Vinyl Anion Equivalents. Part 3.† Diastereoselective Allylation of 2-Phenylseleno-3-trialkylsilyl- and 2-Phenylthio-3-(tributylstannyl)cyclopentanone Enolates

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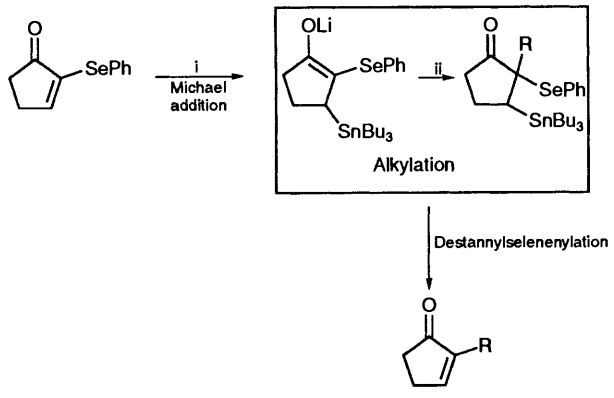
Diastereoselective allylation of enolates derived from 2-phenylseleno(thio)cyclopent-2-enone by conjugate addition of a silyl or stannyl nucleophile has been investigated. All allylated compounds are formed in high *cis* preference. Calculation of the energies of the formation and the stereochemical outcome at equilibrium show higher stability of the *cis* compounds than of the corresponding *trans* isomers. The efficient transformation of the allylated products into 2-allylcyclopent-2-enone is also described.

The tandem dialkylation reaction of cyclopentenones has provided efficient procedures for constructing many natural products having one or more cyclopentane rings.[1] The stereochemistry in the alkylation of 3-alkylcyclopentanone enolates, generated by conjugate addition to cyclopentenones, has been well studied,[2] but there are no ample stereochemical studies on the alkylation of 2,3-dialkylated cyclopentanone enolates derived from conjugate addition of nucleophiles to 2-substituted cyclopent-2-enones.[3,4]

We recently reported an efficient synthesis of 2-substituted cycloalkenones involving the prostaglandin key intermediate *via* a novel α-keto vinyl anion equivalent (Scheme 1).[5] This



Scheme 1 *Reagents:* i, Bu_3SnLi; ii, RX

enone synthesis is composed of three consecutive reactions, starting with 2-(phenylseleno)cyclopent-2-enone; first, conjugate addition of (tributylstannyl)lithium followed by alkylation of the resulting enolate, and destannylselenenylation at the final stage. Interestingly, the alkylation in the above reaction proceeds with high diastereoselectivity, leading to the exclusive formation of the *cis* isomer. We have been interested in undertaking further studies on the reaction of the α-keto vinyl anion equivalent having other functional groups. We describe herein the diastereoselective allylation of the enolates derived from conjugate addition of (trialkylsilyl)lithium or cuprate to 2-(phenylseleno)cyclopent-2-enone and (tributylstannyl)lithium to 2-(phenylthio)cyclopent-2-enone. Transformation of the resulting cyclopentanones into 2-allylcyclopent-2-enone is also described.

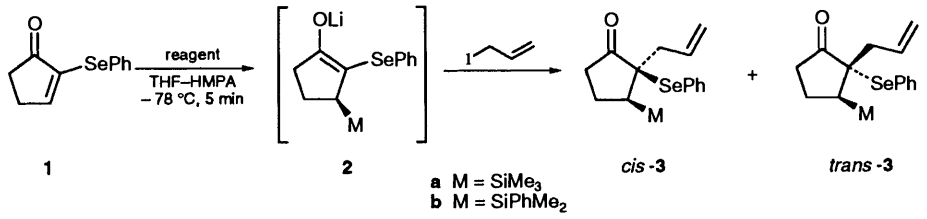
† For Part 2, see ref. 5(*b*).
‡ The results will be published elsewhere.

Results and Discussion

Readily available 2-(phenylseleno)cyclopent-2-enone[6] **1** was treated with (trialkylsilyl)lithium or cuprates in tetrahydrofuran (THF) at −78 °C,[7] and the resulting enolate **2** was allylated with allyl iodide (2 mol equiv.) in the presence of hexamethylphosphoric triamide (HMPA, 3 mol equiv.) to give the diastereoisomeric mixture of the allylated product **3**. The results are summarized in Table 1. Allylation of the enolate **2a** (M = $SiMe_3$), generated by the addition of (trimethylsilyl)lithium,[7a] gave an 86:14 mixture of products *cis*-**3a** and *trans*-**3a** in 68% yield (entry 1). In this reaction, the α'-monoallylated and α',α'-diallylated compounds were formed in 20–30% yield. In order to reduce the formation of these undesired products, reactions under a variety of conditions were examined. Given the results in entries 2 and 3, the yield of **3a** was not improved by using smaller amounts of the silyllithium reagent, because these undesired products seemed to be formed immediately after the addition of allyl iodide under these conditions. The homosilylcuprate[7d] gave compound **3a** in poor yield (entry 4). The selenocyclopentanone enolate generated by the addition of the higher order mixed silylcuprate[7g] seemed not so reactive toward the allylation, and gave a *cis*:*trans* (87:13) mixture of compound **3a** in lower yield (60%, entry 5) than that expected from the high-yield formation of the enolate: the above mixed silylcuprate afforded the 1,4-conjugate addition product in high yield when the reaction mixture was quenched with aq. NH_4Cl before the addition of allyl iodide.‡ Apparently all these reactions gave the allylated product **3** in the similar *cis*:*trans* ratio. It should be noted that the formation of the *cis* isomer increased when the mixed dimethylphenylsilylcuprate was used.

The stereochemistry of the allylated compounds **3** was determined by a nuclear Overhauser effect (NOE) study in the ^1H NMR spectrum as follows. In the spectrum of *cis*-**3a**, obtained as the major product, the signal of the allylic methylene protons showed an 8% NOE on irradiation at the H^a proton, whereas no appreciable NOE was observed between the corresponding protons in *trans*-**3a** (Fig. 1). These data indicate that the phenylseleno and trimethylsilyl groups of the major product are in a *cis* orientation. The stereochemistry was further confirmed on the basis of the chemical evidence obtained by the oxidative elimination of the phenylseleno group. Both isomers were separately treated with H_2O_2 in methylene dichloride at 0 °C. The *trans* isomer *trans*-**3a** afforded 2-allyl-3-(trimethylsilyl)cyclopent-2-enone **4** quantitatively after stirring for 10 min, whereas *cis*-**3a** did not give enone **4** (1%), but instead yielded 2-allylcyclopent-2-enone and 2-(prop-2-enylidene)-3-tri-

