The signal was irradiated during the 25-s delay with sufficient power to just saturate that signal. This process was repeated until 16 transients were accumulated. The process was repeated with the decoupler set far off resonance, and then the total procedure was repeated until 608 transients were collected at each decoupler setting. The resulting FID's were subtracted, and the spectra obtained after fourier transformation were displayed as the NOE difference spectra. Quantitation was obtained by measuring the integral of the enhanced signals and dividing by the integral of the signal being saturated.

3-Hydroxy-4-methoxybiphenyl. Methyl iodide (17.1 g, 0.12 mol) was added to a mixture of 4-phenylpyrocatechol (18.6 g, 0.1 mol) and potassium carbonate (13.8 g, 0.1 mol) in dry dimethylformamide (100 mL). The reaction was stirred overnight at room temperature and then heated at 90 °C for 2 h. After cooling, the mixture was diluted with water (400 mL), acidified with HCl, and extracted with diethyl ether (200 mL) and tetrahydrofuran (50 mL). The ether–tetrahydrofuran layer was washed with water, dried over anhydrous sodium sulfate, and evaporated to dryness under reduced pressure to give a semisolid (19.3 g). This was distilled in a Kugelrohr apparatus (130–135 °C, 0.01 mmHg) to give a white semisolid (17.3 g). Crystallization from hexane–anhydrous ether gave a white solid (12.4 g). Recrystallization from acetonitrile gave a white crystalline solid (6.1 g) with mp 115–116 °C (literature 118 °C):[8] ^{1}H NMR δ 7.54 (d, 2 H, J = 7.6 Hz, 2′), 7.40 (t, 2 H, J = 7.6 Hz, 3′), 7.29 (t, 1 H, J = 7.6 Hz, 4′), 7.20 (d, 1 H, J = 2.2 Hz, 2), 7.09 (dd, 1 H, J = 8.5, 2.2 Hz, 6), 6.91 (d, 1 H, J = 8.5 Hz, 5), 5.68 (s, 1 H, OH), 3.92 (s, 3 H, CH_3).

Registry No. 1, 37055-80-4; 4-phenylpyrocatechol, 92-05-7.

(8) Blatchly, J. M.; McOmie, J. F. W.; Watts, M. L. *J. Chem. Soc.* **1962**, 5085–5090.

Radical α-Allylation of Alkyl-Substituted α-(Phenylseleno)cycloalkanones

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Irradiation and thermal reaction of 3-, 4-, or 6-alkyl-2-(phenylseleno)cycloalkanones with tributyl-2-propenyltin gave 2-allylated products in high yields. Either *trans*- or *cis*-selenocycloalkanones afforded the identical distribution of cis- and trans-allylated products, the trans isomer being predominant. The stereochemical course of these radical allylations is discussed in terms of steric and torsional effects.

Introduction

It is important to develop a method for α-monoallylation of carbonyl compounds, since the α-monoallylation reactions have often been used for construction of natural products or complex molecules. A number of methods for the monoallylation so far have been developed. α-Allylation of ketones attached to a carbanion-stabilizing functionality such as an alkoxycarbonyl,[1] arylthio,[2] or arylseleno[3] group, followed by removal of the functionality, is a widely used method for achieving regioselectivity together with avoiding multiallylation. Methods for direct allylation of enolates such as tin[4] or boron[5] enolates, or enolates[6] formed by the Michael addition to α,β-unsaturated ketones, have also been reported. Recently, palladium-catalyzed allylations have been developed.[7] These allylations substantially proceed through ionic processes. We have reported[8] the efficient allylation via a free-radical intermediate by irradiation of a solution of α-(phenylseleno)cycloalkanone derivatives and (substituted) tributyl-2-propenyltin compounds and succeeded in the α-allylation of the intermediate leading to a prostaglandin (PG) derivative, where the trans-allylated product was exclusively isolated. This result prompted us to study the stereochemistry of the radical allylation in a more general aspect. In this report we describe the stereochemical features of the α-allylation of alkyl-substituted α-(seleno)cycloalkanones.

Results and Discussion

Preparation of Alkyl-Substituted α-(Phenylseleno)cycloalkanones 1. Starting selenides such as 3-methyl-2-(phenylseleno)cyclopentanone[9] (**1a**), 3-butyl-2-(phenylseleno)cyclopentanone[9] (**1b**), 3-methyl-2-(phenylseleno)cyclohexanone[10] (**1c**), and 3-butyl-2-(phenylseleno)cyclohexanone[9] (**1d**) were prepared by conjugate addition of organocuprates to the corresponding 2-(phenylseleno)-2-cycloalken-1-ones.[11] All the reactions gave mixtures of cis and trans isomers, the latter being always major isomers.[12] The structures of these isomers were assigned by NMR spectral analysis.[10] The structures of *trans*- and *cis*-3-methyl-2-(phenylseleno)cyclopentanone (*trans*-**1a** and *cis*-**1a**) were further confirmed by isomeri-

(1) For a general review on allylation of enolates, see: House, H. O. *Modern Synthetic Reactions*, 2nd ed.; W. A. Benjamin: Menlo Park, CA, 1972. Negishi, E. *Organometallics in Organic Synthesis*; Wiley-Interscience: New York, 1980. Jung, M. E. *Tetrahedron* **1976**, *32*, 3.

