(s), 1486 (m), 1455 (m), 1445 (m), 1401 (s), 1309 (w); UV–vis (CH_2Cl_2) [λ, nm (log ε)] 226 (4.25), 238 (4.28), 283 (4.61), 332 (3.79), 348 (3.82), 362 (3.26), 581 (2.56), 621 (2.48), 689 (2.03); mass sectrum, calcd for $C_{17}H_{14}S$ 250.082, found 250.083. Anal. Calcd: C, 81.11; H, 5.49. Found: C, 81.55; H, 5.63.

6-(Thiocyanatomethyl)azulene. An acetone solution containing 277 mg (1.57 mmol) of **3** (along with some 6-methylazulene) and 263 mg (2.71 mmol) of potassium thiocyanate was refluxed for 9 h. The solvent was evaporated and the residue chromatographed on silica gel with carbon tetrachloride as the elution solvent. The 6-(thiocyanatomethyl)azulene was obtained from the third of the four bands eluted; 245 mg (79%). Final purification by sublimation at 42–55 °C (0.005 torr) provided a blue solid: mp 118–119 °C dec.; ^{1}H NMR ($CDCl_3$) δ 4.27 (s, 2 H, CH_2), 7.13 (d, 2 H, J = 10 Hz, $H_{5,7}$), 7.42 (d, 2 H, J = 4 Hz, $H_{1,3}$), 7.93 (t, 1 H, H_2), 8.30 (d, 2 H, $H_{4,8}$); IR (CaF_2, $CHCl_3$; in cm^{-1}) 2930, 2850 (vs), 2160 (w) [SCN], 1730 (w), 1575 (m), 1450 (s). Anal. Calcd for $C_{12}H_9NS$: C, 72.33; H, 4.55; N, 7.03. Found: C, 71.83; H, 4.30; N, 6.74.

Pentacarbonyl[(6-azulenyl)methyl]manganese. A mixture containing 150 mg (0.850 mmol) of 6-(chloromethyl)azulene (and 26 mg of 6-methylazulene) was placed in a 50-mL Schlenk flask and dissolved in 4 mL of anhydrous ether. The flask was sealed with a septum cap and degassed with two freeze–thaw cycles. An ether solution (20 mL) containing 0.85 mmol of sodium manganese pentacarbonyl was added to the stirred mixture maintained at room temperature. The color of the blue solution changed to blue-green, and a white precipitate was formed. After 2 h of stirring, 5 mL of water was added to the solution and the two layers separated in a separatory funnel. The ether layer was dried with anhydrous magnesium sulfate and the solvent removed under reduced pressure to afford a blue-green solid. 6-Methylazulene was removed by sublimation at 22 °C (0.03 torr) to leave 212 mg (74%) of the desired product, a dark green solid. This compound was further purified by sublimation at 60–70 °C (0.01 torr): mp 108–110 °C dec; ^{1}H NMR ($CDCl_3$) δ 2.66 (s, 2 H, CH_2), 7.02 (d, J = 10.5 Hz, 2 H, 2 H, $H_{5,7}$), 7.19 (d, J = 3.5 Hz, 2 H, $H_{1,3}$), 7.60 (t, J = 3.5 Hz, 1 H, H_2), 8.10 (d, J = 10.5 Hz, 2 H, $H_{4,8}$); mass spectrum, calcd for $C_{16}H_9MnO_5$ 335.983, found 335.984. Anal. Calcd: C, 57.14; H, 2.68. Found: C, 57.02; H, 2.50.

