Hexamethylphosphoramide-Mediated Conjugate Addition of (Alkylthio)-, (Phenylthio)-, and (Phenylseleno)allyllithium Reagents to 2-Cyclopentenone[1]

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(Methylthio)- and (*tert*-butylthio)allyllithium react irreversibly with 2-cyclopentenone by α- and γ-1,2-addition in THF at −78 °C. (Phenylthio)- and (phenylseleno)allyllithium also react in this way but in addition display a small tendency to undergo α- and γ-1,4-addition. In the presence of 1 equiv of HMPA, the major reaction pathway for all anions is α-1,4-addition, with barely detectable γ-1,4-addition (~5%) also taking place. The enolate resulting from the HMPA-mediated conjugate addition of (methylthio)allyllithium to 2-cyclopentenone reacts readily with 3-iodo-1-(trimethylsilyl)-1-propyne to produce the corresponding 2,3-disubstituted and 2,3,5-trisubstituted cyclopentanones in 75% and 4% yields, respectively, from 2-cyclopentenone.

The conjugate (1,4 or Michael) addition of organocuprates, obtained by treatment with copper(I) salts of Grignard and organolithium reagents, to α-enones is a well established reaction of basic synthetic importance.[2] Direct conjugate addition of organolithium reagents such as tritylithium,[3] (trimethylsilyl)lithium,[4] and acyl carbanion equivalents has also been reported.[5] Thus, dithioacetal monosulfoxides,[6] tris(phenylthio)methane,[7] trimethylsilyl- and -stannyl dithioacetals,[8] 1,3-dithiane[9] and its derivatives,[5,10] and dithio- and diselenoacetals[11] upon metalation either undergo direct conjugate addition or can be made to do so by an increase in reaction temperature and/or solvent polarity. Dilithium carboxylates,[12] ester enolates bearing α-phenoxy,[13] phenylthio,[13] and phenylseleno[14] substituents, and (arylthio)-[15,16] and (phenylthio)acetonitriles[17] display a similar propensity toward conjugate addition, yielding, in most cases, the 1,4-adduct under conditions of increasing solvent polarity. The outstanding reagent for inducing 1,4-addition is hexamethylphosphoric triamide (HMPA). A number of stabilized carbanions, which normally react by 1,2-addition with α-enones in tetrahydrofuran alone, yield the 1,4-adducts in the presence of HMPA, either under conditions of thermodynamic[10a,13,14,18] or, as very recently shown, of kinetic[9a,11,16] control.

As a synthetic tool, use of organolithium reagents as Michael donors has advantages over the use of organocuprates. They are readily prepared, relatively stable, and upon addition to α-enones generate lithium enolates suitable for alkylation. Conjugate addition of organocuprates yields enolates whose precise structures are as yet unknown[19,20] and which display low or moderate reactivity toward alkylating agents. Hence, a delineation of the type of organolithium (or other group 1 metal derived) reagents which undergo conjugate addition to α-enones is a worthwhile objective.

In view of the ability of HMPA to induce 1,4-addition of the carbanions indicated above, it was felt that the organolithium reagents derived from allylic sulfides and selenides could also be made to undergo conjugate addition to α-enones such as 2-cyclopentenone. The synthetic utility of allylic sulfides, sulfoxides, and selenides as well established[21] and is amply illustrated by the use of sulfides and sulfoxides in the latter stages of several prostaglandin syntheses for stereospecific introduction of the 15-α-hydroxyl substituent.[22] Thus, successful 1,4-addition, provided that it proceeded α to the sulfur or selenium atom, would have the potential of providing a stereospecific and highly convergent route to prostaglandins and other cyclopentanoid natural products. As introductory work to this objective, we now describe the reactions of a series of allyllithium reagents derived from allylic sulfides and allyl phenyl selenide with 2-cyclopentenone.[1]

Discussion

Deprotonation of methyl, *tert*-butyl, and phenyl allyl sulfides by using *sec*-butyllithium and of phenyl allyl selenide by using lithium diisopropylamide in tetrahydrofuran at −50 °C produced the orange anions **1a–d**

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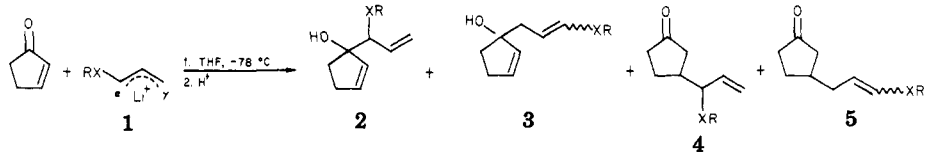
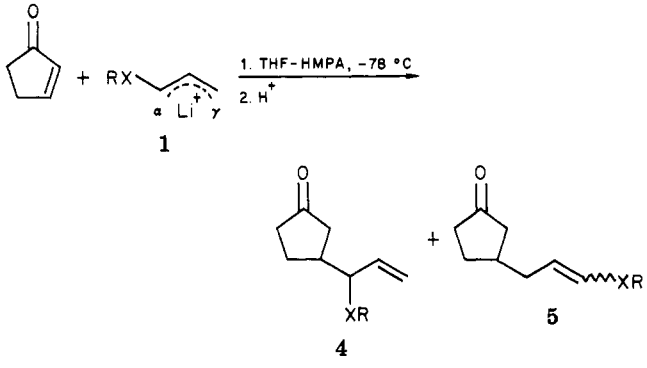
Table I. Reaction of 1 with 2-Cyclopentenone in THF at −78 °C



1	% yield 2[a]	3[b]	4	5[b]
a, X = S; R = CH_3	43 (3:2)	44 (5:3)	0	0
b, X = S; R = t-C_4H_9	33 (13:10)	45 (25:1)	0	0
c, X = S; R = C_6H_5	52 (16:11)	16 (10:11)	~10	~10 (1:4)
d, X = Se; R = C_6H_5	46 (10:11)	16 (10:11)	~10	~8 (7:10)

[a] Diastereomer ratio in parentheses. [b] E:Z ratio in parentheses.

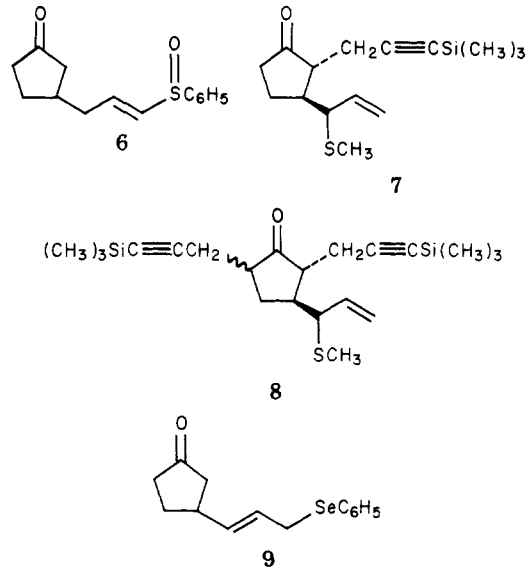
Table II. Reaction of 1 with 2-Cyclopentenone in THF at −78 °C Containing 1 Equiv of HMPA



1	% yield[b] of 4	1	% yield[b] of 4
a, X = S; R = CH_3	89 (3:2)[a]	c, X = S; R = C_6H_5	89 (7:6)
b, X = S; R = t-C_4H_9	85 (9:5)	d, X = Se; R = C_6H_5	81 (12:10)

[a] Diastereomer ratio. [b] The yield of 5 was ~5% in all cases.