(2) Coates, R. M. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 586.

(3) For a review, see: Reich, H. J. *Organoselenium Chemistry*; Liotta, D., Ed.; Wiley: New York, 1987; Chapter 5.

(4) (a) Nishiyama, H.; Sakuta, K.; Itoh, K. *Tetrahedron Lett.* **1984**, *25*, 223, 2487. (b) Yamamoto, Y.; Yatagai, H.; Maruyama, K. *Silicon, Germanium, Tin, Lead Compd* **1986**, *9*, 25.

(5) Negishi, E.; Idacavage, M. J.; DiPasquale, F.; Silveira, A., Jr. *Tetrahedron Lett.* **1979**, 845.

(6) For a review of organocopper conjugate addition–enolate trapping reactions, see: Taylor, R. J. K. *Synthesis* **1985**, 365.

(7) Trost, B. M.; Keinan, E. *Tetrahedron Lett.* **1980**, *21*, 2591. Fiaud, M. C.; Malleron, J. L. *J. Chem. Soc., Chem. Commun.* **1981**, 1159. Negishi, E.; Matsushita, H.; Chatterjee, S.; John, R. A. *J. Org. Chem.* **1982**, *47*, 3188. Kosugi, M.; Suzuki, M.; Hagiwara, I.; Goto, K.; Saito, K.; Migita, T. *Chem. Lett.* **1982**, 939. Kosugi, M.; Hagiwara, I.; Migita, T. *Ibid.* **1983**, 839. Tsuji, J.; Minami, I.; Shimizu, I. *Ibid.* **1983**, 1325. Tsuji, J.; Minami, I.; Shimizu, I. *Tetrahedron Lett.* **1983**, *24*, 4713. Tsuji, J.; Minami, I.; Shimizu, I. *Ibid.* **1983**, *24*, 1793. Tsuji, J.; Shimizu, I.; Minami, I.; Ohashi, Y.; Sugiura, T.; Takahashi, K. *J. Org. Chem.* **1985**, *50*, 1523. Tsuda, T.; Okada, M.; Nishi, S.; Saegusa, T. *Ibid.* **1986**, *51*, 421. Tsuji, J. *Tetrahedron* **1986**, *42*, 4361.

(8) Toru, T.; Yamada, Y.; Ueno, T.; Ueno, Y. *J. Am. Chem. Soc.* **1988**, *110*, 4815.

(9) Liotta, D.; Saindane, M.; Barnum, C.; Zima, G. *Tetrahedron* **1985**, *41*, 4881.

(10) Zervos, M.; Wartski, L., Jr. *J. Org. Chem.* **1986**, *51*, 1293.

(11) Zima, G.; Liotta, D. *Synth. Commun.* **1979**, *9*, 697.

(12) These results are in accord with those reported by Zervos and Wartski,[10] although Liotta and his co-workers have reported the preferential formation of *cis*-selenides.[9]

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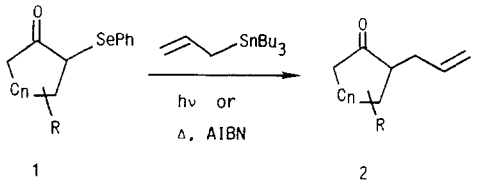

a: n = 1 R = 3-Me
b: n = 1 R = 3-Bu
c: n = 2 R = 3-Me
d: n = 2 R = 3-Bu
e: n = 2 R = 4-tert-Bu
f: n = 2 R = 2-Me [6-PhSe or 6-(2-propenyl)]

Figure 1.

Table I. Allylation of 2-(Phenylseleno)cycloalkanones 1 with Tributyl-2-propenyltin[a]

cyclo-alkanone	CH_2CH-CH_2SnBu_3, equiv	reactn time, h	product	yield,[e] %	trans:cis[e]
trans-**1a**	1.5	1	**2a**	76	77:23
trans-**1a**	2.0	1	**2a**	93	78:22
trans-**1a**	2.0	1	**2a**	71	76:24
trans-**1a**	3.0	0.5	**2a**	98	78:22
cis-**1a**	1.5	1	**2a**	83	78:22
cis-**1a**	2.0	1	**2a**	94	78:22
trans-**1b**	2.0	2	**2b**	95	79:21
trans-**1b**	2.0	2[d]	**2b**	88	83:17
cis-**1b**	1.5	2	**2b**	72	78:22
cis-**1b**	2.0	1	**2b**	91	79:21
1c[b]	1.5	2.5	**2c**	70	67:33
trans-**1d**	3.0	1	**2d**	67	66:34
trans-**1d**	3.0	2[d]	**2d**	91	73:27
cis-**1d**	3.0	1	**2d**	54	66:34
cis-**1d**	3.0	2[d]	**2d**	82	72:28
trans-**1e**	3.0	1	**2e**	72	85:15
cis-**1e**	3.0	1	**2e**	60	87:13
trans-**1f**	2.0	2	**2f**	66	86:14
trans-**1f**	3.0	1	**2f**	85	86:14
cis-**1f**	2.0	3	**2f**	62	86:14
1f[c]	3.0	1	**2f**	82	86:14

