spectrum (rel intensity), m/z 290 ($M^+ - 64$, 1), 149 (68), 133 (43), 107 (94), 93 (100). Anal. Calcd for $C_{17}H_{22}O_4S_2$: C, 57.60; H, 6.26. Found; C, 57.63; H, 6.26.

***cis*-7-(Phenylsulfonyl)-1,2,3,4,5,6,4a,8a-octahydronaphthalene (10) and *trans*-7-(Phenylsulfonyl)-1,2,3,4,5,6,4a,8a-octahydronaphthalene (11).** A solution of **6b** (87 mg, 2.56 mmol) in toluene (2 mL) and pyridine (0.1 mL) was heated in a sealed tube at 175 °C for 21 h. The workup procedure was the same as that for the preparation of **7** and **8** to give **10** (19 mg, 27%) and **11** (18 mg, 26%). **10**: IR (neat) 2927, 2856, 1446, 1301, 1151, 1089, 690, 584, 563 cm^{-1}; ^1H NMR (400 MHz) δ 1.15–1.75 (1 H, m), 2.0–2.2 (2 H, m), 2.35–2.45 (1 H, m), 6.88 (1 H, t, J = 1.3 Hz), 7.46 (2 H, t, J = 7.6 Hz), 7.53 (1 H, t, J = 7.4 Hz), 7.79 (2 H, d, J = 7.5 Hz); mass spectrum (rel intensity), m/z 276 (M^+, 41), 274 (45), 167 (31), 151 (72), 135 (100); exact mass calcd for $C_{16}H_{20}O_2S$ m/z 276.1184, found 276.1180. **11**: IR (neat) 2925, 2854, 1315, 1301, 1151, 1089, 584, 563 cm^{-1}; ^1H NMR (400 MHz) δ 0.9–1.4 (6 H, m), 1.55–1.85 (6 H, m), 2.05–2.25 (2 H, m), 6.83 (1 H, s), 7.46 (2 H, t, J = 7.6 Hz), 7.54 (1 H, t, J = 7.3 Hz), 7.79 (2 H, d, J = 7.3 Hz); mass spectrum (rel intensity), m/z 276 (M^+, 24), 274 (61), 167 (20), 151 (26), 135 (100); exact mass calcd for $C_{16}H_{20}O_2S$ m/z 276.1184, found 276.1178.

(*E*)-4-Methyl-2-(phenylsulfonyl)-1,3,8-nonatriene (12). A solution of **9a** (70 mg, 0.21 mmol) in *p*-xylene (10 mL) was heated at reflux for 5 h. The solvent was removed by a rotary evaporator, and the crude product was purified by flash column chromatography using hexane/ethyl acetate (6:1) as eluent to give **12** (23 mg, 48%) and **13** (6 mg, 11%). **12**: IR (neat) 2933, 1446, 1313, 1305, 1157, 1133, 1081, 746, 688 cm^{-1}; ^1H NMR (400 MHz) δ 1.44 (3 H, s), 1.3–1.4 (2 H, m), 1.92 (2 H, q, J = 7.3 Hz), 2.03 (2 H, t, J = 7.4 Hz), 4.85–4.95 (2 H, m), 5.6–5.75 (1 H, m), 5.69 (1 H, d, J = 1.3 Hz), 5.78 (1 H, s), 6.51 (1 H, s), 7.4–7.5 (2 H, m), 7.5–7.55 (1 H, m), 7.7–7.8 (2 H, m); the NOE experiment showed that irradiation at δ 1.44, 2.03, and 6.51 resulted in enhancements at δ 5.68, 5.78, and 5.68, respectively; mass spectrum (rel intensity), m/z 276 (M^+, 18), 135 (100), 93 (68); exact mass calcd for $C_{16}H_{20}O_2S$ m/z 276.1184, found 276.1191.

***cis*-7a-Methyl-6-(phenylsulfonyl)-2,3,4,5,4a,7a-hexahydroindene (13).** A solution of **9a** (14 mg, 0.041 mmol) in toluene (2 mL) and pyridine (0.1 mL) was heated in a sealed tube at 250 °C for 19 h. The crude product was purified by HPLC using hexane/ethyl acetate (10:1) as eluent to give **13** (10 mg, 88%): mp 66–67 °C; IR (KBr) 2950, 1446, 1303, 1149, 690, 570 cm^{-1}; ^1H NMR (300 MHz) δ 1.06 (3 H, s), 1.23–1.35 (1 H, m), 1.40–1.50 (1 H, m), 1.50–1.66 (5 H, m), 1.66–1.80 (2 H, m), 2.02 (2 H, td, J = 5.66, 1.67 Hz), 6.68 (1 H, s), 7.45–7.65 (3 H, m), 7.8–7.85 (2 H, m); mass spectrum (rel intensity), m/z 276 (M^+, 9), 135 (46), 108 (100); exact mass calcd for $C_{16}H_{20}O_2S$ m/z 276.1184, found 276.1187.

