1-Phenylindole (2a): bp 150 °C (2 mmHg) [lit.[13] bp 110 °C (0.5 mmHg)]; IR (film) 1595, 1495, 1450, 765, 740, 720, 695 cm^{-1}; ^1H NMR δ 6.61 (d, 1 H, J = 3.4 Hz), 7.08–7.70 (m, 10 H); ^{13}C NMR 103.5 (d), 120.3 (d), 121.0 (d), 122.2 (d), 124.1 (d), 126.2 (d), 127.7 (d), 129.2 (s), 129.4 (s), 135.7 (s), 139.6 ppm (s); MS, m/z 193 (M^+).

Bis(1-phenylindol-2-yl) disulfide (3a): mp 230–232 °C; IR (KBr) 1585, 1490, 1440, 740, 695 cm^{-1}; ^1H NMR δ 7.13–7.67 (m, 20 H); ^{13}C NMR 110.6 (d), 111.5 (d), 120.1 (d), 121.1 (d), 123.2 (s), 125.2 (d), 126.9 (d), 128.2 (d), 129.3 (d), 137.3 (s), 138.4 ppm (s). Anal. Calcd for $C_{28}H_{20}N_2S_2$: C, 74.96; H, 4.49; N, 6.24. Found: C, 75.16; H, 4.32; N, 5.98.

3-Methyl-1-phenylindole (2b): bp 150 °C (2 mmHg); IR (film) 1600, 1500, 1450, 770, 740, 695 cm^{-1}; ^1H NMR δ 2.36 (d, 3 H, J = 1.5 Hz), 7.01–7.68 (m, 10 H); ^{13}C NMR 9.6 (q), 110.3 (d), 112.7 (s), 119.1 (d), 119.7 (d), 122.2 (d), 123.9 (d), 125.3 (d), 125.8 (d), 129.4 (d), 129.7 (s), 135.9 (s), 139.9 ppm (s); MS, m/z 207 (M^+). Anal. Calcd for $C_{15}H_{13}N$: C, 86.92; H, 6.32; N, 6.75. Found: C, 86.77; H, 6.34; N, 6.87.

Bis(3-methyl-1-phenylindol-2-yl) disulfide (3b): mp 116–117 °C; IR (KBr) 1590, 1495, 1445, 740, 695 cm^{-1}; ^1H NMR δ 2.00 (s, 6 H), 6.89–7.30 (m, 18 H), 7.41–7.55 (m, 2 H); ^{13}C NMR 9.5 (q), 110.6 (d), 119.6 (d), 119.9 (d), 122.5 (d), 124.3 (d), 127.2 (d), 127.4 (s), 128.5 (d), 128.6 (d), 137.1 (s), 139.0 ppm (s); MS, m/z 476 (M^+), 238 (M^+ - 238, 100%). Anal. Calcd for $C_{30}H_{24}N_2S_2$: C, 75.61; H, 5.08; N, 5.88. Found: C, 75.93; H, 5.27; N, 5.81.

3-Ethyl-1-phenylindole (2c): bp 145 °C (2 mmHg); IR (film) 1595, 1500, 1455, 770, 740, 695 cm^{-1}; ^1H NMR δ 1.37 (t, 3 H), 2.83 (q, 2 H), 7.10–7.72 (m, 10 H); ^{13}C NMR 14.3 (q), 18.3 (t), 110.4 (d), 119.2 (d), 119.7 (d), 119.8 (s), 122.3 (d), 124.3 (d), 123.9 (d), 125.6 (d), 128.9 (d), 136.0 (s), 140.0 ppm (s); MS, m/z 221 (M^+). Anal. Calcd for $C_{16}H_{15}N$: C, 86.83; H, 6.83; N, 6.32. Found: C, 86.51; H, 6.76; N, 6.19.