[a] The reactions were carried out by irradiation of the mixture unless otherwise noted. [b] A trans/cis (9:1) mixture was used. [c] A trans/cis (1:1) mixture was used. [d] The 1 M toluene solution was refluxed with 10 mol % AIBN. [e] Determined by GC.

zation of *cis*-**1a** to *trans*-**1a** by the action of potassium acetate in ethanol. *trans*- and *cis*-3-Butyl-2-(phenylseleno)cyclopentanones (*trans*-**1b** and *cis*-**1b**) were oxidized separately by *m*-chloroperbenzoic acid at −50 °C and then warmed up to room temperature, to give 3-butyl-2-cyclopenten-1-one[9] in 97% and 18% yields, respectively. Smooth syn-elimination[13] of phenylselenenic acid confirmed the structures of *trans*-**1b** and *cis*-**1b**. 4-*tert*-Butyl-2-(phenylseleno)cyclohexanone[14] (**1e**) and 2-methyl-6-(phenylseleno)cyclohexanone[15] (**3f**) were prepared from the corresponding cyclohexanones.

Allylation of 2-(Phenylseleno)cycloalkanones 1. A benzene solution of each isomer of 2-(phenylseleno)-cycloalkanones 1 and a 2–3-fold excess amount of allyltributyltin was irradiated (Figure 1). The results are shown in Table I. Irradiation of a 1 M benzene solution of *trans*-3-methyl-2-(phenylseleno)cyclopentanone

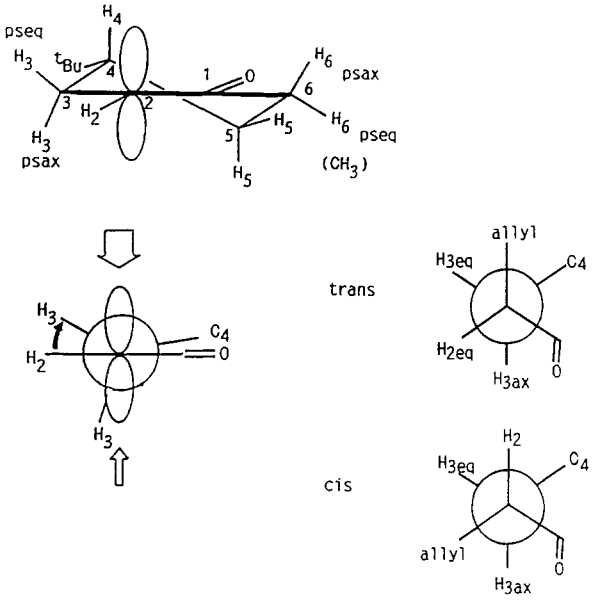

Figure 2.

(*trans*-**1a**) and 2 molar equiv of allyltributyltin for 1 h gave 3-methyl-2-(2-propenyl)cyclopentanone (**2a**) in 93% yield. The yield increased to 98% in the reaction of **1a** with 3 molar equiv of allyltributyltin. The yield of **2a** was lowered when a lesser amount of allyltributyltin was employed as well as when the reaction was carried out in a 0.1 M solution of **1a**. It should be noted that both *cis*- and *trans*-2-(phenylseleno)cyclopentanone (**1a** and **1b**) yielded the same distribution of the trans/cis allylated isomers, i.e., ca. 78:22 and 79:21 from each isomer of **1a** and **1b**, respectively. The reaction of *trans*-3-butyl-2-(phenylseleno)cyclopentanone (*trans*-**1b**) under reflux in toluene with 10 mol % azobis(isobutyronitrile) (AIBN) gave the allylated products **2b** in 88% yield. The allylation of 2-(phenylseleno)cyclohexanone derivatives proceeded in a comparable manner. Both *trans*- and *cis*-3-butyl-2-(phenylseleno)cyclohexanone (*trans*-**1d** and *cis*-**1d**) gave a trans/cis (66:34) mixture of allylcyclohexanone **2d**. More predominant formation of trans isomers was observed in the reactions of 4-*tert*-butyl- and 6-methyl-2-(phenylseleno)cyclohexanones (**1e** and **1f**). The thermal reaction seems to be a better choice than the photolytic reaction in (seleno)cyclohexanones as exemplified in 3-butylcyclohexanones *trans*-**1d** and *cis*-**1d**, because the competitive decomposition of (seleno)cyclohexanones gradually occurs on irradiation. Acceptable yields of allylcyclohexanones were obtainable in the irradiation with a 3-fold excess of allyltributyltin.