Table 1 Diastereoselective allylation of 2,3-disubstituted enolates **2**



Entry	Reagent (mol equiv.)	Allylation conditions		Product	Yield (%)[a]	Ratio[b]
		Temp. (T/°C)[c]	Time (t/h)			*cis*:*trans*
1	Me_3SiLi (1.02)	−78 → 0	1.5	**3a**	68	86:14
2	Me_3SiLi (0.90)	−78 → 0	1.5	**3a**	57	86:14
3	Me_3SiLi (1.21)	−78 → 0	1.5	**3a**	47	86:14
4	$(Me_3Si)_2CuLi$ (1.12)	−78 → rt	2.0	**3a**	23	85:15
5	$Me_3Si(Me)Cu(CN)Li_2$ (1.02)	−78 → rt	2.0	**3a**	60	87:13
6	$PhMe_2Si(Me)Cu(CN)Li_2$ (1.02)	−78 → rt	2.0	**3b**	58	94:6

[a] Isolated yield. [b] Determined by ^1H NMR spectroscopy and HPLC. [c] rt = room temp.

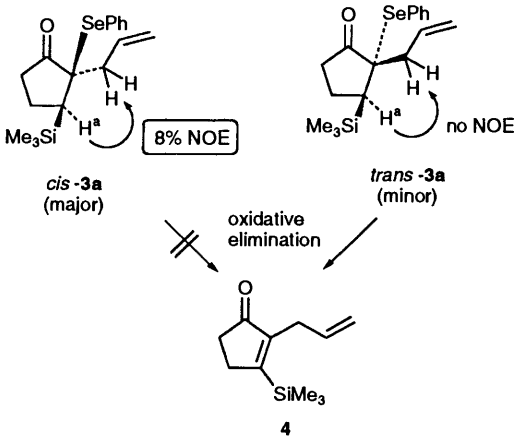
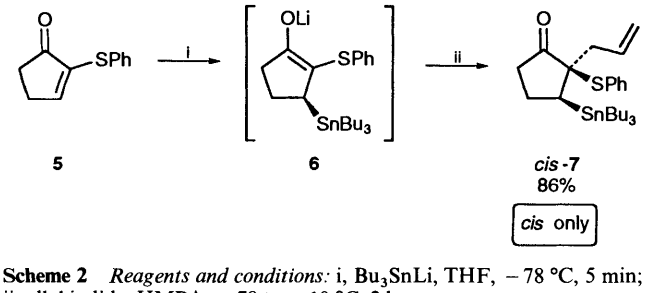


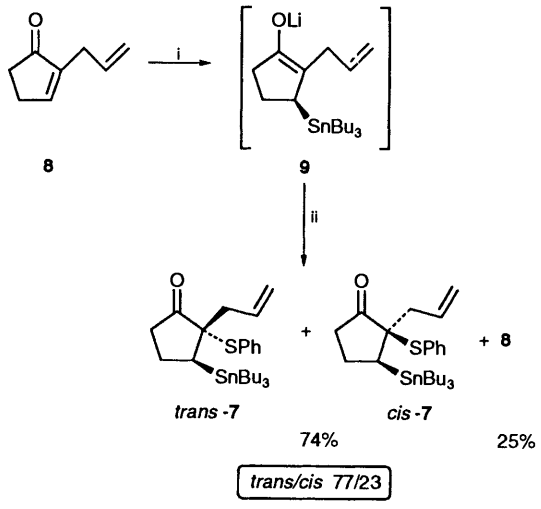
Fig. 1 Stereochemical determination of compounds **3a**

methylsilyl)cyclopentanone. These results are in good accord with the assigned stereochemistries for *cis*-**3a** and *trans*-**3a**, since *syn* elimination is well demonstrated in selenoxide eliminations.[8]

We next examined allylation of the enolate **6** bearing phenylthio and tributylstannyl groups at the 2- and 3-position, respectively. A solution of 2-(phenylthio)cyclopent-2-enone[9] **5** was treated at −78 °C with (tributylstannyl)lithium (1.1 mol equiv.) formed *in situ* from hexabutyldistannane and butyllithium.[10,11] Then allyl iodide (2.0 mol equiv.) and HMPA (3.0 mol equiv.) were added, and the reaction mixture was allowed to warm to −10 °C over a period of 2 h. *cis*-2-Allyl-2-phenylthio-3-(tributylstannyl)cyclopentanone (*cis*-**7**) was obtained in 86% yield as the sole product (Scheme 2). Careful HPLC analysis of the crude reaction mixture showed no formation of the *trans* isomer. The stereochemistry of the product in this allylation was deduced * to be *cis* from the results obtained in reactions of 2-phenylseleno-3-(trimethylsilyl)cyclopentanone enolates (Table 1) and 2-phenylseleno-3-(tributylstannyl)cyclopentanone enolates.[5] On the other hand, *trans*-**7** could be prepared as the predominant product by conjugate addition of (tributylstannyl)lithium to 2-allylcyclopent-2-enone **8** followed by treatment of the resulting enolate **9** with benzenesulfenyl chloride at −78 °C. When the reaction mixture was subjected to purification by silica gel chromatography (Scheme 3), a 77:23



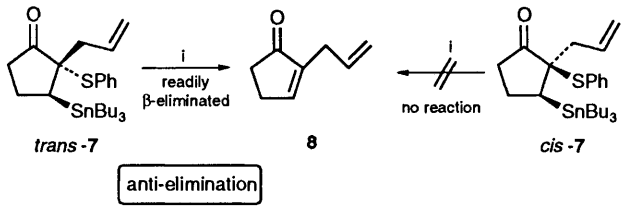
Scheme 2 *Reagents and conditions:* i, Bu_3SnLi, THF, −78 °C, 5 min; ii, allyl iodide, HMPA, −78 to −10 °C, 2 h.



Scheme 3 *Reagents and conditions:* i, Bu_3SnLi, THF, −78 °C, 5 min; ii, PhSCl, −78 °C, 5 min.

(determined by HPLC) mixture of *trans*-**7** and *cis*-**7** was obtained in 74% yield together with the enone **8** (25% recovery). We found that *trans*-**7** was extremely susceptible to silica gel to form the enone **8**. Thus, to a THF solution of *trans*-**7** was added silica gel at room temperature and the mixture was stored for

* Both isomers gave the enone **8** in the oxidative elimination of the phenylthio group. In the ^1H NMR spectra of each isomer **7** neither 3-H proton could be discriminated from the protons corresponding to the tributylstannyl group. The terminal olefin protons of both *cis*-**7** and *cis*-**3a** appeared as a multiplet within the small range from 4.98–5.04 ppm, whereas the corresponding protons in *trans*-**7** and *trans*-**3a** appeared over a wider range from 5.00–5.24 ppm.



