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Supplementary Material Available: A description of X-ray crystal structure determination and listings of positional and thermal parameters and bond distances and angles for 6 (6 pages). Ordering information is given on any current masthead page.

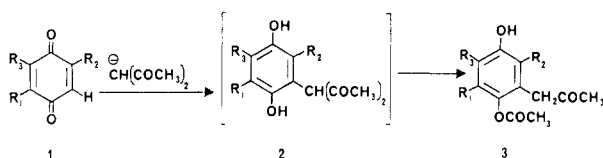
Base-Induced Reaction of Acetylacetone with Substituted Benzoquinones¹

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Among the prodigious efforts of Lee Irwin Smith and his co-workers in unraveling the rich chemistry enjoyed by quinone/enolate anion interactions³ is the report of the reaction of the sodium salt of acetylacetone (2,4-pentanedione) with 2,3,5-trimethyl-1,4-benzoquinone (**1a**).⁴ The product was identified as the (diacetylmethyl)hydroquinone adduct **2a** apparently on the basis of analysis and conversion products. We desired the quinones deriving from such adducts⁵ in connection with other work⁶ and have studied the reaction of acetylacetone with a variety of substituted benzoquinones under basic conditions. The results described herein suggest a revised structure for Smith's adduct **2a** and reveal an additional reaction pathway for the base-induced reaction of quinones and acetylacetone.⁷

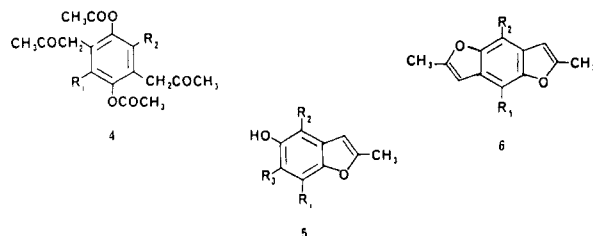


- a R₁ = R₂ = R₃ = CH₃
 b R₁ = R₂ = CH₃, R₃ = H
 c R₁ = R₂ = C₆H₄, R₃ = H
 d R₁ = R₂ = Cl, R₃ = H
 e R₁ = H, R₂ = R₃ = Cl

The reaction of trimethylbenzoquinone (**1a**) and acetylacetone in the presence of 1 equiv of sodium ethoxide

in ethanol, as described by Smith,⁴ gave varying yields of a white solid after acidification, melting as previously reported (129–130 °C). However, the spectral data obtained for this compound were consistent with the hydroquinone monoacetate **3a** resulting from **2a** via an acyl transfer. Particularly diagnostic were the two-proton singlet (benzylic hydrogens) at δ 3.52 in the ¹H NMR spectrum of **3a** and the ester and ketone carbonyl resonances in the ¹³C NMR spectrum at 169.9 and 206.5 ppm, respectively. Treatment of **3a** with acetic anhydride gave the corresponding hydroquinone diacetate, while refluxing in acidic methanol converted **3a** to the benzofuran **5a**. Both of these transformations were described by Smith⁴ for the supposed (diacetylmethyl)hydroquinone, **2a**, and are consistent with the actual structure **3a**. The formation of **5a** from **3a** results from initial hydrolysis, intramolecular hemiketal formation, and dehydration.

Similar reactions of 2,5-dimethyl-1,4-benzoquinone (**1b**) and 2,5-diphenyl-1,4-benzoquinone (**1c**) with acetylacetone enolate gave the analogously rearranged adducts **3b** and **3c**, respectively, in 60–75% yields. We found benzyltrimethylammonium hydroxide (Triton B) to be a convenient base for promoting the reaction, although KOH and NaOCH₃ produced almost identical results. In the case of these disubstituted quinones a small (<10%) amount of a minor product was obtained that is formulated respectively as **4b** and **4c** on the basis of spectral data. The formation of such diadducts apparently arise via a second addition of the enolate to the quinone formed by oxidation of the hydroquinone resulting from initial conjugate addition. The corresponding benzofurans **5** and benzodifurans **6** were obtained after refluxing in acidic methanol, thus establishing a convenient two-step synthesis of these substituted heterocyclic systems.⁸