Bis(3-ethyl-1-phenylindol-2-yl) disulfide (3c): mp 105–106 °C; IR (KBr) 1585, 1495, 1440, 750, 740, 695 cm^{-1}; ^1H NMR δ 1.06 (t, 3 H), 2.62 (q, 4 H), 6.84–7.31 (m, 16 H), 7.51–7.64 (m, 2 H); ^{13}C NMR 15.2 (q), 18.5 (t), 110.8 (d), 119.6 (d), 119.8 (d), 124.1 (d), 126.6 (d), 127.3 (d), 127.6 (s), 128.5 (d), 128.8 (d), 137.2 (s), 139.3 ppm (s); MS, m/z 504 (M^+), 252 (M^+ - 252, 100%). Anal. Calcd for $C_{32}H_{28}N_2S_2$: C, 76.17; H, 5.59; N, 5.55. Found: C, 76.32; H, 5.65; N, 5.49.

1,3-Diphenylindole (2d): mp 103–104 °C; IR (KBr) 1595, 1500, 1450, 765, 735, 695 cm^{-1}; ^1H NMR δ 7.02–7.75 (m, 14 H), 7.84–8.06 (m, 1 H); ^{13}C NMR 110.8 (d), 119.1 (s), 120.1 (d), 120.8 (d), 122.7 (d), 124.4 (d), 125.4 (d), 126.1 (d), 126.6 (d), 127.1 (d), 127.5 (d), 128.8 (d), 129.6 (d), 135.0 (s), 136.6 (s), 139.4 ppm (s). Anal. Calcd for $C_{20}H_{15}N$: C, 89.18; H, 5.61; N, 5.20. Found: C, 88.87; H, 5.56; N, 5.12.

Bis(1,3-diphenylindol-2-yl) disulfide (3d): mp 192–194 °C; IR (KBr) 1595, 1495, 1440, 760, 750, 740, 695 cm^{-1}; ^1H NMR δ 6.90–7.39 (m, 26 H), 7.35–7.65 (m, 2 H); ^{13}C NMR 110.8 (d), 120.2 (d), 120.8 (d), 124.6 (d), 126.1 (s), 126.5 (d), 127.6 (d), 128.6 (d), 129.1 (d), 130.0 (d), 133.3 (s), 136.8 (s), 139.4 ppm (s). Anal. Calcd for $C_{40}H_{28}N_2S_2$: C, 79.98; H, 4.70; N, 4.66. Found: C, 79.85; H, 4.65; N, 4.56.

5-Methyl-1-*p*-tolylindole (2e): bp 140 °C (2 mmHg); IR (film) 1605, 1515, 1475, 820, 795, 760, 715 cm^{-1}; ^1H NMR δ 2.33 (s, 3 H), 2.43 (s, 3 H), 6.52 (d, 1 H, J = 3.9 Hz), 6.93–7.43 (m, 8 H); ^{13}C NMR 20.9 (q), 21.3 (q), 102.7 (d), 110.1 (d), 120.6 (d), 123.7 (d), 123.9 (d), 127.8 (d), 128.2 (s), 129.2 (s), 129.9 (s), 134.2 (s), 135.8 (s), 137.8 ppm (s); MS, m/z 221 (M^+). Anal. Calcd for $C_{16}H_{15}N$: C, 86.83; H, 6.83; N, 6.32. Found: C, 86.96; H, 6.63; N, 6.06.

1-Butylindole (2f): bp 125 °C (2 mmHg); IR (film) 1610, 1505, 1460, 760, 740, 715 cm^{-1}; ^1H NMR δ 0.91 (t, 3 H), 1.13–1.54 (m, 2 H), 1.64–1.94 (m, 2 H), 4.07 (t, 2 H, J = 6.8 Hz), 6.47 (d, 1 H, J = 3.4 Hz), 6.98–7.38 (m, 4 H), 7.56–7.67 (m, 1 H); ^{13}C NMR 13.7 (q), 20.1 (t), 32.3 (t), 46.0 (t), 100.7 (d), 109.3 (d), 119.1 (d), 120.8 (d), 121.2 (d), 127.6 (d), 128.5 (s), 135.9 ppm (s); MS, m/z 173 (M^+). Anal. Calcd for $C_{12}H_{15}N$: C, 83.18; H, 8.72; N, 8.08. Found: C, 82.92; H, 8.72; N, 8.03.