Chart I



which upon being cooled to −78 °C were treated directly with cyclopentenone. The reactions were rapid, were exothermic, and gave good yields of the α- and γ-1,2-addition products **2** and **3**. Small and approximately equal amounts of the α- and γ-1,4-addition products **4** and **5** were also obtained from anions **1c** and **1d** (Table I). The latter products could not be separated from each other; yields of each were determined by ^{1}H NMR spectroscopy on the mixture on **4** and **5**. The identity of each was established by comparison of the ^{1}H NMR spectrum of the mixture with spectra of separate samples of **4c** (see below) and **5c**. The latter was independently prepared by phosphorus triiodide reduction[23] of the sulfoxide **6**. This sulfoxide is obtained as the sole product of HMPA-mediated conjugate addition of the anion derived from phenyl allyl sulfoxide with cyclopentenone.[1,24]

In the presence of 1 equiv of HMPA the course of the reaction is markedly altered. The α-1,4-addition products **4a–d** containing small amounts (~5%) of the γ-1,4-addition products **5a–d** were formed exclusively (Table II). No traces of the 1,2-addition products **2** and **3** were able to be detected. Decreasing the amount of HMPA to 0.2 equiv still resulted in a significant amount of 1,4-addition, with **4a** being obtained in 32% yield as well as the 1,2-addition products **2a** and **3a** from anion **1a**. Exclusive formation of **4b** (75%) also took place with the organocopper reagent derived from **1b** and copper(I) iodide. Hexamethylphosphorus triamide and tetramethylethylenediamine did not induce detectable 1,4-addition for this anion. Attempts to use tris[4-(dimethylamino)phenyl]phosphine oxide as a potential 1,4-directing agent in place of HMPA were unfortunately thwarted by the insolubility of the compound in tetrahydrofuran at −78 °C.

The alkoxides of the 1,2-addition products **2b** and **3b**, prepared in situ from **1b** and cyclopentenone, or of **2c**, prepared from isolated **2c** and lithium diisopropylamide, on treatment with HMPA did not undergo detectable isomerization. Thus, kinetic control is operating in formation of the 1,4-addition products, three other examples of which were reported during the course of this work.[9a,11,16]

Crucial to the use of organolithium reagents as Michael donors is the trapping of the enolates with alkylating agents. Examples of successful trapping have been reported.[3,8,25] In the present case, treatment of the enolate resulting from HMPA-mediated conjugate addition of **1a** to cyclopentenone with 3-iodo-1-(trimethylsilyl)-1-propyne (whose preparation is described in the Experimental Section) yielded the disubstituted and trisubstituted cyclopentanones **7** and **8** (Chart I) in yields of 75% and 4%, respectively, from 2-cyclopentenone. As in a previous case,[26] the relative stereochemistry at C-2 and C-3 could

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not be derived from ^1H NMR measurements by using europium shift reagents. The diastereomeric ratio in this product was the same as that for the simple 1,4-addition product **4a**, indicating that stereochemically homogeneous alkylation had taken place. Use of less than 1 equiv of the iodide in the enolate trapping also yielded the same product. It is thus assigned the trans configuration in line with its greater thermodynamic stability as compared to that of cis isomer.

The foregoing results indicate that HMPA-mediated conjugate addition has synthetic potential, especially as the reaction should be applicable to allylic anions more highly functionalized than those described here. From a mechanistic viewpoint, present evidence does not allow a distinction between a two-electron-transfer process operating under frontier orbital control[15,27] or a one-electron-transfer process[25a] to be made. The intercession of one-electron-transfer processes during reactions of organocopper reagents with α-enones has not been unequivocally established.[20,28] Thus the formation of **4b** from 2-cyclopentenone and the organocopper reagent derived from **1b** cannot be used as evidence for operation of such a process in the corresponding reactions of **1a–d** in the presence of HMPA.

Experimental Section

^1H and ^{13}C NMR spectra were recorded on Varian HA-100 and CFT-20 spectrometers by using $CDCl_3$ solutions. Chemical shifts are reported in parts per million relative to tetramethylsilane. In cases where separate assignment of resonances to each diastereomer of a diastereomeric mixture was not possible, values for diastereotopic protons are given together with an asterisk to indicate values of δ and J corresponding to the second diastereomer. IR spectra were recorded on a Perkin-Elmer 221 spectrophotometer by using neat liquid (sodium chloride plates) unless otherwise stated. Mass spectra were recorded on an AEI MS-902 spectrometer with a DS-30 data system for high-resolution spectra.

Tetrahydrofuran (THF) was distilled from sodium/benzophenone immediately prior to use. Hexamethylphosphoric triamide (HMPA) was dried by stirring with calcium hydride under nitrogen for 36 h, followed by distillation at reduced pressure and storage over molecular sieves. Cyclopentenone was prepared by the method of Alder and Flock,[29] a procedure which in our hands is more convenient on a large scale than that involving the use of cyclopentenediol.[30] Preparative thin-layer chromatography was carried out on Merck silica gel $60PF_{254+366}$ by using dichloromethane as developing solvent. Internal (reaction) temperatures are given throughout.

Allyl Methyl Sulfide. A commercial sample (Aldrich) had the following: bp 92–94 °C; ^1H NMR δ 1.70 (3 H, s, SCH_3), 3.09 (2 H, dt, J = 7.0, ~1.0 Hz, H-1), 5.08 (1 H, ddt, J = 17.5, 2.0, 1.1 Hz, H-3), 5.09 (1 H, ddt, J = 9.0, 2.0, 1.0 Hz, H-3), 5.80 (1 H, ddt, J = 17.5, 9.0, 7.1 Hz, H-2); ^{13}C NMR δ 14.3 (q, SCH_3), 36.8 (t, C-1), 116.9 (t, C-3), 134.1 (d, C-2).

Allyl *tert*-Butyl Sulfide. Prepared according to a literature procedure[31] it had the following: bp 139–140 °C (lit.[31] bp 139–141.5 °C); ^1H NMR δ 1.34 (9 H, s, S-*t*-C_4H_9), 3.20 (2 H, ddd, J = 6.8, 1.3, 1.1 Hz, H-1), 5.03 (1 H, ddt, J = 9.8, 1.8, 1.1 Hz, H-3), 5.88 (1 H, ddt, J = 17.0, 9.8, 6.8 Hz, H-2); ^{13}C NMR δ 31.0 [q, SC-$(CH_3)_3$], 32.1 (t, C-1), 42.6 [s, $SC(CH_3)_3$], 116.6 (t, C-3), 135.5 (d, C-2).

Allyl Phenyl Sulfide. Prepared according to a literature procedure,[32] it had the following: bp 55–58 °C (1 mm) [lit.[32] bp 82–84 °C (4.9 mm)]; ^1H NMR δ 3.52 (2 H, ddd, J = 6.8, 1.4, 1.0 Hz, H-1), 5.04 (1 H, ddt, J = 9.7, 1.6, 1.0 Hz, H-3), 5.11 (1 H, ddt, J = 16.9, 1.6, 1.4 Hz, H-3), 5.88 (1 H, ddt, J = 17.1, 9.7, 6.8 Hz, H-2), 7.1–7.4 (5 H, m, C_6H_5); ^{13}C NMR δ 37.0 (t, C-1), 117.5 (t, C-3), 126.0 (d, para C), 128.7 (d, ortho or meta C), 129.6 (d, meta or ortho C), 133.5 (d, C-2), 135.9 (s, ipso C).

