culated electrostatic potential of a gas-phase molecule can be quantitatively related to its ability in solution to *donate* a proton in a solvent-to-solute hydrogen bond, and thus provide a predictive capability for determining unknown $\alpha$ values. The fact that the two groups of molecules must be treated separately is indicative of roles played by other factors.

**Acknowledgment.** We thank Dr. George R. Famini for very useful discussions. We greatly appreciate the support of this work by the Office of Naval Research through contract No. N00014-85-K-0217.

**Registry No.** $F_3CCH(OH)CF_3$, 920-66-1; $F_3CCH_2OH$, 75-89-8; $H_2O$, 7732-18-5; $CH_3COOH$, 64-19-7; $CH_3OH$, 67-56-1; $HOCH_2CH_2OH$, 107-21-1; $CH_3CH_2OH$, 64-17-5; $CH_3CH_2CH_2CH_2OH$, 71-36-3; $CH_3CH_2CH_2OH$, 71-23-8; $CH_2CH(OH)XH_3$, 67-63-0; $(CH_3)_3COH$, 75-65-0; $CH_3NO_2$, 75-52-5; $CH_3C(O)CH_3$, 67-64-1; $CH_3CN$, 75-05-8; $CH_3CH_2C(O)CH_3$, 78-93-3.

## Cyclopenta[*cd*]pyrene and Monomethyl Isomers

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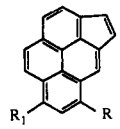
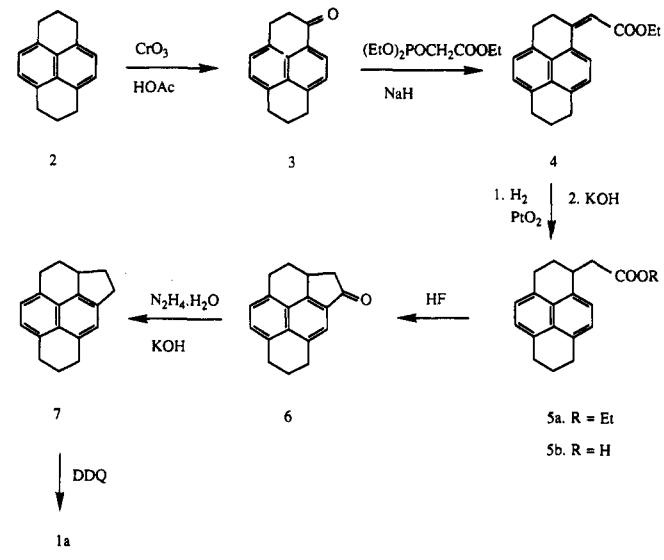
### Introduction

Polycyclic aromatic hydrocarbons (PAH) and their methyl congeners are important environmental contaminants.[1] Cyclopenta[*cd*]pyrene (CPP) is an active mutagen[2] and carcinogen,[3] identified as a major extractable component of particulates from gasoline, kerosine, and coal combustion,[4-6] and its co-occurrence with methylated isomers is suggested in GCMS analyses.[7] Although the effects of methylation on the biological activity of a number of PAH have been extensively investigated,[8] nothing is known about the methyl-CPP isomers. Structure–activity studies in progress require CPP and its methyl isomers in quantity, and we report here a convenient, large-scale synthesis of CPP (**1a**) and its 6-methyl (**1b**) and 8-methyl (**1c**) isomers.




1a. R = H, $R_1$ = H
1b. R = Me, $R_1$ = H
1c. R = H, $R_1$ = Me

**Scheme I**




### Results and Discussion

**Cyclopenta[*cd*]pyrene.** Although synthesis of cyclopenta[*cd*]pyrene has been the focus of considerable attention, no route reported to date is readily applicable to large-scale synthesis. In particular, most strategies[9] require formation of the cyclopenta ring by Lewis acid catalyzed cyclization of 4-pyrenylacetic acid. This reaction is characterized by yields that are inconsistent and tend to decrease with increasing reaction scale. In seeking an alternative route, we wished to avoid this cyclization, since facile decarbonylation of 4-pyrenylacetic acid to a benzylic carbonium ion under acid conditions may account for the difficulty in optimizing this step. Key to the strategy (Scheme I) was cyclopenta ring formation via acid-catalyzed cyclization of (1,2,3,6,7,8-hexahydropyrenyl)acetic acid (**5b**), readily accessible from the commercially available starting compound 1,2,3,6,7,8-hexahydropyrene (**2**). Oxidation of **2** with $CrO_3$[10] or sodium dichromate[11] in benzene/acetic acid gave the 1-oxo intermediate **3** in yields of 40% and 37%, respectively. Compound **3** was condensed with the Wittig reagent[12] triethyl phosphonoacetate to give the olefinic ester **4** in 60% yield, which was hydrogenated over $PtO_2$ to yield quantitatively the corresponding hexahydropyrenyl acetate **5a**, from which the desired acid **5b** was obtained in 93% yield by basic hydrolysis.