1-Butyl-3-methylindole (2g): bp 130 °C (2 mmHg); IR (film) 1605, 1465, 735 cm^{-1}; ^1H NMR δ 0.90 (t, 3 H), 1.12–1.49 (m, 2 H), 1.53–1.90 (m, 2 H), 2.31 (d, 3 H, J = 1.0 Hz), 4.08 (t, 2 H), 6.81 (d, 1 H, J = 1.0 Hz), 6.98–7.34 (m, 3 H), 7.45–7.60 (m, 1 H); ^{13}C NMR 9.6 (q), 13.7 (q), 20.2 (t), 32.5 (t), 45.7 (t), 109.1 (d), 109.9 (s), 118.3 (d), 118.9 (d), 121.2 (d), 125.4 (d), 128.6 (s), 136.3 ppm (s). Anal. Calcd for $C_{13}H_{17}N$: C, 83.37; H, 9.14; N, 7.47. Found: C, 83.57; H, 9.23; N, 7.46.

1-Butyl-3-phenylindole (2h): bp 185 °C (2 mmHg); IR (film) 1600, 1540, 1460, 760, 735, 695 cm^{-1}; ^1H NMR δ 0.90 (t, 3 H), 1.14–1.52 (m, 2 H), 1.63–1.68 (m, 2 H), 4.06 (t, 2 H), 7.01–7.71 (m, 9 H), 7.83–8.02 (m, 1 H); ^{13}C NMR 13.7 (q), 20.2 (t), 32.2 (t), 46.1 (t), 109.7 (d), 116.5 (s), 119.7 (d), 119.9 (d), 121.7 (d), 125.5 (d), 126.2 (s), 127.2 (d), 128.6 (d), 135.7 (s), 136.7 ppm (s). Anal. Calcd for $C_{18}H_{19}N$: C, 86.70; H, 7.68; N, 5.61. Found: 86.47; H, 7.69; N, 5.67.

Bis(1-butyl-3-phenylindol-2-yl) disulfide (3h): bp 200 °C (2 mmHg); IR (film) 1595, 1480, 1445, 760, 695 cm^{-1}; ^1H NMR δ 0.87 (t, 6 H), 1.12–1.81 (m, 8 H), 4.02 (t, 4 H), 6.77–7.61 (m, 18 H); ^{13}C NMR 13.7 (q), 20.3 (t), 31.9 (t), 43.4 (t), 110.1 (d), 120.0 (d), 120.5 (d), 124.1 (d), 124.4 (s), 126.0 (d), 126.3 (d), 127.4 (d), 127.6 (s), 129.8 (d), 133.4 (s), 133.7 ppm (s). Anal. Calcd for $C_{36}H_{36}N_2S_2$: C, 77.10; H, 6.47; N, 4.99. Found: C, 76.97; H, 6.48; N, 4.90.

1-Benzylindole (2i): bp 155 °C (2 mmHg); IR (film) 1605, 1505, 1455, 755, 735, 720, 695 cm^{-1}; ^1H NMR δ 5.23 (s, 2 H), 6.50–6.60 (m, 1 H), 6.77–7.34 (m, 9 H), 7.53–7.69 (m, 1 H); ^{13}C NMR 50.0 (t), 101.6 (d), 109.6 (d), 119.4 (d), 120.9 (d), 121.6 (d), 126.0 (d), 127.5 (d), 128.1 (d), 128.6 (d), 130.1 (s), 136.2 (s), 137.4 ppm (s). Anal. Calcd for $C_{15}H_{13}N$: C, 86.92; H, 6.32; N, 6.75. Found: C, 87.06; H, 6.06; N, 6.40.

1-Methyl-3-phenylindole (2k): bp 170 °C (2 mmHg); IR (film) 1600, 1545, 1480, 1465, 765, 695 cm^{-1}; ^1H NMR δ 3.59 (s, 3 H), 7.00–7.67 (m, 8 H), 7.85–8.02 (m, 1 H); ^{13}C NMR 32.6 (q), 109.5 (d), 116.5 (s), 119.8 (d), 121.9 (d), 125.6 (d), 126.0 (s), 126.5 (d), 127.2 (d), 128.7 (d), 135.6 (s), 137.4 ppm (s). Anal. Calcd for $C_{15}H_{13}N$: C, 86.92; H, 6.32; N, 6.75. Found: C, 86.74; H, 6.33; N, 6.62.