The reaction of 2,5-dichloro-1,4-benzoquinone (**1d**) under similar conditions produced the unrearranged hydroquinone **7** which precipitated from the methanolic reaction mixture. The rearranged adducts **3d** and **4d** were detected in the ¹H NMR spectrum of the crude product but were not isolated. The high oxidation potential of the starting quinone apparently causes oxidation of the initially formed hydroquinone **2d** prior to acyl transfer, and then a second addition of enolate occurs. The limited solubility of **7** precludes subsequent rearrangement. But when **7** was dissolved in THF and treated with Triton B, **4d** was isolated in nearly quantitative yield. Concomitant reduction of starting quinone during the reaction is evident from the isolation of the diacetate of 2,5-dichloro-1,4-benzohydroquinone after acetylation of the concentrated filtrate from the removal of **7**. The diacetate of **2d** was also isolated from the acetylation mixture by fractional crystallization.

The slow addition of the quinone to acetylacetone (2 equiv) in the presence of Triton B gave **7** in 68% yield (based on **1b**). A simple recycling procedure utilizing Ag₂O oxidation of the crude reaction mixture and addition of excess acetylacetone resulted in an aggregate 78% con-

(1) Portions of this work were presented at the 1977 Pacific Conference on Chemistry and Spectroscopy, Anaheim, CA, Oct 1977, abstr no. 44.

(2) Address correspondence to the University of Connecticut.

(3) For a fine review see: Finley, K. T. In "The Chemistry of the Quinonoid Compounds"; Patei, S., Ed.; Wiley: London, 1974; pp 877-1144, Chapter 17.

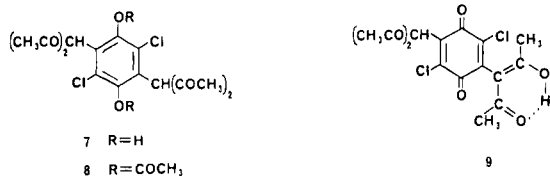
(4) Smith, L. I.; Kaiser, E. W. *J. Am. Chem. Soc.* 1940, 62, 133-8.

(5) For previous reports of such quinones see: (a) Bernatek, E.; Ramstad, S. *Acta Chem. Scand.* 1953, 7, 1351-6. (b) Bernatek, E.; Johnsgard, M.; Stensrud, T. *Ibid.* 1967, 21, 575-5. (c) Kallmayer, H. J. *Arch. Pharm. (Weinheim, Ger.)* 1973, 306, 257-67. (d) Wikholm, R. J. Ph.D. Dissertation, University of California, Irvine, 1971; pp 105-6.

(6) Wikholm, R. J.; Moore, H. W. *J. Am. Chem. Soc.* 1972, 94, 6152-8.

(7) After this work was completed and disclosed,¹ the correct structure for Smith's adduct was reported in the Russian literature: Makovetskii, V. P.; Dzvinchuk, I. B.; Svishchuck, A. A. *Ukr. Khim. Zh. (Russ. Ed.)* 1978, 44, 996-8; *Chem. Abstr.* 1978, 90, 22500.

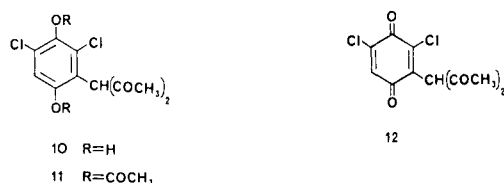
(8) These benzofurans and benzodifurans will be the subject of a future communication: Wikholm, R. J., to be submitted for publication.



version of **1b** to **7** after three cycles.

The recently reported⁹ nickel-catalyzed conjugate addition reaction proved a convenient alternate method for the preparation of **7** and **10**. When the high potential quinones **2,5**- and **2,6**-dichloro-**1,4**-benzoquinone (**1d** and **1e**) were reacted with acetylacetone in the presence of a catalytic amount of Ni(acac)₂, the adduct hydroquinones **7** and **10** were obtained in yields of 72% and 62%, respectively. Again, total conversions of >70% were conveniently obtained after three passes through the recycling procedure. No evidence of **4d** was obtained from NMR analysis of the concentrated filtrate after isolation of **7**. The quinones **1b** and **1c** were isolated unchanged upon prolonged treatment under similar conditions.

The structures of **7** and **10** are based on spectral considerations and chemical transformations. The diacetate derivatives **8** and **11** and the derived quinones **9** and **12** exhibit IR and NMR spectra completely consistent with the assigned structures.