The single-step oxidation of **2** with $Cr^{VI}$ represents a considerable improvement over the reported[13] synthesis of **3** via a multistep route starting with naphthalene. An important advantage of oxidation by $CrO_3$ in Scheme I is that unreacted starting material can be conveniently re-

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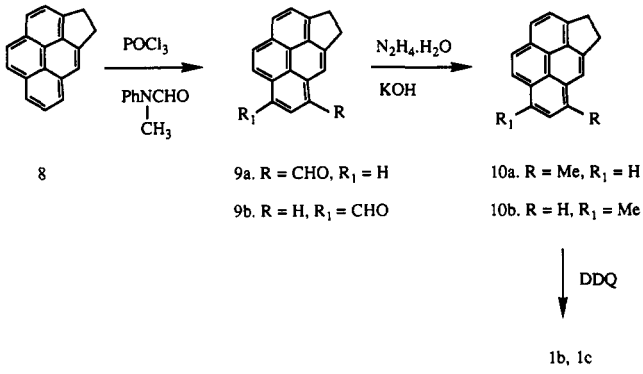
**Scheme II**




covered in the workup, making an effective yield of 68%, based on reacted **2**. The structure of **3** was confirmed by a carbonyl band in the IR spectrum at 1684 $cm^{-1}$ and its $^1H$ NMR spectrum, the salient feature of which is an aromatic doublet at 8.10 ppm for H8, adjacent to the carbonyl group. The exocyclic methylene structure was assigned to the product of the Wittig reaction (4) on the basis of a vinylic singlet in the $^1H$ NMR spectrum.

Acid **5b** cyclized quantitatively in HF to cyclopenta-fused ketone **6**, thus accomplishing formation of the CPP carbon skeleton with considerably greater efficiency than by cyclization of 4-pyrenylacetic acid with the pyrenyl moiety fully aromatized. The structure of ketone **6** is supported by a carbonyl band in the IR spectrum at 1700 $cm^{-1}$ and an $^1H$ NMR spectrum having three aromatic resonances, indicating the expected substitution at one of the aromatic positions. Wolff–Kishner reduction of the carbonyl followed by dehydrogenation with 4 molar equiv of DDQ gave CPP in 63% yield from **6**. The overall yield of CPP, based on reacted **2**, is 26%. While the overall yield of CPP is comparable to yields reported for several published procedures, this scheme is particularly suited to synthesis on a large scale. In addition, the oxidation of hexahydropyrene provides ketone **3** as a synthon potentially useful in routes to substituted pyrenes or in expansion of the pyrene system to larger PAH frames.

**6-Methyl- and 8-Methylcyclopenta[*cd*]pyrene.** Although cyclopenta[*cd*]pyrenes with methyl substitution on the etheno bridge have been reported,[14] no methyl homologues substituted on the pyrene nucleus are known. Scheme II shows the route to the 6-methyl and 8-methyl isomers **1b** and **1c**, respectively. CPP was hydrogenated quantitatively to 3,4-dihydrocyclopenta[*cd*]pyrene (**8**) with $PtO_2$ catalyst. Carbon substitution on the pyrene periphery of **8** was accomplished by the Vilsmeier reaction,[15] using phosphorus oxychloride and *N*-methylformanilide in *o*-dichlorobenzene. The nucleophilic C6 and C8 positions were formylated to give an 83% combined yield of aldehydes **9a** and **9b** in a 1:1 mixture, which was separated by fractional crystallization. No formylation at C1 was observed. Aldehydes **9a** and **9b** were distinguished by their $^1H$ NMR spectra, the 6-formyl structure **9a** being assigned on the basis of the strongly deshielded H5 singlet at 9.19 ppm. For **9b**, an aromatic doublet appears at 9.38 ppm, consistent with deshielding of K region H9 by formyl substitution at C8, while the H5 singlet resonance occurs at a relatively upfield shift of 7.89 ppm. The separated aldehydes **9a** and **9b** each underwent Wolff–Kishner reduction to yield quantitatively the corresponding 3,4-dihydromethylcyclopenta[*cd*]pyrene derivatives **10a** and **10b**, which were aromatized to 6-methylcyclopenta[*cd*]pyrene (**1b**) and 8-methylcyclopenta[*cd*]pyrene (**1c**), respectively, by DDQ in toluene. The structural assignments **1b,c** are supported by analysis of the 2D COSY $^1H$ NMR spectra, and both high resolution mass spectrometry and elemental analysis confirm the elemental composition of **1b** and **1c**. In accord with behavior reported[9a,16] for other cyclopenta-PAH, **1b** and **1c** do not fluoresce under long-wavelength UV light.

