normal reactivity of the propenone moiety such that C-3 has nucleophilic character (n_3 reactivity,[3] 1) have been developed.[4] These include the lithium reagent from metalation of

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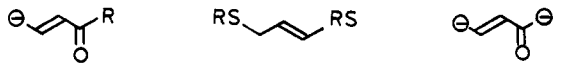
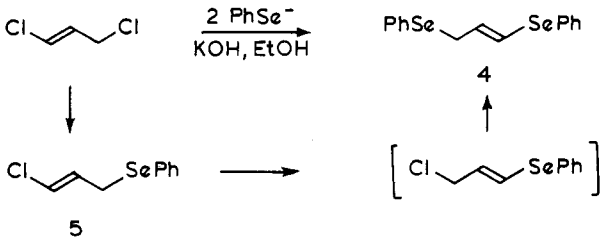
1,3-bis(methylthio)propene (**2a**) introduced by Corey et al.[4a] and the copper reagent prepared from it,[4b] as well as a number of heterosubstituted allyl-,[1a,4c,d,e] allenyl-,[4f-h] and propargyllithium[1b] reagents. We have been particularly



1 2a R = CH_3 b R = Ph 3

interested in reagents of this type exhibiting both n_1 and n_3 reactivity (**3**), since these could permit the preparation of silyl enones which we required for our studies of synthetic applications of the Brook rearrangement.[1c,d,k] The dianions prepared from propargyl phenyl selenide[1b] and 3-phenyl-1-methoxypropadiene[4e] have been used in this way, but there are serious limitations to their general applicability.

We report here our work on the preparation of 1,3-bis(phenylseleno)propene (**4**) and its utilization as a synthetic equivalent for **1** (R = H, $SiMe_3$). The lithium reagent

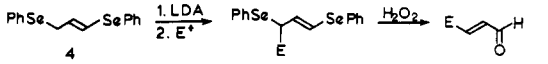


5

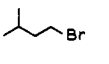
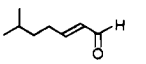
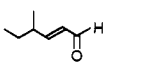
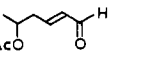
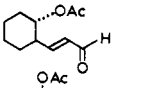
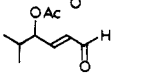
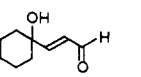
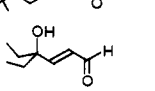
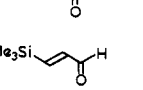
prepared from compound **4** shares the extraordinary nucleophilicity of the one prepared from **2a**, but the oxidative unmasking conditions are different from and milder than for any of the other β-acylvinyl anions (**1**) reported.

Our one-pot synthesis of **4** involves treatment of commercially available 1,3-dichloropropene with benzeneselenolate under strongly basic conditions. This transformation proceeds by S_N2 displacement to give 1-chloro-3-(phenylseleno)propene (**5**, which can be isolated if desired),[5] followed by base-catalyzed 1,3-proton transfer and a second displacement. This same procedure also provides an effective route to the sulfur analogue **2b**.[6]

Table I. Preparation of α,β-Unsaturated Aldehydes with 1,3-Bis(phenylseleno)propene (4)

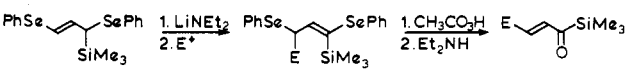


4

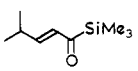
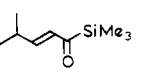
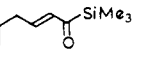
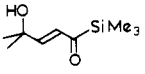
electrophile	product	% yield
		75
		76
		71[a]
		78[a]
		88[a]
		76[b]
		77
		75

[a] The crude reaction mixture after treatment of the lithium reagent with the electrophile was quenched with acetic anhydride. [b] A 62:38 ratio of axial/equatorial alcohols was formed.

Table II. Preparation of Silyl Enones



6 7 8

electrophile	product	% yield[a]
		75
		68
		65
		60

[a] Yields are overall based on 6 → 7 → 8.

Selenide **4** is rapidly deprotonated at −78 °C with lithium diisopropylamide (LDA) in THF, and the anion can be alkylated with primary or secondary halides and epoxides and reacts smoothly with aldehydes, ketones, and chlorosilanes. The single example of addition to an enone studied (4-phenyl-3-buten-2-one) gave a 2.8/1 ratio of 1,2- to 1,4-addition.

Unmasking can be accomplished by simply oxidizing with **4** equiv of 30% hydrogen peroxide (excess oxidant should be avoided). This reaction probably involves [2,3] sigmatropic rearrangement of the allylic selenoxide, followed by a hydrolysis step.[7] No β-hydroxy aldehydes have

(1) For previous papers in this series, see (a) Reich, H. J. *J. Org. Chem.* **1975**, *40*, 2750. (b) Reich, H. J.; Shah, S. K.; Gold, P. M.; Olson, R. E. *J. Am. Chem. Soc.* **1981**, *103*, 3112. (c) Reich, H. J.; Rusek, J. J.; Olson, R. E. *Ibid.* **1979**, *101*, 2225. (d) Reich, H. J.; Olson, R. E.; Clark, M. C. *Ibid.* **1980**, *102*, 1423. Reich, H. J.; Olson, R. E., unpublished results. (e) Reich, H. J.; Cohen, M. L.; Clark, P. S. *Org. Synth.* **1979**, *59*, 141. (f) Reich, H. J.; Chow, F.; Peake, S. L. *Synthesis* **1978**, 299. (g) Reich, H. J.; Shah, S. K. *J. Org. Chem.* **1977**, *42*, 1773. (h) Reich, H. J.; Chow, F.; Shah, S. K. *J. Am. Chem. Soc.* **1979**, *101*, 6638. Reich, H. J.; Shah, S. K.; Chow, F. *Ibid.* **1979**, *101*, 6648. (i) Reich, H. J.; Willis, W. W., Jr.; Clark, P. D. *J. Org. Chem.* **1981**, *46*, 2775. (j) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434. (k) Reich, H. J.; Kelly, M. J. *J. Am. Chem. Soc.* **1982**, *104*, 1119.