The spectral data for each of the diacetylmethyl-substituted compounds obtained in this study suggest no evidence of the keto tautomer, and the 1,3-dicarbonyl system appears to be 100% in the enol form. The IR spectra show broad absorption bands for the hydroxyl and hydrogen-bonded carbonyl groups at 3300 and 1600 cm⁻¹, respectively.¹⁰ The ¹H NMR spectra contain a single methyl absorption as a six-proton signal at ca. δ 1.9, in addition to the enol hydrogen signal at ca. δ 16.9. The ¹³C NMR spectra contain only the three signals of the symmetrical enol form: the hydrogen-bonded carbonyl carbon appears ca. δ 191, the sp²-hybridized 2-carbon is observed at ca. δ 105, and the methyl carbon is observed at ca. δ 23.¹¹

In summary, the initial Michael adduct of quinones and acetylacetone anion has been found to typically undergo further reaction of the retro Claisen variety. The acyl-transfer reaction of the diacetylmethyl-substituted hydroquinones provides a route to selectively protected acetyl hydroquinones that may prove useful in quinone synthesis. The isolated diacetylmethyl-substituted compounds are being studied for the interesting chelating and hydrogen-bonding possibilities imparted by the β-diketone moiety.

Experimental Section

Melting points were determined on a Thomas-Hoover apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer 137 or 283 spectrophotometer. ¹H NMR spectra were recorded at 60 MHz on either a Perkin-Elmer R12B or a Varian EM360 spectrometer using tetramethylsilane as an internal standard. ¹³C

(9) Nelson, J. H.; Howells, P. N.; DeLullo, G. C.; Landen, G. L.; Henry, R. A. *J. Org. Chem.* 1980, 45, 1246-1249.

(10) Cf. Greens, E.; Grinvalde, A.; Stradins, J. *Spectrochim. Acta, Part A* 1975, 31A, 555-564 and references therein.

(11) Cf. Olah, G. A.; Grant, J. L.; Westerman, P. W. *J. Org. Chem.* 1975, 40, 2102-2108 and references therein.

NMR spectra were recorded on a Bruker WH-90 spectrometer at 22.6 MHz. Chemical shifts are given as δ values in parts per million relative to Me₄Si (δ 0.0). Microanalyses were performed by Spang Microanalytical Laboratory, Eagle Harbor, MI, or by Baron Consulting Co., Orange, CT. Mass spectral data were obtained on an AEI MS-10 mass spectrometer.

1-(2-Acetoxy-5-hydroxy-3,4,6-trimethylphenyl)-2-propanone (3a). The procedure described by Smith and Kaiser⁴ gave varying yields of a tan solid which was recrystallized from EtOH-water to give white crystals: mp 129-130 °C [lit.⁴ mp 129-130 °C]; IR (Nujol) 3300 br, 1745, 1690 cm⁻¹; ¹H NMR (CDCl₃) δ 3.52 (s, 2 H), 2.28 (s, 3 H), 2.06 (s, 9 H), 2.00 (s, 3 H); ¹³C NMR (CDCl₃) δ 206.5, 169.9, 150.3, 141.6, 126.9, 123.6, 122.8, 121.4, 43.3, 28.8, 20.4, 13.2, 12.4, 12.3.

The acetate derivative of **3a** (Ac₂O-py) had a melting point of 130-131 °C [lit.⁴ 135.5-136.0 °C]; IR (Nujol) 1750, 1700 cm⁻¹; ¹H NMR (CDCl₃) δ 3.55 (s, 2 H), 2.33 and 2.30 (6 H), 2.05 (s, 12 H).

1-(2-Acetoxy-5-hydroxy-3,6-dimethylphenyl)-2-propanone (3b). 2,5-Dimethyl-1,4-benzoquinone (2.7 g, 20 mmol) was added slowly and in small portions to a stirred solution of 4.0 g (40 mmol) of acetylacetone and of 1 mL of Triton B (2.4 mmol) in 10 mL of MeOH. The reaction mixture became dark immediately. After 1 h a white solid (0.7 g) was filtered off and was identified as the rearranged diadduct **4b** (vide infra). The filtrate was concentrated, and a white solid was filtered off. Recrystallization from MeCN gave colorless prisms (2.0 g, 43% yield): mp 184-186 °C; IR (Nujol) 3450 (OH), 1735 (ester C=O), 1715 (ketone C=O), 1234, 1200 cm⁻¹; ¹H NMR (CDCl₃) δ 3.51 (s, 2 H), 2.26 (s, 3 H), 2.10, 2.05, 2.04 (9 H); ¹³C NMR (CDCl₃) δ 206.1, 169.6, 151.9, 142.0, 128.5, 127.2, 122.0, 116.4, 43.3, 28.9, 20.4, 16.3, 12.1. Anal. Calcd for C₁₃H₁₆O₄: C, 66.08; H, 6.83. Found: C, 66.17; H, 6.87.