The fact that identical distributions of the trans/cis isomers were obtained from both the cis and trans starting selenides shows that allylations from both the trans and cis selenides proceed via the same α-carbon radical intermediate, which is formed by trapping the seleno group with a tributyltin radical. Since the α-radical of cyclopentanone has been reported[16] to be planar by ESR measurement, the preferential formation of the trans isomer could be reasonably explained by the preferential approach of allyltributyltin to the carbon radical from the less hindered direction opposite to the adjacent methyl or

(13) Sharpless, K. B.; Young, M. W.; Lauer, R. F. *Tetrahedron Lett.* **1973**, 1979. We feel that elimination of selenenic acid under nonbasic conditions is still a good method for the stereochemical assignment, although Liotta and his co-workers pointed out that the same elimination product was obtained from either *cis*- or *trans*-seleno compounds under basic conditions via isomerization.[9]
(14) Ozbal, H.; Zajac, W. W. *Tetrahedron Lett.* **1979**, 4821.
(15) Reich, H. J.; Renga, J. M.; Reich, I. L. *J. Am. Chem. Soc.* **1975**, *97*, 5434.
(16) Walter, H. F.; Beaudry, W. T.; Camaioni, D. M.; Pratt, D. M. *J. Am. Chem. Soc.* **1985**, *107*, 793. Gilbert, B. C.; Trenwith, M. *J. Chem. Soc., Perkin Trans. 2*, **1975**, 1083. Gilbert, B. C.; Norman, R. O. C.; Sealy, R. C. *J. Chem. Soc., Perkin Trans. 2* **1973**, 2174. Camaioni, D. M.; Pratt, D. W. *J. Am. Chem. Soc.* **1972**, *94*, 9258. Camaioni, D. M.; Walter, H. F.; Jordan, J. E.; Pratt, D. W. *J. Am. Chem. Soc.* **1973**, *95*, 7978.

butyl group. The product distributions from cyclohexanoyl radicals, however, cannot be explained solely by such steric effects. The conformation of the cyclohexanoyl radical intermediate is likely a half-chair, on the basis of the ESR data[16] as shown in Figure 2, i.e., four carbons (C_1, C_2, C_3, and C_6) lie in a plane. In the reaction of 4-*tert*-butyl-2-(phenylseleno)cyclohexanone (**1e**), the attack of allyltributyltin from the bottom side will result in development of torsional interactions,[17] which attain a maximum during the course of the formation of the cis isomer. In contrast, torsional strain is relieved during the course of the attack from the top side, which will give the trans isomer. The steric environment also favors the formation of the trans isomer. The above torsional effect together with the steric environment favored the formation of the trans isomer over the cis isomer in the reaction of **1e**. A comparable feature can be seen in the allylation of 2-methyl-6-(phenylseleno)cyclohexanone (**1f**), where the preferred conformation of the methyl group in the radical intermediate may be *pseudo*equatorial. A similar stereochemical consideration has been presented[18] in the reaction of 4-substituted cyclohexyl radicals, although the configurations are different from those of the cyclohexanoyl radicals.

Conclusion

The present radical allylation method has the following characteristic features: (i) This one-step allylation enables us to use mixtures of cis and trans isomers as starting selenides[19] and proceeds with moderate stereoselectivity and in some cases with higher stereoselectivity than in the ionic reactions.[20] (ii) Complete regiospecificity is achieved; however, the enolate exchange often causes undesired side reactions as exemplified in the enolate-trapping reaction with alkyl halides for the synthesis of prostaglandins.[21] (iii) The reaction can be conducted under neutral conditions substantially different from those of the ionic reaction,[22] and synthetically important functional groups such as a hydroxyl or amino group may be tolerable to radicals without protection.[23] Thus, the present method serves as an extremely convenient intermolecular allylation of cyclopentanones and cyclohexanones.

(17) Schleyer, P. v. R. *J. Am. Chem. Soc.* **1967**, *89*, 699, 701.

(18) Jensen, F. R.; Gale, L. H.; Rodgers, J. E. *J. Am. Chem. Soc.* **1968**, *90*, 5793. Gruselle, M.; Fossey, J.; Lefort, D. *Tetrahedron Lett.* **1970**, 2069. Gruselle, M.; Tichy, M. *Tetrahedron* **1972**, *28*, 3885. Gruselle, M.; Fossey, J.; Lefort, D. *Can. J. Chem.* **1976**, *54*, 905. Lefort, D.; Fossey, J.; Gruselle, M.; Nedelec, J. Y.; Sorba, J. *Tetrahedron* **1985**, *41*, 4237.

(19) In this aspect, the allylation starting with phenylselenenyl enolates is a comparable reaction to our radical allylation, although the former consists of two reaction processes, allylation and reductive deselenenylation.[3]

(20) The following are several examples of stereochemical results of the ionic reactions. We obtained trans/cis distributions of 3-butyl-2-(2-propenyl)cyclopentanone and -cyclohexanone in ratios of 81:19 and 76:24, respectively, from the conjugate addition and subsequent enolate trapping according to Posner's process.[27] The trans:cis ratio of 4-*tert*-butyl-2-methylcyclohexanone is 49:51 in the methylation of the lithium enolate (House, H. O.; Tefertiller, B. A.; Olmstead, H. D. *J. Org. Chem.* **1968**, *33*, 935) and 35:65 from the tin enolate.[4b] The trimethylsilyl enol ether of 4-*tert*-butyl- or 2-methylcyclohexanone gave a trans:cis ratio of 70:30 or 64:36, respectively, by treatment with tetrabutylammonium fluoride and methyl iodide or butyl iodide: Kuwajima, I.; Nakamura, E.; Shimizu, M. *J. Am. Chem. Soc.* **1982**, *104*, 1025. The palladium-catalyzed allylation of 4-*tert*-butylcyclohexanone gives a trans/cis (50:50) mixture of allylated product.[29]

