JOC*Note*

Ruthenium(III) Chloride Catalyzed Oxidation of Pyrene and 2,7-Disubstitued Pyrenes: An Efficient, One-Step Synthesis of Pyrene-4,5-diones and Pyrene-4,5,9,10-tetraones

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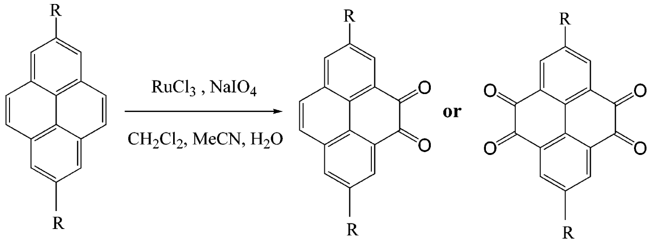
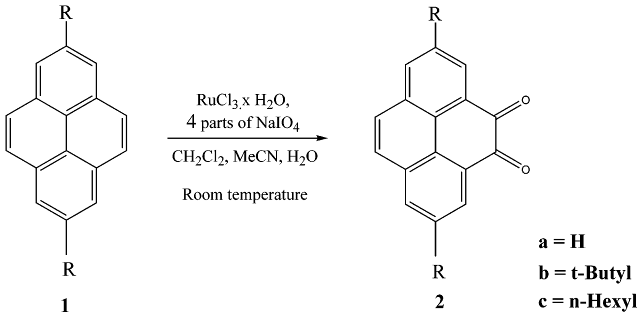


R = H, t-Butyl, or n-Hexyl

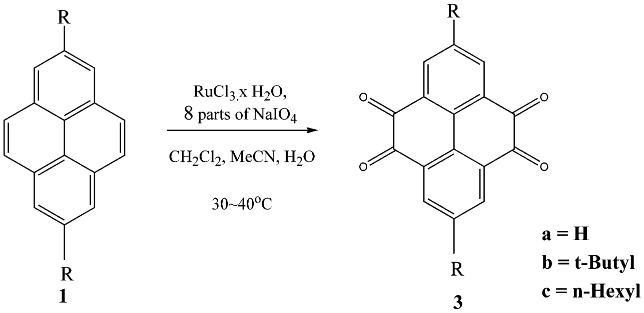
Pyrene and 2,7-disubstituted pyrenes have been oxidized with ruthenium(III) chloride (RuCl$_3$) and sodium periodate (NaIO$_4$) under very mild conditions to 4,5-diones or 4,5,9,10-tetraones. Thus, the oxidation has been controlled by varying the amount of oxidant and reaction temperature to proceed exclusively at the pyrene 4- and 5-positions or at the 4-, 5-, 9-, and 10-positions.

K-region oxidation of pyrene has been studied extensively because of its suspected role in the carcinogenicity of fused arenes.[1] One of the oxidation products, pyrene-4,5-dione (**2a**), is also important because it serves as an intermediate in the preparation of other fused-ring molecules, which are of interest from both a theoretical and a practical point of view.[2] Further oxidation of pyrene-4,5-dione gives pyrene-4,5,9,10-tetraone (**3a**), which has been used in metal complex formation and as a monomer in step growth polymerizations.[2a,3] Previous attempts to prepare **2** and **3** directly from pyrene have been largely unsuccessful since sites other than C(4) and C(5) more readily undergo oxidation.[2c,4] Dione **2a** has been prepared in low yield by the oxidation of pyrene with the highly toxic osmium tetroxide.[2c] Compound **2a**, **3a**, the 2,7-disubstituted pyrenedione **2b**, and the pyrene tetraone **3b** have been prepared by multistep synthetic routes.[3f,5]

SCHEME 1



SCHEME 2



We recently prepared a series of fused, liquid crystalline, substituted bisphenazines by treating pyrene-4,5,9,10-tetraones with 1,2-dialkoxy-4,5-diaminobenzenes.[6] To avoid the multistep routes to the tetraones, we reinvestigated the oxidation of pyrene. A heterogeneous mixture of ruthenium(III) chloride (RuCl$_3$) and sodium periodate (NaIO$_4$) in methylene chloride (CH$_2$Cl$_2$), water, and acetonitrile (CH$_3$CN)[7] selectively provided the dione **2a** or the tetraone **3a** depending on the reaction temperature and the amount of oxidant used. The reaction conditions were very mild. The diones were obtained at room temperature with 4 equiv of NaIO$_4$ (Scheme 1) while the tetraone was formed at 30−40 °C with 8 equiv of NaIO$_4$ (Scheme 2). This was surprising since previous work with ruthenium-catalyzed oxidations of arenes had resulted in either dicarboxylic acids, tetacarboxylic acids, or diols.[8]

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These procedures were then used to prepare the 2,7-disubstituted pyrenediones **2b**, **2c** and tetraones **3b**, **3c**. 2,7-Di(*n*-hexyl)pyrene-4,5-dione (**2c**) and 2,7-di-*n*-hexylpyrene-4,5,9,10-tetraone (**3c**) were prepared from the previously unknown 2,7-di-*n*-hexylpyrene, which was synthesized in three steps from 4,5,9,10-tetrahydropyrene.