Scheme 4 *Reagents:* i, silica gel

1 h, when *trans*-**7** was found to be converted completely into the enone **8**. On the other hand, similar treatment of *cis*-**7** (10 h) did not give enone **8** at all (Scheme 4). In addition, the NMR spectrum of the crude reaction mixture (before purification) showed no signals commensurate with the enone **8**. Therefore, provided that the enone **8**, recovered from the above reaction to the extent of 25%, was formed during silica gel column chromatography and was completely derived from β-elimination of the once formed *trans*-**7**, the above reaction would have given compound **7** in a 92:8 *trans*:*cis* ratio.

As mentioned above, allyl iodide always approaches the enolates from the less hindered side (pathway b in Fig. 2),

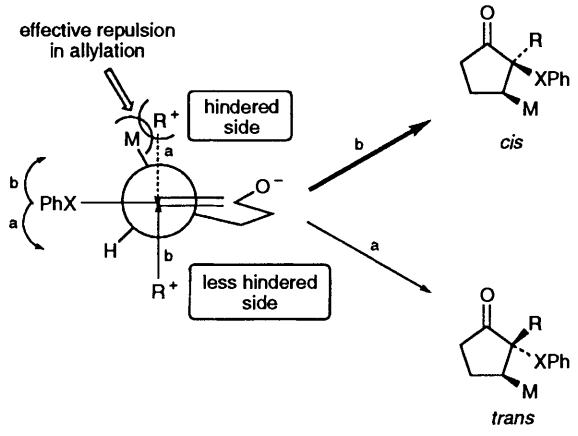
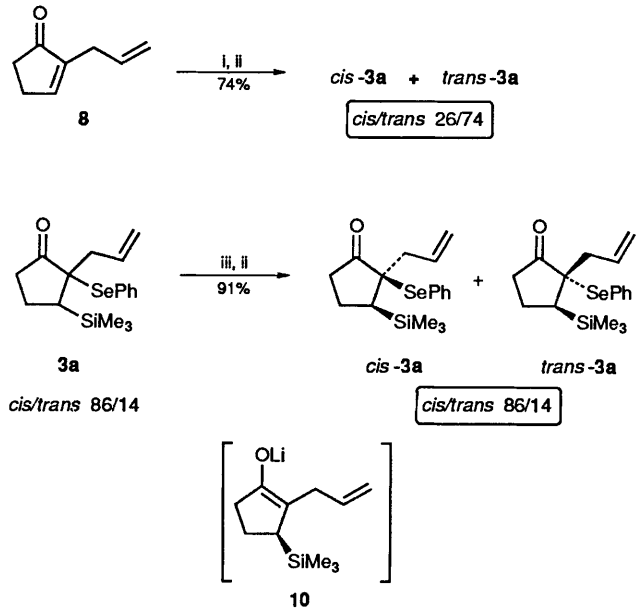


Fig. 2

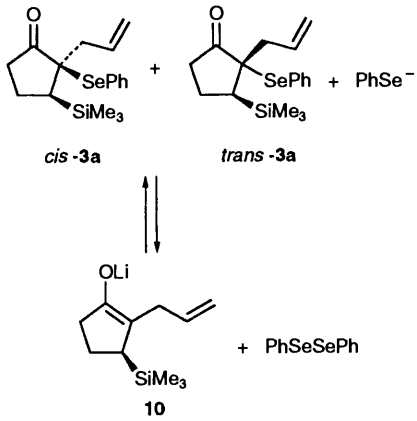
resulting in the exclusive or predominant formation of the *cis* isomer (steric-approach-controlled[12] product) in the present reactions. This stereochemical outcome is in good accord with the data generally obtained in the alkylation of the 2,3-dialkylcyclopentanone enolates. It has been reported, however, that when cyclopentanone enolates have two bulky substituents at the 2- and 3-position, sometimes certain electrophiles such as methyl iodide approach from the same side as the 3-substituent to give the product-development-controlled[12] products (pathway a).*[,4] Although the enolates in our reaction have two bulky substituents such as the phenylseleno or phenylthio group and the trimethylsilyl or tributylstannyl group, the stereochemical outcome was that resulting from attack of allyl iodide from the less hindered side, *i.e.*, from the side opposite the 3-substituent. This discrepancy could be ascribed to the difference in the electrophiles used in these reactions. A higher repulsive effect between the electrophile and the 3-substituent would be expected in allylation compared with that in methylation. Indeed, in addition, as proposed by McGarvey and Williams, the electron-donating silyl and stannyl groups would be disposed perpendicular to the plane of the enolate to participate efficiently in hyperconjugative interactions.[11d] This stereoelectronic effect may enhance the steric hindrance between allyl iodide and the trialkyl-silyl or -stannyl group, leading to the preferential formation of the steric-approach-controlled product in our allylation of the cyclopentanone enolate.

We have previously observed that the reaction of the enone **8** with (trimethylsilyl)lithium followed by treatment with benzeneselenenyl chloride gave compound **3a** in a *cis*:*trans* ratio of 26:74[5] (Scheme 5). Treatment of the selenocyclopent-



Scheme 5 *Reagents and conditions:* i, Me_3SiLi, THF–HMPA (4:1), −78 °C, 5 min; ii, PhSeCl, −78 °C; iii, PhSeLi, THF, −78 °C, 30 min.

anone **3a** (*cis*:*trans* 86:14) with lithium benzeneselenolate[13] at −78 °C and subsequently with benzeneselenenyl chloride, however, resulted in the predominant formation of *cis*-**3a**, the product formed by attack of benzeneselenenyl chloride from the more hindered side of the lithium enolate **10**. This seemingly contradictory result suggests that there should be an equilibrium between *cis*- and *trans*-**3a** and the lithium enolate **10**; *i.e.*, *cis*- and *trans*-**3a** were converted into the lithium enolate **10**, which was then selenenylated with diphenyl diselenide formed during the formation of the enolate (Scheme 6).[4c] However, it

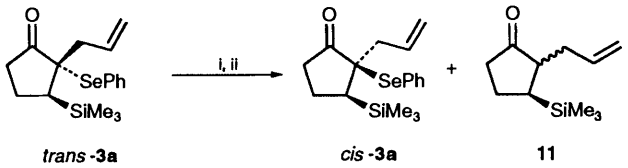


Scheme 6

should be noted that the *cis*:*trans* ratio of product **3a** obtained in the latter reaction is not the one thermodynamically controlled, since the products are composed of a mixture of *cis*- and *trans*-**3a** formed before the addition of benzeneselenenyl chloride plus **3a** (possibly *cis*-**3a**), kinetically formed by the selenenylation of the enolate **10** with benzeneselenenyl chloride. In order to confirm the equilibrium, *trans*-**3a** was treated with

* Unfortunately, attempts to trap the enolate **2** with methyl iodide failed. In addition, protonation of the enolate **2** led to the predominant formation of the *trans* isomer.

lithium benzeneselenolate at −78 °C for 1 h and the resulting mixture was quenched with dry ethanol at −78 °C. Interestingly, we found exclusive formation of *cis*-**3a** (39%) in addition to the allylcyclopentanone **11** (32%) which was derived from ethanolysis of the lithium enolate **10** (Scheme 7). These results



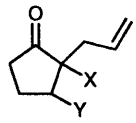
Scheme 7 *Reagents and conditions:* i, PhSeLi, −78 °C, 1 h; ii, abs. EtOH, −78 °C

show that *cis*-**3a** is thermodynamically more stable than *trans*-**3a**.