(2) Deceased Nov 4, 1979.

(3) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 239.

(4) (a) Corey, E. J.; Erickson, B. W.; Noyori, R. *J. Am. Chem. Soc.* **1971**, *93*, 1724. (b) Oshima, K.; Yamamoto, H.; Nozaki, H. *Bull Chem. Soc. Jpn.* **1975**, *48*, 1567. (c) Nakai, T.; Shiono, H.; Okawara, M. *Tetrahedron Lett.* **1974**, 3625. Wada, M.; Nakamura, H.; Taguchi, T.; Takei, H. *Chem. Lett.* **1977**, 345. (d) Cohen, T.; Bennett, D. A.; Mura, A. J., Jr. *J. Org. Chem.* **1976**, *41*, 2506. (e) Lansbury, P. T.; Britt, R. W. *J. Am. Chem. Soc.* **1976**, *98*, 4577. (f) Leroux, Y.; Mantione, R. *Tetrahedron Lett.* **1971**, 591. *J. Organomet. Chem.* **1971**, *30*, 295. (g) Mantione, R.; Leroux, Y. *Tetrahedron Lett.* **1971**, 593; *J. Organomet. Chem.* **1971**, *31*, 5. Leroux, Y.; Roman, C. *Tetrahedron Lett.* **1973**, 2585. Corbel, B.; Paugam, J.-P.; Dreux, M.; Savignac, P. *Ibid.* **1976**, 835. Carlson, R. M.; Jones, R. W.; Hatcher, A. S. *Ibid.* **1975**, 1741. (h) Clinet, J.-C.; Linstrumelle, G. *Ibid.* **1980**, *21*, 3987. (i) Bakuzis, P.; Bakuzis, M. L. F.; Weingarten, T. F. *Ibid.* **1978**, 2371. Kondo, K.; Tunemoto, D. *Ibid.* **1975**, 1007.

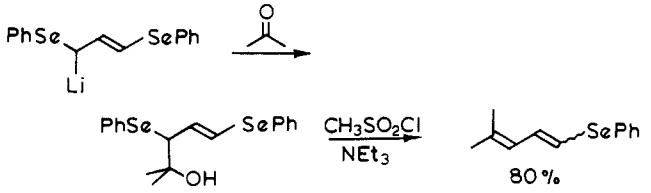
(5) Attempts to deprotonate and alkylate **5** have not been successful. This is in contrast to 3-chloro-1-(phenylseleno)-2-butene which can be metalated.[1a]

(6) Compounds **2a** and **2** (R = Et) can also be prepared, but here removal of impurities which appear to originate from impurities present in the commercial sample of 1,3-dichloropropane (75% technical, Pfalz and Bauer) is more difficult.

(7) Several γ-halo allyl sulfides[4e] and selenides[1a] react in a similar fashion when oxidized.

been observed; this rules out a double [2,3] sigmatropic shift of a possible diselenoxide intermediate. As summarized in Table I, only the trans isomer is formed.

The addition products from the reaction of [1,3-bis(phenylseleno)allyl]lithium carbonyl compounds can also be converted to dienes by reductive elimination of PhSeOH,[1h,i] as in the example below.



The trimethylsilylated derivative **6** can be deprotonated with lithium diethylamide (LDA works less well, probably for steric reasons). Other analogues of **6** having a dimethylphenylsilyl or dimethyl-*tert*-butylsilyl substituent can also be prepared but have not been successfully deprotonated. The anion formed from **6** again shows impressive nucleophilicity, reacting cleanly with 2-bromopropane and 2-bromobutane as well as acetone and other ketones (Table II) to give essentially one regioisomer. With less sterically demanding eletrophiles such as methyl iodide, a mixture of regioisomeric products is obtained. Unmasking of the silanes **7** must be carried out under carefully controlled conditions to avoid destruction of the sensitive silyl enones formed. Low-temperature oxidation with 2 equiv of peracetic acid followed by buffering with diethylamine and warmup works well in the cases shown. As for the aldehyde synthesis discussed earlier, only the trans enones are formed. This route to silyl enones,[8] while not completely general because of regiochemical problems during the alkylation and restrictions on the size of the trialkylsilyl group, does provide a preparatively useful route to several compounds we have not been able to prepare by other routes. For example, a procedure we have used for preparation of silyl enones, using metalated 1-alkoxy-1-(trimethylsilyl)allenes[4f,h] as synthetic equivalents of **1** (R = $SiMe_3$), fails to work well for most of the cases in Table II.[1k,l]

Summary

1,3-Bis(phenylseleno)propene (**4**) can be easily prepared and metalated. Reaction with electrophiles followed by oxidation to selenoxide results in transformation to β-substituted α,β-unsaturated aldehydes. A similar reaction sequence with 1-(trimethylsilyl)-1,3-bis(phenylseleno)-propene (**6**) gives β-substituted α,β-unsaturated silyl ketones (**8**).

Experimental Section

General Procedures. Nuclear magnetic resonance (NMR) spectra were obtained on a JEOL MH-100, Varian FX-60, or Brucker WH-270 spectrometer. Chemical shifts are reported in δ units, parts per million relative to either tetramethylsilane, methylene chloride (δ 5.32), or chloroform (δ 7.24) as internal standard. Infrared spectra were recorded on a Beckman Acculab 7 or Perkin-Elmer 267 spectrophotometer. Unless otherwise specified NMR spectra were measured on CCl_4 solutions and IR spectra of neat liquid between salt plates. Mass spectra were obtained on an AEI-MS-902 spectrometer at an ionizing voltage of 70 eV.

Starting materials were commercially available or prepared according to the literature references cited. Diphenyl diselenide was prepared according to literature procedure.[1e] *n*-Butyllithium in hexane was purchased from Foote Mineral Co. and was titrated using *n*-propanol with 1,10-phenanthroline as indicator.[12] Peracetic acid (40% in acetic acid) was purchased from FMC Corp. Diethyl ether and tetrahydrofuran (THF) were freshly distilled from sodium benzophenone ketyl. Diisopropylamine and diethylamine were distilled from potassium hydroxide and stored over 4A molecular sieves. All other reagents were used as received, unless otherwise stated. Solutions of lithium diisopropylamide (LDA), 1 M in THF, were prepared as in ref 1j and were titrated with diphenylacetic acid in THF.[13] Solutions of lithium diethylamide were prepared as needed, using 1 equiv each of diethylamine and *n*-butyllithium in 1 mL of THF/mmol. All reactions involving strong base chemistry were run under an atmosphere of dry nitrogen in oven-dried glassware.