Allyl Phenyl Selenide. Sodium borohydride (3.8 g, 0.1 mol) was added in small portions to a stirred suspension of diphenyl diselenide (12.5 g, 0.04 mol) in absolute ethanol (100 mL) under nitrogen. The resultant solution was cooled to 0 °C, and 3-bromo-1-propene (12.1 g, 0.1 mol) was added dropwise. After being stirred for 2 h at 0 °C, the reaction mixture was poured into water (200 mL) and extracted with ether (3 × 50 mL). The ether extracts were washed with water, dried (Na_2SO_4), and evaporated under reduced pressure to leave a pale amber liquid, which was distilled under reduced pressure to yield allyl phenyl selenide: 11.4 g (72%); bp 65–68 °C (1.0 mm) [lit.[33] 82–83 °C (3mm)]; ^1H NMR δ 3.5 (2 H, ddd, J = 7.6, 1.3, ~0.7 Hz, H-1), 5.19 (1 H, ddt, J = 9.8, 1.5, ~0.7 Hz, H-3), 5.23 (1 H, ddt, J = 17.0, 1.7, 1.2 Hz, H-3), 5.94 (1 H, ddt, J = 17.0, 9.8, 7.4 Hz, H-2), 7.1–7.6 (5 H, m, C_6H_5); ^{13}C NMR δ 30.6 (t, C-1), 116.7 (t, C-3), 127.0 (d, para C), 128.8 (d, ortho or meta C), 130.0 (s, ipso C), 133.2 (d, meta or ortho C), 134.3 (d, C-2).

Reaction of 2-Cyclopenten-1-one in THF. (i) With (Methylthio)allyllithium (1a). *sec*-Butyllithium (1.84 M in pentane) was added dropwise to a stirred solution of allyl methyl sulfide (0.88 g, 0.01 mol) in THF (40 mL) under nitrogen at -50 °C until an initial coloration due to the anion persisted in the solution. More *sec*-butyllithium (5.4 mL, 0.01 mol) was then added, and after 10 min, the temperature of the solution was lowered to -78 °C. Neat cyclopentenone (0.82 g, 0.01 mol) was slowly added until the yellow color of the anion disappeared, the temperature of the solution being kept below -70 °C during the addition. After 5 min, the solution was quenched with aqueous ammonium chloride (1.5 g in water, 30 mL), warmed to 0 °C, diluted with water (45 mL), and extracted with ether (3 × 100 mL). The combined ether extracts were washed with water (75 mL), brine (50 mL), dried (Na_2SO_4), and evaporated under reduced pressure to leave a pale yellow oil which was separated by preparative TLC into two fractions. The more polar fraction, R_f 0.3, was a 5:3 mixture of (*E*)- and (*Z*)-1-[3′-(methylthio)-2′-propenyl]-2-cyclopenten-1-ol (**3a**; 0.95 g, 44%), as determined by ^1H NMR. The isomers were unable to be separated by using either TLC or VPC under a variety of conditions. The mixture had the following: IR 3700–3100 (s, OH) cm^{-1}; ^1H NMR (*E* isomer) δ 1.6–2.6 (4 H, m, H-4, H-5), 2.12 (1 H, s, $W_{h/2}$ = 3Hz, OH), 2.27 (3 H, s, SCH_3), 2.42 (2 H, dd, J = 7.5, 1.2 Hz, H-1′), 5.44 (1 H, dt, J = 14.2, 7.5 Hz, H-2′), 5.70 (1 H, dm, J = 5.4 Hz, H-3), 5.88 (1 H, dt, J = 5.4, 2.2 Hz, H-2), 6.09 (1 H, dt, J = 14.4, 1.2 Hz, H-3′); ^{13}C NMR δ 16.8 (q, SCH_3), 31.0 (t, C-4), 37.1 (t, C-5), 44.3 (t, C-1′), 85.2 (s, C-1), 123.8 (d, C-2′ or C-3′), 129.3 (d, C-3′ or C-2′), 133.4 (d, C-3), 135.9 (d, C-2); ^1H NMR (*Z* isomer) δ 1.6–2.6 (4 H, m, H-4, H-5), 2.12 (1 H, s, $W_{h/2}$ = 3 Hz, OH), 2.24 (3 H, s, SCH_3), 2.91 (2 H, dd, J = 7.5, 1.2 Hz, H-1′), 5.62 (1 H, dt, J = 9.6, 7.5 Hz, H-2′), 5.70 (1 H, dm, J = 5.4 Hz, H-3), 5.87 (1 H, dt, J = 5.4, 2.2 Hz, H-2), 6.03 (1 H, dt, J = 9.4, 1.2 Hz, H-3′); ^{13}C NMR δ 14.7 (q, SCH_3), 31.0 (t, C-4), 37.0 (t, C-5), 40.1 (t, C-1′), 85.6 (s, C-1), 121.6 (d, C-2′ or C-3′), 127.2 (d, C-3′ or C-2′), 133.6 (d, C-3), 135.9 (d, C-2); mass spectrum, calcd for $C_9H_{14}OS$ (M^+) m/e 170.0764, found 170.0767.

The less polar component, R_f 0.5, was a 3:2 diastereomeric mixture of 1-[1′-(methylthio)-2′-propenyl]-2-cyclopenten-1-ol (**2a**; 0.92 g, 43%), as determined by ^1H NMR. The mixture displayed chromatographic homogeneity in solution on silica gel in a variety of solvent systems: IR 3700–3100 (s, OH) cm^{-1}; ^1H NMR (major diastereomer) δ 1.6–2.8 (5 H, m, H-4, H-5, OH), 2.0 (3 H, s, SCH_3), 3.22 (1 H, dm, J = 9.6 Hz, H-1′), 5.06 (1 H, ddd, J = 16.4, 2.0, ~0.3 Hz, H-3′), 5.15 (1 H, ddd, J = 10.2, 2.0, ~0.2 Hz, H-3′), 5.63 (1 H, ddd, J = 16.2, 10.2, 9.7 Hz, H-2′), 5.76 (1 H, dt, J = 5.4, 2.0 Hz, H-3), 5.96 (1 H, dt, J = 5.4, 2.0 Hz, H-2); ^{13}C NMR (major diastereomer) δ 14.3 (q, SCH_3), 31.2 (t, C-4), 35.6 (t, C-5), 61.8 (d, C-1′), 86.6 (s, C-1), 117.0 (t, C-3′), 134.0 (d, C-2′), 134.7 (d, C-3 or C-2), 135.0 (d, C-2 or C-3); mass spectrum, calcd for $C_9H_{12}S$

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($M^+ - H_2O$) m/e 152.0659, found 152.0668.

(ii) With *tert*-(Butylthio)allyllithium (1b). Allyl *tert*-butyl sulfide (1.30 g, 0.01 mol) was submitted to the foregoing conditions to yield a pale yellow oil, which was resolved by preparative layer TLC into two fractions.