(*E*)-4-Methyl-2-(phenylsulfonyl)-1,3,9-decatriene (14), (*Z*)-4-Methyl-2-(phenylsulfonyl)-1,3,9-decatriene (15), and (2*E*,4*E*)-4-Methyl-2-(phenylsulfonyl)-2,4,9-decatriene (16). A solution of **9b** (67 mg, 0.19 mmol) in toluene (2 mL) and pyridine (0.1 mL) was heated in a sealed tube at 160 °C for 18 h. The crude product was purified by HPLC using hexane/ethyl acetate (10:1) as eluent to give **14** (30 mg, 55%), **15** (7 mg, 13%), and **16** (6 mg, 11%). **14**: IR (neat) 2933, 1446, 1315, 1305, 1160, 1133, 1081, 748, 688 cm^{-1}; ^1H NMR (300 MHz) δ 1.15–1.4 (4 H, m), 1.40 (3 H, d, J = 1.2 Hz), 1.95–2.05 (4 H, m), 4.9–5.0 (2 H, m), 5.65 (1 H, d, J = 1.6 Hz), 5.65–5.8 (2 H, m), 6.48 (1 H, s), 7.4–7.5 (2 H, m), 7.5–7.6 (1 H, m), 7.75–7.85 (2 H, m); the NOE experiment showed that irradiation at δ 2.0 and 5.65 resulted in enhancements for δ 6.8 and 6.47, respectively; mass spectrum (rel intensity), 290 (M^+, 13), 149 (100); exact mass calcd for $C_{17}H_{22}O_2S$ m/z 290.1341, found 290.1336. **15**: ^1H NMR (300 MHz) δ 1.0–1.15 (4 H, m), 1.71 (3 H, d, J = 0.8 Hz), 1.75–1.95 (4 H, m), 4.85–5.0 (2 H, m), 5.62 (1 H, d, J = 1.7 Hz), 5.6–5.8 (1 H, m), 5.76 (1 H, s), 6.44 (1 H, s), 7.75–7.85 (2 H, m); the NOE experiment showed that irradiation at δ 1.7, 5.6, and 6.4 resulted in enhancements at δ 5.76, 6.4, and 5.6, respectively. **16**: ^1H NMR (300 MHz) δ 1.4–1.55 (2 H, m), 1.77 (3 H, s), 1.94 (3 H, s), 2.0–2.2 (4 H, m), 4.9–5.05 (2 H, m), 5.65–5.85 (2 H, m), 7.19 (1 H, s), 7.45–7.65 (3 H, m), 7.8–7.9 (2 H, m).

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Registry No. 1, 64741-13-5; **2a**, 124243-68-1; **2b**, 124243-69-2; 3, 104664-79-1; **4a**, 124243-70-5; **4b**, 124243-71-6; **6a**, 124266-43-9; **6b**, 124243-72-7; **7**, 124243-73-8; **8**, 124243-74-9; **9a**, 124266-44-0; **9b**, 124266-45-1; **10**, 124243-75-0; **11**, 124243-76-1; **12**, 124243-77-2; **13**, 124243-78-3; **14**, 124243-79-4; **15**, 124243-80-7; **16**, 124243-81-8; $CH_2{=}CH(CH_2)_3I$, 7766-48-5; $CH_2{=}CH(CH_2)_4I$, 18922-04-8.

Application of NMR Techniques to the Structural Elucidation of Isomeric Phenolic Biphenyls

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3-Hydroxy-4-methoxybiphenyl has been synthesized and its structure confirmed by using NMR techniques. Complete ^{13}C NMR assignments of the biphenyl system were made by using a long-range HETCOR spectrum. The position of the hydroxy versus methoxy substituent was then established by using the long-range HETCOR spectrum, ^{13}C spin-lattice relaxation measurements, deuterium-induced ^{13}C chemical shift effects, and NOE difference spectroscopy.

