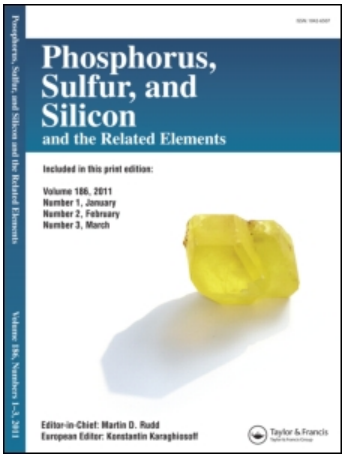

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STEREOCHEMISTRY IN THE PROTONATION OF ENOLATES GENERATED FROM 2-SUBSTITUTED 2-CYCLOPENTEN-1-ONES BY THE 1,4-ADDITION OF TRIALKYLSILYL AND TRIBUTYLSTANNYL ANIONS

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The 1,4-addition of trialkylsilyl anions to 2-(phenylseleno)-2-cyclopenten-1-one affords trans cyclopentanone derivatives. A similar trans selectivty was observed in the protonation of enolates derived from phenylseleno- or phenylthiocyclopentenones by the addition of the vinyl anion corresponding to the prostaglandin ω-chain. On the other hand, the 1,4-additions of trialkylsilyl and tributylstannyl anions to 2-(2-propenyl)-2-cyclopenten-1-one lead to a predominant formation of the cis compounds.

Key words: Stereoselectivity, 1,4-addition, cycleopentenone, trialkylsilyl anion, tributylstannyl anion.

INTRODUCTION

There has been little data on the stereoselectivity in the protonation of enolates derived from the 1,4-addition to α,β-unsaturated ketones, but preferential formation of 2,3-trans products is generally observed.[1] We have been studying efficient synthetic methods starting with α-(phenylseleno)-α,β-unsaturated ketones as attractive 1,4-addition substrates.[2] Liotta and co-workers have reported high selectivity for the 2,3-cis product in the protonation via the 1,4-addition of alkyl groups to selenoenones.[3] We have recently reported an efficient synthesis of 2-alkyl-2-cycloalken-1-ones, starting with selenocycloalkenones, in which the allylation of enolates derived from the conjugate addition of tributylstannyl- or trialkylsilyllithium proceeds with high stereoselectivity.[2c,f] We describe herein the protonation reaction via the 1,4-addition of trialkylsilyl groups to 2-(phenylseleno)- and 2-(2-propenyl)-2-cyclopenten-1-ones.

RESULTS AND DISCUSSION

Conjugate addition of (trialkylsilyl)lithium or cuprates[4] to 2-(phenylseleno)-2-cyclopenten-1-one[5] (**1a**) was studied. The results are summarized in Table I. A THF solution of selenocyclopentenone **1a** was treated at −78°C for 5 min with (trimethylsilyl)lithium,[4a] prepared *in situ* from hexamethyldisilane and methyllithium in THF-hexamethylphosphoric triamide (HMPA). A mixture of an aqueous NH_4Cl and ethyl ether was poured into the reaction mixture with vigorous stirring, giving *trans*- and *cis*-2-(phenylseleno)-3-(trimethylsilyl)-1-cyclopentanones (trans-**2** and cis-**2**) in 57 and 10% yield, respectively (trans:cis = 84:16, entry 1).

TABLE I

The 1,4-addition of various nucleophiles to 2-substituted 2-cyclopenten-1-ones

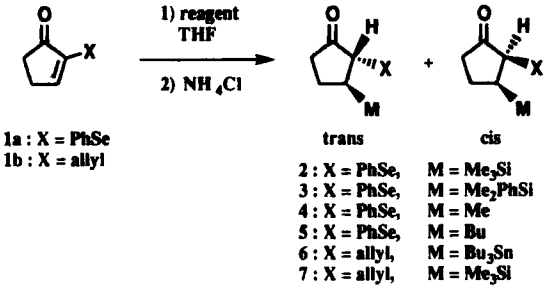
Entry	Substr.	Reagent	Temp °C	Time	Product	Yield %	Ratio [a] trans : cis
1	**1a**	Me_3SiLi	-78	5 min	**2**	67	84 : 16
2	**1a**	$(Me_3Si)_2Li$	-78 → -20	30 min	**2**	59	80 : 20
3	**1a**	$PhMe_2SiLi$	-78 → r t	3 h	**3**	—[b]	———
4	**1a**	$PhMe_2Si(Me)$-$Cu(CN)Li_2$	-78	15 min	**3**	94	89 : 11
5[c]	**1a**	Me_2CuLi	-20	30 min	**4**	95	84 : 16
6[c]	**1a**	Bu_2CuLi	-20	30 min	**5**	97	< 1 : >99
7[d]	**1b**	Bu_3SnLi	-78	5 min	**6**	90	13 : 87 [e]
8	**1b**	Me_3SiLi	-78	5 min	**7**	91	61 : 39 [e]