Preparative thin-layer chromatography (preparative TLC) was carried out with Merck PF-254 silica gel, eluting with the solvents indicated. All melting points and boiling points are uncorrected; all reaction temperatures were measured externally.

Oxidation Procedures. While the oxidation of divalent organoselenium compounds with peracids at low temperatures is straightforward, oxidation with hydrogen peroxide is highly exothermic and appears to be autocatalytic (i.e., $PhSeO_2H$ is catalyst, due either to its acidity or by formation of $PhSeO_3H$[1f]). Under no circumstances should oxidations of amounts greater than 5 mmol be carried out by adding the full amount of H_2O_2 before oxidation had commenced.

1,3-Bis(phenylseleno)propene (4). Into a 250-mL, three-neck, round flask equipped with a mechanical stirring apparatus, gas inlet tube, and reflux condenser were placed Ph_2Se_2 (9.36 g, 30 mmol), sodium formaldehyde sulfoxylate[14] (Rongalite, 5.39 g, 30 mmol), and 100 mL of ethanol. This mixture was stirred and heated to 50 °C under nitrogen. Alcoholic KOH (18 mL of a 5 m solution) was slowly added. After 30–45 min, the reaction solution was colorless and 1,3-dichloropropene (2.73 mL, 30 mmol) was added followed by solid KOH (8.4 g, 150 mmol). The thick white suspension was heated to 80 °C for 24 h. The reaction vessel was cooled to 0 °C and monochloroacetic acid (1 g) was carefully added in small portions to alkylate any remaining PhSeNa. The reaction mixture was diluted with water and extracted with 1:1 ether/pentane. The organic extracts were washed with dilute HCl solution, followed by 7% $NaHCO_3$ and brine. Drying (Na_2SO_4) and solvent evaporation yielded 9.63 g (90% yield) of 1,3-bis(phenylseleno)propene as a very pale yellow liquid. Analytical TLC and NMR analysis indicated no PhSeSePh or other impurities; thus this material was used without further purification. **4**: NMR (*Z,E* mixture) δ 3.43, 3.62 (d, *J* = 6.5 Hz; d, *J* = 8 Hz, 2 H), 5.84–6.50 (m, 2 H), 7.2–7.6 (m, 10 H); IR 3050, 2990, 2900, 1940 (w), 1570, 1468, 1430, 1070, 1010, 940, 740, 685 cm^{-1}; mass spectrum, M^+ calcd for $C_{15}H_{14}Se_2$ 353.94259, found, 353.94260.

1,3-Bis(phenylthio)propene (2b). A 100-mL, three-neck, round flask fitted with a reflux condenser, magnetic stir bar, and gas inlet tube was charged with solid KOH (5.6 g, 100 mmol) and 50 mL of ethanol. Thiophenol (3.18 mL, 30 mmol) was added followed by 1,3-dichloropropene (1.37 mL, 15 mmol). This solution was stirred at reflux for 24 h, cooled, and subjected to a normal workup to afford 3.8 g of a brown liquid. Kugelrohr distillation of this liquid (bath 120 °C, 0.12 mm) gave 3.29 g (85% yield) of **2b**[4d] as a pale-yellow liquid: NMR (2:3 *E/Z* isomer ratio) δ 3.53, 3.66 (d, *J* = 7 Hz; d, *J* = 8 Hz, 2 H), 5.6–6.28 (m, 2 H), 7.05–7.40 (m, 10 H); IR 3060, 2950, 2860, 1945 (w), 1870 (w), 1800 (w), 1735 (w), 1580, 1475, 1440, 1020, 750, 690 cm^{-1}.

(*E,Z*)-1-Chloro-3-(phenylseleno)-1-propene ((*E,Z*)-γ-Chloroallyl Phenyl Selenide; 5). To a stirred suspension of

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(11) The allenyllithium reagents do not react cleanly with secondary halides, and the reaction products with ketones and aldehydes are not hydrolyzed to silyl enones in good yield (Reich, H. J.; Kelly, M. J., unpublished results).

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PhSeSePh (5.0 g, 16 mmol) in 40 mL of absolute ethanol under N_2 was added powdered $NaBH_4$ in small portions until a colorless solution was obtained. To this was added 1,3-dichloropropene (2.92 mL, 32 mmol) neat via syringe. The resulting solution was stirred for 1 h at 25 °C. Normal workup gave 7.08 g of pale-yellow liquid. Distillation (Kugelrohr, bath 75–80 °C, 0.2 mm) afforded 6.72 g (91% yield) of **5** as a colorless liquid: NMR (ca. 60:40 cis/trans mixture, $CDCl_3$) δ 3.32, 3.60 (d, J = 8 Hz; d, J = 7 Hz, 2 H), 6.00 (m, 2 H), 7.2–7.6 (m, 5 H); IR 3040, 2910, 1610, 1540, 1470, 1430, 945, 730, 680 cm^{-1}; mass spectrum, M^+ calcd for C_9H_9SeCl 231.9558, found 231.9555.

Preparation of β-Substituted α,β-Unsaturated Aldehydes from 4. The procedures below for preparation of **6** and *trans*-6-methyl-2-heptenal illustrate in detail the techniques used for the preparation and derivatization of [1,3-bis(phenylseleno)allyl]lithium and for conversion of the products to α,β-unsaturated aldehydes.