1,1'-(2,5-Diacetoxy-3,6-dimethyl-1,4-phenylene)bis(2-propanone) (4b). The rearranged diadduct was isolated from the reaction described above. Recrystallization from MeOH-CHCl₃ gave white needles (0.5 g, 8% yield): mp 230.5-231.5 °C; IR (Nujol) 1750, 1720 cm⁻¹; ¹H NMR (CDCl₃) 3.57 (s, 2 H), 2.28 (s, 3 H), 2.05 (s, 3 H), 2.04 (s, 3 H); ¹³C NMR (CDCl₃) δ 205.0, 168.7, 146.5, 128.7, 126.9, 43.5, 28.9, 20.4, 13.5. Anal. Calcd for C₁₈H₂₂O₆: C, 64.65; H, 6.63. Found: C, 64.95; H, 6.81.

1-(2-Acetoxy-5-hydroxy-3,6-diphenylphenyl)-2-propanone (3c). A total of 2.0 g (7.7 mmol) of 2,5-diphenyl-1,4-benzoquinone was added in small portions to a stirred solution of 0.8 g of 2,4-pentanedione (8.0 mmol) and 1 mL of Triton B in 25 mL of dioxane. After 12 h the reaction mixture was poured into ca. 250 mL of water and acidified with a few drops of concentrated H₂SO₄. Extraction with CH₂Cl₂ gave a brown oil which yielded the rearranged diadduct **4c** after trituration with a few milliliters of EtOH and cooling. The filtrate was concentrated and taken up in a few milliliters of MeOH. Cooling and stirring induced crystallization of **3c** (1.7 g, 62% yield after recrystallization from EtOH): mp 116-117 °C (EtOH) (most samples melted ca. 80 °C and were contaminated with the diadduct **4c**); IR (Nujol) 3500, 3160, 1755, 1715, 1685, 1205, 1190, 1170 cm⁻¹; ¹H NMR (CDCl₃) δ 7.3-7.6 (m, 10 H), 6.96 (s, 1 H), 3.39 (s, 2 H), 1.97 (s, 3 H), 1.94 (s, 3 H) (a broad peak between 5-6 ppm disappeared on shaking with D₂O). Anal. Calcd for C₂₅H₂₀O₄: 360.1362. Found: 360.1355 (by MS). This material was never completely separated from **4c**.

The acetate derivative was prepared (Ac₂O-py): mp 196-197 °C; IR (Nujol) 1775, 1750, 1710, 1200, 1170 cm⁻¹; ¹H NMR (CDCl₃) 7.1-7.6 (m, 10 H), 7.12 (s, 1 H), 3.44 (s, 2 H), 1.96 (s, 6 H), 1.87 (s, 3 H). Anal. Calcd for C₂₅H₂₂O₅: 402.1467. Found: 402.1469.

1,1'-(2,5-Diacetoxy-3,6-diphenyl-1,4-phenylene)bis(2-propanone) (4c). The rearranged diadduct isolated from the procedure described above was recrystallized from MeOH (0.2 g, 6% yield): mp 226-228 °C; IR (Nujol) 1760, 1720, 1195, 1175, 1150 cm⁻¹; ¹H NMR (CDCl₃) δ 7.2-7.5 (m, 5 H), 3.40 (s, 2 H), 1.95 (s, 3 H), 1.80 (s, 3 H). Anal. Calcd for C₂₈H₂₆O₆: 458.1729. Found: 458.1770 (by MS). Calcd: C, 73.25; H, 5.72. Found: C, 73.54; H, 5.65.