The more polar fraction, R_f 0.31, was a 25:1 mixture of (*E*)- and (*Z*)-1-[3′-(*tert*-butylthio)-2′-propenyl]-2-cyclopenten-1-ol (**3b**): 0.96 g (45%); IR ($CHCl_3$) 3595 (m, OH) cm^{-1}; ^1H NMR (*E* isomer) δ 1.34 (9 H, s, S-*t*-C_4H_9), 1.6–2.7 (4 H, m, H-3, H-4), 1.79 (1 H, s, OH), 2.45 (2 H, dd, J = 7.0, ~0.6 Hz, H-1′), 5.67 (1 H, dt, J = 5.6, 2.1 Hz, H-3), 5.88 (1H, dt, J = 14.9, 7.0 Hz, H-2′), 5.90 (1 H, dt, J = 5.6, 2.2 Hz, H-2), 6.22 (1 H, dt, J = 14.7, ~0.6 Hz, H-3′); ^{13}C NMR δ 30.8 [q, $SC(CH_3)_3$], 31.0 (t, C-4), 37.3 (t, C-5), 43.7 [s, $SC(CH_3)_3$], 44.6 (t, C-1′), 85.3 (s, C-1), 124.1 (d, C-2′ or C-3′), 131.4 (d, C-3′ or C-2′), 134.0 (d, C-3), 135.8 (d, C-2); mass spectrum, calcd for $C_{12}H_{20}OS$ (M^+) m/e 212.1234, found 212.1237. Anal. Calcd for $C_{12}H_{20}OS$: C, 67.89; H, 9.50; S, 15.1 found: C, 68.08; H, 9.45; S, 15.3.

The less polar fraction, R_f 0.50, was a 13:10 diastereomeric mixture of 1-[1′-(*tert*-butylthio)-2′-propenyl]-2-cyclopenten-1-ol (**2b**): 0.69 g (33%); IR 3700–3100 (m, OH) cm^{-1}; ^1H NMR δ 1.34 (9 H, s, S-*t*-C_4H_9), 1.6–2.7 (4 H, m, H-4, H-5), 3.1 (1 H, s, $W_{h/2}$ = 10 Hz, OH), 3.46 (1 H, dm, J = 9.4 Hz, H-1′), 5.06, 5.10* (1 H, ddd, J = 9.6, 9.6*, 1.9, 1.9*, ~0.5, ~0.8* Hz, H-3′), 5.15, 5.22* (1 H, ddd, J = 16.8, 16.8*, 1.9, 1.9*, ~0.5, ~0.8* Hz, H-3′), 5.55–6.09 (3 H, m, H-2, H-2′, H-3); ^{13}C NMR δ 31.5 [q, $SC(CH_3)_3$], 31.79 (t, C-4), 35.0 (t, C-5), 43.9, 44.2* [s, $SC(CH_3)_3$], 56.8, 57.6* (d, C-1′), 86.2, 86.6* (s, C-1), 115.9, 116.6* (t, C-3′), 133.8 (d, C-3), 134.6, 135.2* (d, C-2′), 138.4, 138.9* (d, C-2); mass spectrum, calcd for $C_{12}H_{18}S$ ($M^+ - H_2O$) m/e 194.1129, found 194.1134.

(iii) With (Phenylthio)allyllithium (1c). Allyl phenyl sulfide (1.50 g, 0.01 mol) was submitted to the foregoing conditions to yield a pale yellow oil, which was resolved by preparative layer TLC into three fractions.

The most polar fraction, R_f 0.20, was a 10:11 mixture of (*E*)- and (*Z*)-1-[3′-(phenylthio)-2′-propenyl]-2-cyclopenten-1-ol (**3c**): 0.36 g (16%); IR ($CHCl_3$) 3595 (m, OH) cm^{-1}; ^1H NMR (*E* isomer) δ 1.8–2.7 (4 H, m, H-4, H-5), 1.82 (1 H, s, $W_{h/2}$ = 3 Hz, OH), 2.50 (2 H, dd, J = 6.8, ~0.4 Hz, H-1′), 5.69 (1 H, dt, J = 5.5, 2.0 Hz, H-3), 5.92 (1 H, dt, J = 5.5, 2.2 Hz, H-2) 5.95 (1 H, dt, J = 15.1, 7.0 Hz, H-2′), 6.27 (1 H, dt, J = 14.8, ~0.4 Hz, H-3′), 7.2–7.4 (5 H, m, C_6H_5); ^1H NMR (*Z* isomer) δ 1.8–2.7 (4 H, m, H-4, H-5), 1.82 (1 H, s, $W_{h/2}$ = 3 Hz, OH), 2.62 (2 H, dd, J = 7.2, ~1.2 Hz, H-1′), 5.73 (1 H, dt, J = 5.7, 2.0 Hz, H-3), 5.90 (1 H, dt, J = 9.4, 7.2 Hz, H-2′), 5.91 (1 H, dt, J = 5.8, 2.2 Hz, H-2), 6.35 (1 H, dt, J = 9.2, 1.2 Hz, H-3′), 7.2–7.4 (5 H, m, C_6H_5); ^{13}C NMR (*E* and *Z* isomers) δ 31.2 (t, C-4), 37.4 (t, C-5), 40.25 (t, C-1′, Z isomer), 44.3 (t, C-1′, *E* isomer), 85.3 (s, C-1). Mass spectrum, calcd for $C_{14}H_{16}OS$ (M^+) m/e 232.0922, found 232.0919.

The fraction of intermediate polarity, R_f 0.40, was a 16:11 diastereomeric mixture of 1-[1′-(phenylthio)-2′-propenyl]-2-cyclopenten-1-ol (**2c**): 1.20 g (52%); IR ($CHCl_3$) 3590 (m, OH) cm^{-1}; ^1H NMR (major diastereomer) δ 1.7–2.6 (4 H, m, H-4, H-5), 2.73 (1 H, s, $W_{h/2} \approx$ 4 Hz, OH), 3.69 (1 H, dm, J = 9.7 Hz, H-1′), 5.31 (1 H, ddd, J = 16.6, 1.8, ~0.6 Hz, H-3′), 5.39 (1 H, ddd, J = 10.5, 1.8, ~0.4 Hz, H-3′), 5.65–5.87 (1 H, m, H-3), 5.76 (1 H, ddd, J = 16.6, 10.5, 9.7 Hz, H-2′), 5.91–6.03 (1 H, m, H-2), 7.2–7.5 (5 H, m, C_6H_5); ^{13}C NMR δ 31.4 (t, C-4), 35.9 (t, C-5), 63.7 (d, C-1′), 86.9 (s, C-1); mass spectrum, m/e 212 (M^+). Anal. Calcd. for $C_{14}H_{16}OS$: C, 72.39; H, 6.94; S, 13.8. Found: C, 72.43; H, 7.02; S, 13.9.

The least polar fraction, R_f 0.45, was an inseparable mixture of 3-[1′-(phenylthio)-2′-propenyl]-1-cyclopentanone (**4c**) (~0.2 g, ~10%) and the *E* and *Z* isomers (1:4) of 3-[3′-(phenylthio)-2′-propenyl]-1-cyclopentanone (**5c**) (~0.2 g, ~10%), as estimated by ^1H NMR spectroscopy. The preparation of **4c** and **5c** by alternative routes is described below.