## Experimental Section

**Physical Data.** $^1H$ NMR spectra were recorded on a Varian XL-400 spectrometer at 400 MHz. Mass spectra were obtained by direct insertion probe on a VG 70S 250SEQ mass spectrometer in the EI mode at 70 eV. IR spectra were recorded on a Nicolet 20DX-FTIR spectrophotometer, and UV–vis on a Milton–Roy Spectronic 1201 spectrophotometer. Melting points were determined in a Fisher-Johns melting point apparatus and are uncorrected. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

**Materials.** 1,2,3,6,7,8-Hexahydropyrene and triethyl phosphonoacetate were purchased from Aldrich Chemical Co. and used as received.

**1-Oxo-1,2,3,6,7,8-hexahydropyrene (3). a. Oxidation by $CrO_3$.** 1,2,3,6,7,8-Hexahydropyrene (7.0 g, 34 mmol) in glacial acetic acid (100 mL) was heated to 80° C with stirring and sufficient benzene (~15 mL) added to dissolve the hydrocarbon. To this solution at 80 °C were added $CrO_3$ (4.48 g, 45 mmol) in glacial acetic acid (10 mL) and water (4 mL) dropwise. The reaction was stirred at 80 °C for 30 min after completion of the addion (~15 min) and then at room temperature for 2 h. The reaction was poured into distilled water (1 L) and extracted with chloroform (3 × 200 mL), and the organic layers were combined, washed with water, dried over $Na_2SO_4$, and evaporated. The product was purified by chromatography on silica with benzene eluant. The first band (purple fluorescence) was starting material **2** (2.58 g) and the second band (blue fluorescence) yielded ketone **3** as a pale yellow solid: 3.0 g (40%); mp 108–109 °C (lit.[13] mp 105–106 °C); $^1H$ NMR (400 MHz, chloroform-*d*) 2.08 (quintet, 2 H, $J_{ave}$ = 6.2 Hz, C7-methylene), 2.91 (t, 2 H, $J_{ave}$ = 7.1 Hz, C2-methylene), 3.12 (t, 2 H, $J_{ave}$ = 6.2 Hz, C6- or C8-methylene), 3.14 (t, 2 H, $J_{ave}$ = 6.2 Hz, C8- or C6-methylene), 3.36 (t, 2 H, $J_{ave}$ = 7.0 Hz, C3-methylene), 7.22 (d, 1 H, $J$ = 7.40 Hz, H (4 or 5), 7.34 (overlapping d, 2 H, $J$ = 7.40 Hz, H (5 or 4 and 9)), 8.10 (d, 1 H, $J$ = 7.40 Hz, H10) ppm; IR(KBr) 1684 $cm^{-1}$ ($\nu_{C=O}$).

**b. Oxidation by $Na_2CrO_7$.** To a solution of hexahydropyrene (700 mg, 3.37 mmol) in glacial acetic acid (20 mL) and benzene (10 mL) was added $Na_2Cr_2O_7$ (2.0 g, 6.73 mmol). The reaction mixture was stirred at room temperature for 22 h and poured into distilled water (200 mL). Workup as described above afforded ketone **3**: 277 mg (37%).

**1-(Carbethoxymethylene)-1,2,3,6,7,8-hexahydropyrene (4).** To a suspension of NaH (0.34 g, 14.16 mmol) in dry benzene (50 mL) at 0 °C under nitrogen was added triethyl phosphonoacetate (3.03 g, 13.52 mmol) in dry benzene (50 mL) dropwise. After the addition was complete, the reaction mixture was stirred at room temperature for 1 h. The reaction was then cooled to 0 °C, ketone **3** was added dropwise in benzene (50 mL), and the mixture was refluxed for 72 h. The reaction mixture was cooled to room temperature and treated with distilled water (100 mL), the benzene layer was separated, and the aqueous layer was extracted with ether (2 × 100 mL). The organic phases were combined, washed with brine, dried over $Na_2SO_4$, and evaporated. The residue was purified by chromatography on silica with benzene eluant. Collection of the first light fluorescent band gave olefinic ester **4**: 2.38 g (60%); mp 87 °C (methanol); UV (methanol) [$\lambda_{max}$, nm ($\epsilon \times 10^{-4}$)] 341 (1.75), 250 (2.69), 229 (2.86); $^1H$ NMR (400 MHz, chloroform-*d*) 1.36 (t, 3 H, $J$ = 7.15 Hz, ester $CH_3$), 2.08 (quintet, 2 H, C7-methylene), 3.10 (m, 4 H, C6- and C8-methylenes), 3.18 (t, 2 H, $J_{2,3}$ = 6.14 Hz, C2-methylene), 3.47 (t,