6-(Oximinomethyl)azulene. Freshly distilled isoamyl nitrite (1.47 g, 12.5 mmol) was placed in a 50-mL, round-bottomed flask, flushed with nitrogen, sealed with a septum cap, and cooled with a −40 °C cold bath. A 0.4 M solution of the sodium azulenate in THF was prepared from 1.19 g (8.4 mmol) of 6-methylazulene, chilled to −20 °C, and subsequently added, via syringe, over a period of 10 min to the flask containing the nitrite. A green color developed immediately. The solution was stirred at ice bath temperature (ca. 0 °C) for 1$^1/_2$ h and poured into 300 mL of cold water, and the aqueous layer was extracted with ether. The ether layer was washed three times with 5% aqueous hydrochloric acid solution and twice with water, and then dried over anhydrous sodium sulfate. The ether was removed under reduced pressure and the residue subjected to reduced pressure (0.05 torr) for 1 h. The residue was extracted with 200 mL of 5% aqueous potassium hydroxide solution and washed four times with petroleum ether. The alkaline layer was acidified, in the presence of dichloromethane, with cold 10% aqueous acetic acid. The oxime was extracted into the dichloromethane layer. The combined organic layers were washed with water and dried over anhyrous sodium sulfate. Evaporation of the solvent yielded 1.10 g (77%) of essentially pure oxime as a blue-green solid. Further purification of this oxime for elemental analysis was effected by recrystallization from petroleum ether/dichloromethane and subsequent sublimation at 60 °C (0.01 torr): mp 138–140 °C; ^{1}H NMR ($CDCl_3$) δ 8.32 (d, J = 10 Hz, 2 H, $H_{4,8}$), 8.28 (s, 1 H, N=CH), 7.92 (t, J = 4 Hz, 1 H, H_2), 7.48 (d, J = 10 Hz, 2 H, $H_{5,7}$), 7.40 (d, J = 4 Hz, 2 H, $H_{1,3}$); mass spectrum, calcd for C_9H_9NO 171.068, found 171.068. Anal. Calcd: C, 77.17; H, 5.30. Found: C, 77.23; H, 5.15.

Competition Experiments. A 1:1 (molar) mixture of 1-(chloromethyl)naphthalene and 6-(chloromethyl)azulene was dissolved in a measured amount (typically in the order of 0.3 mL, concentration typically 0.06 M for each of the chlorides) of deuterated acetone or DMF. A small measured amount of nucleophile was added and the progress of the reaction monitored by NMR spectroscopy, via multiple integration of the methylene proton absorption of the chlorides and their corresponding substitution products. The assignment of the proton signals was ascertained by comparison with authentic derivatives of both the 1-methylnaphthalene and the 6-methylazulene. The reactions with SCN^- and $HNEt_2$ were carried to 7 and 10% completion, respectively. In the case of PhS, the displacement was too fast to be monitored by NMR; 0.55 equiv (with respect to the total amount of chloride) of the nucleophile was added and the product distribution of the completed reaction (less than 5 min after addition) determined by multiple integration of the CH_2 singlets in the ^{1}H NMR spectrum.

Registry No. **3**, 99458-96-5; **4**, 99459-00-4; **5** (Y = H), 1654-52-0; **5** (Y = NEt_2), 99458-97-6; **5** (Y = SPh), 99458-98-7; **5** (Y = SCN), 99458-99-8; **5** (Y = $Mn(CO)_5$), 99459-01-5; sodium thiophenoxide, 930-69-8; potassium thiocyanate, 333-20-0; sodium pentacarbonyl manganate, 13859-41-1; 1-(chloromethyl)naphthalene, 86-52-2.

Efficient Synthesis of 5,6-Diacetoxyindole: A Stable Eumelanin Precursor

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5,6-Diacetoxyindole (**7**) is a stable, protected form of 5,6-dihydroxyindole (DHI), a key intermediate in melanogenesis.[1] Diacetate **7** is of interest because it can be hydrolyzed in situ for studies of eumelanin formation and structure, thus eliminating handling of the unstable diol.

Classical procedures[2,3] for conversion of piperonal (**1**) to **7** involve steps that are inefficient or tedious. For example, the iron salts generated during Fe–CH_3CO_2H cyclization of 4,5-diacetoxy-2,β-dinitrostyrene (**6**) are difficult to separate from **7**, and they cause polymerization of the DHI generated during cyclization. In addition, standard catalytic methods[4,5] for reductive cyclization of 2,β-dinitrostyrenes have not been used for **6**, due to the variety of side reactions that occur under the cyclization conditions (50 psi H_2, 10% Pd/C, ethyl acetate–acetic acid–ethanol).