(iv) With (Phenylseleno)allyllithium (1d). *n*-Butyllithium (Merck, 15% w/v solution in hexane, 4.7 mL, 0.011 mol) was added at −40 °C to a stirred solution of diisopropylamine (1.11 g, 0.011 mol) in THF (40 mL) under dry nitrogen. After 30 min the solution temperature was lowered to −55 °C, and allyl phenyl selenide (1.97 g, 0.01 mol) was added dropwise. After a further 30 min, the solution temperature was lowered to −78 °C. Addition of cyclopentenone (0.82 g, 0.01 mol) and subsequent workup of the reaction mixture as previously described yielded a pale yellow oil. Preparative layer TLC resolved the oil into three fractions.

The most polar fraction, R_f 0.3, was a 10:11 mixture of (*E*)- and (*Z*)-1-[3′-(phenylseleno)-2′-propenyl]-2-cyclopenten-1-ol (**3d**): 0.44 g (16%); IR 3700–3100 (m, OH) cm^{-1}; ^1H NMR (*E* isomer) δ 1.6–2.6 (5 H, m, H-4, H-5, OH), 2.48 (2 H, dd, J = 7.0, ~0.9 Hz, H-1′), 5.73 (1 H, dt, J = 5.5, 2.0 Hz, H-3), 5.89 (1 H, dt, J = 5.5, 2.2 Hz, H-2), 6.07 (1 H, dt, J = 15.1, 7.2 Hz, H-2′), 6.52 (1 H, dt, J = 15.1, ~0.9 Hz, H-3′), 7.2–7.6 (5 H, m, C_6H_5); ^1H NMR (*Z* isomer) δ 1.6–2.6 (5 H, m, H-4, H-5, OH), 2.55 (2 H, dd, J = 7.2, 1.0 Hz, H-1′), 5.67 (1 H, dt, J = 5.6, 2.1 Hz, H-3), 5.90 (1 H, dt, J = 5.6, 2.1 Hz, H-2), 6.13 (1 H, dt, J = 9.0, 7.2 Hz, H-2′), 6.60 (1 H, dt, J = 8.8, 1.0 Hz, H-3′), 7.2–7.6 (5 H, m, C_6H_5); ^{13}C NMR (*E* and *Z* isomers) δ 31.2 (t, C-4), 37.5 (t, C-5), 42.3 (t, C-1′, *Z* isomer), 45.6 (t, C-1′, *E* isomer), 85.3 (s, C-1); mass spectrum, calcd for $C_{14}H_{16}OSe$ (M^+), m/e 280.0365, found 280.0367.

The fraction of intermediate polarity, R_f 0.45, was a 12:10 diastereomeric mixture of 1-[1-(phenylseleno)-2-propenyl]-2-cyclopenten-1-ol (**2d**): 1.3g (46%); IR 3700–3100 (m, OH) cm^{-1}; ^1H NMR δ 1.7–2.6 (5 H, m, H-4, H-5, OH), 3.81, 3.84* (1 H, d, J = 10.0, 10.2* Hz, H-1′), 4.72, 4.75* (1 H, ddd, J = 16.8, 17.0*, 1.8, 1.6*, ~0.6, ~0.6* Hz, H-3′), 4.87, 4.90* (1 H, ddd, J = 10.2, 10.2*, 1.7, 1.6*, ~0.3, ~0.3* Hz, H-3′), 5.68–6.0 (2 H, m, H-2, H-3), 5.90, 5.97* (1 H, dt, J = 16.8, 17.0*, ~10, ~10* Hz, H-2′), 7.2–7.7 (5 H, m, C_6H_5); ^{13}C NMR δ 31.3, 31.65* (t, C-4), 36.4, 36.8* (t, C-5), 61.0, 61.2* (d, C-1′), 87.3 (s, C-1); mass spectrum, calcd for $C_{14}H_{16}OSe$ (M^+) m/e 280.0365, found 280.0375.

The least polar fraction, R_f 0.55, was a mixture of 3-[1′-(phenylseleno)-2′-propenyl]-1-cyclopentanone (**4d**; ~0.3g, ~10%) and the *E* and *Z* isomers (7:10) of 3-[3′-(phenylseleno)-2′-propenyl]-1-cyclopentanone (**5d**; ~0.2 g, ~8%), as estimated by ^1H NMR spectroscopy. The preparation of **4d** is described below. Isolation of **5d** was not attempted. It had the following: IR ~1740 (s, C=O) cm^{-1}; ^1H NMR (*E* isomer) δ ~1.4–2.7 (9 H, m, H-2, H-3, H-4, H-5, H-1′), 6.03 (1 H, dt, J = 15.5, 6.8 Hz, H-2′), 6.45 (1 H, dt, J = 15.5, ~0.6 Hz, H-3′); ^1H NMR (*Z* isomer) δ ~1.4–2.7 (9 H, m, H-2, H-3, H-4, H-5, H-1′), 6.01 (1 H, dt, J = 9.0, 5.5 Hz, H-2′), 6.55 (1 H, dt, J = 9.0, ~0.3 Hz, H-3′).

Reaction of 2-Cyclopenten-1-one in THF in the Presence of HMPA. (i) With (Methylthio)allyllithium (1a). *sec*-Butyllithium (1.84 M in pentane) was added dropwise to a stirred solution of allyl methyl sulfide (0.88 g, 0.01 mol) in THF (40 mL) containing HMPA (1.79 g, 0.01 mol) under nitrogen at −50 °C until the color due to the anion persisted. More *sec*-butyllithium (5.4 mL, 0.01 mol) was then added. After 10 min, the resultant deep orange solution was cooled to −78 °C and treated with cyclopentenone (0.82 g, 0.01 mol) as described above. The workup yielded a pale yellow oil, which was submitted to preparative layer TLC to yield a 3:2 diastereomeric mixture of 3-[1′-(methylthio)-2′-propenyl]-1-cyclopentanone (**4a**; 1.51 g, 89%) as a pale yellow oil: R_f 0.53; IR 1743 (s, C=O) cm^{-1}; ^1H NMR (major diastereomer) δ 1.5–2.7 (7 H, m, H-2, H-3, H-4, H-5), 1.96 (3 H, s, SCH_3), 3.01 (1 H, dd, J = 9.0, 7.6 Hz, H-1′), 5.00 (1 H, ddd, J = 16.2, 2.0, ~0.4 Hz, H-3′), 5.15 (1 H, dd, J = 10.0, 2.0 Hz, H-3′), 5.62 (1 H, ddd, J = 16.2, 9.9, 9.0 Hz, H-2′); ^{13}C NMR (major diastereomer) 13.7 (q, SCH_3), 27.4 (t, C-4), 38.2 (t, C-5), 40.1 (d, C-3), 43.2 (t, C-2), 53.5 (d, C-1′), 116.2 (t, C-3′), 136.5 (d, C-2′), 217.5 (s, C-1); mass spectrum, calcd for $C_9H_{14}OS$, (M^+) m/e 170.0764, found 170.0767. Also present in the above sample was ~5% of the γ-1,4-product (**5a**) which could not be removed by further preparative TLC. Its presence was indicated by absorptions at δ 5.95–6.03 in the ^1H NMR spectrum, corresponding to an equimolar mixture of *E* and *Z* isomers.