2,5-Dichloro-3,6-bis(diacetylmethyl)-1,4-hydroquinone (7). The 2,5-dichloro-1,4-benzoquinone (3.5 g, 20 mmol) was added in small portions to a rapidly stirred solution of acetylacetone (4.4 g, 44 mmol) and Triton B (1 mL) in 25 mL of MeOH. The reaction mixture turned dark brown upon addition of each portion of the quinone but became clear and yellow after a few seconds

and before the next portion was added. After ca. half of the quinone had been added, a white precipitate appeared. The reaction mixture was stirred for an hour after the addition of quinone was completed, and the white precipitate was filtered off. Recrystallization from MeCN gave white prisms (2.5 g, 68% yield): mp 234–235 °C; IR (Nujol) 3300 (br), 1600 (br), 1170, 910, 865 cm⁻¹; ¹³C NMR (Me₂SO-*d*₆) δ 190.9, 145.3, 124.4, 122.0, 107.9, 22.8. Anal. Calcd for C₁₆H₁₆O₆Cl₂: 374.0322. Found: 374.0308 (by MS). Calcd: C, 51.22; H, 4.30. Found: C, 50.81; H, 4.31.

A diacetate derivative (8) was prepared (Ac₂O-py) and recrystallized from EtOH: mp 222–228 °C; IR (Nujol) 1770, 1590 (br), 1175, 1005, 920 cm⁻¹; ¹H NMR (CDCl₃) δ 16.8 (s, 1 H), 2.26 (s, 3 H), 1.90 (s, 6 H); ¹³C NMR (CDCl₃) δ 191.4, 167.4, 145.5, 132.1, 129.2, 106.5, 23.4, 20.1. Anal. Calcd for C₂₀H₂₀O₈Cl₂: C, 52.30; H, 4.39. Found: C, 52.14; H, 5.01. Calcd: 458.0532. Found: 458.0520 (by MS).

1,4-Diacetoxy-2,5-dichloro-3-(diacetylmethyl)benzene. The filtrate from the isolation of 7 was evaporated and treated with acetic anhydride and pyridine catalyst. Pouring into cold water and stirring gave a white solid which was recrystallized repeatedly from EtOH giving 1,4-diacetoxy-2,5-dichlorobenzene mp 139–141 °C (lit.¹² 141 °C), and the diacetate derivative of **2d**: mp 126–128 °C; IR (Nujol) 1780, 1770, 1580, 1165 cm⁻¹; ¹H NMR (CDCl₃) δ 16.8 (s, 1 H), 7.28 (s, 1 H), 2.35 (s, 3 H), 2.24 (s, 3 H), 1.87 (s, 6 H); ¹³C NMR (DCCl₃) δ 191.5, 167.7, 167.5, 145.4, 145.0, 132.4, 128.3, 126.7, 124.6, 106.5, 23.4, 20.5, 20.1. Anal. Calcd for C₁₅H₁₄O₆Cl₂: C, 49.88; H, 3.91. Found: C, 49.89; H, 4.17.

2,5-Dichloro-3,6-bis(diacetylmethyl)-1,4-benzoquinone (9). The hydroquinone 7 was smoothly oxidized by Ag₂O (CH₂Cl₂, Na₂SO₄) or by FeCl₃ (diethyl ether, MeOH, water) to the bright orange quinone: mp 205–206 °C; IR (Nujol) 3240 (br), 1730, 1680 (sh), 1580 (br), 1180, 1020 cm⁻¹; ¹H NMR (CDCl₃) δ 16.9 (s, 1 H), 1.95 (s, 6 H); ¹³C NMR (CDCl₃) 190.3, 177.0, 144.9, 141.7, 105.4, 23.8. Anal. Calcd for C₁₆H₁₄O₆Cl₂: 372.0166. Found: 372.0164 (by MS). Calcd: C, 51.49; H, 3.79. Found: C, 51.24; H, 3.65.

1,1'-(2,5-Diacetoxy-3,6-dichloro-1,4-phenylene)bis(2-propanone) (4d). When 1.7 g of 7 was suspended in 35 mL of tetrahydrofuran and treated with ca. 0.5 mL of Triton B, the reaction mixture became homogeneous immediately and turned successively orange and then brown. After 1 h of stirring at room temperature the reaction mixture was concentrated to a brown oil and triturated with MeOH. Filtration gave 0.25 g of a white solid with a melting point of 230–232 °C. The filtrate was poured into H₂O, and the tan solid thus obtained was recrystallized twice from EtOH. The white needles (1.4 g, 80% combined yield) had a melting point of 233–235 °C. IR (Nujol) 1770, 1715, 1175; ¹H NMR (CDCl₃) 3.77 (s, 2 H), 2.33 (s, 3 H), 2.13 (s, 3 H); ¹³C NMR (CDCl₃) δ 202.7, 167.4, 144.8, 128.5, 127.7, 43.9, 29.1, 20.2. Anal. Calcd for C₁₆H₁₆O₆Cl₂: C, 51.22; H, 4.30. Found: C, 50.92; H, 4.29. Calcd: 374.0322. Found: 374.0315 (by MS).