Results and Discussion

Nitration of piperonal (**1**) normally results in a 4.5:1 molar ratio of 6-nitropiperonal to 4-nitro(methylenedioxy)benzene (by displacement of the aldehyde).[5] However, in cold (−15 °C) dichloroethane, 6.4 equiv of fuming HNO_3 cleanly converted 25 g of **1** to **2** in 99% yield. The reaction was less successful at higher temperatures (−10 to 0 °C) or with a larger excess of HNO_3. ^{1}H NMR showed that, under these conditions, displacement of the aldehyde group of **2** resulted in 10–15% of 4,5-dinitro(methylenedioxy)benzene.

Demethylenation of **2**, rather than condensation with nitromethane, was the second step, since 4,5-(methylenedioxy)-2,β-dinitrostyrene is deprotected in low yield. Similarly, the best deprotection reagent (BBr_3) for 5,6-

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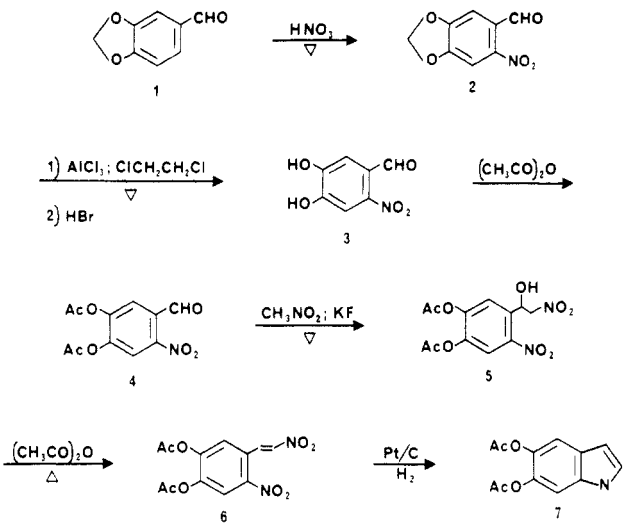
Scheme I



(methylenedioxy)indole gave only 12% of DHI or 40% of **7**, if the reaction was quenched with acetic anhydride.

When **2** is treated with $AlCl_3$ in 1,2-dichloroethane at 0–5 °C, 5-(chloromethoxy)-4-hydroxy-2-nitrobenzaldehyde is formed.[6] Rather than isolate this compound as in earlier procedures,[6,7] the mixture was poured into 48% HBr and stirred at ambient temperature to give 97% yield of 4,5-dihydroxy-2-nitrobenzaldehyde (**3**). Higher temperatures resulted in lower yields of **3**.

Since neither H_2O removal (Dean–Stark trap or dehydrating agents) nor any of the variety of catalysts available for difficult Knoevengel condensations[8] increased the rate of condensation of **3** with nitromethane, condensation of diacetate **4**, which was prepared quantitatively from **3**, was tried next.

Since acetates are susceptible to nucleophilic attack, the nonnucleophilic base KF and low (0 °C) temperature were used. Also, since this synthesis was being designed for incorporation of $^{13}CH_3NO_2$, the procedure had to use a minimum of nitromethane. When **4** was stirred with 3.3 equiv of nitromethane and catalytic amounts of KF and 18-crown-6, it was converted to 1-(4,5-diacetoxy-2-nitrophenyl)-2-nitroethanol (**5**). In dioxane–2-propanol, the reaction was incomplete in 65 h, but when *N*-methylmorpholine or *N*-methylmorpholine–2-propanol was the solvent/catalyst, product was obtained in 24 h. This procedure was simplified further by warming the mixture containing **5** with acetic anhydride–sodium acetate to convert it to 4,5-diacetoxy-2,β-dinitrostyrene (**6**), which was precipitated in ice H_2O. Compound **6** was determined to be the *E* isomer by comparison of the large coupling constant (ca. 13 Hz) to known values.[9]