(ii) With (*tert*-Butylthio)allyllithium (1b). Allyl *tert*-butyl sulfide (1.30 g, 0.01 mol) was subjected to the above conditions to give a pale yellow oil, which was purified by preparative layer TLC to yield a 9:5 diastereomeric mixture of 3-[1′-(*tert*-butylthio)-2′-propenyl]-1-cyclopentanone (**4b**; 1.80 g, 85%) as a pale amber oil: R_f 0.53; IR 1744 (s, C=O) cm^{-1}; ^1H NMR (major diastereomer) δ 1.31 (9 H, s, S-*t*-C_4H_9), 1.6–2.6 (7 H, m, H-2, H-3, H-4, H-5), 3.29 (1 H, dd, J = 8.8, 6.0 Hz, H-1′), 5.08 (1 H, ddd, J = 9.4, 1.7, ~0.4 Hz, H-3′), 5.10 (1 H, ddd, J = 17.0, 1.7, ~0.4 Hz, H-3′), 5.83 (1 H, ddd, J = 17.0, 9.4, 8.8 Hz, H-2′); ^{13}C NMR δ 26.8 (t, C-4), 31.4 [q, $SC(CH_3)_3$], 38.3 (t, C-5), 41.4 (d, C-3), 43.2 (t, C-2), 43.7 [s, $SC(CH_3)_3$], 50.7 (d, C-1′), 115.0 (t, C-3′), 150.5 (d, C-2′), 217.9 (s, C-1); mass spectrum m/e 212 (M^+). Anal. Calcd for $C_{12}H_{20}OS$: C, 67.89; H, 9.50; S, 15.1. Found: C, 67.64; H, 9.33;

S, 15.3.

Also present in the above sample was ~5% of the γ-1, 4-product (**5b**), whose presence as an equimolar mixture of *E* and *Z* isomers was indicated by absorptions at 6.17–6.28 in the ^{1}H NMR spectrum.

(iii) With (Phenylthio)allyllithium (1c). Allyl phenyl sulfide (1.50 g, 0.01 mol) was subjected to the above conditions to give a pale yellow oil, which was purified by preparative layer TLC to yield a 7:6 diastereomeric mixture of 3-[1′-(phenylthio)-2′-propenyl]-1-cyclopentanone (**4c**; 2.06 g, 89%) as a pale yellow oil: R_f 0.45; IR 1739 (s, C=O) cm^{-1}; ^{1}H NMR δ 1.5–2.7 (7 H, m, H-2, H-3, H-4, H-5), 3.49, 3.54* (1 H, dd, *J* = 9.1, 9.2*, 7.4, 6.7* Hz, H-1′), 4.85 (1 H, ddd, *J* = 16.5, 1.5, ~0.6 Hz, H-3′), 5.70, 5.71* (1 H, ddd, *J* = 16.6, 16.6*, 10.2, 10.2*, 9.1, 9.1* Hz, H-2′), 7.2–7.6 (5 H, m, C_6H_5); ^{13}C NMR δ 27.3, 27.5* (t, C-4), 38.4 (t, C-5), 40.5 (d, C-3), 42.9, 43.5* (t, C-2), 57.7, 57.9* (d, C-1), 116.7, 116.9* (t, C-3′), 136.7 (d, C-2′), 217.6 (s, C-1); mass spectrum, *m/e* 212 (M$^+$). Anal. Calcd for $C_{14}H_{16}OS$: C, 72.39; H, 6.94; S, 13.8. Found: C, 72.26; H, 7.00; S, 13.8.

Also present in the sample was ~5% of the γ-1,4-product (**5c**), whose presence as a ~1:4 mixture of *E* and *Z* isomers was indicated by absorptions in the ^{1}H NMR spectrum at δ 5.81 (1 H, dt, *J* = 9.2, 7.0 Hz, H-2′, *Z* isomer), 6.50 (1 H, dt, *J* = 9.2, ~0.9 Hz, H-3′, Z isomer), 5.89 (1 H, dt, *J* = 14.6, 6.9 Hz, H-2′, E isomer), and 6.22 (1 H, dt, *J* = 14.6, ~0.4 Hz, H-3′, E isomer). The preparation and characterization of **5c** is described below.

(iv) With (Phenylseleno)allyllithium (1d). Allyl phenyl selenide (1.97 g, 0.01 mol) was added to a solution of HMPA (1.79 g, 0.01 mol) and lithium diisopropylamide, prepared from *n*-butyllithium (5.4 mL, 0.011 mol) and diisopropylamine (1.11 g, 0.011 mol), in THF (40 mL) at −55 °C. After 30 min, the solution temperature was lowered to −78 °C. The solution was treated with cyclopentenone (0.82 g, 0.01 mol) and worked up as previously described to yield a pale yellow oil, which was purified by preparative layer TLC to yield a 12:10 diastereomeric mixture of 3-[1′-(phenylseleno)-2′-propenyl]-1-cyclopentanone (**4d**; 2.26 g, 81%) as a pale yellow oil: R_f 0.55; IR 1738 (s, C=O) cm^{-1}; ^{1}H NMR δ 1.4–2.7 (7 H, m, H-2, H-3, H-4, H-5), 3.61, 3.63* (1 H, dd, *J* = 9.8, 9.8*, 7.8, 7.0* Hz, H-1′), 4.71, 4.73* (1 H, ddd, *J* = 16.6, 16.6*, 1.5, 1.5*, ~0.4, 0.4* Hz, H-3′), 4.85, 4.88* (1 H, dd, *J* = 10.2, 10.2*, 1.5, 1.5* Hz, H-3′), 5.79, 5.80* (1 H, dt, *J* = 16.6, 16.6*, ~10, ~10* Hz, H-2′); ^{13}C NMR δ 29.7, 29.9* (t, C-4), 38.75 (t, C-5), 41.0 (d, C-3), 43.7, 44.6* (t, C-2), 53.5 (d, C-1′), 115.7, 115.9* (t, C-3′), 137.2 (d, C-2′), 217.7 (s, C-1); mass spectrum, calcd for $C_{14}H_{16}OSe$ (M$^+$) *m/e* 280.0365, found 280.0374.

Also present in the above sample was ~5% of the γ-1,4-product (**5d**), whose presence as a 1:2 mixture of the *E* and *Z* isomers was indicated by absorptions at δ 6.4–6.6 in the ^{1}H NMR spectrum. The α-1,4-addition product (**4d**) is unstable at room temperature. After 1 week, approximately 50% of the allylic isomer **9** was present in a sample originally containing 95% of (**4d**), as indicated by ^{1}H NMR spectroscopy. No attempt was made to purify the allylic isomer **9**, which in the foregoing sample had δ 3.50 (2 H, dt, *J* = 7.2, ~0.6 Hz, H-3′), 5.31 (1 H, dd, *J* = 14.7, 6.5 Hz, H-1′), and 5.63 (1 H, dt, *J* = 14.7, 7.2 Hz, H-2′).

Reaction of 2-Cyclopenten-1-one with (Methylthio)allyllithium (1a) in THF in the Presence of 0.2 Equiv of HMPA. Reaction of (methylthio)allyllithium (1a), from allyl methyl sulfide (0.88 g, 10 mmol), with cyclopentenone (0.82 g, 10 mmol) in THF (40 mL) containing HMPA (0.35 g, 2 mmol) and isolation of the products by preparative TLC as described above gave the 1,2-α (**2a**; 0.49g, 23%), 1,2-γ (**3a**; 0.63 g, 30%), and 1,4-α (**4a**; 0.69 g, 32%) products.