a) Isolated ratio. b) The 1,2-adduct was formed, see ref. 4f. c) Ref. 3. d) Ref.2c.
e) Determined by HPLC and ^1H NMR analysis.

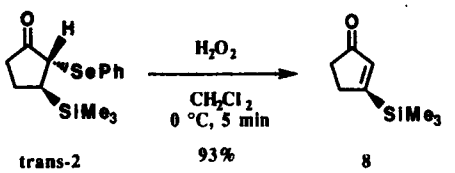
The homosilylcuprate was also capable of being added to selenocyclopentenone **1a** in a 1,4-conjugate fashion to give trans-**2** and cis-**2** in a similar ratio (entry 2). The cis isomer cis-**2** was confirmed not to isomerize to the trans under the purification conditions by silica gel column chromatography. In addition, the reaction mixture derived from the addition of the silyllithium to **1a** was quenched with a mixture of an aqueous NH_4Cl and ethyl ether, and three aliquots of the ethereal solution were taken after stirring the resultant mixture for periods shorter than 1 min, 10 min, and 1 h, respectively. Each ethereal solution was analyzed by HPLC as well as ^1H NMR and found to contain trans- and cis-**2** in the same ratio (84:16). These results suggest that the products are kinetically controlled. Several attempts for the 1,4-addition of (dimethylphenylsilyl)lithium[6] failed, giving only 1,2-adduct (entry 3).[7] The higher order mixed silylcuprate[4g] was found to be superior for the 1,4-addition to **1a**, and *trans*- and *cis*-3-(dimethylphenylsilyl)-2-(phenylseleno)-1-cyclopentanone **3** was formed in 94% yield in a trans/cis ratio of 89:11 (entry 4).

The stereochemistry of the adducts was determined on the basis of the chemical evidence obtained by oxidative elimination of the phenylseleno group (Scheme II): For example, each isomer of compound **2** was separately treated with hydrogen peroxide in CH_2Cl_2 at 0°C. One isomer afforded 3-(trimethylsilyl)-2-cyclopenten-1-one (**8**) in 96% yield after stirring for 5 min at 0°C, whereas the other did not give **8** but the reaction resulted in a complex reaction mixture after stirring for 1 h at 0°C. Thus, the former was assigned as trans-**2** and the latter as cis-**2**, on the basis of the well-defined *syn* elimination of the selenoxide.[8]

The reaction of the selenocyclopentenone **1a** with trialkylsilyl anions resulted in the predominant formation of the trans compounds. The trans selectivity in the reaction of **1a** is in agreement with the stereochemical outcome[9] observed in reactions of α-alkylcycloalkenones with alkylcopper reagents, whereas it does not agree with the data reported by Liotta and co-workers[3] shown in Table I (entries 5 and 6). This discrepancy would arise from the difference in steric bulkiness between the nucleophiles, *i.e.*, the trialkylsilyl group and the methyl or butyl group.