1,3-Bis(phenylseleno)-3-(trimethylsilyl)-1-propene (6). To a cooled (−78 °C) magnetically stirred solution of 1,3-bis(phenylseleno)propene (7.04 g, 20 mmol) in 10 mL of THF was added LDA (1 M, 20 mL, 20 mmol) to give a bright-red suspension. This was stirred for 5 min at −78 °C and then was treated with Me_3SiCl (2.54 mL, 20 mmol). The cold bath was replaced with an ice–water bath and the solution was stirred at 0 °C for 30 min, during which time the red color was discharged, leaving a pale-yellow color. The reaction mixture was poured into 7% aqueous $NaHCO_3$ and extracted with 1:1 ether/pentane. The combined organic extracts were washed with $NaHCO_3$, H_2O, and brine and dried (Na_2SO_4). Concentration gave 8.27 g (98% yield) of **6** as a yellow-orange oil, which solidified upon cooling to −15 °C. Inspection of the NMR spectrum showed the reaction to be complete. Analytical TLC revealed only one compound. This material was used without additional purification. **6**: NMR δ 0.34 (s, 9 H), 3.52 (dd, J = 9, 2 Hz, 1 H), 6.20 (m, 2 H), 7.2–7.6 (m, 10 H); IR 3020, 2940, 1870, 1570, 1430, 1240, 1060, 840, 730, 680 cm^{-1}; mass spectrum, M^+ calcd for $C_{18}H_{22}Se_2Si$ 425.9821, found 425.9837.

***trans*-3-(Trimethylsilyl)-2-propenal.** Crude 1,3-bis(phenylseleno)-3-(trimethylsilyl)-1-propene (0.85 g, 2 mmol; prepared as above) in 10 mL of CH_2Cl_2 was oxidized with 0.89 mL of 30% H_2O_2 by use of the procedure below. After preparative TLC (3:7 ether/pentane eluent, R_f 0.8), 195 mg of *trans*-3-(trimethylsilyl)-2-propenal[15] was isolated as a pale-yellow oil: NMR δ 0.10 (s, 9 H), 6.30 (dd, J = 19, 7.5 Hz, 1 H), 6.95 (d, J = 19 Hz, 1 H), 9.30 (d, J = 7.5 Hz, 1 H); IR 2940, 2790, 2690, 1875, 1685, 1250, 1080, 860, 840, 780 cm^{-1}.

***trans*-6-Methyl-2-heptenal.** A cold (−78 °C) THF solution of [1,3-bis(phenylseleno)allyl]lithium (5 mmol) prepared as above was treated with isoamyl bromide (0.6 mL, 5 mmol), warmed to 0 °C, and stirred for 1 h. Normal workup gave 1,3-bis(phenylseleno)-6-methyl-1-heptene as an oil (100% conversion by NMR): NMR δ 0.88 (d, J = 6 Hz, 6 H), 1.05–1.90 (m, 5 H), 3.64 (m, 1 H), 5.88 (m, 2 H), 7.0–7.6 (m, 10 H).

A solution of 2 mmol (0.85 g) of the crude selenide in 6 mL of CH_2Cl_2 was placed in a 10-mL flask equipped with a magnetic stir bar and 10-mL dropping funnel. A solution of 30% H_2O_2 (0.88 mL, 8 mmol) in 0.9 mL of H_2O was placed in the dropping funnel. Approximately 10% (by volume) of this oxidant solution was added to the vigorously stirred reaction mixture. At the first sign of reaction initiation (solution darkening, warming), the reaction flask was cooled in an ice bath, maintaining the reaction temperature between 0 °C and 10 °C, while the remainder of the oxidant solution was added dropwise over a 15-min period. The solution was stirred for an additional 15 min and then was diluted with 1:1 ether/pentane and H_2O. The organic layer was washed with 7% $NaHCO_3$ solution and the aqueous layer was extracted with ether. Combined organic layers were washed with brine and dried (Na_2SO_4). Concentration afforded 0.3 g of crude yellow oil. Kugelrohr distillation (bath 75–80 °C, aspirator vacuum) gave 0.19 g (75% yield) of *trans*-6-methyl-2-heptenal[16] as a colorless liquid. NMR analysis showed only the trans double bond isomer to be present. *trans*-6-Methyl-2-heptenal: NMR δ 0.94 (d, J = 6 Hz, 6 H), 1.15–1.80 (m, 3 H), 2.33 (dt, J = 8, 7 Hz, 2 H), 5.95 (dd, J = 19, 9 Hz, 1 H), 6.71 (dt, J = 19, 7 Hz, 1 H), 9.29 (d, J = 7 Hz, 1 H); IR 2950, 2860, 2805, 2740, 1685 (s), 1630, 1470, 1150, 980, 790, 760 cm^{-1}; mass spectrum, M^+ calcd for $C_8H_{14}O$ 126.1045, found 126.1042.

***trans*-4-Methyl-2-hexenal.** A cold (−78 °C) magnetically stirred solution of [1,3-bis(phenylseleno)allyl]lithium (2 mmol) in 4 mL of THF was treated with 2-bromobutane (2 mmol, 2.2 mL), warmed to 0 °C for 1 h, and worked up to give 0.79 g of crude 1,3-bis(phenylseleno)-4-methyl-1-hexene: NMR (*E,Z* mixture) δ 0.5–1.9 (m, 9 H), 3.65, 4.15 (m, 1 H), 5.80–6.35 (m, 2 H), 7.00–7.60 (m, 10 H).

Oxidation of this crude product with 8 mmol of H_2O_2 afforded 0.17 g (76% yield) of *trans*-4-methyl-2-hexenal as a colorless liquid after distillation (Kugelrohr, bath 65–70 °C, aspirator): NMR δ 0.99 (t, J = 8 Hz, 3 H), 1.19 (d, J = 8 Hz, 3 H), 1.60 (pentet, J = 8 Hz, 2 H), 2.40 (m, 2 H), 6.10 (dd, J = 16, 8 Hz, 1 H), 6.80 (dd, J = 16, 8 Hz, 1 H), 9.55 (d, J = 8 Hz, 1 H); IR 2960, 2905, 2860, 2800, 2740, 1682, 1625, 1455, 980, 790, 760 cm^{-1}; mass spectrum, M^+ calcd for $C_7H_{12}O$ 112.0888, found 112.0892.