Bis(1-methyl-3-phenylindol-2-yl) disulfide (3k): mp 140–141 °C; IR (KBr) 1600, 1480, 1440, 745, 690 cm^{-1}; ^1H NMR δ 3.52 (s, 6 H), 6.65–7.50 (m, 18 H); ^{13}C NMR 29.7 (q), 110.0 (d), 120.1 (d), 120.2 (d), 124.1 (s), 124.1 (d), 126.0 (d), 127.4 (d), 127.8 (s), 129.6 (d), 133.3 (s), 138.4 ppm (s). Anal. Calcd for $C_{30}H_{24}N_2S_2$: C, 75.59; H, 5.07; N, 5.87. Found: C, 75.29; H, 5.08; N, 5.90.

Registry No. **1a**, 73425-20-4; **1b**, 112817-80-8; **1c**, 112817-81-9; **1d**, 112817-82-0; **1e**, 112817-83-1; **1f**, 112817-84-2; **1g**, 112817-85-3; **1h**, 112817-86-4; **1i**, 104501-75-9; **1j**, 13637-38-2; **1k**, 33693-09-3; **1l**, 496-30-0; **1m**, 112817-87-5; **2a**, 16096-33-6; **2b**, 112817-88-6; **2c**, 112817-89-7; **2d**, 20538-11-8; **2e**, 112817-90-0; **2f**, 22014-99-9; **2g**, 1914-00-7; **2h**, 112817-91-1; **2i**, 3377-71-7; **2k**, 30020-98-5; **2l**, 120-72-9; **3a**, 112817-92-2; **3b**, 112817-93-3; **3c**, 112817-94-4; **3d**, 112817-95-5; **3h**, 112817-96-6; 3k, 51206-75-8; **6**, 112817-97-7; 1-phenylindolin-2-one, 3335-98-6; 3-methyl-1-phenylindolin-2-one, 23210-22-2; 3-ethyl-1-phenylindolin-2-one, 112817-98-8; 1,3-diphenylindolin-2-one, 23210-25-5; 5-methyl-1-*p*-tolylindolin-2-one, 112817-99-9; 1-butylindolin-2-one, 28148-20-1; 1-butyl-3-methylindolin-2-one, 112818-00-5; 1-butyl-3-phenylindolin-2-one, 112818-01-6; 1-benzylindolin-2-one, 7135-32-2; 1-methyl-3-phenylindolin-2-one, 3335-97-5; 1*H*-indolin-2-one, 59-48-3; 1-methylindolin-2-one, 61-70-1.

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Carbonyl to Methylene Conversion: Selenium-Assisted Reduction of Aromatic Ketones with Carbon Monoxide and Water

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There is increasing interest in the organic chemistry of selenium, and much effort is being devoted to the synthesis of new selenium compounds and to their use for a wide

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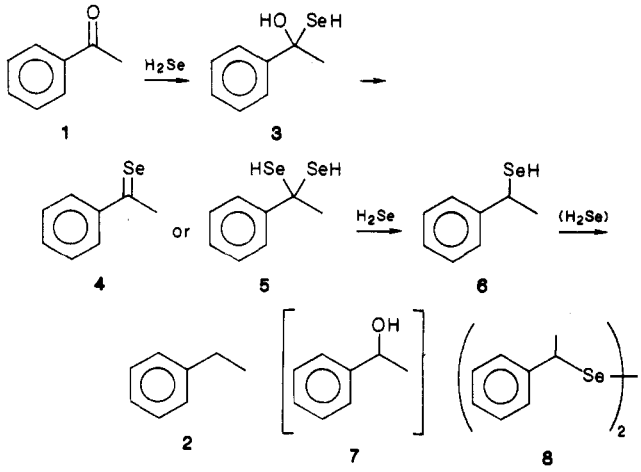
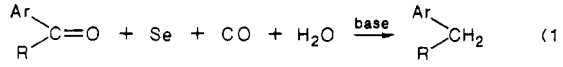
Scheme I



variety of synthetic transformations.[1] Among these, it has been known that compounds containing the SeH group such as selenols and hydrogen selenide have a potent reducing ability toward various organic compounds.[2-4] However, these selenium compounds are unstable against air, so practical use as reducing agents in organic synthesis has been limited to a few cases, which include reduction of nitroso, azo, imino, or sulfoxy groups by ArSeH,[2] reduction or reductive selenation of ketones or benzyl halides by RSeH,[3] and photoreduction of ketones or aldehydes by H_2Se.[4]