(21) Davis, R.; Untch, K. G. *J. Org. Chem.* **1979**, *44*, 3755. Paterson, J. W.; Fried, J. H. *Ibid.* **1974**, *39*, 2506. Very recently, excellent methods for construction of a PG skeleton via the organocopper conjugate addition–enolate trapping process have been reported; see: Suzuki, M.; Yanagisawa, A.; Noyori, R. *J. Am. Chem. Soc.* **1985**, *107*, 3348. Johnson, C. R.; Penning, T. D. *Ibid.* **1986**, *108*, 5655; **1988**, *110*, 4726.

(22) The palladium-catalyzed allylation can be conducted under neutral conditions.[7]

(23) We observed a high-yield formation of the allylated product from 3-butyl-4-hydroxy-2-(phenylseleno)cyclopentanone.

Experimental Section

General Procedures. ^1H and ^{13}C NMR spectra were recorded on either JEOL JNM-PMX60Si (60 MHz), Varian XL-200 (200 MHz), or Varian XL-500 (500 MHz)[24] spectrometers and are reported in δ from Me_4Si. IR spectra were recorded on a JASCO A-102 spectrometer, and the IR figures reproted are ν_{max} in cm^{-1}. Mass spectra were recorded on either ESCO EMD-05B or Hitachi M-2000 spectrometers.

All reactions were performed under argon. All irradiations were carried out with a 400-W high-pressure Toshiba mercury lamp. A Pyrex glass tube containing a benzene solution of a substrate and an allylstannane was externally irradiated under argon at a distance of 15 cm from the mercury lamp. Analyses of the products were performed with a Shimadzu Chromatopac C-R3A instrument attached to either Hitachi 063 or Shimadzu GC-9A gas chromatographs (column; OV-17 3 mm × 2 m), and naphthalene was used as an internal standard for quantitative analyses. HPLC analyses were performed with a JASCO TRIROTAR-VI instrument. All reactions were monitored by thin-layer chromatography carried out on 0.25-mm E. Merck silica gel plates (60F-254), with UV light and 7% phosphomolybdic acid in ethanol/heat as developing agent. Flash column chromatography was carried out with a Michel Miller column packed with Fuji Davison silica gel BW-200, equipped with FMI lab pump RPG150 and FMI pulse damper PD-60LF, normally at a pressure of 1–2 kg cm^{-2}.

3-Methyl-2-(phenylseleno)cyclopentanone (1a). Preparation according to the literature[9] gave *trans*-**1a** and *cis*-**1a** after flash chromatography (silica gel, 10% ethyl acetate in hexane). *trans*-**1a**: ^1H NMR (60 MHz, CCl_4) δ 1.15 (3 H, d, J = 6 Hz), 1.33–2.43 (5 H, m), 3.05 (1 H, d, J = 7 Hz), 7.06–7.73 (5 H, m); IR (thin film) 3025, 1720 cm^{-1}. *cis*-**1a**: ^1H NMR (60 MHz, CCl_4) δ 1.23 (3 H, d, J = 6 Hz), 1.36–2.80 (5 H, m), 3.62 (1 H, d, J = 5 Hz), 7.06–7.67 (5 H, M); IR (thin film) 3025, 1725 cm^{-1}.

A mixture of 3-methyl-2-(phenylseleno)cyclopentanone (**1a**) (trans/cis 6:94) and an excess amount of sodium acetate in ethanol was stirred at room temperature for 3 h. HPLC analysis showed a 79:21 mixture of *trans*-**1a** and *cis*-**1a** (Nakarai Finepak SIL; eluent, 20% ethyl acetate in hexane; flow speed, 1.0 mL/min; t_R, 4.34 min for *trans*-**1a** and 5.39 min for *cis*-**1a**).

3-Butyl-2-(phenylseleno)cyclopentanone (1b). Preparation according to the literature[9] gave *trans*-**1b** and *cis*-**1b** after flash chromatography (silica gel, 5% ethyl acetate in hexane). *trans*-**1b**: ^1H NMR (60 MHz, CCl_4) δ 0.66–2.36 (14 H, m), 3.15 (1 H, d, J = 6 Hz), 7.06–7.73 (5 H, m); ^{13}C NMR ($CDCl_3$) δ 13.99 (q), 22.65 (t), 26.90 (t), 29.19 (t), 33.86 (t), 36.11 (t), 42.51 (d), 53.08 (d), 128.38 (d), 129.05 (d), 135.53 (d), 214.89 (s); IR (thin film) 3050, 1735 cm^{-1}. *cis*-**1b**: ^1H NMR (60 MHz, CCl_4) δ 0.73–2.80 (14 H, m), 3.58 (1 H, d, J = 5.5 Hz), 7.06–7.76 (5 H, m); ^{13}C NMR ($CDCl_3$) δ 14.04 (q), 22.74 (t), 27.07 (t), 30.04 (t), 32.21 (t), 35.66 (t), 41.86 (d), 53.99 (d), 128.36 (d), 129.09 (d), 135.44 (d), 211.88 (s); IR (thin film) 3050, 1720 cm^{-1}.