***trans*-5-Acetoxy-2-hexenal.** A stirred cold (−78 °C) solution of 2 mmol of [1,3-bis(phenylseleno)allyl]lithium in 5 mL of THF was treated with propylene oxide (0.14 mL, 2 mmol) and allowed to warm to 0 °C. After 30 min, this solution was treated with 1 mL of acetic anhydride, stirred for an additional 30 min, and worked up as usual to give 0.98 g of crude 1,3-bis(phenylseleno)-5-acetoxy-1-hexene as a viscous liquid: NMR (*E,Z* mixture) δ 1.18 (d, J = 7 Hz, 3 H), 1.70–2.05 (m, 2 H), 1.90 (s, 3 H), 3.74, 4.20 (m, 1 H), 4.85 (m, 1 H), 5.70–6.33 (m, 2 H) , 7.0–7.6 (m, 10 H).

Oxidation of this crude material in 6 mL of CH_2Cl_2 with 8 mmol of H_2O_2 proceeded cleanly to afford, after preparative TLC, 0.22 g (70.5% yield) of *trans*-5-acetoxy-2-hexenal as a pale-yellow liquid. The NMR spectrum of this compound correlated with that reported:[4a] NMR δ 1.28 (d, J = 6 Hz, 3 H), 2.00 (s, 3 H), 2.60 (dd, J = 7, 6 Hz, 2 H), 5.05 (m, 1 H), 6.10 (dd, J = 16, 7 Hz, 1 H), 6.80 (dt, J = 16, 7 Hz, 1 H), 9.50 (d, J = 7 Hz, 1 H).

4-Acetoxy-5-methyl-*trans*-2-hexenal. Isobutyraldehyde (0.18 mL, 2 mmol) was added to a cold (−78 °C) solution of [1,3-bis(phenylseleno)allyl]lithium (2 mmol) in 4 mL of THF. After 30 min at −78 °C, the red anion color was discharged and acetic anhydride (1 mL) was added. After 1 h at 25 °C, the reaction was worked up as usual to afford 1.13 g of a diastereomeric mixture of 1,3-bis(phenylseleno)-4-acetoxy-5-methyl-1-hexene as a viscous yellow oil: NMR δ 0.90 (m, 6 H), 1.95 (m, 1 H), 2.05 (s, 3 H), 3.82, 4.28, (m, 1 H), 4.87 (m, 1 H), 5.80–6.42 (m, 2 H), 7.05–7.60 (m, 10 H).

Following the normal procedure, the crude selenide from above was oxidized to give, after Kugelrohr distillation (bath 50 °C, 0.8 mm), 0.30 g (88% yield) of 4-acetoxy-5-methyl-*trans*-2-hexenal as a pale-yellow liquid: NMR δ 0.91 (d, J = 7 Hz, 6 H), 1.95 (m, 1 H), 2.05 (s, 3 H), 5.23 (m, 1 H), 6.03 (ddd, J = 16, 7, 1 Hz, 1 H), 6.66 (dd, J = 16, 5 Hz, 1 H), 9.44 (d, J = 7 Hz, 1 H); IR 2980, 2920, 2870, 2810, 2720, 1740, 1685, 1630, 1460, 1440, 1370, 1320, 1240, 1130, 1040, 1020, 980 cm^{-1}.

***trans*-3-(*trans*-2-Acetoxycyclohexyl)-2-propenal.** To a cold (−78 °C) stirred solution of [1,3-bis(phenylseleno)allyl]lithium (2 mmol) in 4 mL of THF was added cyclohexene oxide (0.21 mL, 2 mmol). The solution was warmed to 0° C for 1 h and then treated with 1 mL of acetic anhydride and allowed to stir for an additional 1 h. Workup gave 1.1 g of a diastereomeric mixture of *trans*-2-[1,3-bis(phenylseleno)allyl]cyclohexyl acetate as a viscous yellow oil: NMR δ 0.90–2.20 (m, 9 H), 1.9 (s, 3 H), 3.6, 3.9 (m, 1 H), 4.45, 4.70 (m, 1 H), 5.80–6.38 (m, 2 H), 7.0–7.6 (m, 10 H).

The crude selenide from above was oxidized in 10 mL of CH_2Cl_2 with 8 mmol of H_2O_2 to afford, after preparative TLC (1:4 ether/pentane eluent, R_f 0.25), 0.305 g (78% yield) of *trans*-3-(*trans*-2-acetoxycyclohexyl)-2-propenal[4a] as a pale-yellow oil: NMR δ 1.05–2.60 (m, 9 H), 1.95 (s, 3 H), 4.64 (m, 1 H), 5.96 (dd, J = 16, 8 Hz, 1 H), 6.59 (dd, J = 16, 8 Hz, 1 H), 9.38 (d, J = 8 Hz, 1 H); IR 2930, 2820, 2790, 2720, 1740, 1680, 1630, 1440, 1360, 1230, 1150, 1090, 1030, 970 cm^{-1}.

***trans*-3-[(1-Hydroxy-4-*tert*-butyl)cyclohexyl]-2-propenal.** A solution of 4-*tert*-butylcyclohexanone (0.155 g, 1 mmol) in 2 mL of THF was added to a cold (−78 °C) stirred solution of [1,3-bis(phenylseleno)allyl]lithium (1 mmol) in 2 mL of THF. The

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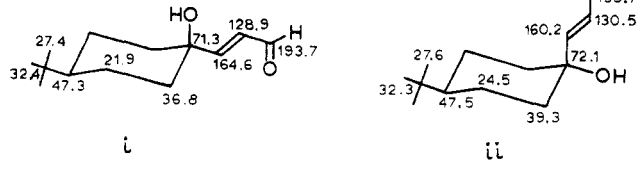
resulting light-pink solution was stirred for an additional 50 min at −78 °C and then worked up to yield 0.65 g of 1-[1,3-bis(phenylseleno)allyl]-4-*tert*-butylcyclohexanol as a yellow oil: NMR δ 0.88 (s, 9 H), 0.9–2.1 (m, 9 H), 3.93, 4.10 (d, J = 9 Hz; d, J = 8 Hz, 1 H), 5.80–6.35 (m, 2 H), 7.0–7.6 (m, 10 H).