2,6-Dichloro-3-(diacetylmethyl)-1,4-hydroquinone (10). A mixture of 1.8 g (10 mmol) of 2,6-dichloro-1,4-benzoquinone, 2.0 g (20 mmol) of 2,4-pentadione, and 0.1 g of Ni(acac)₂ in 30 mL of MeOH was stirred overnight. The reaction mixture was poured into ca. 250 mL of water, and 2.3 g of a tan powder was filtered off. Recrystallization from (EtOH/H₂O) gave **2e** (2.1 g, 76% yield): mp 190–192 °C; IR (Nujol) 3420, 1580 (br), 1185 cm⁻¹; ¹H NMR (CDCl₃) δ 16.9 (s, 1 H), 6.95 (s, 1 H), 4.7–5.7 (br, 1 H), 1.89 (s, 6 H).

A diacetate derivative (11) was prepared (Ac₂O-py): mp 132–133 °C; IR (Nujol) 1770, 1590 (br), 1200, 1165 cm⁻¹; ¹H NMR (CDCl₃) δ 16.9 (s, 1 H), 7.22 (s, 1 H), 2.42 (s, 3 H), 2.20 (s, 3 H), 1.87 (s, 6 H); ¹³C NMR δ 191.6, 168.3, 166.9, 147.9, 142.7, 131.5, 129.6, 128.8, 122.9, 101.1, 23.3, 20.4, 20.1. Anal. Calcd for C₁₅H₁₄Cl₂O₆: 360.0167. Found: 360.0156 (by MS). Calcd: C, 49.88; H, 3.91. Found: C, 49.59; H, 3.84.

2,6-Dichloro-3-(diacetylmethyl)-1,4-benzoquinone (12). A suspension of 0.50 g (1.8 mmol) of **2e** in 50 mL of CH₂Cl₂ was treated with 0.9 g (3.9 mmol) of Ag₂O and 1 g of Na₂SO₄ and stirred overnight at room temperature. The reaction mixture was filtered, and the solvent was evaporated. Recrystallization of the orange residue from EtOH gave 0.42 g (84%) of the bright orange-red quinone: mp 149–150 °C; IR (Nujol) 1685, 1645, 1585

(br), 1195, 1040 cm⁻¹; ¹H NMR (CDCl₃) δ 16.9 (s, 1 H), 7.21 (s, 1 H), 1.94 (s, 6 H); ¹³C NMR (CDCl₃) δ 190.2, 182.0, 172.6, 143.9, 143.7, 141.6, 133.9, 105.1, 23.8. Anal. Calcd for C₁₁H₈Cl₂O₄: C, 48.03; H, 2.93. Found: C, 48.29; H, 3.01. calcd: 273.9800. Found: 273.9801 (by MS).

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Registry No. **1a**, 935-92-2; **1b**, 137-18-8; **1c**, 844-51-9; **1d**, 615-93-0; **1e**, 697-91-6; **2d**, 93645-28-4; **2d** diacetate, 93645-29-5; **2e**, 93645-30-8; **2e** diacetate, 93645-31-9; **3a**, 68591-15-1; **3a** acetate, 93645-32-0; **3c**, 93645-34-2; **3c** acetate, 93645-35-3; **4b**, 93645-36-4; **4c**, 93645-37-5; **4d**, 93645-38-6; **7**, 93645-39-7; **8**, 93645-40-0; **9**, 93645-41-1; **12**, 93645-42-2; acetylacetone, 123-54-6.

Synthesis Utilizing Reducing Ability of Carbon Monoxide. A New Method for Synthesis of Selenocarboxamides: Reaction of Nitriles with Selenium, Carbon Monoxide, and Water

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Recently a variety of metal carbonyl complexes¹ were reported to catalyze the water–gas shift reaction under basic conditions. Furthermore, metal hydrides, which are intermediates in the water–gas shift reaction, have found use in several organic reactions such as reduction² or reductive carbonylation³ of nitrobenzenes and carbonylation of olefins.⁴

During our studies on the selenium-catalyzed carbonylation of various organic compounds with carbon mon-

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