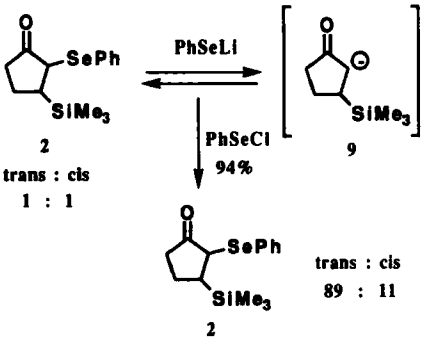


SCHEME I



SCHEME II

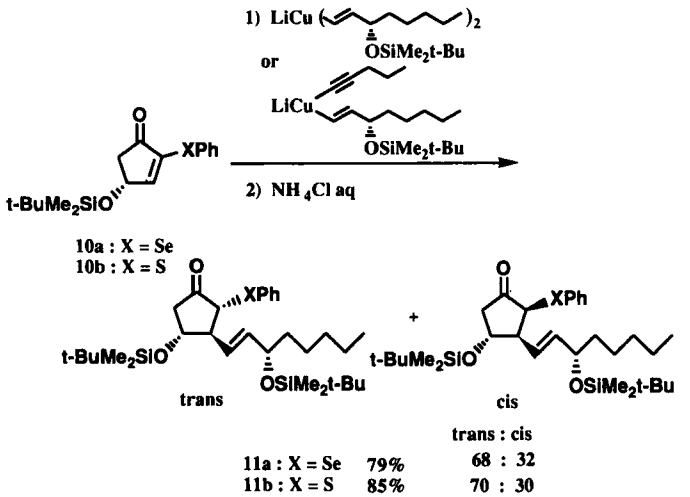
We have observed that allylation of enolates derived from selenocyclopentenone **1a** by the 1,4-addition of silyl or stannyl nucleophiles affords 2-(2-propenyl)-2-(phenylseleno)-3-(trialkylsilyl or tributylstannyl)-1-cyclopentanones with exclusive or high cis selectivity (cis configuration between the phenylseleno and trialkylsilyl or tributylstannyl groups).[2c,f] In these instances, an allyl electrophile approaches the enolate from the less hindered side, resulting in the predominant formation of the cis isomer which is the steric-approach-controlled product.[10] On the other hand, the trans selectivity obtained in the protonation of 3-trialkylsilyl enolates is controlled by the repulsive effect between the phenylseleno and trialkylsilyl groups which would develop during the course of the formation of the cis isomer,[11] namely, the reaction would proceed through a late transition state since the trans compound is more stable than the cis, as reasonably supported by the following results. As shown in Scheme III, a 1:1 mixture of trans-**2** and cis-**2** was treated with lithium phenylselenolate in THF at −78°C for 30 min subsequently it was treated with



SCHEME III

phenylselenyl chloride in the presence of HMPA at −78°C for 15 min to give an 89:11 mixture of trans-**2** and cis-**2** in 94% yield, resulting partly from an equilibrium between **2** and the lithium enolate **9** and partly from selenenylation of **9**.[3] In addition, cis-**2** could be easily transformed to trans-**2** under an equilibrium. Thus, a 57/43 mixture of trans-**2** and cis-**2** was treated with K_2CO_3 in methanol for 1 day to give a mixture of trans-**2** and cis-**2** in a ratio of 94:6. The kinetically-controlled diastereoselectivity (trans:cis = 84:16) observed in the protonation of the enolate fully reflects the thermodynamic stability of compound **2**, giving product-development-controlled products.[10]

We also examined the reaction of several 2-substituted 2-cyclopentenones. The 1,4-addition of a mixed vinylcuprate to 4-[(*tert*-butyldimethylsilyl)oxy]-2-(phenylseleno)-2-cyclopenten-1-one (**10a**) gave, after protonation, the adduct **11a** in a trans/cis ratio of 68:32[2a] (Scheme IV). The addition to 2-(phenylthio)cyclopentenone **10b** also resulted in the predominant formation of the trans compound trans-**11b** (trans:cis = 70:30). In contrast, the 1,4-addition of tributylstannyllithium to 2-(2-propenyl)-2-cyclopenten-1-one (**1b**) yielded the adduct **6** in a trans/cis ratio of 13:87 (Table I, entry 7). The addition of trimethylsilyllithium to **1b** gave the adduct **7** in a trans/cis ratio of 61:39, showing a slight increase of the cis formation as compared with the reaction starting with selenocyclopentenone **1a** (entries 1, 2 and 8). The predominant formation of the cis compound cis-**7** in the reaction of **1b** with tributylstannyllithium is noteworthy. McGarvey and Williams have proposed that the stannyl group is perpendicularly disposed in the transition state of the alkylation of enolates derived from the addition of a stannyl anion to α,β-unsaturated esters, where the approaching reagent is directed antiperiplanar to the stannyl group.[12] Thus, provided that the stannyl group is disposed perpendicularly to the enolate in our reaction, it allows the protonation to occur from the less hindered side to give the cis product. On the other hand, enolates of the 2-(phenylseleno)cyclopentanone having a silyl group or a relatively bulky alkyl group



SCHEME IV

at the 3 position gave the stable trans isomer as the major product. Koga and coworkers have pointed out the importance of the bulkiness of groups at the 2 and 3 positions for the stereoselection in the alkylation of enolates.[13] Our data, together with the reported results, reveal that the protonation of enolates often gives a different stereoselection from the alkylation, and the stereoselectivity depends not only on the groups at the 2 and 3 positions but also on the electrophiles.