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2 H, $J_{3,2}$ = 6.14 Hz, C3-methylene), 4.25 (q, 2 H, $J$ = 7.15 Hz, ester $CH_2$), 6.43 (s, 1 H, exocyclic methylene), 7.18–7.24 (m, 3 H, H4,H5,H9), 7.64 (d, 1 H, $J$ = 7.44 Hz, H10) ppm; IR (KBr) 1709 $cm^{-1}$ ($\nu_{C=O}$), 1625 $cm^{-1}$ ($\nu_{C=C}$); mass spectrum, $m/z$ (rel intensity) 292 (100, $M^+$), 263 (95, M – Et), 245 (74, M – Et – $H_2O$). Anal. Calcd for $C_{20}H_{20}O_2$: C, 82.16; H, 6.90. Found: C, 81.65; H, 7.04.

**Ethyl (1,2,3,6,7,8-Hexahydropyrenyl)acetate (5a).** Ester 4 (3.17 g, 10.86 mmol) was stirred under $H_2$ in methanol (150 mL) with $PtO_2$ (50 mg) overnight. The reaction mixture was filtered and evaporation of solvent quantitatively yielded ester **5a**, which was used directly in the next step: $^1H$ NMR (400 MHz, chloroform-*d*) 1.28 (t, 3 H, $J$ = 7.15 Hz, ester $CH_3$), 2.06 (m, 4 H, C2- and C7-methylenes), 2.62 (dd, 1 H, $J$ = 14.60, 8.99 Hz, exocyclic $CH_2$), 2.69 (dd, 1 H, $J$ = 14.60, 6.19 Hz, exocyclic $CH_2$), 3.09 (m, 6 H, C3-, C6-, and C8-methylenes), 3.65 (m, 1 H, H1), 4.20 (q, 2 H, $J$ = 7.15 Hz, ester $CH_2$), 7.16 (d, 1 H, $J$ = 7.33 Hz, H9), 7.21 (br s, 2 H, H4,H5), 7.22 (d, 1 H, $J$ = 7.33 Hz, H10) ppm.

**(1,2,3,6,7,8-Hexahydropyrenyl)acetic Acid (5b).** Ester **5a** (3.18 g, 10.82 mmol) was heated under reflux with a mixture of aqueous KOH (20%, 50 mL) and methanol (200 mL) for 1 h on a steam bath. The methanol was evaporated and the aqueous solution diluted with distilled water (50 mL) and acidified with HCl (1:1) to precipitate acid **5b**: 2.67 g (93%); mp 154–155 °C (methanol). Anal. Calcd for $C_{18}H_{18}O_2$: C, 81.17; H, 6.81. Found: C, 81.00; H, 6.96.

**4-Oxo-1,2,2a,3,4,6,7,8-octahydrocyclopenta[*cd*]pyrene (6).** Acid **5b** (2.5 g, 9.40 mmol) was stirred with anhydrous HF (150 mL) for 16 h at room temperature. The reaction was worked up by published procedures and the crude product purified by chromatography on alumina with chloroform eluant. Ketone **6** was collected as a pale yellow band with blue fluorescence: 2.26 g (97%); mp 112–113 °C; UV (methanol) [$\lambda_{max}$ ($\epsilon \times 10^{-4}$)] 359 (1.28), 345 (1.08), 304 (1.04), 292 (1.33), 282 (1.20), 252 (4.88), 219 (1.41); $^1H$ NMR (400 MHz, chloroform-*d*) 1.67 (m, 2 H, C2- or C7-methylene), 2.09 (m, 2 H, C7- or C2-methylene), 2.45 (dd, 1 H, $J$ = 17.61, 5.25 Hz, $CH_2$), 2.50 (m, 1 H, $CH_2$), 3.09 (m, 6 H, C1-, C6-, and C8-methylenes), 3.45 (m, 1 H, H2a), 7.29 (d, 1 H, $J_{10,9}$ = 7.18 Hz, H10), 7.34 (d, 1 H, $J_{9,10}$ = 7.18 Hz, H9), 7.42 (s, 1 H, H5); IR (KBr) 1700 $cm^{-1}$ ($\nu_{C=O}$); mass spectrum, $m/z$ (rel intensity) 248 (100, $M^+$), 220 (45, M – CO), 205 (53, M – $C_2H_3O$). Anal. Calcd for $C_{18}H_{16}O$: C, 87.06; H, 6.50. Found: C, 86.91; H, 6.70.