Recently we have developed a new reduction system, in which hydrogen selenide (or HSe^-), formed in situ from elemental selenium, carbon monoxide, and water, acts as the active reducing species.[5] In the course of our studies to clarify the characteristic features of this reaction system, we have found that aromatic ketones are readily reduced to the corresponding aromatic hydrocarbons by using selenium, carbon monoxide, and water (eq 1).

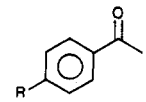
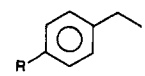
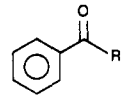
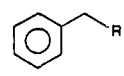
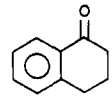
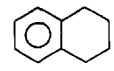
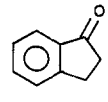
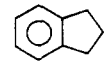
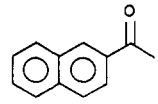
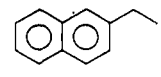
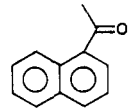
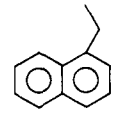
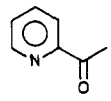
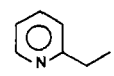
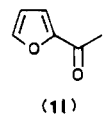
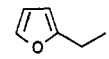
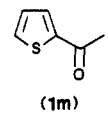
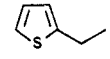


(1)

The reduction of acetophenone with carbon monoxide and water in the presence of a stoichiometric amount of selenium and a base (1,5-diazabicyclo[5.4.0]undec-5-ene, DBU) at 120 °C for 24 h afforded ethylbenzene in 95% yield (Table I, entry 1). Table I summarizes the results of the reduction of some other aromatic ketones. The yields were excellent for alkyl phenyl ketones (entries 1–10). Cyclic ketones (entries 7 and 8) and a nonenolizable ketone (entry 6) also could be reduced to the corresponding hydrocarbons. During the reduction process, chloro (entry 2) and trifluoromethyl groups (entry 3) remained unchanged. Similar reduction of heteroaromatic ketones also took place to give alkyl heterocycles in moderate yields (entries 11–13).

Although the mechanism of the reduction has not been fully established, a possible reaction path is shown in Scheme I. The initial reaction may be the nucleophilic addition of hydrogen selenide to the carbonyl group of the aromatic ketone. The adduct **3** may be reduced to selenol intermediate **6** by hydrogen selenide through a short-lived selenoketone **4** or selenoketal **5**. The presence of selenol intermediate **6** is supported by the following results: when 1-phenylethaneselenol prepared[6] in situ was subjected to

Table I. A Stoichiometric Reduction of Aromatic Ketones[a]

entry	ketone	product	yield,[c] %
			
1	R = H (**1a**)		95
2	R = Cl (**1b**)		(84)
3	R = CF_3 (**1c**)		78
			
4[b]	R = C_2H_5 (**1d**)		95
5[b]	R = $CH(CH_3)_2$ (**1e**)		96
6[b]	R = $C(CH_3)_3$ (**1f**)		72
7[b]	 (**1g**)		94 (92)
8[b]	 (**1h**)		90 (78)
9	 (**1i**)		(84)
10	 (**1j**)		(73)
11	 (**1k**)		61
12	 (**1l**)		61
13	 (**1m**)		72

[a] All reactions were carried out according to the procedure in the text. [b] 150 °C, 48 h. [c] GLC yields. Isolated yields are in parentheses.