In order to confirm this unexpected greater stability of the *cis* isomer compared with the *trans* isomer, a computational analysis of both *cis* and *trans* isomers was performed by the PM3 method.[14] The calculated energies of formation for the most stable conformations of *cis*- and *trans*-**3a** were −81.4 and −76.0 kcal mol^{-1} (1 cal = 4.184 J), respectively, as shown in Fig. 3. A large degree of difference in the energies of formation ($\Delta\Delta H$ 5.4 kcal mol^{-1}) between *cis*- and *trans*-**3a** is in good accord with the result obtained above; the exclusive formation of *cis*-**3a** from the equilibration mixture. Table 2 shows the energies of formation for other related 2-allylcyclopentanones having a phenylseleno or phenylthio group at the 2-position and a tributylstannyl or trimethylsilyl group at the 3-position. The data show that the *cis* isomers are more stable than the *trans* isomers in all sets of compounds. The selected dihedral angles of **3a** are also listed in Fig. 3, showing that the cyclopentanone ring of the *trans* isomer should be more distorted than that of the *cis* isomer.

We have previously demonstrated[5] that when 2-alkyl-2-phenylseleno-3-(tributylstannyl)cyclopentanones are treated with tetrabutylammonium fluoride (TBAF), the phenylseleno and tributylstannyl groups can be easily β-eliminated to give 2-alkylcyclopent-2-enones. We examined the fluoride-induced desilylselenenylation[15] and destannylsulfenylation.[16] The results are shown in Table 3. When the allylated compounds **3** and **7** were treated with TBAF (1.1–2.0 mol equiv.) in THF at ambient or at higher temperature, β-elimination was completed within 15–30 min to afford the allylcyclopentenone **8** in good yield. Noteworthy is the formation of olefin with high regio-

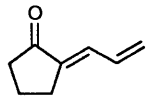
Table 2 The energies of formation for 2-allyl-2-phenylseleno(thio)-3-trimethylsi yl(tributylstannyl)cyclopentanones



Entry	X	Y	*cis* or *trans*[a]	ΔH/kcal mol^{-1}[b]
1	SePh	$SiMe_3$	*cis*	−81.4
2	SePh	$SiMe_3$	*trans*	−76.0
3	SePh	$SnBu_3$	*cis*	−76.2
4	SePh	$SnBu_3$	*trans*	−65.0
5	SPh	$SiMe_3$	*cis*	−34.1
6	SPh	$SiMe_3$	*trans*	−32.9
7	SPh	$SnBu_3$	*cis*	−34.7
8	SPh	$SnBu_3$	*trans*	−27.4

[a] These terms refer to the relative relationships of X and Y. [b] 1 cal = 4.184 J.

specificity; no regioisomer **12** was detected in these reactions. We observed that deselenenylation of 2-allyl-2-(phenylseleno)-cyclopentanone through oxidation with hydrogen peroxide at 0 °C afforded an 81:19 mixture of isomers **12** and **8**.[17] For the regiospecific olefinic formation it is, therefore, important to have the trimethylsilyl or tributylstannyl group at the 3-position of the 2-alkyl-substituted 2-(phenylseleno)- or 2-(phenylthio)-cyclopentanones. In other words, the phenylseleno or phenylthio group and the trimethylsilyl or tributylstannyl group can work together as an olefin-masking group throughout the procedure.



12

In summary, the present allylation of enolates derived from 2-(phenylseleno)- and 2-(phenylthio)-cyclopent-2-enone by conjugate addition of silyl and stannyl nucleophiles afforded allylated cyclopentanones with exclusive or high *cis* selectivity. Both desilylselenenylation and destannylsulfenylation of allylated cyclopentanones afforded 2-allylcyclopent-2-enone **8** in high yield, showing efficient use of the phenylseleno or phenylthio group and the trialkyl-silyl or -stannyl group as an olefin-masking group.

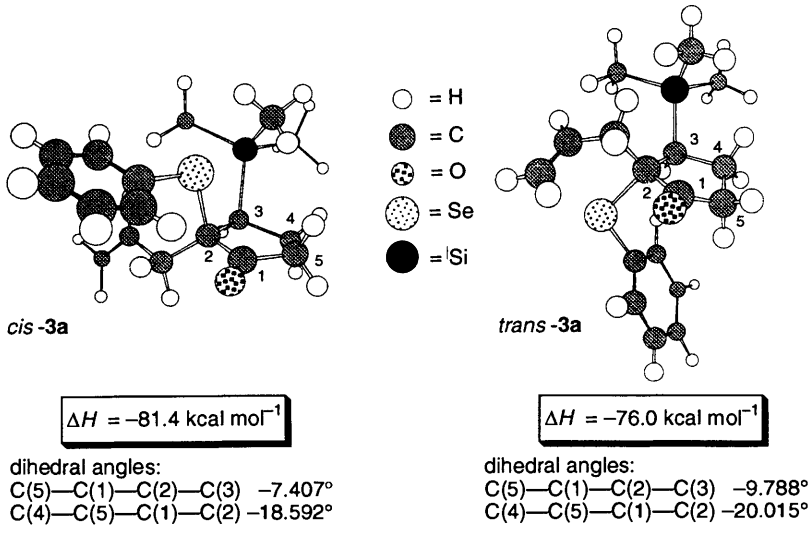
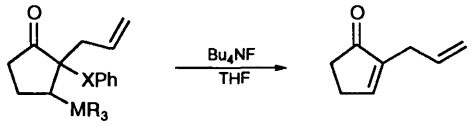


Fig. 3 The most stable conformations of *cis*- and *trans*-**3a**

Table 3 Conversion of allylated compounds **3** and **7** to 2-allylcyclopentenone **8**



3 or **7** **8**

Entry	Allylated compounds X	MR_3	Conditions Temp. (T/°C)[a]	Time (t/min)	Yield of **8** (%)[b]
1	Se	$SiMe_3$	rt	15	70
2	Se	$SiPhMe_2$	rt	15	77
3	S	$SnBu_3$	40–50	30	95

[a] rt = room temp. [b] Isolated yield.