**1,2,2a,3,4,6,7,8-Octahydrocyclopenta[*cd*]pyrene (7).** A mixture of ketone **6** (2.0 g, 8.06 mmol), diethylene glycol (150 mL), hydrazine monohydrate (4 mL), and KOH (4 g) was refluxed for 6 h, cooled to room temperature, and poured into water (500 mL). The water was extracted with chloroform (2 × 100 mL) and the organic extracts were combined, washed with water, dried over $Na_2SO_4$, and evaporated to dryness. Chromatography of the residue over silica with hexane eluant gave **7**: 1.69 g (90%); mp 91–92 °C; $^1H$ NMR (400 MHz, chloroform-*d*) 1.54–1.76 (m, 2 H, C2-methylene), 2.07 (quintet, 2 H, $J$ = 6.18 Hz, C7-methylene), 2.36–2.51 (m, 2 H, C3-methylenes), 2.88–3.16 (m, 8 H, C1-, C4-, C6-, and C8-methylenes), 3.34 (m, 1 H, H3a), 7.07 (d, 1 H, $J_{9,10}$ = 7.05 Hz, H9 or H10), 7.13 (d, 1 H, $J_{9,10}$ = 7.05 Hz, H10 or H9), 7.16 (s, 1 H, H5) ppm; mass spectrum, $m/z$ (rel intensity) 234 (100, $M^+$), 206 (58, M – $C_2H_4$), 191 (29, M – $C_3H_7$). Anal. Calcd for $C_{18}H_{18}$: C, 92.26; H, 7.74. Found: C, 92.79; H, 7.66.

**Cyclopenta[*cd*]pyrene (1a).** A solution of **7** (1.60 g, 6.84 mmol) in toluene (100 mL) and DDQ (6.52 g, 28.7 mmol) was refluxed under nitrogen for 16 h. The cooled solution was filtered, and the filtrate concentrated to 50 mL and passed through a silica column eluted with hexane. Collection of the orange band yielded **1**: 1.08 g (70%; mp 174 °C (lit.[2] mp 174–176 °C). $^1H$ NMR[17] and UV–vis[5,9b] were identical with published data.

**3,4-Dihydrocyclopenta[*cd*]pyrene (8).** Cyclopenta[*cd*]-pyrene (452 mg, 2.0 mmol) in ethyl acetate (50 mL) was stirred with $PtO_2$ (20 mg) under $H_2$ until the solution became colorless (~10 min). Workup according to published procedures yielded **8**: 455 mg (100%); mp 133 °C (lit.[5] mp 133–134 °C). $^1H$ NMR and UV–vis spectra were identical with published data.[5]

**6-Formyl-3,4-dihydrocyclopenta[*cd*]pyrene (9a) and 8-Formyl-3,4-dihydrocyclopenta[*cd*]pyrene (9b).** Phosphorus oxychloride (240 mg, 1.55 mmol) was added dropwise to a solution of **8** (200 mg, 0.88 mmol) and methyl formanilide (240 mg, 1.78 mmol) in *o*-dichlorobenzene (2 mL) at 0 °C. The reaction was stirred at 90–95 °C for 2 h and the dark red solution added to aqueous sodium acetate (4 g in 40 mL $H_2O$). This mixture was heated briefly on a water bath, cooled to room temperature, and extracted with chloroform (2 × 100 mL). The organic extracts were washed with water (100 mL), dried over $Na_2SO_4$, and evaporated to dryness. The residue was chromatographed over silica with benzene eluant. Collection of the yellow band with blue fluorescence yielded a 1:1 mixture of aldehydes **9a** and **9b**: 186 mg (83%). Aldehydes **9a** and **9b** were separated by fractional crystallization from methanol.

