indicated the presence of unreacted olefin. Nevertheless, reaction was quenched to minimize the likelihood of product decomposition. The product was partitioned between ether and water. The organic layer was washed with water, dried, and evaporated under reduced pressure avoiding excessive heating. Chromatography on neutral alumina, activity IV, gave unreacted **7c** (30 mg, 30%) on initial elution with hexanes. Elution with benzene afforded pure **2a** (65 mg, 63%): mp 127–128 °C dec; NMR δ 2.94 (dd, 1, CH_2), 3.31 (dd, 1, CH_2), 4.27 (br t, 1, CH), 7.80–8.30 (m, 9, aromatic); mass spectrum, *m/e* 244.

2,7-Diacetyl-4,5,9,10-tetrahydropyrene (6b). Acetylation of **5** (1.0 g, 5 mmol) was conducted by the procedure previously employed with replacement of CS_2 by CH_2Cl_2 as solvent. There was obtained **6b** (1.42 g, 98%): mp 225–227 °C (benzene–hexane); NMR δ 2.63 (s, 6, CH_3), 2.97 (s, 8, CH_2), 7.80 (s, 4, aromatic).

2,7-Diacetylpyrene (7d). Dehydrogenation of **6b** (1.45 g, 5 mmol) was carried out by the procedure employed for the monoacetyl compound, except that 3 days were required for complete reaction. There was obtained **7d** (1.40 g, 98%): mp >265 °C (CH_2Cl_2); NMR δ 2.96 (s, 6, CH_3), 8.24 (s, 4, $H_{4,5,9,10}$), 9.84 (br s, 4, $H_{1,3,6,8}$).

2,7-Bis(1-hydroxyethyl)pyrene (7e). Reduction of **7d** (1.00 g, 3.5 mmol) with $NaBH_4$ by the procedure employed for 2-acetylpyrene gave **7e** (1.00 g, 98%): mp >250 °C; NMR δ 1.69 (d, 6, CH_3), 2.35 (br s, 2, OH), 5.33 (q, 2, CH), 7.92 (s, 4, $H_{4,5,9,10}$), 8.10 (s, 4, $H_{1,3,6,8}$).

2,7-Divinylpyrene (7f). Dehydration of **7e** (1.45 g, 5 mmol) by the procedure employed for **7b** furnished 2,7-divinylpyrene (1.0 g, 79%): mp 177–178 °C; NMR δ 5.44 (d, 2, CH_2), 6.05 (d, 2, CH_2), 7.13 (dd, 2, CH), 8.00 (s, 4, $H_{4,5,9,10}$), 8.18 (s, 4, $H_{1,3,6,8}$).

2,7-Bisoxiranylpyrene (2b). A mixture of **7f** (100 mg, 0.39 mmol) in CH_2Cl_2 (5 mL) and phosphate buffer (5 mL, pH 8.0) was cooled to 4 °C and *m*-chloroperbenzoic acid (68 mg, 0.39 mmol) was added with stirring. TLC analysis indicated reaction was incomplete after 3 days at 4 °C. Another portion (68 mg) of the peracid was added and stirring was continued for 5 days, when a final portion (68 mg) of peracid was added. The mixture was stirred at 4 °C for 7 days more and then diethyl ether (50 mL) was added. The aqueous layer was removed, and the organic layer was washed with ice-cold 2% NaOH solution (2 × 50 mL) and distilled water (2 × 20 mL) and dried (Na_2SO_4). The solution was filtered and the solvent removed under reduced pressure (no heat). The residue was purified by rapid chromatography on a column of basic alumina, activity IV, eluted with 20% benzene in hexane. Evaporation of the solvent gave **2b** (81 mg, 73%): mp 145–147 °C dec; NMR δ 3.00 (dd, 2, CH_2, $J = 3.1$ Hz), 3.30 (dd, 2, CH_2, $J = 4.9$ Hz), 4.32 (apparent t, 2, CH, $J = 4.3$ Hz), 8.13 (s, 4, aromatic $H_{4,5,9,10}$), 8.26 (s, 4, aromatic $H_{1,3,6,8}$); mass spectrum, *m/e* 286.