Experimental

General Methods.—^{1}H NMR spectra were obtained using a JEOL JNM-PMX60Si (60 MHz), Varian XL-200 (200 MHz), Varian Gemini 200-BB (200 MHz), or Varian XL-400 (400 MHz) spectrometer. ^{13}C NMR spectra were obtained using a Varian XL-200 (50.3 MHz), Varian Gemini 200-BB (50.3 MHz), or Varian XL-400 (79.5 MHz) spectrometer. ^{29}Si NMR spectra were obtained using a Varian XL-400 spectrometer. Chemical shifts of ^{1}H, ^{13}C, and ^{29}Si NMR spectra are reported in δ-values from tetramethylsilane. ^{119}Sn NMR spectra were recorded on a Varian Gemini 200-BB spectrometer and are reported in δ-values from tetramethyltin. J-Values are given in Hz. IR spectra were recorded on JASCO A-102 spectrometer, and the IR figures reported are ν_{max} in cm^{-1}. Mass spectra were recorded on either an ESCO EMD-05B or a Hitachi M-2000 spectrometer. Elemental analyses were recorded on a Perkin-Elmer 240B analyser.

All reactions were performed in oven- and flame-dried glassware under argon. Air- and moisture-sensitive reagents and solvents were transferred *via* syringe or cannula and were introduced into reaction vessels through rubber septa. HPLC analyses were performed on a JASCO TRIROTAR-VI instrument. 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, with heating. Medium-pressure column chromatography was carried out on a Michel Miller column packed with Fuji Davison silica gel BM-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}.

Materials.—Unless otherwise noted, materials were obtained from commercial suppliers and were used without purification. THF was freshly distilled from sodium benzophenone ketyl under argon before use. HMPA was distilled from calcium hydride, and stored over molecular sieves (4 Å). (Dimethylphenylsilyl)lithium was prepared as described[18] and used as a 0.85 mol dm^{-3} THF solution.

cis- *and* trans-2-*Phenylseleno*-2-(*prop*-2-*enyl*)-3-(*trimethylsilyl*)*cyclopentanone* **3a**.—*Method A: with* (*trimethylsilyl*)*lithium.* A solution of hexamethyldisilane (1.68 g, 11.45 mmol) in THF–HMPA (45 cm^3; 4:1) was stirred and cooled at 0 °C. To this solution was added a 1.06 mol dm^{-3} diethyl ether solution of methyllithium (8.5 cm^3, 9.01 mmol, 1.02 mol equiv.) and the resulting red coloured solution of (trimethylsilyl)lithium was stirred for 15 min.[7a] The solution was then cooled to −78 °C and a solution of 2-(phenylseleno)cyclopent-2-enone[6] **1** (2.10 g, 8.85 mmol, 1.0 mol equiv.) in THF (5.0 cm^3 and 0.5 cm^3 for rinse) was added dropwise over a period of 15 min, and the mixture was stirred for 5 min. Then allyl iodide (2.98 g, 17.74 mmol) was added and the bath temperature was allowed to increase to 0 °C over a period of 1.5 h. The reaction mixture was poured into a mixture of hexane (100 cm^3), diethyl ether (30 cm^3), and 1.0 mol dm^{-3} aq. acetic acid (50 cm^3) with ice. The mixture was vigorously stirred for 10 min. The organic layer was separated and the aqueous solution was extracted with diethyl ether (3 × 50 cm^3). The combined extracts were washed successively with water (2 × 50 cm^3) and brine (100 cm^3), and dried over $MgSO_4$. After filtration the solvent was removed under reduced pressure and the residue was purified by column chromatography [silica gel (170 g); hexane–ethyl acetate (95:5)] to give a diastereoisomeric mixture of δ 2-phenylseleno-2-(prop-2-enyl)-3-(trimethylsilyl)cyclopentanone **3a** (2.12 g, 68%). The *cis*:*trans* ratio was determined as 86:14 by HPLC analysis [column Nacalai Finepak SIL; eluent hexane–ethyl acetate (95:5); flow speed 1.0 cm^3 min^{-1}; t_R 8.72 min for the minor, *trans*-**3a** and 9.46 min for the major, *cis*-**3a**] and ^{1}H NMR analysis.

In the same way, when (trimethylsilyl)lithium was used in 0.90 and 1.21 mol equiv. with selenoenone **1**, *cis*:*trans* (86:14) mixtures were obtained in 57 and 47% yield, respectively. Pure *cis*-**3a** (major) and *trans*-**3a** (minor) were isolated by preparative HPLC: *cis*-**3a**; δ_H(400 MHz; $CDCl_3$) 0.23 (9 H, s, 3 × Me), 1.60–1.68 (1 H, m, CHSi), 1.95–2.16 (3 H, m, 4-H_2 and 5-H), 2.61 (2 H, d, J 7.3, allylic CH_2), 2.67–2.78 (1 H, m, 5-H), 4.98–5.04 (2 H, m, terminal CH_2), 5.35 (1 H, ddt, J 9.5, 17.7 and 7.3, C*H*=CH_2), 7.26–7.32 (2 H, m, *o*-Ph), 7.36–7.41 (1 H, m, *p*-Ph) and 7.46–7.51 (2 H, m, *m*-Ph); δ_C(100.6 MHz; $CDCl_3$) −0.330 (q), 20.887 (t), 32.372 (d), 36.196 (t), 38.752 (t), 62.117 (s), 118.586 (t), 125.754 (s), 128.720 (d), 129.418 (d), 134.433 (d), 138.195 (d) and 210.246 (s); δ_{Si}(79.5 MHz; $CDCl_3$) 2.452 (J_{Si-Se} 7.5, J_{Si-C} 47.7); ν_{max}(neat)/cm^{-1} 3060m, 2950m, 2900m, 2825w,1720s,1635w,1570w,1470w,1450w,1430m,1400m,1300w, 1245s, 1195m, 1105m, 1085m, 1065w, 1010m, 1000m, 900m, 835s, 760s, 740s and 690m; m/z 352 (M^+, ^{80}Se, 0.2%), 337 (0.5), 314 (0.02), 230 (4), 215 (3), 195 (52), 157 (3) and 73 (100) (Found: C, 58.2; H, 7.0. $C_{17}H_{24}OSeSi$ requires C, 58.1; H, 6.9%); *trans*-**3a**; δ_H(400 MHz; $CDCl_3$) 0.08 (9 H, s, 3 × Me), 1.65 (1 H, dd, J 2.2 and 8.4, CHCi), 1.97 (1 H, dddd, J 2.2, 2.2, 8.9 and 13.3, 4-H), 2.17 (1 H, ddd, J 8.9, 8.9 and 18.7, 5-H), 2.37 (1 H, dddd, J 2.2, 2.2, 4.4 and 16.9, allylic CH_2), 2.47 (1 H, dddd, J 8.4, 8.9, 9.3 and 13.3, 4-H), 2.57 (1 H, dd, J 8.2 and 16.9, allylic CH_2), 2.70 (1 H, ddd, J 2.2, 9.3 and 18.7, 5-H), 5.03 (1 H, ddd, J 2.0, 3.5 and 17.3, terminal CH_2), 5.22 (1 H, ddd, J 2.0, 3.5 and 10.2, terminal CH_2), 6.00 (1 H, dddd, J 4.4, 8.2, 10.2 and 17.3, C*H*=CH_2), 7.24–7.30 (2 H, m, *o*-Ph), 7.34–7.39 (1 H, m, *p*-Ph) and 7.45–7.50 (2 H, m, *m*-Ph); δ_C(100.6 MHz; $CDCl_3$) −0.338 (q), 20.834 (t), 34.011 (d), 34.641 (t), 35.756 (t), 65.136 (s), 117.668 (t), 127.203 (s), 128.758 (d), 129.289 (d), 134.857 (d),