In summary, the protonation reaction of enolates derived from 2-(phenylseleno)- or 2-(phenylthio)-2-cyclopenten-1-one by the 1,4-addition of trialkylsilyl and vinylic nucleophiles afforded *trans*-2,3-disubstituted cyclopentanones as major products, whereas the 1,4-addition of trimethylsilyl anions to 2-(2-propenyl)-2-cyclopenten-1-one gave *trans*-2-(2-propenyl)-2-(trimethylsilyl)-2-cyclopenten-1-one as a major product but in an increased ratio of the cis isomer.

EXPERIMENTAL

General

^{1}H NMR spectra were obtained using a JEOL JNM-PMX60Si (60 MHz) or Varian Gemini 200 (200 MHz) spectrometer. Chemical shifts of ^{1}H NMR spectra are reported in δ from tetramethylsilane. IR spectra were recorded on JASCO A-102 spectrometer, and the IR figures reported are ν_{max} in cm^{-1} with the following relative intensities: br (broad), s (strong), m (medium), or w (weak). Mass spectra were recorded on either ESCO EMD-05B or Hitachi M-2000 spectrometers. Elemental analyses were recorded on Perkin-Elmer 240B.

All reactions were performed in oven and flame-dried glassware under argon. Air- and moisture-sensitive reagents and solvents were transferred *via* a syringe or cannula and were introduced into reaction vessels through rubber septa. All reactions were monitored by TLC carried out on 0.25-mm E. Merck silica gel plates (60F-254). TLC plates were visualized with UV light and 7% phosphomolybdic acid in ethanol-heat. Medium-pressure column chromatography was carried out on a Michel Miller column packed with Fuji Davison silica gel BW-200, equipped with FMI lab pump RP-G150 and a FMI pulse dampener PD-60-LF, normally at a pressure of 1–2 kg cm^{-2}.

Unless otherwise noted, materials were obtained from commercial suppliers and were used without purification. THF and diethyl ether were freshly distilled from sodium benzophenone ketyl under argon before use. HMPA and CH_2Cl_2 were freshly distilled from calcium hydride under argon before use.