**Aldehyde 9a**: mp 131–132 °C; UV (methanol) [$\lambda_{max}$ ($\epsilon \times 10^{-4}$)] 405 (1.28), 364 (1.10), 348 (0.97), 332 (sh, 0.37), 290 (1.85), 277 (1.32), 267 (sh, 0.69), 239 (2.11), 231 (2.27); $^1H$ NMR (400 MHz, acetone-$d_6$) 3.61–3.70 (m, 4 H, C3- and C4-methylenes), 8.01 (d, 1 H, $J_{2,1}$ = 7.7 Mz, H2), 8.13 (d, 1 H, $J_{9,10}$ = 8.9 Hz, H9 or H10), 8.23 (d, 1 H, $J_{8,7}$ = 7.9 Hz, H8), 8.29 (d, 1 H, $J_{9,10}$ = 8.9 Hz, H10 or H9), 8.33 (d, 1 H, $J_{1,2}$ = 7.7 Hz, H1), 8.45 (d, 1 H, $J_{7,8}$ = 7.9 Hz, H7), 9.19 (s, 1 H, H5), 10.71 (s, 1 H, CHO) ppm; IR (KBr) 1678 $cm^{-1}$ ($\nu_{C=O}$); mass spectrum, $m/z$ (rel intensity) 256 (100, $M^+$), 255 (32, M – H), 227 (92, M – CHO), 226 (M – $CH_2O$). Anal. Calcd for $C_{19}H_{12}O \cdot {}^1/_3(CH_3OH)$ (presence of methanol quantitated by $^1H$ NMR integration): C, 86.96; H, 5.04. Found: C, 87.20; H, 4.65.

**Aldehyde 9b**: mp 157–159 °C; UV (methanol) [$\lambda_{max}$ ($\epsilon \times 10^{-4}$)] 397 (1.75), 381 (1.58), 363 (sh, 1.07), 294 (2.14), 282 (1.37), 251 (sh, 1.79), 244 (sh, 1.92), 234 (2.43), 226 (sh, 1.79); $^1H$ NMR (400 MHz, acetone-$d_6$) 3.62 (t, 2 H, $J$ = 5.3 Hz, C4-methylene), 3.70 (t, 2 H, $J$ = 5.3 Hz, C3-methylene), 7.89 (s, 1 H, H5), 8.03 (d, 1 H, $J_{2,1}$ = 7.7 Hz, H2), 8.25 (d, 1 H, $J_{6,7}$ = 7.8 Hz, H6), 8.34 (d, 1 H, $J_{1,2}$ = 7.7 Hz, H1), 8.36 (d, 1 H, $J_{10,9}$ = 9.4 Hz, H10), 8.46 (d, 1 H, $J_{7,6}$ = 7.8 Hz, H7), 9.38 (d, 1 H, $J_{9,10}$ = 9.4 Hz, H9), 10.72 (s, 1 H, CHO) ppm; IR (KBr) 1678 $cm^{-1}$ ($\nu_{C=O}$). Anal. Calcd for $C_{19}H_{12}O \cdot {}^1/_3(CH_3OH)$ (presence of methanol quatitated by $^1H$ NMR integration): C, 86.96; H, 5.04. Found: C, 87.57; H, 4.97.

**6-Methyl-3,4-dihydrocyclopenta[*cd*]pyrene (10a).** The Wolff–Kishner reduction of **9a** (51 mg, 0.199 mmol) was performed in diethylene glycol (10 mL), hydrazine monohydrate (0.5 mL), and KOH (1.0 g) as described for **6** above to yield quantitatively **10a**: 48 mg; mp 135–136 °C; $^1H$ NMR (400 MHz, chloroform-*d*) 2.87 (s, 3 H, $CH_3$), 3.57 (br t, 2 H, $J_{4,3}$ = 7.2 Hz, ethano H4), 3.62 (br t, 2 H, $J_{3,4}$ = 7.2 Hz, ethano H3), 7.74 (d, 1 H, $J$ = 7.8 Hz, H7), 7.79 (d, 1 H, $J_{2,1}$ = 7.5 Hz, H2), 7.88–7.91 (m, 3 H, H8,H9,H10), 7.89 (s, 1 H, H5), 8.02 (d, 1 H, $J_{1,2}$ = 7.5 Hz, H1) ppm.