1,6- and 1,8-Bis(bromoacetyl)pyrene (8b and 9b). A solution of 1,6-diacetylpyrene[16] (1.43 g, 5 mmol) in EtOAc (20 mL) and $CHCl_3$ (20 mL) was heated to reflux with 4.69 g (20 mmol) of finely powdered $CuBr_2$ with vigorous stirring for 3.5 h. The yellow precipitate was filtered off, washed with CH_2Cl_2, dried, and combined with the residue obtained from evaporation of the filtrate. This material (5.28 g) was extracted with boiling benzene (5 × 125 mL), filtered, and concentrated. Crystallization gave **8b** (908 mg, 41%): mp 169.5–171 °C dec; NMR δ 8.29–9.07 (m, 8, aromatic), 4.71 (s, 4, CH_2). Analogous reaction of 1,8-diacetylpyrene[16] (1.15 g, 4 mmol) afforded **9b** (1.40 g, 79%), as yellow crystals: mp 194.5–195.5 °C dec; NMR (Me_2SO-d_6) δ 4.70 (s, 4, CH_2), 8.19 (s, 2, $H_{4,5}$), 8.27 (d, 2, $H_{3,6}$), 8.40 (d, 2, $H_{2,7}$), 9.00 (s, 2, $H_{9,10}$, $J_{2,3} = 8.0$ Hz); UV λ_{max}^{EtOH} 204 (ϵ 35 200), 232 (46 900), 243 (40 500), 288 (27 700), 377 (27 700).

1,6- and 1,8-Bisoxiranylpyrene (1b and 1c). To a stirred suspension of **8b** (444 mg, 1 mmol) in boiling EtOH (20 mL) was added dropwise a solution of $NaBH_4$ (112 mg, 3 mmol) in 2 mL of H_2O. The mixture was refluxed for 5 min and filtered hot. The filtrate was cooled at 4 °C for 30 min, and the crystalline precipitate filtered to give **1b** (72 mg), mp 158–159 °C dec. The insoluble material from the reaction was triturated with H_2O, and the yellow crystals were filtered off, washed with H_2O and MeOH, and dried to yield **1b** (113 mg, total yield with previous crop 65%): mp 187–190 °C dec; NMR δ 2.97 (m, 2, CH_2), 3.41 (dd, 2, CH_2), 4.75 (dd, 2, CH), 7.98 (d, 2, $H_{3,8}$), 8.12 (d, 2, $H_{4,9}$), 8.17 (d, 2, $H_{2,7}$), 8.37 (d, 2, $H_{5,10}$, $J_{4,5} = 9.2$ Hz, $J_{2,3} = 7.8$ Hz); UV spectrum λ_{max}^{EtOH} 201 (ϵ 23 600), 233 (32 300), 242 (58 400), 256 (s, 7450), 266 (22 360), 277 (44 700), 317 (9940), 332 (27 950), 349 (41 600). Analogous reaction of **9b** (444 mg, 1 mmol) provided **1c** (191 mg, 67%): mp 142–144 °C; NMR (500 MHz) δ 2.97 (m, 2, CH_2), 3.44 (dd, 2, CH_2), 4.79 (apparent t, 2, CH), 7.97 (d, 2, $H_{3,6}$), 8.03 (s, 2, $H_{4,5}$), 8.16 (d, 2, $H_{2,7}$), 8.47 (s, 2, $H_{9,10}$, $J_{2,3} = 8.0$ Hz); UV spectrum λ_{max}^{EtOH} 202 (ϵ 33 800), 234 (44 200), 242 (69 300), 256 (s, 13 900), 266 (28 600), 277 (51 100), 304 (s, 6100), 318 (13 000), 333 (31 600), 349 (43 300).

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Registry No. **1a**, 61695-74-7; **1b**, 86470-94-2; **1c**, 86470-95-3; **2a**, 86470-96-4; **2b**, 86470-97-5; **3**, 73529-24-5; **5**, 781-17-9; **6a**, 82799-67-5; **6b**, 86470-98-6; **7a**, 789-06-0; **7b**, 86470-99-7; **7c**, 86471-00-3; **7d**, 86471-01-4; **7e**, 86471-02-5; **7f**, 86471-03-6; **8a**, 86471-04-7; **8b**, 86471-05-8; **9a**, 86471-06-9; **9b**, 86471-07-0; DMF, 68-12-2; 4,5-dihydropyrene, 6628-98-4; pyrene-1-carboxaldehyde, 3029-19-4; dimethylsulfonium methylide, 6814-64-8; trimethylsulfonium iodide, 2181-42-2; 4-bromopyrene, 1732-26-9; pyrene-4-carboxaldehyde, 22245-51-8; acetyl chloride, 75-36-5.