The stereochemistries of *trans*-**1b** and *cis*-**1b** were further confirmed by subjecting each isomer to the oxidation–elimination reaction of the phenylseleno group as follows. Although the elimination of the selenenic acid was usually effected by adding a base such as pyridine, the elimination without base was found to be able to discriminate the reaction between the trans and cis isomers, i.e., the reaction of *trans*-**1b** proceeds far more rapidly than that of *cis*-**1b**.

Oxidation–Elimination of the Phenylseleno Group of *trans*-1b. To a solution of *trans*-3-butyl-2-(phenylseleno)-cyclopentanone (*trans*-**1b**) (62 mg, 0.21 mmol) in dichloromethane (0.6 mL) was added a solution of *m*-chloroperbenzoic acid (*m*-CPBA) (40 mg, 0.23 mmol) in dichloromethane (1.0 mL). After 20 min, disappearance of the starting selenide and formation of the selenoxide were confirmed by TLC (R_f 0.50; 5% methanol in $CHCl_3$). Then the cooling bath was removed, and the mixture was stirred for 2.5 h. Ether (10 mL) was added, and the resulting solution was washed successively with aqueous $NaHCO_3$, water, and brine, dried over anhydrous $MgSO_4$, and evaporated under reduced pressure. The residue was purified by flash chroma-

(24) We are indebted to the Ono Pharmaceutical Co. for 500-MHz NMR spectra.

tography (30% ethyl acetate in hexane), to afford 3-butyl-2-cyclopenten-1-one[9] (28 mg, 97%).

Oxidation–Elimination of the Phenylseleno Group of *cis*-1b. The same reaction as above was carried out starting with *cis*-3-butyl-2-(phenylseleno)cyclopentanone (24 mg, 0.08 mmol) and gave 3-butyl-2-cyclopenten-1-one (2 mg, 18%).

3-Methyl-2-(phenylseleno)cyclohexanone[12] (1c). The product prepared according to the literature[9] was shown as a 93:7 trans/cis mixture of the isomers by HPLC analysis (Finepak SIL; eluent, 3% ethyl acetate in hexane; flow speed, 1.0 mL/min; t_R, 12.7 min for *trans*-**1c** and 16.0 min for *cis*-**1c**): ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.11 (2.7 H, d, J = 6 Hz), 1.22 (0.3 H, d, J = 6 Hz), 1.49–2.36 (5 H, m), 2.42–2.60 (H, m), 2.99–3.29 (H, m), 3.56–3.66 (0.9 H, m), 3.76–3.84 (0.1 H, m), 7.24–7.72 (5 H, m).

3-Butyl-2-(phenylseleno)cyclohexanone (1d). Preparation according to the literature[9] gave *trans*-**1d** and *cis*-**1d** after flash chromatography (silica gel, 5% ethyl acetate in hexane). *trans*-**1d**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (3 H, t, J = 6.0 Hz), 1.23–1.46 (6 H, m), 1.65 (1 H, ddddd, J = 13.5, 4.0, 3.5, 3.5, 1.5 Hz, H_{4eq}), 1.79–1.93 (2 H, m, H_5), 2.04 (1 H, dddd, J = 13.5, 12.5, 4.5, 4.5 Hz, H_{4ax}), 2.23 (1 H, dddd, J = 14.5, 6.5, 3.0, 1.5 Hz, H_{6eq}), 2.23 (1 H, dddd, J = 14.5, 6.5, 3.0, 1.5 Hz, H_{3eq}), 2.30 (1 H, dddt, J = 7.0, 4.5, 3.5, 3.5 Hz, H_{3eq}), 3.11 (1 H, ddd, J = 14.5, 11.5, 7.5 Hz, H_{6ax}), 3.64 (1 H, ddd, J = 3.5, 1.5, 1.5 Hz, H_{2eq}), 7.23–7.56 (5 H, m); IR (thin film) 3050, 1690 cm^{-1}. *cis*-**1d**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 0.88 (3 H, t, J = 6.0 Hz), 1.20–1.35 (6 H, m), 1.46–1.78 (3 H, m, H_{4ax}, H_{5ax}, H_{4eq}), 1.92 (1 H, dddt, J = 11.3, 7.5, 3.7, 3.6 Hz, H_{3ax}), 2.04 (1 H, ddddd, J = 13.0, 7.0, 6.5, 3.0, 3.0 Hz, H_{5eq}), 2.24 (1 H, dddd, J = 15.0, 6.0, 3.0, 2.0 Hz, H_{6eq}), 3.16 (1 H, ddd, J = 15.0, 13.0, 7.0 Hz, H_{6ax}), 3.77 (1 H, ddd, J = 3.7, 2.0, 2.0 Hz, H_{2eq}), 7.20–7.60 (5 H, m); IR (thin film) 3050, 1690 cm^{-1}.

The trans and cis isomers of 4-*tert*-butyl-2-(phenylseleno)-cyclohexanone[14] (**1e**) and 2-methyl-6-(phenylseleno)cyclohexanone[15] (**1f**) showed reasonable spectral data.