**6-Methylcyclopenta[*cd*]pyrene (1b).** A solution of **10a** (40 mg, 0.165 mmol) and DDQ (39 mg, 0.173 mmol) in toluene (15 mL) was refluxed under nitrogen for 2 h, and the cooled solution was transferred onto a column of silica. Elution with hexane and collection of the red-orange band yielded **1b**: 28 mg (70%); mp 138–139 °C; UV (heptane) [$\lambda_{max}$ ($\epsilon \times 10^{-4}$)] 387 (0.78), 379 (1.33), 368 (1.05), 358 (1.57), 343 (0.96), 307 (0.72), 289 (1.99), 266 (0.84), 2.43 (2.77), 235 (3.19); $^1H$ NMR (400 MHz, acetone-$d_6$) 3.12 (s, 3 H, $CH_3$), 7.31 (d, 1 H, $J_{4,3}$ = 5.1 Hz, H4), 7.47 (d, 1 H, $J_{3,4}$ = 5.1 Hz, H3), 7.96 (d, 1 H, $J_{7,8}$ = 7.5 Hz, H7), 8.06 (d, 1 H, $J_{2,1}$ = 7.3 Hz, H2), 8.12 (d, 1 H, $J_{1,2}$ = 7.3 Hz, H1), 8.14 (d, 1 H, $J_{9,10}$ = 9.1 Hz, H9 or H10), 8.18 (d, 1 H, $J_{9,10}$ = 9.1 Hz, H10 or H9), 8.30 (d, 1 H, $J_{8,7}$ = 7.5 Hz, H8), 8.75 (s, 1 H, H5) ppm; mass spectrum, $m/z$ (rel intensity) 240 (100, $M^+$), 239 (69, M – H), 120 (15, $M^{2+}$). Anal. Calcd for $C_{19}H_{12}$: C, 94.96; H, 5.04. Found: C, 95.35; H, 4.65.

**8-Methyl-3,4-dihydrocyclopenta[*cd*]pyrene (10b).** The Wolff–Kishner reduction of **9b** (51 mg, 0.199 mmol) was performed as described for **9a** above to yield quantitatively **10b**: 48 mg; mp 141–142 °C; $^1H$ NMR (400 MHz, chloroform-*d*) 2.86 (s, 3 H, $CH_3$), 3.52 (t, 2 H, $J_{4,3}$ = 7.5 Hz, ethano H4), 3.62 (t, 2 H, $J_{3,4}$ = 7.5 Hz, ethano H3), 7.67 (s, 1 H, H5), 7.73 (d, 1 H, $J_{7,6}$ = 7.9 Hz, H7), 7.80 (d, 1 H, $J_{2,1}$ = 7.5 Hz, H2), 7.92 (d, 1 H, $J_{6,7}$ = 7.5 Hz, H6), 8.00 (d, 1 H, $J_{10,9}$ = 9.2 Hz, H10), 8.03 (d, 1 H, $J_{1,2}$ = 7.5 Hz, H1), 8.09 (d, 1 H, $J_{9,10}$ = 9.2 Hz, H9) ppm.

**8-Methylcyclopenta[*cd*]pyrene (1c).** Dehydrogenation of **10b** (40 mg, 0.165 mmol) was carried out as described for **10a** above to yield **1c**: 28 mg (70%); mp 142–143 °C; UV (heptane) [$\lambda_{max}$ ($\epsilon \times 10^{-4}$) 382 (1.99), 375 (1.08), 362 (1.75), 345 (0.72), 309 (0.48),

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289 (1.81), 268 (0.78), 246 (2.29), 2.38 (3.07); $^1$H NMR (400 MHz, acetone-$d_6$) 3.05 (s, 3 H, $CH_3$), 7.24 (d, 1 H, $J_{4,3}$ = 5.1 Hz, H4), 7.42 (d, 1 H, $J_{3,4}$ = 5.1 Hz, H3), 7.96 (d, 1 H, $J_{7,6}$ = 7.8 Hz, H7), 8.14 (d, 1 H, $J_{2,1}$ = 7.5 Hz, H2), 8.20 (d, 1 H, $J_{1,2}$ = 7.5 Hz, H1), 8.22 (d, 1 H, $J_{10,9}$ = 9.2 Hz, H10), 8.31 (d, 1 H, $J_{9,10}$ = 9.2 Hz, H9), 8.45 (d, 1 H, $J_{6,7}$ = 7.8 Hz, H6), 8.37 (s, 1 H, H5) ppm; mass spectrum (rel intensity), $m/z$ 240 (100, $M^+$), 239 (67, M - H), 120 (18, $M^{2+}$). Anal. Calcd for $C_{19}H_{12}$: C, 94.96; H, 5.04. Found: C, 95.18; H, 4.82.