Phenolic biphenyl compounds are natural products commonly observed as metabolites of biphenyl.[1] In many such substances, some of the phenolic hydroxyl groups are substituted, and O-methylation is often observed. In establishing the structures of partially O-methylated phenolic biphenyl compounds, ^{13}C NMR spectroscopy is a valuable and much used tool. However, signal assignment between hydroxylated and O-methylated carbons based on shift value calculations is often ambiguous since the substituent effects of OH and OCH_3 groups are comparable.[2] It was therefore necessary to develop NMR techniques to differentiate these carbons so that complete NMR assignments and therefore structure assignments could be made. The techniques used included 2D long-range heteronuclear correlated spectroscopy (HETCOR), spin-lattice relaxation

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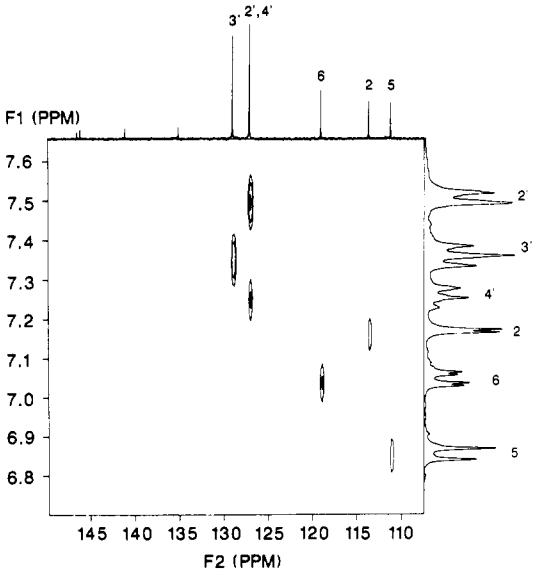
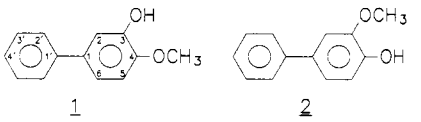


Figure 1. Aromatic region of 1D proton (side), ^{13}C (top), and 2D HETCOR spectra.

measurements, deuterium-induced chemical shift effects, and nuclear Overhauser effect (NOE) difference spectroscopy. Here we present results obtained using these techniques to differentiate the model compound 3-hydroxy-4-methoxybiphenyl **1** from the possible positional isomer 4-hydroxy-3-methoxybiphenyl **2**.



1 **2**

Results and Discussion

The aromatic region of the 1D proton and ^{13}C NMR spectra of **1** are shown along with the HETCOR spectrum in Figure 1. Assignments of the proton resonances follow from inspection of integrals, chemical shifts, and coupling constants. Protons 2, 5, and 6 are observed upfield (relative to normal aromatic protons) due to their proximity to the methoxy and hydroxy substituents and are differentiated by the coupling constants observed. Similarly, all five protons of the second aromatic ring are assigned based on the integrals and couplings observed.

Once the proton assignments are made, the attached carbons can be deduced from the HETCOR spectrum by examination of the position of the cross-peaks observed. The HETCOR spectrum does not lead to assignment of the quaternary carbons, however, as the delays in the HETCOR pulse sequence are optimized for large (140 Hz) one-bond coupling.

The quaternary carbon assignments are paramount in differentiating between **1** and **2**. In particular, the specific assignments for carbons 3 and 4, which differ in chemical shift by only 25 Hz (vide infra), are needed. To assign these carbons the delays in the HETCOR pulse sequence were optimized for three-bond aromatic (9 Hz) coupling. The long-range HETCOR spectrum thus obtain is shown in Figure 2. The most prominant cross-peaks are observed between protons and carbons separated by three bonds, although for some protons weak cross-peaks were observed due to residual one-bond coupling.

The farthest downfield quaternary carbon (146.11 ppm) has cross-peaks to protons 2 and 6 and is therefore assigned to carbon 4, para to the second aromatic ring. The resonance slightly upfield (145.77 ppm) has a cross-peak only

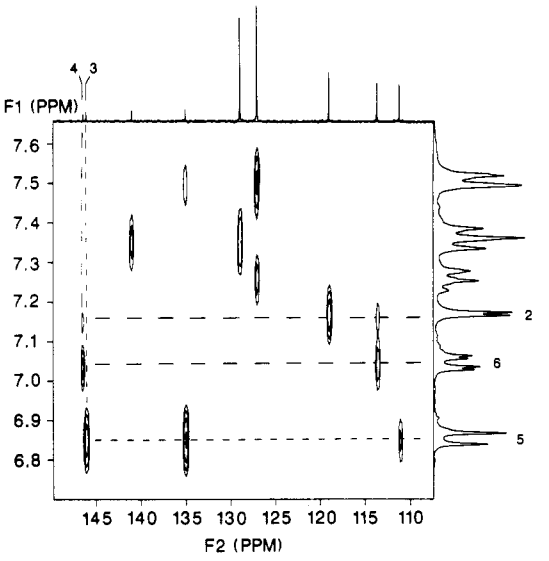


Figure 2. Aromatic region of long-range HETCOR spectrum.