When the standard method (10% Pd/C, 50 psi H_2, ethyl acetate–acetic acid–ethanol) for cyclization of 4,5-disubstituted 2,β-dinitrostyrenes was used for (*E*)-4,5-diacetoxy-2,β-dinitrostyrene, trace 5,6-diacetoxyindole and several other indoles were obtained. The major product isolated by column chromatography was unidentified, but its ^1H NMR spectrum showed no resonances corresponding to acetyl groups, the M^+ peak was 398 (**7**; 233), and the elemental analysis was inconsistent with **7**. However, cyclizations run in acetic acid over 5% Pt/C at less than 20 psi H_2 gave **7** in up to 73% yield after acetylation of the mixture, removal of the solvent in vacuo, and HPLC purification (Scheme I).

Therefore, this work has shown the best order of steps in syntheses involving 2,β-dinitrostyrenes as intermediates and describes a method for preparation of reasonable quantities of **7**, or its labeled derivatives, for structural investigations of eumelanin, free from other biologically derived impurities, and also for investigations of the pigment-forming process. Increased yield in the cyclization would make this process even more desirable, though.

Experimental Section

Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. ^1H NMR and ^{13}C NMR (300 and 75.48 MHz, respectively) spectra were obtained on a General Electric QE-300 NMR spectrometer, and chemical shifts are reported in parts per million (ppm) relative to external tetramethylsilane. The ^{13}C NMR spectra of aldehydes **2–4** showed (at ca. 125 ppm) the expected small (ca. 25 Hz) two-bond coupling of C-1 to the aldehyde proton. HPLC separations of **7** were done on a Waters Prep 500A, with 3:1 toluene–ethyl acetate.

6-Nitropiperonal (2). Fuming HNO_3 (50 mL) was added to a −30 °C solution of piperonal (**1**) (25 g, 167 mmol) in 100 mL of 1,2-dichloroethane. The reaction was stirred at ca. −15 °C until no piperonal remained (ca. 6.5 h). The mixture was poured into 500 mL of ice H_2O, extracted with ethyl acetate, and dried over $MgSO_4$. Removal of the solvent gave 32.2 g (99%) of 6-nitropiperonal: mp 93–94 °C (lit.[5] mp 93–94 °C); ^1H NMR (acetone-d_6) δ 10.18 (s, 1 H), 7.58 (s, 1 H), 7.25 (s, 1 H), 6.35 (s, 2 H); ^{13}C NMR (Me_2SO-d_6) δ 188.40 (d, ArCHO), 152.41, 151.80 (s, s; C-4, C-5), 146.11 (s, C-2), 128.02 (d, C-1), 107.4 (d, C-6), 105.39 (d, C-3), 105.00 (t, OCH_2O).

4,5-Dihydroxy-2-nitrobenzaldehyde (3). Sublimed $AlCl_3$ (42 g) was added to 105 mL of cold (−5 °C), dry 1,2-dichloroethane under Ar, followed by a solution of 21 g of **2** in 85 mL of dry 1,2-dichloroethane. The reaction was maintained at −5 to +5 °C until no 6-nitropiperonal remained (ca. 1.25 h), then poured into 250 mL of cold 48% HBr, and stirred at ambient temperature until none of the intermediate chloromethyl ether remained (ca. 2 days). The reaction mixture was diluted with H_2O, extracted with ethyl acetate, and dried over $MgSO_4$, and the solvent was removed to give 18.9 g (97%) of **3**: mp 203–204 °C (lit.[6] mp 203–204); ^1H NMR (acetone-d_6) δ 10.59 (br s, 1 H), 10.20 (s, 1 H), 7.60 (s, 1 H), 7.30 (s, 1 H); ^{13}C NMR (Me_2SO-d_6) δ 188.76 (d, ArCHO), 151.34, 150.12 (s, s; C-4, C-5), 142.53 (s, C-2), 124.78 (d, C-1), 114.78 (d, C-6), 112.6 (d, C-3).