137.543 (d) and 210.079 (s); δ_{Si}(79.5 MHz; $CDCl_3$) 3.370 (J_{Si-Se} 9.9, J_{Si-C} 51.1); ν_{max}(neat)/cm^{-1} 3050m, 2950m, 2880m, 1715s, 1630w, 1570w, 1460w, 1425m, 1405m, 1310w, 1250s, 1210w, 1200m, 1145w, 1100m, 1060w, 1020w, 1005w, 990w, 970w, 905m, 930w, 890w, 850s, 830s, 760m, 740s and 690m; *m/z* 352 (M^+, ^{80}Se, 0.05%), 337 (0.63), 314 (0.15), 230 (3), 215 (1), 195 (36) and 73 (100) (Found: C, 58.0; H, 6.95%).

Method B: with bis(trimethylsilyl)cuprate. To a solution of (trimethylsilyl)lithium obtained from hexamethyldisilane (197 mg, 1.35 mmol) and a 1.30 mol dm^{-3} diethyl ether solution of methyllithium (0.80 cm^3, 1.04 mmol) in THF–HMPA (6.0 cm^3; 4:1), kept at 0 °C for 15 min, was added copper(I) iodide (99 mg, 0.52 mmol) to the solution at −30 °C and the mixture was stirred for 1 h.[7d] The solution was cooled to −50 °C and a solution of enone **1** (110 mg, 0.46 mmol) in THF (0.5 cm^3 and 0.2 cm^3 for rinse) was added dropwise during 5 min. After having been stirred for an additional 1.5 h at −30 to −20 °C, the mixture was recooled to −78 °C. To this solution was added allyl iodide (169 mg, 1.00 mmol) and the bath temperature was allowed to increase to ambient over a period of 2 h. Saturated aq. NH_4Cl (5 cm^3), ammonia water (5 cm^3) and diethyl ether (10 cm^3) were added successively with vigorous stirring of the mixture. The organic layer was separated, the water layer was extracted with diethyl ether (3 × 15 cm^3) and the combined organic phases were washed with brine (10 cm^3) and dried over $MgSO_4$. After filtration the solvent was removed under reduced pressure and the residue was purified by column chromatography [silica gel (20 g); hexane–ethyl acetate (96:4)] to give a diastereoisomeric mixture of compound **3a** (37 mg, 23%). The *cis*:*trans* ratio was determined as 85:15 by ^{1}H NMR and HPLC analyses as described above. HPLC: t_R of the minor, *trans*-**3a** 8.72 min, and t_R of the major, *cis*-**3a** 9.46 min.

Method C: with higher order mixed trimethylsilylcuprate. To a suspension of copper(I) cyanide (48 mg, 0.54 mmol) in THF (1.5 cm^3) at −50 °C was added a 1.30 mol dm^{-3} diethyl ether solution of methyllium (0.4 cm^3, 0.52 mmol). After having been stirred for 10 min, the reaction mixture was cooled to −78 °C. To this mixture was added a solution of (trimethylsilyl)lithium obtained from hexamethyldisilane (95 mg, 0.65 mmol) and a 1.30 mol dm^{-3} diethyl ether solution of methyllithium (0.42 cm^3, 0.55 mmol) as described in Method A. The reaction mixture was stirred for 30 min.[7g] Then a solution of enone **1** (118 mg, 0.50 mmol) in THF (0.5 cm^3 and 0.2 cm^3 for rinse) was added dropwise over a period of 5 min and the mixture was stirred for an additional 5 min. Allyl iodide (412 mg, 2.45 mmol) was added and the bath temperature was allowed to increase to ambient over a period of 2 h. The same work-up as described in Method B gave a residual oil, which was purified by column chromatography [silica gel (35 g); hexane–ethyl acetate (96:4)] to give a diastereoisomeric mixture of compound **3a** (105 mg, 60%). The *cis*:*trans* ratio was determined as 86:14 by ^{1}H NMR and HPLC analysis described above. HPLC: t_R of the minor, *trans*-**3a** 8.72 min, and t_R of the major, *cis*-**3a** 9.46 min.