Reaction of selenocyclopentenone **1a** *with (trimethylsilyl)lithium*: To a solution of hexamethyldisilane (255 mg, 1.74 mmol) in THF-HMPA (7.5 ml, 4:1) was added a 1.3 M diethyl ether solution of methyllithium (1.0 ml, 1.30 mmol) at 0°C and the resultant red-colored solution was stirred for 15 min to form (trimethylsilyl)lithium.[4a] The solution was then cooled to −78°C and a solution of **1a** (237 mg, 1.00 mmol) in THF (0.5 ml and 0.1 ml for rinse) was added dropwise. The reaction mixture was stirred for an additional 5 min, when the 1,4-addition was complete as judged by TLC. Then a mixture of a saturated aq NH_4Cl (5 ml) and diethyl ether (10 ml) was added to the vigorously stirred solution. The organic layer was separated and the aqueous layer was extracted with diethyl ether (3 × 10 ml). The combined organic layer was washed successively with water (2 × 10 ml) and brine (10 ml), dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel 18 g, 95:5 hexane/ethyl acetate) to give *trans*-**2** (176 mg, 57%) and *cis*-**2** (31 mg, 10%). *trans*-**2**: ^{1}H NMR (60 MHz; CCl_4) δ 0.06 (9 H, s, 3 × CH_3), 1.02–2.39 (5 H, m), 3.38 (1 H, d, J = 5.6 Hz) and 7.08–7.65 (5 H, m); IR (neat) 3050 (w), 2955 (m), 2880 (m), 1725 (s), 1575 (w), 1475 (m), 1425 (m), 1400 (m), 1300 (w), 1250 (s), 1200 (w), 1155 (m), 1095 (m), 1063 (w), 1020 (w), 1005 (w), 1000 (w), 960 (w), 905 (m), 850 (s), 835 (s), 735 (s), 690 (m) cm^{-1}; MS m/e (rel intensity) 312 (M^+, ^{80}Se, 11), 230 (40), 215 (10), 155 (100), 135 (21). Anal. Calcd for $C_{14}H_{20}OSeSi$: C, 54.01; H, 6.47. Found: C, 54.10; H, 6.51. *cis*-**2**: ^{1}H NMR (60 MHz; CCl_4) δ 0.17 (9 H, s, 3 × CH_3), 1.11–2.79 (5 H, m), 3.60 (1 H, d, J = 6.0 Hz), and 7.06–7.66 (5 H, m, Ph); IR (neat) 3060 (w), 2960 (m), 2905 (m), 2820 (w), 1725 (s), 1580 (w), 1480 (m), 1455 (w), 1440 (m), 1405 (w), 1310 (w), 1250 (s), 1190 (w), 1155 (m), 1115 (m), 1065 (w), 1040 (w), 1020 (w), 1000 (w), 980 (m), 920 (m), 850 (s), 840 (s), 775 (w), 740 (s), 690 (m) cm^{-1}; MS m/e 312 (M^+, ^{80}Se, 32), 230 (18), 215 (33), 155 (100), 135 (33). Anal. Calcd for $C_{14}H_{20}OSeSi$: C, 54.01; H, 6.47. Found: C, 54.12; H, 6.53.

Reaction of **1a** *with bis(trimethylsilyl)cuprate*: To a red solution of (trimethylsilyl)lithium obtained from hexamethyldisilane (255 mg, 1.74 mmol) and a 1.3 M diethyl ether solution of methyllithium (1.0 ml, 1.30 mmol) in THF-HMPA (7.5 ml, 4:1) as described above was added copper (I) cyanide (58 mg, 0.65 mmol) at 0°C and the reaction mixture was stirred for 20 min. The mixture was then cooled to −78°C and a solution of **1a** (128 mg, 0.54 mmol) in THF (0.6 ml) was added dropwise. The mixture was stirred for 30 min, during which time the temperature was allowed to increase gradually to −20°C. Workup and purification as described above gave *trans*-**2** (79 mg, 47%) and *cis*-**2** (20 mg, 12%).

Reaction of **1a** *with (dimethylphenylsilyl)(methyl)cyanocuprate*: To a suspension of copper (I) cyanide (47 mg, 0.52 mmol) in THF (1.0 ml) was added a 1.3 M diethyl ether solution of methyllithium (0.4 ml, 0.52 mmol) at −50°C. The resultant clear solution was stirred at the same temperature for 10 min and then cooled to −78°C and a 0.85 M THF solution of (dimethylphenylsilyl)lithium[6] (0.61 ml, 0.52 mmol) was added. The resultant deep red solution was stirred for 30 min at −78°C and a solution of **1a** (98 mg, 0.41 mmol) in THF (0.7 ml) was added dropwise over 5 min. After stirring for an additional 5 min, a saturated aq NH_4Cl (2 ml) and 25–28% ammonia water (1 ml) were successively added to the vigorously stirred solution. The organic layer was separated and the water layer was extracted with diethyl ether (3 × 10 ml). The combined organic extracts were washed with brine (10 ml), dried over $MgSO_4$, and filtered. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel 20 g, 93:7 and 90:10 hexane/ethyl acetate) to give *trans*-**3** (129 mg, 84%) and *cis*-**3** (16 mg, 10%). *trans*-**3**: ^1H NMR (60 MHz; CCl_4) δ 0.32 (6 H, s, 2 × CH_3), 1.02–2.50 (5 H, m), 3.41 (1 H, d, J = 5.6 Hz), and 7.05–7.70 (10 H, m, 2 × Ph); IR (neat) 3050 (m), 3000 (w), 2950 (m), 2870 (w), 1950 (w, br), 1880 (w, br), 1805 (w, br), 1710 (s), 1570 (w), 1470 (m), 1455 (w), 1420 (m), 1400 (w), 1300 (w), 1250 (m), 1200 (w), 1150 (m), 1110 (m), 1065 (w), 1020 (w), 1000 (w), 955 (w), 900 (m), 830 (s), 815 (s), 775 (m), 730 (s), 690 (s) cm^{-1}; MS m/e 374 (rel intensity) (M^+, ^{80}Se, 0.7), 314 (0.5), 292 (0.8), 217 (15), 157 (4), 135 (100). Anal. Calcd for $C_{19}H_{22}OSeSi$: C, 61.11; H, 5.94. Found: C, 61.01; H, 6.04. *cis*-**3**: ^1H NMR (60 MHz; CCl_4) δ 0.48 (3 H, s, CH_3), 0.52 (3 H, s, CH_3), 1.60–2.78 (5 H, m), 3.55 (1 H, d, J = 5.0 Hz), and 7.05–7.61 (10 H, m, 2 × Ph); IR (neat) 3050 (w), 3000 (w), 2950 (m), 2860 (w), 1950 (w, br), 1870 (w, br), 1800 (w, br), 1720 (s), 1570 (w), 1475 (w), 1450 (w), 1430 (w), 1420 (m), 1400 (w), 1300 (w), 1245 (m), 1190 (w), 1150 (m), 1110 (m), 1060 (w), 1035 (w), 1020 (w), 995 (w), 970 (w), 915 (w), 830 (s), 810 (s), 780 (m), 730 (s), 690 (s) cm^{-1}; MS m/e 374 (M^+, ^{80}Se, 2), 292 (0.8), 217 (16), 157 (5), 135 (100). Anal. Calcd for $C_{19}H_{22}OSeSi$: C, 61.11; H, 5.94. Found: C, 61.19; H, 6.14.