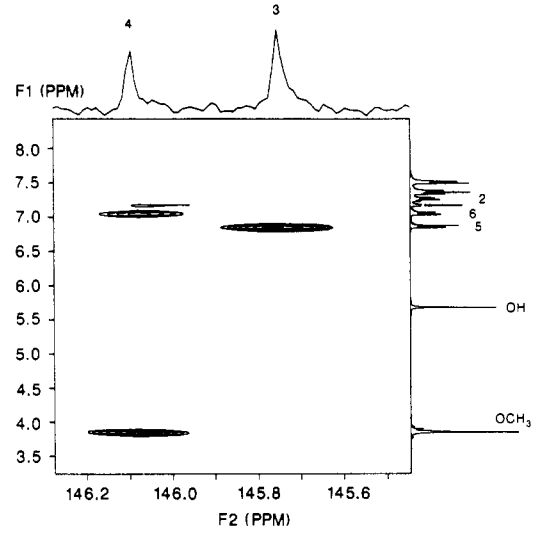


Figure 3. Long-range HETCOR spectrum. Carbon axis expanded to show carbons 3 and 4 only.

Table I. ^{13}C Chemical Shifts and Deuterium-Induced Isotope Shifts

chemical shift (ppm versus TMS)	carbon	deuterium-induced isotope shift (ppm)
146.11	4	−0.06
145.77	3	−0.10
140.71	1′	<0.01
134.79	1	<0.01
128.66	3′	<0.01
126.79	4′	<0.01
126.76	2′	<0.01
118.71	6	−0.02
113.37	2	−0.08
110.89	5	<0.01
56.02	methyl	−0.01

to proton 5 and is therefore assigned to the meta position, carbon 3. Complete carbon assignments obtained from the HETCOR and long-range HETCOR spectra are given in Table I.

The assignment of the positions of the methoxy/hydroxy substituents to either the para or meta carbons was then undertaken by four independent methods. The first of these methods was the long-range HETCOR spectrum previously discussed to observe coupling from the down-

field quaternary carbon and the methoxy protons. In Figure 3 the long-range HETCOR spectrum is shown with the carbon axis expanded so that only the two quaternary carbons of interest are shown while the entire window is shown on the proton axis. As can be seen, coupling is observed between the methoxy protons and carbon 4, establishing the site of the methoxy substituent as the para position. It should be noted that when acquisition of the long-range HETCOR was repeated with the delays set for 6 or 12 Hz coupling this correlation was not observed, emphasizing the importance of properly setting this parameter for successful assignment to be made. Conversely, most of the aromatic proton–carbon correlations were observed with all three parameter sets.

As an alternate means of assignment of the methoxy/hydroxy positions the spin–lattice relaxation times (T_1) of carbons 3 and 4 were studied. For most carbon atoms in typical organic molecules such as **1** and **2**, dipolar relaxation with nearby protons is usually the major relaxation mechanism. This mechanism is dependent on the inverse sixth power of the C–H distance and therefore decreases quickly as the C–H distance increases. It is the reduced level of these interactions (relative to carbons directly bearing protons) which leads to the long relaxation times and therefore weak signals typical of quaternary carbons. Despite the long T_1's, the presence of one extra proton close to a hydroxy-substituted aromatic carbon should make dipole–dipole relaxation more efficient than for methoxy-substituted aromatic carbons. This will result in lower T_1 values.

Malterud and Anthonsen[3] have recently reported T_1 measurements on 15 partially O-methylated phenolic substances (phenols, benzaldehydes, acetophenones and flavonoids) and found this to be true with the typical ratio of T_1(C–OH)/T_1(C–OCH_3) to be 0.74. Using a typical inversion–recovery T_1 experiment a T_1 value of 34.7 s for the downfield carbon and 26.2 s for the upfield carbon was determined. It is therefore possible to assign the downfield carbon (longest T_1) to the methoxy-substituted carbon. Since we know this carbon is para to the second aromatic ring from the long-range HETCOR spectrum, the isomer assignment can be made. The ratio of T_1 values observed (0.76) is in good agreement with the results of Malterud and Anthonsen.