3-*Dimethylphenylsilyl*-2-*phenylseleno*-2-(*prop*-2-*enyl*)*cyclopentanone* **3b**.—To a suspension of copper(I) cyanide (51 mg, 0.57 mmol) in THF (1.5 cm^3) at −50 °C, was added a 1.30 mol dm^{-3} diethyl ether solution of methyllithium (0.4 cm^3, 0.52 mmol) and the mixture was stirred at the same temperature for 10 min. The reaction mixture was then cooled to −78 °C and a 0.85 mol dm^{-3} THF solution of (dimethylphenylsilyl)lithium (0.62 cm^3, 0.53 mmol) was added dropwise. The resulting deep red solution was stirred for 30 min, a solution of enone **1** (119 mg, 0.50 mmol) in THF (0.6 cm^3 and 0.2 cm^3 for rinse) was added dropwise over a period of 5 min, and the mixture was stirred for an additional 15 min. Allyl iodide (412 mg, 2.45 mmol) was added and the bath temperature was allowed to increase to ambient over a period of 2 h. The same work-up as described above gave a residual oil, which was purified by column chromatography [silica gel (35 g); hexane–ethyl acetate (98:2–95:5)] to give a diastereoisomeric mixture of 3-dimethylphenylsilyl-2-phenylseleno-2-(prop-2-enyl)cyclopentanone **3b** (120 mg, 58%). The *cis*:*trans* ratio was determined as 94:6 by ^{1}H NMR and HPLC analyses as described above. HPLC: t_R of the minor, *trans*-**3b** 10.72 min, and t_R of the major, *cis*-**3b** 12.13 min: compound **3b**; δ_H(60 MHz; CCl_4) 0.34 (3 H, s, Me for the minor, *trans*-**3b**), 0.36 (3 H, s, Me for the minor, *trans*-**3b**), 0.52 (3 H, s, Me for the major, *cis*-**3b**), 0.54 (3 H, s, Me for the major, *cis*-**3b**), 1.49–2.86 (7 H, m), 4.56–5.66 (3 H, m) and 6.99–7.72 (10 H, m, 2 × Ph); ν_{max}(neat)/cm^{-1} 3075m, 3010w, 2960m, 2830w, 1950br, w, 1880br, w, 1820br, w, 1720s, 1635w, 1575w, 1475m, 1455w, 1430m, 1405m, 1300w, 1250s, 1200m, 1150w, 1110s, 1090m, 1065w, 1010m, 1000m, 970w, 920m, 895m, 830s, 810s, 780m, 735s, 700s and 690s; *m/z* 414 (M^+, ^{80}Se, 0.3%), 314 (0.3), 257 (23), 157 (6) and 135 (100) (Found: C, 63.8; H, 6.5. $C_{22}H_{26}OSeSi$ requires C, 63.9; H, 6.3%).

cis-2-*Phenylthio*-2-(*prop*-2-*enyl*)-3-(*tributylstannyl*)*cyclopentanone* cis-**7**.—To a solution of hexbutyldistannane (1.86 g, 3.21 mmol) in THF (6 cm^3) at −20 °C was added butyllithium (1.53 mol dm^{-3} in hexane; 2.0 cm^3, 3.06 mmol) and the mixture was stirred for 15 min during which time it warmed to −10 °C.[10] To the recooled (−78 °C) mixture was added a solution of 2-(phenylthio)cyclopent-2-enone[9] **5** (530 mg, 2.79 mmol) in THF (2.0 cm^3 and 0.5 cm^3 for rinse), and the mixture was stirred for 5 min. Then allyl iodide (937 mg, 5.58 mmol) and HMPA (1.45 cm^3, 8.31 mmol) were added successively. The bath temperature was allowed to increase to −10 °C during 2 h, and saturated aq. NH_4Cl (5 cm^3) and diethyl ether (10 cm^3) were added. The organic layer was separated, the aqueous solution was extracted with diethyl ether (3 × 10 cm^3), and the combined organic phases were washed successively with water (2 × 10 cm^3) and brine (10 cm^3) and dried over $MgSO_4$. After filtration the solvent was removed under reduced pressure to leave a residue, which was purified by column chromatography [silica gel (110 g); hexane–ethyl acetate (96:4)] to give cis-2-*phenylthio*-2-(*prop*-2-*enyl*)-3-(*tributylstannyl*)*cyclopentanone* cis-**7** (1.25 g, 86%), which was shown to be pure by HPLC analysis [column Nacalai Finepak SIL; eluent hexane–ethyl acetate (97:3); flow speed 1.0 cm^3 min^{-1}; t_R 8.79 min]: *cis*-**7**; TLC R_f 0.49 [(90:10) hexane–ethyl acetate]; δ_H(200 MHz; $CDCl_3$) 0.94 (9 H, t, *J* 7.2, Me), 1.00–1.13 (6 H, m), 1.38 (6 H, tq, *J* 7.2 and 7.2), 1.50–1.67 (6 H, m), 2.00–2.42 (4 H, m), 2.32 (1 H, dd, *J* 9.4 and 13.7, allylic CH_2), 2.53 (1 H, dd, *J* 5.2 and 13.7, allylic CH_2), 2.62–2.80 (1 H, m), 4.95–5.08 (2 H, m, CH=CH_2), 5.42 (1 H, dddd, *J* 5.2, 9.4, 11.6 and 16.9, C*H*=CH_2) and 7.29–7.45 (5 H, m, Ph); δ_C(50.3 MHz; $CDCl_3$) 10.40 (t), 13.69 (q), 23.24 (t), 27.55 (t), 29.26 (t), 32.01 (d), 37.12 (t), 38.10 (t), 64.25 (s), 118.65 (t), 128.67 (d), 129.61 (d), 130.04 (s), 133.94 (d), 137.16 (d) and 211.06 (s); δ_{Sn}($CDCl_3$) −19.34; ν_{max}(neat)/cm^{-1} 3050w, 2915s, 2850s, 1720s (C=O), 1632w (C=C), 1570w (Ph), 1450m, 1433m, 1399w, 1370w, 1334w, 1300w, 1277w, 1248w, 1190m, 1170w, 1140w, 1065m, 1000m, 958w, 910m, 862w, 740m and 684m; *m/z* 465 (M^+ − Bu, ^{120}Sn, 6%), 413 (M^+ − SPh, 2), 400 (4), 343 (96), 291 (5), 229 (78), 177 (32), 153 (22), 121 (27), 109 (15) and 79 (100) (Found: C, 60.0; H, 8.3. $C_{26}H_{42}OSSn$ requires C, 59.9; H, 8.1%).

trans- *and* cis-2-*Phenylthio*-2-(*prop*-2-*enyl*)-3-(*tributylstannyl*)*cyclopentanone* **7**.—To the reaction mixture obtained from hexabutyldistannane (306 mg, 0.528 mmol) and butyllithium (1.57 mol dm^{-3} in hexane; 0.32 cm^3, 0.502 mmol) as described above, at −78 °C, was added a solution of 2-(prop-2-enyl)-cyclopent-2-enone[5] **8** (55 mg, 0.450 mmol) in THF (0.5 cm^3 and 0.1 cm^3 for rinse) and the mixture was stirred for 5 min at the same temperature. Then benzenesulfenyl chloride (3.02 mol