Oxidation of this material gave after preparative TLC (3:7 ether/pentane eluent, three elutions), the two stereoisomers of the title aldehyde. The leading band at R_f 0.3–0.45 yielded 100 mg of white crystals (i): mp 72–73 °C; NMR ($CDCl_3$) δ 0.85 (s, 9 H), 0.8–1.84 (m, 9 H), 2.58 (br s, 1 H), 6.24 (dd, J = 16, 8 Hz, 1 H), 6.79 (d, J = 16 Hz, 1 H), 9.43 (d, J = 8 Hz, 1 H). The trailing band at R_f 0.15–0.28 gave 60 mg of white crystalt (ii): mp 59–60 °C; NMR ($CDCl_3$) δ 0.84 (s, 9 H), 0.8–2.0 (m, 9 H), 2.57 (br s, 1 H), 6.30 (dd, J = 16, 8 Hz, 1 H), 7.00 (d, J = 16 Hz, 1 H), 9.50 (d, J = 8 Hz, 1 H). Total yield of aldehyde was 160 mg (76% yield): IR (mull) 3320, 2720, 1687, 1365, 1150, 1130, 1065, 985 cm^{-1}; mass spectrum, M^+ calcd for $C_{13}H_{22}O_2$ 210.1620, found 210.1615.

The ^{13}C NMR spectra given for i and ii allowed assignment of structure i to the less polar compound and ii to the more polar one on the basis of the upfield shift of the axial vinyl carbon of ii.[17]



i

ii

***trans*-4-Ethyl-4-hydroxy-2-hexenal.** A 2-mmol sample of **3** was deprotonated and treated with 0.22 mL (2 mmol) of 3-pentanone as in the previous run. Workup gave crude 4,6-bis(phenylseleno)-3-ethyl-5-hexen-3-ol as a 1:1 E/Z mixture: NMR ($CDCl_3$) δ 0.88 (t, J = 7.5 Hz, 6 H), 1.72 (m, 4 H), 1.99 (br s, 1 H), 3.92, 4.42 (d, J = 10 Hz; d, J = 8.5 Hz, 1 H), 5.95–6.50 (m, 2 H), 7.2–7.6 (m, 10 H); IR 3450, 3020, 2950, 2860, 1570, 1470, 1430, 1110, 1010, 740, 685 cm^{-1}.

The sample above was oxidized as usual and purified by preparative TLC (3:7 ether/pentane eluent, R_f 0.2) to give 0.2 g (77% yield) of 4-ethyl-4-hydroxy-*trans*-2-hexenal as white crystals: mp 54–55 °C; NMR ($CDCl_3$) δ 0.85 (t, J = 7 Hz, 6 H), 1.64 (q, J = 7 Hz, 4 H), 2.84 (s, 1 H), 6.45 (dd, J = 16.5, 8 Hz, 1 H), 6.78 (d, J = 16.5 Hz, 1 H), 9.50 (d, J = 8 Hz, 1 H); IR (mull) 3400, 2770, 1680, 1460, 1120, 1050, 980 cm^{-1}; mass spectrum, M^+ calcd for $C_8H_{14}O_2$ 142.0994, found 142.0993.

1-(Phenylseleno)-4-methyl-1,3-pentadiene. To a solution of 0.54 g (1.5 mmol) of 1,3-bis(phenylseleno)propene in 5 mL of THF at −78 °C under N_2 was added 1.6 mL (1.6 mmol) of a 1.0 M LDA solution. After 5 min, 0.117 mL (1.6 mmol) of dry acetone was added. The solution was stirred for 5 min, quenched with HCl, and worked up. After solvent removal, the crude product was dissolved in a solution of 10 mL of CH_2Cl_2 and 1.05 mL (7.5 mmol) of triethylamine and cooled to 0 °C under N_2 with stirring. Methanesulfonyl chloride (0.35 mL, 4.5 mmol) was added dropwise over a 15-min period. The solution was stirred an additional 30 min at 0 °C and then 15 min at room temperature. The solution was then poured into 50 mL of ether and washed with 10% HCl, 7% $NaHCO_3$, and saturated salt. Solvent removal and TLC with pentane (r_f 0.8 after three elutions) gave 0.289 g (80%) of the desired product: NMR ($CDCl_3$; mixture of double bond isomers) δ 1.80 (m, 6 H), 5.80–7.0 (m, 3 H), 7.18–7.6 (m, 5 H); IR 3010, 2950, 1675, 1560, 1460, 1420, 1140, 1100, 1010, 960, 720 cm^{-1}; mass spectrum, M^+ calcd for $C_{12}H_{14}Se$ 238.0261, found 238.0251.

Preparation of β-Substituted α,β-Unsaturated Silyl Ketones 8 from 6. The following procedure illustrates the method used for the preparation and derivatization of [1-(trimethysilyl)-1,3-bis(phenylseleno)allyl]lithium and conversions of the products to silyl enones. Note that α,β-unsaturated silyl ketones are light-sensitive compounds and should be treated accordingly.

4-Methyl-1-(trimethylsilyl)-*trans*-2-hexen-1-one. To a cold (−78 °C) magnetically stirred solution of $LiNEt_2$ (10 mmol) in 10 mL of THF was added via syringe 1,3-bis(phenylseleno)-3-(trimethylsilyl)-1-propene (**6**, 4.24 g, 10 mmol; diluted with 5 mL of THF). The resulting deep-purple solution was stirred for 5 min and then was treated with 2-bromobutane (1.1 mL, 10 mmol). The cold bath was replaced with an ice–water bath, and after 1 h of stirring at 0 °C, the reaction was worked up as in previous alkylation runs to obtain 1,3-bis(phenylseleno)-4-methyl-1-(trimethylsilyl)-1-hexene, which was oxidized without purification: NMR δ 0.04 (s, 9 H), 0.95–2.05 (m, 9 H), 4.84 (m, 1 H), 6.65 (dd, J = 9, 3 Hz, 1 H), 7.18–7.8 (m, 10 H); mass spectrum, M^+ calcd for $C_{22}H_{30}Se_2Si$ 482.0447, found 482.0430.