Oxidation of **2**: To an ice-cooled CH_2Cl_2 (2.0 ml) solution of trans-**2** (137 mg, 0.44 mmol) was added H_2O_2 (31%, 0.5 ml, 5.95 mmol) at 0°C, and the mixture was stirred for 5 min. The mixture was then washed successively with an aqueous $NaHCO_3$ solution (3 ml) and H_2O (3 ml). The aqueous solution was extracted with CH_2Cl_2 (3 × 5 ml). The combined organic solution was dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel 3 g, 88:12 hexane/ethyl acetate) to give 3-(trimethylsilyl)-2-cyclopenten-1-one[14] (**8**) (63 mg, 93%). ^1H NMR (200 MHz; $CDCl_3$) δ 0.21 (6 H, s, 3 × CH_3), 2.32–2.38 (2 H, m, H-4), 2.69–2.76 (2 H, m, H-5), and 6.35 (1 H, t, J = 2.1 Hz, H-3); IR (neat) 2950 (m), 2910 (m), 1700 (s), 1560 (w), 1435 (w), 1400 (w), 1320 (w), 1250 (m), 1180 (w), 1020 (m), 975 (m), 840 (s), 810 (m), 750 (m), 695 (w) cm^{-1}. On the other hand, similar treatment of cis-**2** (98 mg, 0.31 mmol) with H_2O_2 (31%, 0.4 ml, 4.76 mmol) at 0°C for 1 h afforded a complicated reaction mixture.

Reaction of **2** *with lithium benzenselenolate and benzenselenenyl chloride*: To a solution of benzenselenol (37 mg, 0.24 mmol) in THF (1.0 ml) was added butyllithium (1.58 M/hexane, 0.15 ml, 0.24 mmol) at room temperature, and the mixture was stirred for 10 min.[15] The mixture was cooled to −78°C, and a solution of **2** (cis:trans = 1:1, 66 mg, 0.21 mmol) in THF (0.7 ml) was added. Immediately after the addition, the color of the solution turned to yellow. The mixture was stirred for 30 min. Then was added HMPA (0.08 ml, 0.46 mmol) and a solution of benzeneselenenyl chloride (49 mg, 0.26 mmol) in THF (0.5 ml), and the mixture was stirred for 10 min. A mixture of saturated aq NH_4Cl (5.0 ml) and diethyl ether (8.0 ml) was added. The aqueous solution was extracted with diethyl ether (2 × 5 ml) and the combined organic extracts were washed successively with water (5 ml) and brine (5 ml), and dried over $MgSO_4$. After filtration the solvent was removed under reduced pressure and the residue was purified by column chromatography (silica gel 3g, 98:2 hexane/ethyl acetate) to give a trans/cis mixture of **2** (62 mg, trans:cis = 89:11, 94%).