Reaction of 2-Cyclopenten-1-one with *tert*-(Butylthio)allylcopper in THF. (*tert*-Butylthio)allyllithium (**1b**) was prepared in THF as described above. The solution was cooled to −55 °C, and copper(I) iodide (1.90 g, 0.01 mol) was added in one portion. The color of the solution changed from clear orange to opaque green. After the mixture was stirred for 30 min, the temperature was lowered to −70 °C, cyclopentenone was added, and after the reaction temperature was allowed to rise to 0 °C during 2 h, the reaction mixture was worked up in the usual way to yield a pale yellow oil, which after preparative TLC afforded the diastereomeric 1,4-γ-adduct **4b** (1.59 g, 75%).

Enolate Trapping. (Methylthio)allyllithium (**1a**) was generated from allyl methyl sulfide (0.49 g, 5.6 mmol, 1.0 equiv) and *sec*-butyllithium (3.04 mL, 5.6 mmol) in THF (20 mL) containing HMPA (1.0 g, 5.6 mmol) at −50 °C as previously described. The temperature was lowered to −78 °C, cyclopentenone (0.46 g, 5.6 mmol) was added slowly, and after 2 min, 3-iodo-1-(trimethylsilyl)-1-propyne (2.52 g, 10.1 mmol, 1.8 equiv) was added dropwise to the reaction mixture at −78 °C. The temperature of the reaction mixture was raised to −45 °C during 90 min. The reaction was quenched with aqueous ammonium chloride and then worked up to give a pale yellow oil, which was subjected to preparative layer TLC to yield two fractions.

The more polar fraction, R_f 0.5, a pale yellow oil, was a 3:2 diastereomeric mixture of (*E*)-2-[3′-(trimethylsilyl)-2-propynyl]-3-[1″-(methylthio)-2″-propenyl]-1-cyclopentanone (**7**): 2.65 g (75%); IR 2180 (m, C≡C), 1750 (s, C=O) cm^{-1}; ^{1}H NMR (major diastereomer) δ 0.13 [9 H, s, $Si(CH_3)_3$], 1.6–2.7 (8 H, m, H-2, H-3, H-4, H-5, H-1′), 3.40 (1 H, ddd, *J* = 9.4, 5.6, ~0.5 Hz, H-1″), 5.11 (1 H, ddd, *J* = 16.3, 2.0, ~0.5 Hz, H-3″), 5.22 (1 H, ddd, *J* = 10.2, 2.0, ~0.2 Hz, H-3″) 5.77 (1 H, ddd, *J* = 16.3, 10.2, 9.5 Hz,H-2″); ^{13}C NMR δ [q, $Si(CH_3)_3$], 14.3 (q, SCH_3), 19.6 (t, C-1′), 24.2 (t, C-4), 37.6 (t, C-5), 44.2 (d, C-3), 50.5 (d, C-2), 53.3 (d, C-1″) 86.8 (s, C-3′), 103.7 (s, C-2′), 117.9 (t, C-3″), 137.0 (d, C-2″), 217.0 (s, C-1); mass spectrum, calcd for $C_{15}H_{24}OSSi$ (M$^+$) *m/e* 280.1316, found 280.1306.

The less polar fraction, R_f 0.7, was a mixture of two major diastereomers (3:2) and one minor diastereomer of 2,5-bis[3′-(trimethylsilyl)-2′-propynyl]-3-[1″-(methylthio)-2″-propenyl]-1-cyclopentanone: 0.32 g (4%); IR 2179 (s, C≡C), 1745 (s, C=O) cm^{-1}; ^{1}H NMR (major diastereomer) δ 0.14 [18 H, s, $Si(CH_3)_3$], 1.8–2.8 (9 H, m, H-2, H-3, H-4, H-5, H-1′), 2.02 (3 H, s, SCH_3), 3.29 (1 H, ddd, *J* = 9.5, 6.1 Hz, H-1″), 5.09 (1 H, ddd, *J* = 16.4, 2.0, ~0.3 Hz, H-3″), 5.15 (1 H, ddd, *J* = 10.1, 2.0, ~0.2 Hz, H-3″), 5.72 (1 H, ddd, *J* = 16.4, 10.1, 9.4 Hz, H-2″); ^{13}C NMR δ 0.06 [q, $Si(CH_3)_3$], 14.2 (q, SCH_3), 20.3 (t, C-1′), 28.6 (t, C-4), 41.8 (d, C-3), 45.5 (d, C-5), 50.9 (d, C-2), 55.2 (d, C-1″), 86.2 (s, C-1′), 104.2 (s, C-2′), 117.8 (t, C-3″), 135.6 (d, C-2″), 217.3 (s, C-1); mass spectrum, calcd for $C_{21}H_{34}OSSi$ (M$^+$) *m/e* 390.1868, found 390.1867.

Preparation of 3-[3′-(Phenylthio)-2′-propenyl]-1-cyclopentanone (5c). A mixture of anhydrous potassium carbonate (0.1 g) and phosphorus triiodide (1.8 g, 4.37 mmol) in dichloromethane (20 mL) was stirred overnight. The supernatant liquid was then added dropwise to a stirred solution of the sulfoxide **6**[1,24] (1.0 g, 4.03 mmol) in dichloromethane (10 mL) at 0 °C containing anhydrous potassium carbonate (1 g). Immediate reaction took place as indicated by TLC, and the exotherm accompanying addition of the phosphorus triiodide. The sulfoxide **6** had completely reacted upon addition of ca. $^1/_3$ equiv of the reagent solution (0.65 mL, 1.42 mmol, 0.35 equiv). The reaction mixture was then quenched with excess aqueous sodium hydrogen sulfite and extracted into ether (3 × 20 mL). The extracts were washed with water and brine and then dried ($MgSO_4$). Removal of solvent under reduced pressure left a dark viscous oil, which was chromatographed on a silica gel column (1 × 10 mm). Dichloromethane eluted 3-[3′-(phenylthio)-2′-propenyl]-1-cyclopentanone (**5c**) as a colorless oil, 0.42 g (45%). While the starting sulfide **6** was the pure *E* isomer,[24] the product sulfide was a 6:1 mixture of *E* and *Z* isomers, which could not be separated by TLC. It had the following: IR 1741 (s, C=O) cm^{-1}; ^{1}H NMR δ 1.5–2.6 (9 H, m, H-2, H-3, H-4, H-5, H-1′), 5.80 (1 H, dt, *J* = 9.2, 7.0 Hz, H-2′, *Z* isomer), 5.96 (1 H, dt, *J* = 14.8, 6.4 Hz, H-2′, *E* isomer), 6.23 (1 H, dt, *J* = 14.5, ~0.7 Hz, H-3′, *E* isomer), 6.29 (1 H, dt, *J* = 9.0, 1.0 Hz, H-3′, *Z* isomer); mass spectrum, *m/e* 232 (M$^+$). Anal. Calcd for $C_{14}H_{16}OS$: C, 72.39; H, 6.94; S, 13.78. Found C, 72.55; H, 6.79; S, 14.0.