The selenide obtained above was combined with 2.5 mmol of identical material which had been prepared earlier. To a cold (−78 °C) solution of 6.0 g (12.5 mmol) of 1,3-bis(phenylseleno)-4-methyl-1-(trimethylsilyl)-1-hexene in 25 mL of CH_2Cl_2 was added a solution of CH_3CO_3H (3.23 mL, 25 mmol) in 2 mL of THF. Efficient stirring of the reaction solution is required during this addition as much yellow precipitate is formed. After 15 min, diethylamine (5 mL) was added (the precipitate dissolved), the cold bath was replaced by an ice–water bath, and the flask was covered with aluminum foil to exclude light. After being stirred for 30 min at 0 °C, the reaction mixture was diluted with 1:1 ether/pentane and washed several times with cold H_2O, followed by a single wash with 7% aqueous $NaHCO_3$ and brine. The organic layer was dried (Na_2SO_4) and concentrated on a rotary evaporator to give 4.2 g of red oil. Short-path distillation (bath 30–35 °C, 0.2 mm) afforded 1.73 g (75% yield) of 4-methyl-1-(trimethylsilyl)-*trans*-2-hexen-1-one as a brilliant yellow liquid: NMR δ 0.18 (s, 9 H), 0.88 (t, J = 8 Hz, 3 H), 1.04 (d, J = 7 Hz, 3 H), 1.43 (m, 2 H), 2.22 (m, 1 H), 6.10 (d, J = 16 Hz, 1 H), 6.51 (dd, J = 16, 8 Hz, 1 H); IR 2950, 2900, 2860, 1690,1630, 1590 (s), 1460, 1250, 1185, 980, 850, 760 cm^{-1}; mass spectrum, M^+ calcd for $C_{10}H_{20}SiO$ 184.1276, found 184.1279.

4-Methyl-1-(trimethylsilyl)-*trans*-2-penten-1-one. Following the procedure given above, 4.24 g (10 mmol) of **6** in 5 mL of THF was deprotonated with $LiNEt_2$ (10 mmol) and the lithium reagent was alkylated with 0.94 mL (10 mmol) of 2-bromopropane. Normal workup gave 4.56 g of 1,3-bis(phenylseleno)-4-methyl-1-(trimethylsilyl)-1-pentene: NMR δ 0.00 (s, 9 H), 1.04 (m, 6 H), 1.85 (br m, 1 H), 4.60 (dd, J = 11, 6 Hz, 1 H), 6.56 (d, J = 11 Hz, 1 H), 7.05–7.65 (m, 10 H).

The selenide obtained was oxidized as above with a solution of 2.6 mL of CH_3CO_3H (20 mmol). After 5 mL of diethylamine was added, the reaction mixture was worked up. Solvent evaporation yielded 3.4 g of red oil. Short-path distillation (Kugelrohr, bath 27–30 °C, 0.2 mm) gave 1.17 g (68% yield) of 4-methyl-1-(trimethylsilyl)-*trans*-2-penten-1-one as a brilliant yellow liquid: NMR δ 0.20 (s, 9 H), 1.18 (d, J = 7 Hz, 6 H), 2.42 (octet, J = 7 Hz, 1 H), 6.04 (d, J = 16 Hz, 1 H), 6.59 (dd, J = 16, 7 Hz, 1 H); IR 2950, 2880, 1870, 1680, 1630, 1590 (s), 1460, 1245, 1180, 980, 850, 755 cm^{-1}; mass spectrum, M^+ calcd for $C_9H_{18}SiO$ 170.1126, found 170.1126.

4-Hydroxy-4-methyl-1-(trimethylsilyl)-*trans*-2-penten-1-one. A solution of **6** (4.24 g, 10 mmol) was deprotonated as above and treated with freshly distilled acetone (0.74 mL, 10 mmol). Workup gave 5.02 g of crude 1,3-bis(phenylseleno)-1-(trimethylsilyl)-4-hydroxy-4-methyl-1-pentene: NMR (mixture of double bond isomers) δ 0.10, 0.20 (s, 9 H), 1.40 (m, 6 H), 2.68 (br s, 1 H), 5.10, 5.82 (d, J = 12 Hz; d, J = 10 Hz, 1 H), 6.48, 6.68 (d, J = 12 Hz; d, J = 10 Hz, 1 H), 7.07–7.64 (m, 10 H). There were some small spurious absorptions in the $SiCH_3$ region also.

The selenide obtained above was treated with CH_3CO_3H (2.6 mL, 20 mmol) buffered and worked up as before to give 3.28 g of red oil. Kugelrohr distillation (bath 40 °C, 0.4 mm) provided 1.11 g (60% yield) of 4-hydroxy-4-methyl-1-(trimethylsilyl)-*trans*-2-penten-1-one as a brilliant yellow liquid: NMR δ 0.14 (s, 9 H), 1.25 (s, 6 H), 3.30 (br s, 1 H), 6.25 (d, J = 17 Hz, 1 H), 6.64 (d, J = 17 Hz, 1 H); IR 3450, 2960, 1875, 1635, 1590, 1370, 1250, 1180, 1140, 980, 850 cm^{-1}; mass spectrum, M^+ calcd for $C_9H_{18}SiO_2$ 186.1076, found 186.1075.

5-Methyl-1-(trimethylsilyl)-*trans*-2-hexen-1-one. Alkylation of **6** (1 mmol) with isobutyl bromide as above gave 1,3-bis(phenylseleno)-1-(trimethylsilyl)-5-methyl-1-hexene, which was used without purification: NMR δ 0.0 (s, 9 H), 0.92–2.00 (m, 9

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H), 4.86 (m, 1 H), 6.48 (d, J = 10 Hz, 1 H), 7.2–7.7 (m, 10 H).

Oxidation and workup as in preceding runs gave 5-methyl-1-(trimethylsilyl)-*trans*-2-hexen-1-one (65% NMR yield): NMR δ 0.32 (s, 9 H), 1.04 (d, J = 7 Hz, 6 H), 1.80 (m, 1 H), 2.18 (t, J = 7 Hz, 2 H), 6.10 (d, J = 16 Hz, 1 H), 6.60 (dt, J = 16, 7 Hz, 1 H).