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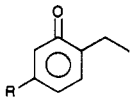
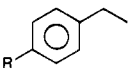
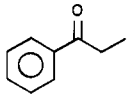
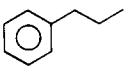
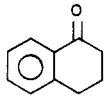
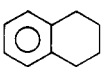
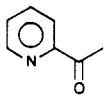
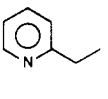
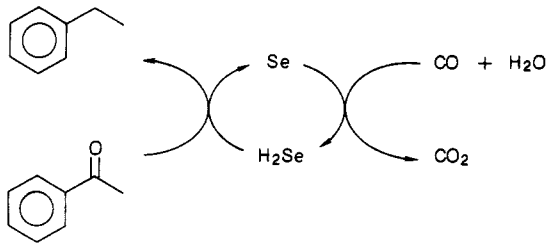
Table II. A Catalytic Reaction[a]

ketone	product	yield, %
		
R = H		100
R = CH_3		98
R = CF_3		100
		100[b]
		100[b]
		64

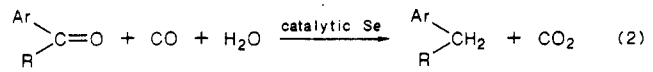
[a] Reactions were carried out under the conditions shown in the text. [b] 150 °C, 48 h.

Scheme II



the same conditions as those involved in the reduction of acetophenone with Se–CO–H_2O, ethylbenzene was formed in 60% yield.[7] On the other hand, the presence of alcohol **7** as an intermediate may be ruled out: when 1-phenylethanol was allowed to react with carbon monoxide, water, and selenium, formation of ethylbenzene was not observed and 1-phenylethanol was recovered unchanged.

After the reduction was completed, starting selenium was recovered by exposing the reaction mixture to air. This fact shows regeneration of hydrogen selenide in the reaction mixture at the last stage of the reduction. Then, catalytic use of selenium in this reaction system was examined. Thus, catalytic reduction of aromatic ketones was successfully achieved by using a catalytic amount of selenium (0.2 equiv) (eq 2).



(2)

Representative results of the selenium-catalyzed reaction are summarized in Table II. The catalytic cycle is shown in Scheme II.

Carbonyl to methylene conversion is a widely employed transformation in organic synthesis,[8] and a number of methods have been reported for this transformation, for example: (1) Wolff–Kishner reduction;[9] (2) Clemmensen reduction;[10] (3) hydrogenation by metal catalysts;[11] (4) reduction using metal hydrides;[12] (5) reduction using hydrosilanes.[13] However, we believe that the present method using in situ formed hydrogen selenide offers a convenient alternative to them.

Experimental Section

General Methods. The instruments used were as follows: ^1H NMR, Hitachi R-24B; IR, Shimadzu IR-400; MS, Hitachi RMU-6A; GLC, Shimadzu GC-3BF.

Metallic selenium (99%) from Wako Chemical Co. and carbon monoxide (99.9%) from Seitetsu Chemical Co. were used. Aromatic ketones **1a–e** and **1g–m**, 1,5-diazabicyclo[5.4.0]undec-5-ene (DBU), and tetrahydrofuran (THF) were all purchased from commercial sources and purified by distillation. Aromatic ketone **1f** was prepared according to the literature.[14] 1-Phenylethanol (**7**) was prepared by the reduction of acetophenone with $LiAlH_4$. Bis(1-phenylethyl) diselenide (**8**) was prepared by the reaction of (1-bromoethyl)benzene with NaSeH.[15]

General Procedure for the Reduction of Aromatic Ketones with Carbon Monoxide and Water Using a Stoichiometric Amount of Selenium. In a 50-mL stainless steel autoclave were placed aromatic ketone (10 mmol), selenium (0.79 g, 10 mmol), water (1.8 mL, 100 mmol), DBU (1.5 mL, 10 mmol), and THF (5 mL), and the mixture was heated at 120 °C for 24 h under CO (30 atm). After the reaction was complete, carbon monoxide was purged in a well-ventilated hood, and air was blown into the solution for 10 min in order to oxidize the remaining hydrogen selenide to elemental selenium. Selenium deposited was filtered off, the filtrate was acidified to slightly acidic end with hydrochloric acid (2 N), and then the product was extracted with diethyl ether (100 mL × 3). The combined extracts were analyzed by GLC and dried over $MgSO_4$. Evaporation of the solvent and purification by column chromatography on silica gel gave corresponding alkanes. Results are given in Table I. The structures of the products were assigned by a comparison of their GLC retention times, ^1H NMR, IR, and mass spectra with those of authentic materials.