General Procedure for the Allylation of α-Seleno Carbonyl Compounds. (a) Photolytic Procedure. 3-Methyl-2-(2-propenyl)cyclopentanone[25] (2a). A solution of *trans*-3-methyl-2-(phenylseleno)cyclopentanone (*trans*-**1a**) (20 mg, 0.08 mmol) and tributyl-2-propenyltin (53 mg, 0.16 mmol) in degassed benzene (0.08 mL) was irradiated for 1 h. Both the yield of **2a** (93%) and the trans:cis ratio (78:22) were determined by GC analysis (oven temperature, 70 °C; t_R, 2.79 min for *trans*-**2a** and 3.75 min for *cis*-**2a**).

(b) Thermal Reaction. 3-Butyl-2-(2-propenyl)cyclopentanone[4b] (2b). A solution of *trans*-3-butyl-2-(phenylseleno)cyclopentanone (*trans*-**1b**) (17 mg, 0.06 mmol), tributyl-2-propenyltin (38 mg, 0.12 mmol), and AIBN (0.5 mg) in toluene (0.06 mL) was heated under reflux for 2 h. The yield (88%) of **2b** and the trans:cis ratio (83:17) were determined by GC analysis (column temperature, 100 °C; t_R, 4.52 min for trans-**2b** and 5.49 min for *cis*-**2b**). The spectral data of **2b** were reasonable for the assigned structure. Furthermore, a solution of a cis-rich mixture (trans/cis, 10:90) of **2b** was heated under reflux with an excess amount of sodium acetate for 3 h, to give an 89:11 trans/cis mixture of isomers.

3-Methyl-2-(2-propenyl)cyclohexanone[26] (2c). The yield (70%) of **2c** and the trans:cis ratio (67:33) were determined by GC analysis (column temperature, 70 °C; t_R, 4.49 min for *trans*-**2c** and 5.38 min for *cis*-**2c**). The spectral data were in good accord with those reported.[26]

3-Butyl-2-(2-propenyl)cyclohexanone (2d). The yield (67%) of **2d** and the trans:cis ratio (66:34) were determined by GC analysis (column temperature, 120 °C; t_R, 3.85 min for *trans*-**2d** and 4.26 min for *cis*-**2d**). **2d**: ^{1}H NMR (60 MHz, CCl_4) δ 0.60–2.60 (19 H, m), 4.63–5.15 (2 H, m), 5.26–6.16 (1 H, m); IR (thin film) 3060, 1705 cm^{-1}; GC–MS m/e (relative intensity) (*trans*-**2d**) 194 (M^+, 20), 151 (14), 137 (95), 109 (84), 96 (100), (*cis*-**2d**) 194 (M^+, 7), 151 (14), 137 (99), 109 (84), 96 (100); MS m/e 194.1658, $C_{13}H_{22}O$ requires 194.1671. Trans-rich (trans/cis, 76:24 and 58:42) mixtures of **2d** were separately treated with sodium ethoxide in ethanol at room temperature, to give the same trans/cis mixture in a ratio of 62:38. Hydrogenation of **2d** (trans/cis, 89:11) with Pd/C gave trans-rich 3-butyl-2-propylcyclohexanone (**3**): ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.80–0.96 (6 H, m), 1.12–1.82 (13 H, m), 1.85–2.04 (2 H, m), 2.13 (1 H, dt, J = 5,[27] 7.5 Hz, H_2), 2.24 (1 H, ddd, J = 14, 8, 4.5 Hz, H_6), 2.41 (1 H, ddd, J = 14, 8, 6.5 Hz, H_6); IR (thin film) 1705 cm^{-1}; MS m/e 196.1839, $C_{13}H_{24}O$ requires 196.1827.

4-*tert*-Butyl-2-(2-propenyl)cyclohexanone[28] (2e). The yield (72%) of **2e** and the trans:cis ratio (85:15) were determined by GC analysis (column temperature, 105 °C; t_R, 7.84 min for *trans*-**2e** and 8.84 min for *cis*-**2e**). Trans and cis isomers were isolated by flash chromatography (eluent; 2% ethyl ether in light petroleum ether). *trans*-**2e**: ^{1}H NMR (60 MHz, CCl_4) δ 0.87 (9 H, s), 1.10–2.56 (10 H, m), 4.73–5.16 (2 H, m), 5.33–6.22 (1 H, m); ^{13}C NMR ($CDCl_3$) δ 26.64 (t), 27.42 (q), 30.30 (t), 32.47 (s), 35.52 (t), 38.61 (t), 41.15 (d), 48.58 (d), 116.90 (t), 135.48 (d), 215.05 (s); IR (thin film) 3060, 1705 cm^{-1}. *cis*-**2e**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.90 (9 H, s), 1.00–2.68 (10 H, m), 4.92–5.14 (2 H, m), 5.70–5.94 (1 H, m); ^{13}C NMR ($CDCl_3$) δ 27.66 (q), 28.69 (t), 32.52 (s), 33.74 (t), 34.55 (t), 41.61 (t), 47.10 (d), 49.37 (d), 116.17 (t), 136.64 (d), 212.71 (s); IR (thin film) 3080, 1710 cm^{-1}.