Reaction of allylcyclopentenone **1b** *with (trimethylsilyl)lithium*: To a red solution of (trimethylsilyl)lithium obtained from hexamethyldisilane (195 mg, 1.20 mmol) and 1.16 M diethyl ether solution of methyllithium (0.8 ml, 0.93 mmol) in THF-HMPA (5.0 ml, 4:1) as described above was added a solution of **1b** (87 mg, 0.71 mmol) in THF (0.6 ml and 0.1 ml for rinse) at −78°C, and the mixture was stirred for 5 min. Then a saturated aq NH_4Cl (5 ml) and diethyl ether (5 ml) were added. The

usual workup afforded a crude oil, which was purified by column chromatography (silica gel 14 g, 92:8 hexane/ethyl acetate) to give **7** (126 mg, 91%), which was shown to be a 61:39 mixture of *trans*-**7** and *cis*-**7** by ^{1}H NMR. ^{1}H NMR (200 MHz; $CDCl_3$) δ 0.05 (9 H, s, *trans* $Si(CH_3)_3$), 0.08 (9 H, s, *cis* $Si(CH_3)_3$), 1.14–1.31 (1 H, m), 1.45–1.70 (1 H, m), 1.86–2.46 (5 H, m), 2.50–2.64 (1 H, m), 4.96–5.09 (2 H, m, CH=CH_2), 5.54–5.76 (1 H, m, *trans* CH=CH_2), and 5.77–5.98 (1 H, m, *cis* CH=CH_2); IR (neat) 3090 (w), 2960 (s), 1735 (s), 1640 (m), 1435 (m), 1405 (m), 1250 (s), 1165 (m), 1140 (w), 1105 (w), 1060 (w), 1010 (m), 1000 (m), 910 (m), 880 (s), 835 (s), 750 (m), 730 (m), 690 (m) cm^{-1}; MS m/e (rel intensity) 196 (M^+, 25), 195 (100), 181 (13), 155 (57), 123 (8), 82 (3). Anal. Calcd for $C_{11}H_{20}OSi$: C, 67.28; H, 10.27. Found: C, 67.31; H, 10.41.

1,4-Addition of a vinylcuprate to (4R)-4-[(tert-butyldimethyl)silyloxy]-2-(phenylseleno)-2-cyclopenten-1-one **10a**: A 2.2 M pentane solution of *tert*-butyllithium (1.18 ml, 2.61 mmol) was added dropwise to a diethyl ether solution (5 ml) of (3S)-(E)-[(*tert*-butyldimethylsilyl)oxy]-1-iodo-1-octene[16] (481 mg, 2.61 mmol) at −78°C, and the mixture was stirred at −78°C for 2 h. To this solution was added CuBr-trimethylphosphite complex (175 mg, 0.65 mmol), prepared according to the literature,[17] and the mixture was stirred for 1 h. Then a solution of phenylselenocyclopentenone[2a] **10a** (160 mg, 0.44 mmol) in diethyl ether (1 ml) was added. After 10 min, NH_4Cl saturated aq solution (5 ml) and diethyl ether (5 ml) were added. The usual workup afforded a crude oil, which was purified by column chromatography (silica gel 40 g, 99:1 hexane/ethyl acetate) to give **11a** (207 mg, 79%), which was shown to be a 68:32 mixture of *trans*-**11a** and *cis*-**11a** by HPLC and ^{1}H NMR. HPLC t_R 33.5 and 46.0 min (Finepack SIL, eluent, hexane/AcOEt = 99:1, flow speed, 1.0 ml/min): ^{1}H NMR (200 MHz; $CDCl_3$) δ 0.04, 0.06 (12 H, s), 0.84 (18 H, s), 1.10–1.70 (11 H, m), 2.22 (1 H, dd, J = 16.0, 5.0 Hz), 2.59 (1 H, dd, J = 16.0, 7.0 Hz), 2.68–2.90 (1 H, m), 3.32 (1 H, d, J = 7.0 Hz, *trans*-PhSe—CH; a small d appeared at 3.89, J = 12.0 Hz, *cis*-PhSeCH), 4.02–4.24 (2 H, m, 2 × O—CH), 5.02–5.88 (2 H, m, CH=CH), 7.22–7.80 (5 H, m); IR (neat) 2950 (s), 2900 (s), 1730 (s), 1570 (w), 1460 (m), 1350 (m), 1250 (s), 1110 (s), 1060 (m), 1000 (w), 960 (m), 830 (s), 760 (s); MS m/e (rel intensity) 610 (M^+, 16), 553 (56), 453 (184), 396 (50), 369 (15), 322 (58), 294 (100), 157 (22). Anal. Calcd for $C_{31}H_{54}O_3SeSi_2$: C, 61.05; H, 8.92. Found: C, 61.04; H, 9.21.