Catalytic Reduction of Aromatic Ketones. A stirred mixture of aromatic ketone (10 mmol), Se (2 mmol), water (100 mmol), DBU (20 mmol), and THF (5 mL) was heated under CO (30 atm) at 120 °C for 24 h. The subsequent workup was carried out as described above, and the resulting extract was analyzed by GLC with n-C_nH_{2n+2} as the internal standard. Results are given in Table II.

Reaction of 1-Phenylethaneselenol (6), Generated in Situ, with Selenium, Carbon Monoxide, and Water.[7] A mixture of bis(1-phenylethyl) diselenide (**8**) (1.85 g, 5 mmol), Se (10 mmol), water (100 mmol), DBU (10 mmol), and THF (5 mL) was stirred under CO (30 atm) at 120 °C for 24 h. The same workup was performed as described in the reduction of aromatic ketones using a stoichiometric amount of selenium, and the following analysis by GLC indicated the formation of ethylbenzene (60% yield).

Reaction of 1-Phenylethanol (7) with Selenium, Carbon Monoxide, and Water. A stirred mixture of 1-phenylethanol (1.22 g, 10 mmol), selenium (10 mmol), water (100 mmol), DBU (10 mmol), and THF (5 mL) was heated under CO (30 atm) at

(7) A relevant interesting observation has been described in light of our recent report: Similar reaction of aromatic ketones and aldehyde with sulfur, carbon monoxide, and water gave the corresponding thiols as the reductive thiolation products. See: Nishiyama, Y.; Ohtori, Y.; Hamanaka, S.; Ogawa, A.; Murai, S.; Sonada, N. *Nippon Kagaku Kaishi* **1987**, 1502.

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120 °C for 24 h. A similar workup as described in the general procedure for the reduction of aromatic ketones and purification by column chromatography on silica gel resulted in the recovery of 1-phenylethanol (94%).

Registry No. **1a**, 98-86-2; **1b**, 99-91-2; **1c**, 709-63-7; **1d**, 93-55-0; **1e**, 611-70-1; **1f**, 938-16-9; **1g**, 529-34-0; **1h**, 83-33-0; **1i**, 93-08-3; **1j**, 941-98-0; **1k**, 1122-62-9; **1l**, 1192-62-7; **1m**, 88-15-3; **2**, 100-41-4; **7**, 98-85-1; **8**, 109445-64-9; DBU, 6674-22-2; *p*-ClC_6H_4Et, 622-98-0; *p*-$CF_3C_6H_4Et$, 27190-69-8; $Ph(CH_2)_2CH_3$, 103-65-1; $PhCH_2CH(CH_3)_2$, 538-93-2; $PhCH_2C(CH_3)_3$, 1007-26-7; Se, 7782-49-2; H_2O, 7732-18-5; CO, 630-08-0; *p*-MeC_6H_4Ac, 122-00-9; NaSeH, 12195-50-5; *p*-MeC_6H_4Et, 622-96-8; 1,2,3,4-tetrahydronaphthalene, 119-64-2; 2,3-dihydro-1*H*-indene, 496-11-7; 2-ethylnaphthalene, 939-27-5; 1-ethylnaphthalene, 1127-76-0; 2-ethylpyridine, 100-71-0; 2-ethylfuran, 3208-16-0; 2-ethylthiophene, 872-55-9; (1-bromoethyl)benzene, 585-71-7.

Synthesis of Bay-Region Diol Epoxides and Other Derivatives of Benzo[*h*]quinoline