Preparation of 3-Iodo-1-(trimethylsilyl)-1-propyne. Method 1. Iodine (12.7 g, 0.05 mol) was added to a stirred solution of [3-(trimethylsilyl)-2-propynyl]-*o*-phenylene phosphite (13.3 g, 0.05 mol), prepared from 3-(trimethylsilyl)-2-propyn-1-ol[34] and *o*-phenylene phosphorochloridite according to the method of Corey and Anderson,[35] in dichloromethane (160 mL) at 0 °C. The mixture was protected from light and allowed to warm to room temperature. After being stirred for 6 h, the solution was washed successively with aqueous sodium hydroxide (20%, 100 mL) and

(34) Mironov, V. F.; Maksimova, N. G., *Izv. Akad. Nauk SSSR, Ser. Khim* **1960**, 2059; *Chem. Abstr.* **1961**, *55*, 142976.
(35) Corey, E. J., Anderson, J. E. *J. Org. Chem.* **1967**, *32*, 4160.

saturated aqueous sodium disulfite (100 mL) and then dried (Na_2SO_4). Removal of the dichloromethane under reduced pressure left a dark liquid which was distilled under reduced pressure to yield 3-iodo-1-(trimethylsilyl)-1-propyne: 6.2 g (52%); bp 42 °C (2 mm); pale yellow liquid; IR 2951 (s, C≡C) cm^{-1}; ^1H NMR δ 0.84 [9 H, s, $Si(CH_3)_3$], 3.70 (2 H, s, CH_2); mass spectrum, calcd for C_6H_{11} ISi (M^+) m/e 237.9675, found 237.9688; calcd for $C_6H_{11}Si$ (M^+-I) m/e 111.0630, found 111.0634.

Method 2. Iodine (5.06 g, 0.02 mol) was added at once to a stirred solution of 3-(trimethylsilyl)-2-propyn-1-ol (2.56 g, 0.02 mol), tri-*n*-butylphosphine (4.06 g, 0.02 mol), and HMPA (7.16 g, 0.04 mol) in ether (20 mL) at 0 °C under nitrogen. After 15 min the mixture was treated with saturated aqueous sodium disulfite (100 mL) and worked up as described above to yield a dark semicrystalline residue which on distillation at reduced pressure afforded the foregoing iodopropyne (2.3 g, 47%). Entrapment and subsequent decomposition of the product by residual tributylphosphine oxide took place during the distillation. The distilled iodopropyne slowly darkenedand was found by ^1H NMR to have decomposed to the extent of approximately 20% after 5 days at −10 °C in the dark.

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Registry No. 1a, 70597-22-7; **1b**, 74472-75-6; **1c**, 74472-73-4; **1d**, 74472-76-7; **2a** (isomer 1), 78199-65-2; **2a** (isomer 2), 78199-66-3; **2b** (isomer 1), 78199-67-4; **2b** (isomer 2), 78199-68-5; **2c** (isomer 1), 78199-69-6; **2c** (isomer 2), 78199-70-9; **2d** (isomer 1), 78199-71-0; **2d** (isomer 2), 78199-72-1; (*E*)-**3a**, 74472-94-9; (*Z*)-**3a**, 74472-95-0; (*E*)-**3b**, 74472-98-3; (*Z*)-**3b**, 74472-99-4; (*E*)-**3c**, 74472-87-0; (*Z*)-**3c**, 74472-92-7; (*E*)-**3d**, 78199-73-2; (*Z*)-**3d**, 78199-74-3; **4a** (isomer 1), 78199-75-4; **4a** (isomer 2), 78199-76-5; **4b** (isomer 1), 78217-47-7; **4b** (isomer 2), 78199-77-6; **4c** (isomer 1), 78217-48-8; **4c** (isomer 2), 78199-78-7; **4d** (isomer 1), 78199-79-8; **4d** (isomer 2), 78199-80-1; (*E*)-**5a**, 78199-81-2; (*Z*)-**5a**, 78199-82-3; (*E*)-**5b**, 78199-83-4; (*Z*)-**5b**, 78199-84-5; (*E*)-**5c**, 74472-88-1; (*Z*)-**5c**, 74472-93-8; (*E*)-**5d**, 74473-03-3; (*Z*)-**5d**, 74473-04-4; **6**, 77548-22-2; **7** (isomer 1), 78199-85-6; **7** (isomer 2), 78246-83-0; **8**, 78199-86-7; **9**, 78199-87-8; allyl methyl sulfide, 10152-76-8; allyl *tert*-butyl sulfide, 37850-75-2; allyl phenyl sulfide, 5296-64-0; allyl phenyl selenide, 14370-82-2; diphenyl diselenide, 1666-13-3; 3-bromo-1-propene, 106-95-6; 2-cyclopenten-1-one, 930-30-3; hexamethylphosphoramide, 1608-26-0; 3-iodo-1-(trimethylsilyl)-1-propyne, 78199-88-9; [3-(trimethylsilyl)-2-propynyl]-*o*-phenylene-phosphite, 78199-89-0; 3-(trimethylsilyl)-2-propyn-1-ol, 5272-36-6.

Base-Catalyzed Reactions of α,β-Unsaturated Esters and Nitriles. 4. Dimerization of β-Alkyl-Substituted Acrylates[1]

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2-Butenoates [$CH_3CH{=}CHCO_2R$ (**1**), where R = C_1–C_4 alkyl, cyclohexyl, or 1-bornyl] and higher β-alkyl-substituted acrylates [$R'CH{=}CHCO_2C_2H_5$ (**2**), where R′ = C_2–C_9 *n*-alkyl] undergo highly selective (>95%) dimerization in the presence of promoted potassium or sodium catalysts to yield corresponding 2-alkylidene-3-alkylglutarates (**3**). The reaction involves metalation of the β-alkylacrylate at the C-2 position, followed by addition at C-3 of a second monomeric molecule. Changes in the relative extent of dimerization (K_r) as a function of structural and experimental variables were determined. K_r is strongly dependent upon the inductive and steric characteristics of the alcoholic (R) group and of the β-alkyl substituent (R′). For an *n*-alkyl group as R′ the K_r value increases with increase in chain length from C_1 to C_4 but then decreases for longer substituents (C_5–C_9). Among the two geometric isomers in the dimeric product **3**, the isomer with an α-vinylic hydrogen cis to the carboalkoxy group is predominant in all cases, but its relative concentration decreases with an increase in the size of R′. Branched or cyclic β-substituents in **2** prevent dimerization due to steric hindrance in the rate-determining addition step. Promoted potassium or sodium catalysts show much higher dimerization activity compared to supported alkali metals or to alkoxides. For conversions of up to 60%, K_r values in proton-exchanging alkylbenzene solvents and in nonexchanging alkylcyclohexanes are closely similar, indicating faster abstraction of an α-vinylic hydrogen from the monomer, rather than a benzylic hydrogen from the solvent, in the chain regeneration step of the reaction.

It was shown[2] previously that ethyl crotonate undergoes selective dimerization at 110 °C in the presence of potassium–benzylpotassium as catalyst to give the diethyl ester of 2-ethylidene-3-methylglutaric acid in 90% yield. In the present study the possibility of enlarging the scope of base-catalyzed oligomerization reactions was investigated by determining the approximate relative dimerization rates of higher β-alkyl-substituted acrylates ($R'CH{=}CHCO_2Et$, where R′ = C_2–C_9 alkyl or cycloalkyl). The effect of the alcoholic group in 2-butenoates ($CH_3CH{=}CHCO_2R$, where R = C_1–C_4 alkyl, cyclohexyl or 1-bornyl) was also studied. Another purpose of this investigation was to determine the effect of experimental variables, i.e., the temperature, solvent, and type of base catalyst, upon relative dimerization rate.

The experimental procedure and analytical methods were similar to those used previously.[1,2]

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