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## New Agents for the Selective Reduction of the Carbon-Carbon Double Bond of α,β-Unsaturated Carbonyl Compounds

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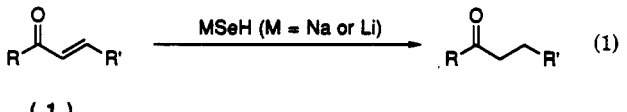
There is increasing interest in the chemistry of organoselenium compounds, and much effort is being devoted to synthesizing new selenium compounds and applying them to organic synthesis.[1] Among such compounds, the alkali metal salts of hydrogen selenide, which can be readily prepared in situ by the reaction of elemental selenium and an appropriate reducing agent (e.g., Li,[2] Na,[2] $NaBH_4$,[3] $LiBEt_3H$,[4] and $NaBEt_3H$[5]), have frequently been used as reagents for introducing of selenium into various organic compounds. However, the utilization of these salts as reducing agents has, so far, been limited to the reduction of organic disulfides and organic thiosulfates[6] and to the reductive dehalogenation of *vic*-dihaloalkanes.[7]

We therefore set out to evaluate the alkali metal salts of hydrogen selenide as reagents for the reduction of various organic functional groups. Here we show that sodium hydrogen selenide (NaSeH) and lithium hydrogen selenide (LiSeH) can be used for the selective reduction of the olefinic linkage of α,β-unsaturated carbonyl compounds (eq 1).[8]




(1)

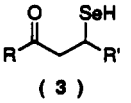
( 1 ) ( 2 )

The results of the reduction of various α,β-unsaturated carbonyl compounds by NaSeH (generated in situ by the reaction of elemental selenium with $NaBH_4$ in ethanol) are shown in Table I. The reduction of 4-phenyl-3-buten-2-one (**1a**) by treatment with a slight excess (1.5 equiv) of NaSeH provided 4-phenylbutan-2-one (**2a**) in 84% yield (entry 5). Under the reaction conditions employed, overreduced products (e.g., alcohols) were not formed (entries 1-5). Decreasing the amount of NaSeH (from 1.5 to 1.0 or 1.2 equiv) or lowering the reaction temperature (from 50 to 25 °C) led to a decrease in the yield of **2a** (entries 1-4). During the reduction of compounds **1d** and **1e**, chloro and methoxy groups were unaffected (entries 8 and 9). The olefinic carbon-carbon double bond of 4-(2-furyl)-3-buten-2-one (**1f**) and 4-(2-thienyl)-3-buten-2-one (**1g**) underwent reduction without affecting the furyl and thienyl groups (entries 10 and 11). α,β-Unsaturated ketones like 3-undecene-2-one (**1h**) and 1-phenyl-3-buten-1-one (**1i**), which possess no aromatic β-substituent, were also reduced by NaSeH in good yields (entries 12 and 13). In the case of dihydrocarvone (**1j**), which possesses both isolated and conjugated carbon-carbon double bonds, the conjugated double bond was reduced selectively (entry 14). The carbon-carbon double bonds of the α,β-unsaturated ester (**1k**) and the α,β-unsaturated dicarboxylic acid ester (**1l**) were also reduced selectively (entries 15 and 16). Unfortunately, however, reduction of the carbon-carbon double bond of the α,β-unsaturated carboxylic acid (**1m**) did not occur to any great extent and, at best, only a small quantity (<10%) of the saturated acid **2m** was produced.

The effectiveness of NaSeH as a reducing agent was compared with that of LiSeH, which was generated in situ by the reaction of Se and $LiEt_3BH$ in the presence of water. The α,β-unsaturated carbonyl compounds **1a**, **1h**, **1i**, and **1j** served as the substrates. Reductions with LiSeH proceeded smoothly and gave the corresponding ketones in fair to good yields (entries 1-4, Table II). Unlike reductions with NaSeH, it was necessary to use only a stoichiometric amount of LiSeH. The α,β-unsaturated carboxylic acid (**1m**) was reduced by LiSeH to the corresponding saturated acid in 57% yield (entry 5, Table II), whereas, as noted above, when NaSeH was the reducing agent, the yield was less than 10%.

To permit a better comparison at the two reagents, NaSeH was also generated in situ in a manner similar to that used to generate LiSeH, i.e., by the reaction of Se, $NaBEt_3H$, and $H_2O$. Treatment of **1m** with NaSeH prepared in this manner (1.0 equiv) gave **2m** in only 5% yield. Thus, the nature of the cation of the salt does have a significant influence on the extent of reduction. However, the reasons why this is so are not clear.

Although the details of the mechanism remain to be elucidated, it is probable that the reductions proceed through the Micheal adduct **3**.[12,13]

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(12) Reports describing the Micheal addition of compounds bearing a Se-H group, e.g., benzeneselenol, to α,β-unsaturated carbonyl compounds have appeared. See: Miyashita, M.; Yoshikoshi, A. *Synthesis* **1980**, 664 and references cited therein.

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