Experimental Section

Pyrene (**1a**) was purchased from Acros and used as received. 2,7-Di-*tert*-butylpyrene (**1b**) was synthesized by using the reported procedure in greater than 90% yield.[9] Preparation of 2,7-di-*n*-hexylpyrene (**1c**) is described in the Supporting Information.

General Procedure for the Preparation of Pyrene-4,5-diones (2) (Scheme 1). To a solution of pyrenes (**1**) (10 mmol) in CH_2Cl_2 (40.0 mL) and CH_3CN (40.0 mL) were added $NaIO_4$ (10.0 g, 46.8 mmol), H_2O (50.0 mL), and $RuCl_3 \cdot xH_2O$ (0.20 g, 0.96 mmol). The dark brown suspension was stirred at room temperature overnight. The reaction mixture was poured into 500 mL of H_2O and the organic phase was separated. The aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The CH_2Cl_2 extracts were combined with the organic phase and washed with H_2O (3 × 200 mL) to give an dark orange solution. The solvent was removed under reduced pressure to afford a dark orange solid. Thin-layer chromatography (TLC), using an ethyl acetate/hexanes (2/5) mixture, indicated the presence of several byproducts, which were not isolated. Column chromatography (CH_2Cl_2) gave pure products as bright orange crystals.

2a: yield 45%; mp 299−302 °C (lit.[5a] mp 302−304 °C); ^1H NMR (300 MHz, $CDCl_3$) δ 8.47 (dd, 2H), 8.16 (dd, 2H), 7.82 (s, 2H), 7.76 (t, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.5, 135.9, 132.1, 130.2, 130.20, 128.5, 128.1, 127.4; mass calcd for $C_{16}H_8O_2$ 232.05, found 232.05 (ESI).

2b: yield 46%; mp 241−244 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.54 (dd, 2H), 8.12 (dd, 2H), 7.79 (s, 2H), 1.49 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 181.2, 51.3, 132.1, 132.0, 130.0, 128.5, 127.5, 126.7, 35.4, 31.4; mass calcd for $C_{24}H_{24}O_2$ 344.18, found 344.18 (ESI).

2c: yield 40%; mp 138−140 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.15 (dd, 2H), 7.78 (dd, 2H), 7.60 (s, 2H), 2.78 (t, 4H), 1.72 (p, 4H), 1.32 (m, 12H), 0.89 (t, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 180.6, 142.8, 134.9, 131.9, 130.7, 129.6, 127.0, 126.6, 35.9, 31.9, 31.3, 29.2, 22.8, 14.3; mass calcd for $C_{28}H_{32}O_2$ 400.24, found 400.24 (ESI).

General Procedure for the Preparation of Pyrene-4,5,9,-10-tetraones (3) (Scheme 2). To a solution of the pyrene (**1**) (10 mmol) in CH_2Cl_2 (40.0 mL) and CH_3CN (40.0 mL) were added $NaIO_4$ (17.5 g, 81.8 mmol), H_2O (50.0 mL), and $RuCl_3 \cdot xH_2O$ (0.25 g, 1.2 mmol). The dark brown suspension was heated at 30−40 °C overnight. The reaction mixture was poured into 200 mL of H_2O, and the solid was removed by filtration. After the dark green product was washed with 500 mL of H_2O, the organic phase was separated. The aqueous phase was extracted with CH_2Cl_2 (3 × 50 mL). The CH_2Cl_2 extracts were combined with the organic phase and washed with H_2O (3 × 200 mL) to give a dark green solution. The solvent was removed under reduced pressure to afford a dark green solid that was combined with the dark green product. Thin-layer chromatography (TLC), using an ethyl acetate/hexanes (2/5) mixture, indicated the presence of several byproducts, which were not isolated. Column chromatography (CH_2Cl_2) gave pure products as bright orange crystals.

3a: yield 36%; mp >350 °C; ^1H NMR (300 MHz, DMSO-d_6) δ 8.32 (d, 4H), 7.71 (t, 2H); ^{13}C NMR (N/A, solubility too low); mass calcd for $C_{16}H_6O_4$ 262.03, found 262.03 (ESI).

3b: yield 47%; mp 339−342 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.47(s, 4H), 1.42 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.4, 155.1, 134.05 132.4, 130.8, 35.6, 30.9; mass calcd for $C_{24}H_{22}O_4$ 374.15, found 374.15 (ESI).

3c: yield 30%; mp 199−202 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.25 (s, 4H), 2.75 (t, 4H), 1.69 (t, 4H), 1.33 (m, 12H), 0.89 (t, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 178.3, 146.8, 136.8, 132.7, 130.9, 35.6, 31.7, 30.8, 29.0, 22.7, 14.2; mass calcd for $C_{28}H_{30}O_4$ 430.21, found 430.21 (ESI).

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Supporting Information Available: Preparation of 2,7-di-*n*-hexyl-pyrene (**1c**) and ^1H and ^{13}C spectra of all the compounds were not listed in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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