Reaction of thiocyclopentenone **10b** *with mixed vinylcuprate*: A 2.2 M pentane solution of *tert*-butyllithium (0.17 ml, 0.37 mmol) was added dropwise to a diethyl ether solution (0.5 ml) of (3S)-(E)-[(*tert*-butyldimethylsilyl)oxy]-1-iodo-1-octene (69 mg, 0.19 mmol) at −78°C, and the mixture was stirred at −78°C for 2 h. Then a solution of pentynylcopper(I)[18] (25 mg, 0.19 mmol) and hexamethylphosphorous triamide (76 mg, 0.47 mmol) in diethyl ether (0.5 ml) was added. The resulting mixture was stirred for 1 h before thiocyclopentenone[19] **10b** (50 mg, 0.16 mmol) in diethyl ether (0.5 ml) was added. After 15 min, a saturated aq NH_4Cl (1 ml) and diethyl ether (1 ml) were added. The usual workup afforded a crude oil, which was purified by column chromatography (silica gel 10 g, 99:1 hexane/ethyl acetate) to give **11b** (69 mg, 85%), which was shown to be a 70:30 mixture of *trans*-**11b** and *cis*-**11b** by ^{1}H NMR. ^{1}H NMR (200 MHz; $CDCl_3$) δ 0.03–0.08 (12 H, m, 4 × CH_3), 0.86 (9 H, s, *trans t*-Bu), 0.87 (9 H, s, *cis t*-Bu), 0.89 (9 H, s, *trans t*-Bu), 0.90 (9 H, s, *cis t*-Bu), 1.17–1.60 (11 H, m), 2.19 (1 H, dd, J = 8.5, 18.3 Hz, *trans* H-5), 2.21–2.35 (1 H, m, *cis* H-5), 2.57 (1 H, ddd, J = 7.4, 7.4, 10.9 Hz, *trans* H-3), 2.65 (1 H, dd, J = 1.6, 18.1 Hz, *cis* H-5), 2.71 (1 H, dd, J = 6.5, 18.3 Hz, *trans* H-5), 3.00–3.12 (1 H, m, *cis* H-3), 3.16 (1 H, d, J = 10.8 Hz, *trans* H-2), 4.00–4.18 (2 H, m, *trans* 2 × CHOSi, 1 H, m, *cis* CHOSi), 4.09 (1 H, d, J = 10.4 Hz, *cis* H-2), 4.30–4.38 (1 H, m, *cis* H-4), 5.43 (1 H, dd, J = 8.9, 15.4 Hz, *cis*), 5.51 (1 H, dd, J = 7.9, 15.4 Hz, *trans*), 5.66 (1 H, dd, J = 4.9, 15.4 Hz, *cis*), 5.69 (1 H, dd, J = 4.9, 15.4 Hz, *trans*), and 7.20–7.50 (5 H, m, Ph); IR (neat) 3050 (w), 2930 (s), 2855 (s), 1745 (s), 1580 (w), 1460 (m), 1360 (m), 1250 (s), 1110 (s), 1085 (m), 1005 (w), 965 (m), 835 (s), 775 (s); MS m/e (rel intensity) 562 (M^+, 5), 547 (1.5), 505 (84), 453 (4), 447 (1), 430 (50), 405 (56), 373 (47), 359 (12), 321 (8), 295 (65), 273 (100). Anal. Calcd for $C_{31}H_{54}O_3SSi_2$: C, 66.13; H, 9.65. Found: C, 66.07; H, 9.81.

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