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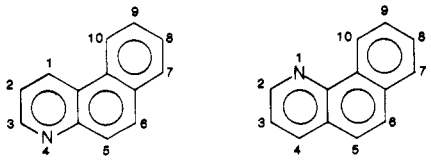
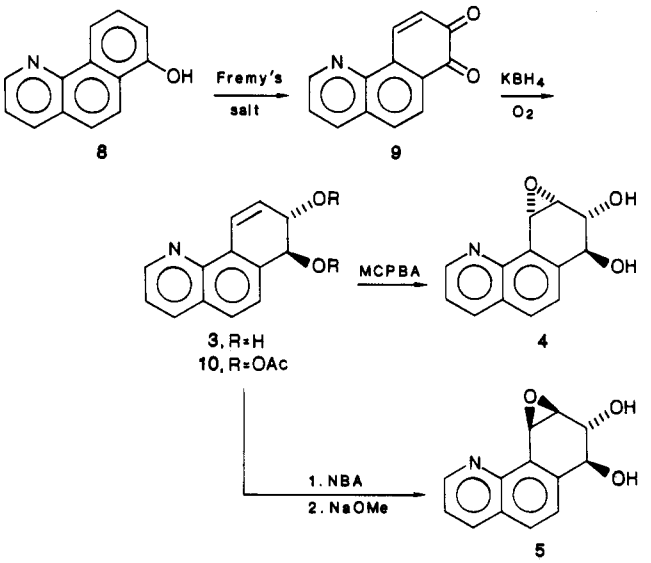
The azaphenanthrenes, benzo[*f*]quinoline (BfQ, **1**) and benzo[*h*]quinoline (BhQ, **2**), are environmental contaminants that have been detected in automobile exhaust, urban air particulates, and cigarette smoke.[2-4] BfQ and BhQ have been shown to be metabolically activated to products mutagenic to *Salmonella typhimurium*.[5-8] In contrast to BfQ and BhQ, their carbon analogue phenanthrene is nonmutagenic.[9] In a previous paper,[10] we have described the synthesis of dihydrodiol and diol epoxide derivatives of benzo[*f*]quinoline. Since we are interested in understanding (i) the mechanism by which the presence and position of aza substitution influence the biological activity of azaphenanthrenes and (ii) the metabolism of these chemicals, we require dihydrodiol and diol epoxide derivatives of benzo[*h*]quinoline. The present paper describes the synthesis of dihydro diol **3**, diol epoxides **4** and **5**, and tetrahydro epoxides **6** and **7**.



Scheme I



Treatment of 7-hydroxy-BhQ (**8**)[11] with Fremy's salt readily afforded BhQ-7,8-dione (**9**) (see Scheme I) in 76% yield. The ^1H NMR and mass spectra of the dione were consistent with its structure. The potassium borohydride reduction of dione **8** in ethanol bubbled with air produced the crude dihydro diol **3** which was purified as dihydro diacetate **10** in an overall yield of 20%. The significant shift of H_{10} in the ^1H NMR spectra (δ 8.01) of **10** compared to that of H_4 in the ^1H NMR spectra (δ 6.29)[12] of *trans*-1,2-diacetoxy-1,2-dihydrophenanthrene is due to the presence of the nitrogen in the bay region of **10**. A similar observation has been made with the analogous dihydro diol diacetates of benz[*c*]acridine,[13] dibenz[*c*,*h*]acridine,[14] and dibenz[*a*,*h*]acridine.[15] The hydrolysis of diester **10** with methanol–ammonia afforded 78% yield of the required dihydro diol **3**. The large coupling constant ($J_{7,8}$ = 10.8) between carbinol protons of **3** compared to that ($J_{7,8}$ = 5.7) of the corresponding protons of diacetate **10** suggested that the trans hydroxyl groups of **3** occupy quasi-diequatorial conformation.

The epoxidation of the dihydro diol **3** with an excess of *m*-chloroperoxybenzoic acid yielded anti diol epoxide **4**. A large coupling constant ($J_{7,8}$ = 9.4) between carbinol protons and small coupling constant ($J_{9,10}$ = 4.4) between H_9 and H_{10} confirmed the structure of **4** and indicated that vicinal hydroxyl groups are in quasi-diequatorial conformations. There was no evidence for the presence of an *N*-oxide based on UV, mass, and ^1H NMR spectra. The mass spectrum showed a molecular ion only at *m*/*e* 229 and the expected upfield shift of the H_2 and H_4 for an *N*-oxide was not observed in the ^1H NMR spectrum of **4**.[10] This observation was in contrast to the previous observation[10] that indicated that the similar oxidation of *trans*-7,8-dihydroxy-7,8-dihydro-BfQ with *m*-chloroperoxybenzoic acid produced only N-oxidation products. The

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