4,5-Diacetoxy-2-nitrobenzaldehyde (4). Compound **3** (19.1 g, 104 mmol) was stirred at 60 °C in 80 mL of acetic anhydride with 1 g of sodium acetate for 45 min. The reaction mixture was poured onto ice and stirred until the original gummy precipitate became a powdery solid. The dispersion was filtered, and the solid was washed well with cold H_2O and dried. 4,5-Diacetoxy-2-nitrobenzaldehyde (**4**) was obtained in 99% yield (27.6 g): mp 113–116 °C (lit.[11] mp 113 °C); ^1H NMR (acetone-d_6) δ 10.36 (s, 1 H), 8.18 (s, 1 H), 7.83 (s, 1 H), 2.36 (s, 6 H); ^{13}C NMR (Me_2SO-d_6) δ 188.62 (d, ArCHO), 168.17 (s, ester carbonyl), 147.09, 146.7 (s, s; C-4, C-5), 145.73 (s, C-2), 129.96 (s, C-1), 125.15 (d, C-6), 121.45 (d, C-3), 20.85 (q, ester CH_3).

(*E*)-4,5-Diacetoxy-2,β-dinitrostyrene (6). Compound **4** (1 g, 3.7 mmol) was stirred for 24 h under Ar at 0 °C with 6 mL of *N*-methylmorpholine, 4 mL of 2-propanol, 0.05 g of KF, and 0.75 g of CH_3NO_2, then poured into 5 mL of acetic anhydride with 0.1 g of sodium acetate, and warmed to 60 °C for 1 h. The reaction mixture was poured onto ice and stirred until a fine powder resulted. The dispersion was filtered, and the solid was washed well with cold H_2O and dried to give 1.15 g (99%) of **6**: mp 129–132 (lit.[3] mp 128–132 °C); ^1H NMR (Me_2SO-d_6) δ 8.41 (d, J = 13.47 Hz, 1 H), 8.26 (s, 1 H), 8.04 (d, J = 13.45 Hz, 1 H), 7.97 (s, 1 H), 2.35 (s, 3 H) 2.33 (s, 3 H); ^{13}C NMR (Me_2SO-d_6) δ 168.17

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(s, ester carbonyl), 146.55 (s, C-5), 146.22 (s, C-2), 144.38 (s, C-4), 141.48 (d, C-β), 134.61 (d, C-α), 125.71 (d, C-6), 125.27 (s, C-1), 122.15 (d, C-3), 20.78 (q, ester CH_3).

5,6-Diacetoxyindole (7). Compound **6** (3.1 g, 10 mmol) and 0.31 g of 5% Pt/C were dispersed in 60 mL of CH_3CO_2H and hydrogenated on a Parr apparatus at 15 psi for 5 h. Thirty milliliters of acetic anhydride was added, and the reaction was warmed to 30 °C as the solvent was removed at reduced pressure. HPLC purification gave 1.63 g (70%) of **7**: mp 134–136 °C (lit.[3] mp 134–136 °C); ^{1}H NMR (Me_2SO-d_6) δ 11.24 (br s, 1 H), 7.41 (d, J = 2.68 Hz, 1 H), 7.36 (s, 1 H), 7.27 (s, 1 H), 6.45 (d, J = 2.59 Hz, 1 H), 2.27 (s, 6 H); ^{13}C NMR (Me_2SO-d_6) δ 169.47 (s, ester carbonyl), 137.84 (s, C-8), 136.28 (s, C-6), 133.52 (s, C-5), 127.55 (d, C-2), 125.59 (s, C-9), 113.75 (d, C-4), 106.12 (d, C-7), 101.56 (d, C-3), 21.00 (q, ester CH_3).

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Registry No. 1, 120-57-0; 2, 712-97-0; 3, 73635-75-3; 4, 15794-35-1; 5, 99459-13-9; 6, 99459-14-0; 7, 15069-79-1; 5-(chloromethoxy)-4-hydroxy-2-nitrobenzaldehyde, 73635-74-2.