The stereochemistry of 4-*tert*-butyl-2-(2-propenyl)cyclohexanone (**2e**) was further confirmed by isomerization (sodium ethoxide in ethanol, room temperature, 1.5 h) of *trans*-**2e** to a 9:91 trans/cis mixture of isomers.

2-Methyl-6-(2-propenyl)cyclohexanone[29] (2f). The yield (85%) of **2f** and the trans:cis ratio (84:16) were determined by GC analysis (column temperature, 70 °C; t_R, 5.17 min for *cis*-**2f** and 5.53 min for *trans*-**2f**). Each isomer was separated by flash chromatography (silica gel; eluent, 3% ethyl ether in light petroleum ether). *trans*-**2f**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.09 (3 H, d, J = 6 Hz), 1.44–2.30 (7 H, m), 2.38–2.68 (3 H, m), 4.98–5.16 (2 H, m), 5.63–5.88 (1 H, m); ^{13}C NMR ($CDCl_3$) δ 15.68 (q), 20.30 (t), 31.79 (t), 34.83 (t), 35.00 (t), 42.99 (d), 48.29 (d), 116.50 (t), 135.90 (d), 215.95 (s); IR (thin film) 3080, 1705 cm^{-1}. *cis*-**2f**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.02 (3 H, d, J = 6 Hz), 1.68–2.70 (10 H, m), 4.88–5.26 (2 H, m), 5.70–5.90 (1 H, m); ^{13}C NMR ($CDCl_3$) δ 14.56 (q), 25.52 (t), 33.74 (t), 34.69 (t), 37.38 (t), 45.65 (d), 50.41 (d), 116.01 (t), 136.89 (d), 213.59 (s).

Each isomer was reduced with 10% Pd/C to 2-methyl-6-propylcyclohexanone[30] (**4**). *trans*-**4**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (3 H, t, J = 6.5 Hz), 1.05 (3 H, d, J = 6.5 Hz), 1.16–1.56 (4 H, m), 1.60–2.10 (6 H, m), 2.24–2.52 (1 H, m), 2.56 (1 H, ddd, J = 10.0, 6.5, 5.2 Hz, H_2). *cis*-**4**: ^{1}H NMR (200 MHz, $CDCl_3$) δ 0.89 (3 H, J = 6.5 Hz), 1.00 (3 H, d, J = 6.0 Hz), 1.06–1.48 (5 H, m), 1.62–1.92 (3 H, m), 2.03–2.38 (2 H, m), 2.24 (1 H, m, coalescing to dd, J = 12.4, 4.6 Hz, by irradiation at 1.22, H_6), 2.42 (1 H, ddd, J = 12.8, 6.0, 5.6 Hz, H_2).

Registry No. *trans*-**1a**, 73824-96-1; *cis*-**1a**, 73824-93-8; *trans*-**1b**, 73824-97-2; *cis*-**1b**, 73824-94-9; *trans*-**1c**, 73824-98-3; *cis*-**1c**, 73824-95-0; *trans*-**1d**, 106352-55-0; *cis*-**1d**, 106352-54-9; *trans*-**1e**, 73843-13-7; *cis*-**1e**, 73843-14-8; *trans*-**1f**, 57204-94-1; *cis*-**1f**, 57204-93-0; *trans*-**2a**, 124244-30-0; *cis*-**2a**, 124244-31-1; *trans*-**2b**, 109900-41-6; *cis*-**2b**, 109900-42-7; *trans*-**2c**, 61674-94-0; *cis*-**2c**, 61674-93-9; *trans*-**2d**, 124244-32-2; *cis*-**2d**, 124244-33-3; *trans*-**2e**, 15781-18-7; *cis*-**2e**, 15781-11-0; *trans*-**2f**, 124244-34-4; *cis*-**2f**, 124244-35-5; **3**, 124244-38-8; *trans*-**4**, 124244-36-6; *cis*-**4**, 124244-37-7; allyltributyltin, 24850-33-7; 3-butyl-2-cyclopenten-1-one, 53253-06-8.

(25) Zima, G.; Barnum, C.; Liotta, D. *J. Org. Chem.* **1980**, *45*, 2737.
(26) Caine, D.; Chao, S. T.; Smith, H. A. *Org. Synth.* **1978**, *56*, 52.
(27) The vicinal coupling constant between H_2 and H_3 of *trans*-2,3-dibutylcyclohexanone is 6 Hz; see: Posner, G. H.; Sterling, J. J.; Whitten, C. E.; Lentz, C. M.; Brunelle, D. J. *J. Am. Chem. Soc.* **1975**, *97*, 107.
(28) Conia, J. M.; Briet, P. *Bull. Chim. Soc. Fr.* **1966**, 3881, 3888. Hiroi, K.; Yamada, S. *Chem. Pharm. Bull.* **1973**, *21*, 47.
(29) Trost, B. M.; Self, C. R. *J. Org. Chem.* **1984**, *49*, 468.
(30) Yamada, K.; Yano, T.; Miyaura, N.; Suzuki, A. *Bull. Chem. Soc. Jpn.* **1979**, *52*, 275.