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Registry No. (*E*)-**2b**, 80780-63-8; (*Z*)-**2b**, 80780-64-9; (*Z*)-**4**, 80780-65-0; (*E*)-**4**, 80780-66-1; (*Z*)-**5**, 80780-67-2; (*E*)-**5**, 80789-27-1; **6**, 80780-68-3; i, 80780-69-4; ii, 80796-73-2; Ph_2Se_2, 1666-13-3; 1,3-dichloropropene, 542-75-6; thiophenol, 108-98-5; *trans*-3-trimethylsilyl-2-propenal, 33755-86-1; *trans*-6-methyl-2-heptenal, 80780-70-7; 1,3-bis(phenylseleno)allyllithium, 80780-71-8; isoamyl bromide, 107-82-4; 1,3-bis(phenylseleno)-6-methyl-1-heptene, 80780-72-9; *trans*-4-methyl-2-hexenal, 80780-73-0; 2-bromobutane, 78-76-2; 1,3-bis(phenylseleno)-4-methyl-1-hexene, 80780-74-1; *trans*-5-acetoxy-2-hexenal, 31849-96-4; propylene oxide, 75-56-9; 1,3-bis(phenylseleno)-5-acetoxy-1-hexene, 80780-75-2; 4-acetoxy-5-methyl-*trans*-2-hexenal, 80780-76-3; isobutyraldehyde, 78-84-2; 1,3-bis(phenylseleno)-4-acetoxy-5-methyl-1-hexene, 80780-77-4; cyclohexene oxide, 286-20-4; *trans*-2-[1,3-bis(phenylseleno)allyl]cyclohexyl acetate, 80780-78-5; *trans*-3-(*trans*-2-acetoxycyclohexyl)-2-propenal, 31849-91-9; 4-*tert*-butylcyclohexanone, 98-53-3; 1-[1,3-bis(phenylseleno)allyl]-4-*t*-butyl-cyclohexanol, 80780-79-6; 3-pentanone, 96-22-0; (*E*)-4,6-bis(phenylseleno)-3-ethyl-5-hexen-3-ol, 80780-80-9; (*Z*)-4,6-bis(phenylseleno)-3-ethyl-5-hexen-3-ol, 80780-81-0; 4-ethyl-4-hydroxy-*trans*-2-hexenal, 80780-82-1; (*E*)-phenylseleno-4-methyl-1,3-pentadiene, 80780-83-2; (*Z*)-1-phenylseleno-4-methyl-1,3-pentadiene, 80780-84-3; 4-methyl-1-trimethylsilyl-trans-2-hexen-1-one, 80780-85-4; 1,3-bis(phenylseleno)-4-methyl-1-trimethylsilyl-1-hexene, 80789-28-2; 4-methyl-1-trimethylsilyl-*trans*-2-penten-1-one, 73341-03-4; 2-bromopropane, 75-26-3; 1,3-bis(phenylseleno-4-methyl-1-trimethylsilyl)-1-pentene, 80780-86-5; 4-hydroxy-4-methyl-1-trimethylsilyl-*trans*-2-penten-1-one, 80789-29-3; acetone, 67-64-1; (*E*)-1,3-bis(phenylseleno)-1-(trimethylsilyl)-4-hydroxy-4-methyl-1-pentene, 80780-87-6; (*Z*)-1,3-bis(phenylseleno)-1-trimethylsilyl)-4-hydroxy-4-methyl-1-pentene, 80780-88-7; 5-methyl-1-(trimethylsilyl)-*trans*-2-hexen-1-one, 80780-89-8; isobutyl bromide, 78-77-3; 1,3-bis(phenylseleno)-1-(trimethylsilyl)-5-methyl-1-hexene, 80780-90-1.

Reactions of Bis(acetoxymethyl) Ether and Several of Its Aryloxy Analogues

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Displacement of acetoxy groups from bis(acetoxymethyl) ether by a variety of phenols is demonstrated. The effect of various catalysts on the reaction is documented, and a possible role of the catalyst is discussed. Several (aryloxy)methyl ethers are used for the preparation of (alkylthio)methyl ethers.

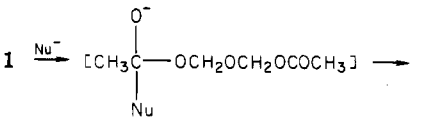
Bis(acetoxymethyl) ether (1), known for many years[1] and easily prepared in large quantity from acetic anhydride and *s*-trioxane (eq 1a), has found very little use because of its facile hydrolysis and decomposition (eq 1b). We report here the efficient displacement of acetoxy in 1 by aryloxy to form intermediates more useful in subsequent displacement reactions.[2]

$$(CH_2O)_3 + (CH_3CO)_2O \xrightarrow{H^+} (CH_3COOCH_2)_2O \qquad (1a)$$

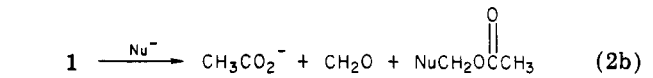
$$\underset{1}{(CH_3COOCH_2)_2O} \xrightarrow{H^+ \text{ or } OH^-} [(HOCH_2)O] \rightarrow CH_2O + CH_3COOH \qquad (1b)$$

Results and Discussion

An attempt to develop a synthesis of bis(phenoxymethyl) ether and bis[(alkylthio)methyl] ethers[3] without using bis(chloromethyl) ether[4,5] prompted investigation of bis(acetoxymethyl) ether (1) as an intermediate. Many attempts to displace the acetoxy groups in 1 with strong nucleophiles such as mercaptide or aryl oxide gave either disubstituted methylenes or intractable mixtures of paraformaldehyde and other polymeric compounds, with no formation of substituted methyl ether. Attack on the carbonyl carbon or cleavage of the formal ether linkage is the predominant reaction (eq 2a,b). To minimize these



$$CH_3CONu + CH_2O + CH_3COO^- \qquad (2a)$$



(2b)

Nu^- = strong nucleophile

undesirable additions, reactions with weak nucleophiles such as phenols and mercaptans, which might hydrogen bond with the carbonyl oxygen of 1, were investigated. At

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