dm^{-3} in methylene dichloride; 0.18 cm^3, 0.544 mmol) was added and the mixture was stirred for an additional 5 min. The same work-up as mentioned above gave a residual oil, which was purified by column chromatography [silica gel (40 g); hexane–ethyl acetate–triethylamine (97:3:0.1–96:4:0.1)] to give a diastereoisomeric mixture of 2-phenylthio-2-(prop-2-enyl)-3-(tributylstannyl)cyclopentanone **7** (173 mg, 74%). The *trans*:*cis* ratio was determined as 77:23 by HPLC analysis as described above. HPLC: t_R of *trans*-**7** 6.21 min, and t_R of *cis*-**7** 8.79 min. 2-Allylcyclopent-2-en-1-one[19] **8** (14 mg, 25%) was also obtained, which was the decomposition product of *trans*-**7** on silica gel. The pure *trans* isomer was obtained by column chromatography of a diastereoisomeric mixture of compound **7**: trans-**7**; R_f 0.54 [(90:10) hexane–ethyl acetate]; δ_H(200 MHz; $CDCl_3$) 0.83–0.92 (15 H, m), 1.20–1.60 (12 H, m), 1.89–2.21 (4 H, m), 2.46–2.78 (3 H, m), 5.14 (1 H, dd, *J* 1.6 and 17.2), 5.24 (1 H, dd, *J* 1.6 and 10.4), 5.96 (1 H, dddd, *J* 5.0, 7.6, 10.4 and 17.2) and 7.22–7.41 (5 H, m); ν_{max}(neat)/cm^{-1} 3050w, 2920s, 2850s, 1720s (C=O), 1635w (C=C), 1575w (Ph), 1455m, 1433m, 1400w, 1370w, 1190w, 1145w, 1070m, 1020w, 1000w, 960w, 910w, 860w, 742m and 688m; *m/z* 465 (M^+ − Bu, ^{120}Sn, 2%), 413 (M^+ − SPh, 3), 400 (12), 343 (92), 291 (11), 229 (94), 177 (45), 153 (62), 122 (90), 109 (13) and 79 (100) (Found: C, 59.7; H, 8.3. $C_{26}H_{42}OSSn$ requires C, 59.9; H, 8.1%). For compound **8**; δ_H(60 MHz; CCl_4) 2.15–2.69 (4 H, m), 2.84 (2 H, d, *J* 7.5), 4.78–5.23 (2 H, m), 5.44–6.19 (1 H, m) and 7.01–7.24 (1 H, m); ν_{max}(neat)/cm^{-1} 1698s and 1638m.

Conversion of Allylated Compound **7** *with Silica Gel.*—To a solution of *trans*-**7** (135 mg, 0.26 mmol) in THF (5 cm^3) was added silica gel (Fuji Davison BM-200, 1 g). After 1 h, the disappearance of *trans*-**7** was confirmed by TLC. THF was evaporated off under reduced pressure and the residue was purified by column chromatography [silica gel (15 g); hexane–ethyl acetate (90:10)] to give enone **8** (31 mg, 98%). On the other hand, the reaction of *cis*-**7** with silica gel for 10 h resulted only in the recovery of substrate.

Reaction of Compound **3a** *with Lithium Benzeneselenolate and Benzeneselenenyl Chloride.*—To a solution of benzeneselenol (52 mg, 0.33 mmol) in THF (1.5 cm^3) at room temperature was added methyllithium (1.3 mol dm^{-3} in diethyl ether; 0.25 cm^3, 0.33 mmol) and the mixture was stirred for 10 min[13] before being cooled to −78 °C, and to this solution was added a solution of compound **3a** (104 mg, 0.30 mmol; *cis*:*trans* 86:14) in THF (0.5 cm^3 and 0.2 cm^3 for rinse). Immediately after the addition, the colourless solution turned to yellow and the mixture was stirred for 30 min. To this solution was added HMPA (0.1 cm^3, 0.59 mmol) followed by a solution of benzeneselenenyl chloride (70 mg, 0.37 mmol) in THF (0.5 cm^3 and 0.2 cm^3 for rinse), and the mixture was stirred for 10 min. Saturated aq. NH_4Cl (5.0 cm^3) and diethyl ether (8.0 cm^3) were added. The aqueous solution was extracted with diethyl ether (2 × 5 cm^3) and the combined organic phases were washed successively with water (5 cm^3) and brine (5 cm^3), and dried over $MgSO_4$. After filtration the solvent was removed under reduced pressure and the residue was purified by column chromatography [silica gel (30 g); hexane–ethyl acetate (95:5)] to give a diastereoisomeric mixture of compound **3a** (95 mg, 91%). The *cis*:*trans* ratio was determined as 86:14 by HPLC analysis as described above, and by ^{1}H NMR analysis.

Reaction of Compound **3a** *with Lithium Benzeneselenolate and Absolute Ethanol.*—To the reaction mixture obtained from benzeneselenol (31 mg, 0.20 mmol) and *trans*-**3a** (62 mg, 0.18 mmol) as above was added cooled (−78 °C) absolute ethanol (0.05 cm^3) *via* cannula, and the reaction mixture was stirred for 1 h. Saturated aq. NH_4Cl (3.0 cm^3), diethyl ether (2.0 cm^3), and hexane (2.0 cm^3) were added successively to the vigorously stirred mixture. The aqueous layer was extracted with diethyl ether (2 × 5 cm^3) and the combined organic phases were dried over $MgSO_4$. After filtration the solvent was removed under reduced pressure and the residue was purified by column chromatography [silica gel (10 g); hexane–ethyl acetate (96:4)] to give *cis*-**3a** (24 mg, 39%) and 2-allyl-3-(trimethylsilyl)cyclopentanone **11** (11 mg, 32%). The *cis*:*trans* ratio of compound **3a** was determined as >99:1 by ^{1}H NMR analysis.

Calculation Method.—Molecular orbital calculations were performed on a Silicon-Graphics IRIS240GTX computer by the PM3 method[14] with MOPAC Version 6.01.[20]

Conversion of Allylated Compounds **3** *and* **7** *into 2-Allylcyclopent-2-enone* **8** *with TBAF.*—(a) *From compound* **3a**. To a solution of compound **3a** (103 mg, 0.29 mmol; *cis*:*trans* 86:14) in THF (0.5 cm^3) was added a THF solution of TBAF (1.0 mol dm^{-3}; 0.3 cm^3, 0.3 mmol). The mixture was stirred for 15 min at room temperature and then was directly subjected to column chromatography [silica gel (18 g); hexane–ethyl acetate (95:5–90:10)] to give 2-allylcyclopent-2-enone **8** (25 mg, 70%).

(b) *From compound* **3b**. The same treatment of compound **3b** (110 mg, 0.27 mmol, *cis*:*trans* 94:6) gave compound **8** (25 mg, 77%).

(c) *From compound* cis-**7**. Treatment of compound *cis*-**7** (135 mg, 0.26 mmol) with TBAF (1.0 mol dm^{-3}; 0.5 cm^3, 0.5 mmol) at 40–50 °C for 30 min and the same purification as above gave compound **8** (30 mg, 95%).

Acknowledgements

This work was supported by the Ministry of Education, Science and Culture, Japan (Grant-in-Aid for Developmental Scientific Research No. 03555177).

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Paper 3/02142D
Received 14*th April* 1993
Accepted 26*th April* 1993