Indirect Electrochemical Radical Cyclization of Bromo Acetals by Cobaloxime(I) as an Electron-Transfer Catalyst

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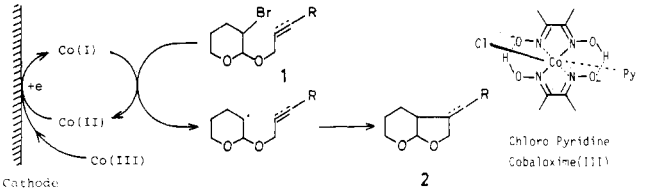
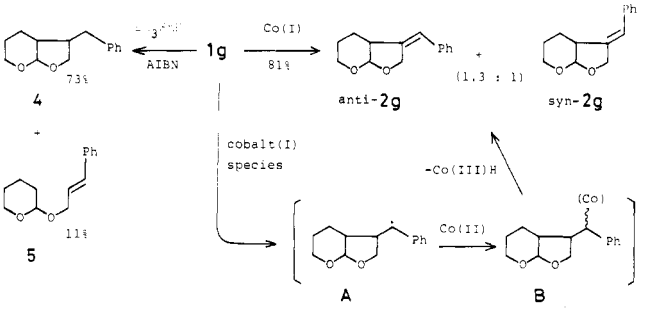
Cyclization by trapping of a free radical with an internal π-bond system is a promising strategy for the construction of carbo- and heteroring molecules under mild conditions.[1] Reported methods utilizing trialkylstannane or -distannane as a radical generator are troublesome in the purification of the products from trialkyltin halide,[2] although a partial solution to this problem has been devised by using polymer-supported organotin compounds.[3] In this paper we disclose a facile procedure for the radical cyclization according to Scheme I, in which electrochemically regenerated cobaloxime(I) (Co(I)) from cobaloxime(III)[4] has been exploited as a mediator for the reductive cleavage of C–Br bonds of brominated olefins and acetylenes **1** to **2**.[5]

Although cobaloxime(I) generated by the reduction of cobaloxime(III), the most simple model compound of vitamin B_{12}, with $NaBH_4$ has been shown to catalyze the reduction of alkyl halides and tosylates to produce alkyl radical and/or organocobaloxime species through an electron-transfer process,[6] no effective electrochemical

Scheme I



Scheme II



versions of these reactions have been explored in spite of intensive and intriguing results on indirect electrochemical reduction of C–halogen bonds[7] assisted by vitamin B_{12} derivatives and its model compounds.[8]

The radical cyclization by electrochemically regenerated cobaloxime(I) has been carried out in methanol containing Et_4NOTs as a supporting electrolyte in a divided cell under argon. Thus, the bromo acetal **1d** was electrolyzed in the presence of about 50 mol % of chloropyridinecobaloxime(III) and a small amount of 40% NaOH under a constant current density of 13.3 mA/cm^2 (terminal voltage 9–11 V) at 50–60 °C. After passage of 2 faraday/mol of electricity, the mixture was subjected to the usual extractive workup followed by purification on column chromatography (SiO_2) to give the desired **2d** in 70% yield. No cyclization was observed in the absence of the cobalt catalyst.

An interesting feature of the present radical cyclization is that the reaction can be carried out in methanol, contrary to the trialkyltin hydride promoted radical reaction in aprotic nonpolar solvents. The formation of **2d** from **1d** by this electrochemical method in polar aprotic solvents such as DMF and MeCN decreased to 30% and 18%, respectively. The electrochemical cyclization can be carried out by using less than 20 mol % of cobaloxime(III), though the reaction becomes sluggish. It is noted that the reactivity of the catalyst can be enhanced by addition of 40% NaOH to the medium: the electrolysis of **1d** in the absence of 40% NaOH afforded **2d** in 57% yield by passage of 4.9 faraday/mol of electricity.

As shown in Table I, various brominated olefins and acetylenes derived from cyclic enol ethers and enamine could be converted into the corresponding tetrahydrofuran derivatives. Thus, the reaction proceeded through a closure in the exo mode to only a five-membered ring. However, similar treatment of **3**, bearing a C=C double

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