A third method of assignment of the substituents on carbons 3 and 4 is measurement of the deuterium-induced isotope shifts. Exchange of the hydroxy proton with deuterium results in an upfield shift of the carbons (in order of decreasing magnitude) ipso, ortho, and para to the hydroxy substituent. Newmark and Hill[4] report deuterium-induced isotope shifts of 2-ethoxyphenol of −0.14, −0.09, and −0.10 ppm for the C-1, C-2, and C-6 carbons, respectively. The observed shifts for **1**, given in Table I, are consistent with those reported for 2-ethoxyphenol but smaller in magnitude. A shift of −0.10 ppm is observed for carbon 3 and −0.06 ppm for carbon 4, establishing that the hydroxy is on carbon 3. Since these carbons are known from the long-range HETCOR spectrum to be meta and para, respectively, to the second aromatic ring, isomer assignment as **1** is complete.

The final method used to make isomer assignment is independent of having complete carbon assignments, but only dependent on the proton NMR spectral assignments. In the NOE difference spectra, shown in Figure 4, positive signals are observed to protons in close spatial proximity

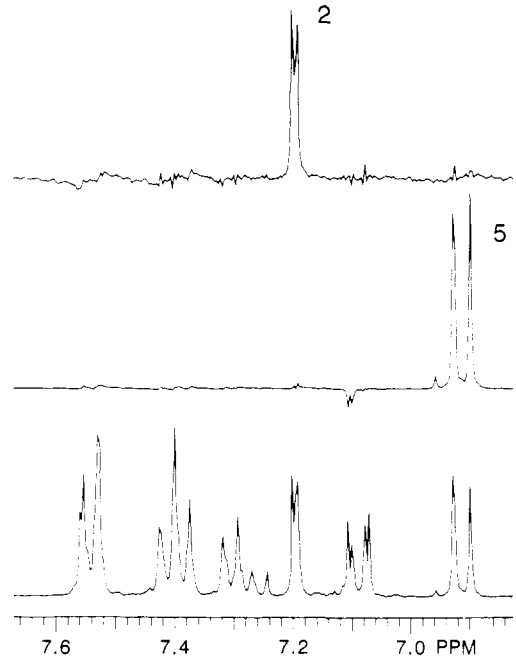


Figure 4. NOE difference experiment. (bottom) Normal spectrum, decoupler set off-resonance, (middle) difference spectrum, decoupler set on methoxy protons, and (top) difference spectrum, decoupler set on hydroxy proton.

of the irradiated proton(s).[5] Thus, when the methoxy protons are irradiated a 5% NOE enhancement is observed for H-5. Similarly, irradiation of the hydroxy proton yields a 3% NOE enhancement in H-2. Since the position of H-2 and H-5 are assigned based on coupling constants the isomer assignment can be made as the methoxy substituent is adjacent to H-5 and the hydroxy substituent is adjacent to H-2. This is only true with **1**.

Experimental Section

All spectra were obtained on a Varian VXR-300 NMR spectrometer operating at 300 MHz for proton and 75 MHz for carbon. All experiments were run on a 150-mg sample made up to 0.7 mL in deuteriochloroform. Chemical shifts are reported versus TMS. Heteronuclear chemical shift correlation spectra (HETCOR) were acquired using the Varian-supplied pulse sequence based on the literature sequence of Bax.[6] The spectra were acquired with 256 time increments zero filled to give a final 512 × 512 data matrix. The minimum sweep width required to observe all proton and carbon resonances was used.

^{13}C spin–lattice relaxation time measurements were made using a standard inversion–recovery pulse sequence.[7] Spectra were acquired with evolution times of 2.8, 5.6, 11.3, 45, 90, and 180 s. A 180-s delay was used between each transient with 36 transients acquired for each evolution time. Calculation of T_1 values was carried out with the programs furnished with the Varian VXR-300 spectrometer.

^{13}C NMR spectra for measurement of the deuterium-induced shifts were acquired in triplicate before and after shaking the deuteriochloroform solution with excess D_2O. Spectra were acquired with a digital resolution of 0.76 Hz/data point. The worst precision in chemical shifts for a given resonance observed in the triplicate acquisitions was 0.02 ppm with most values better than 0.01 ppm.

NOE difference spectra were obtained at 27 °C as follows. The signal of interest was irradiated for 25 s, and then a transient acquired with the decoupler off using an acquisition time of 1 s.

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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).

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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-

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(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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