A Simple, Inexpensive Procedure for the Large-Scale Production of Alkyl Quinones

Dennis Liotta,*[1] Jack Arbiser, James W. Short, and Manohar Saindane

Department of Chemistry, Emory University, Atlanta, Georgia 30322

Received December 28, 1982

Alkyl *p*-benzoquinones are versatile starting materials in the synthesis of many important natural products and are particularly useful as dienophiles in Diels–Alder reactions. Quinones may be produced in high yield through the exposure of *o*-arylhydroxylamines to strong acid or by the oxidation of phenols and aromatic amines with (inter alia) Fremy's salt[2] or thallium(III) nitrate.[3] Unfortunately, each of these methods suffers certain disadvantages. For example, since *o*-arylhydroxylamines are usually prepared by reduction of their corresponding nitro compounds, they are oftentimes produced in low yield and are heavily contaminated with nitroso, amino, azo, and azoxy byproducts. As a consequence, many *o*-arylhydroxylamines are not always readily available as starting materials.

On the other hand, aromatic amines and phenols are readily available and are usually quite inexpensive to purchase. However, the two best reagents for the oxidation of these substrates (i.e., Fremy's salt and thallium(III) nitrate) are relatively expensive reagents. Moreover, although both reagents are effective oxidants, the former exhibits explosive properties, and the latter produces highly toxic byproducts. While these features are certainly quite manageable in small-scale reactions, they have proven to be particularly bothersome to us in large-scale quinone production.

We report herein a simple method for the large-scale production of alkyl quinones which does not suffer from any of the disadvantages discussed above. The method

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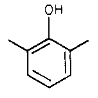
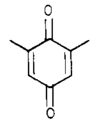
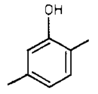
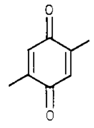
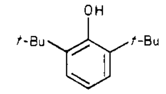
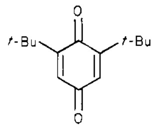
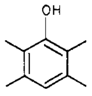
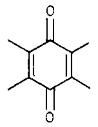
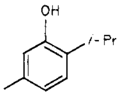
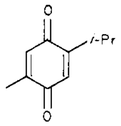
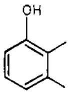
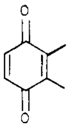
Table I

substrate	product	isolated yield,[a] %
 **1**	 **2**	84
 **3**	 **4**	57
 **5**	 **6**	52
 **7**	 **8**	59
 **9**	 **10**	46
 **11**	 **12**	30

[a] All compounds were characterized by comparison of their physical and spectral properties with literature values.

we have adopted is a modified two-phase Jones oxidation procedure (ether/aqueous chromic acid) which enables us to routinely prepare 30–60 g of alkyl quinones in a one-pot reaction. Although the yields obtained range from modest to very good (see Table I), the process itself is quite simple to carry out and far less expensive than the previously discussed procedures. The bonus associated with this method is that quinones of reasonably high purity are virtually always obtained by simple extraction procedures; i.e., *chromatographic purifications are rarely required.*

This method does not work well with 2-methoxyphenol, presumably due to competitive *o*-quinone formation and subsequent polymerization.

Experimental Section

General Methods. Melting points were determined with a Thomas-Hoover Uni-Melt capillary melting point apparatus. Infrared spectra were determined with Perkin-Elmer Model 257, 457, and 727 spectrophotometers. Nuclear magnetic resonance spectra were recorded by using Varian T-60, EM-360, and EM-390 spectrometers, and chemical shifts are reported in parts per million (δ) relative to an internal tetramethylsilane reference. Nominal mass spectra were recorded by using a Finnigan 4000 GC/MS system and a Varian Associates M-66 spectrometer.

General Procedure for the Conversion of Phenols to Quinones. This procedure will be illustrated by using 2,6-dimethylphenol. The other phenol oxidations listed in Table I can be accomplished by using exactly the same procedure. 2,6-Dimethylphenol (30 g, 0.25 mol) was dissolved in 350 mL of ether and placed in a 2-L round-bottomed flask fitted with an overhead stirrer and an addition funnel. The reaction vessel was immersed in an ice-water bath, and the addition funnel was charged with Jones reagent, produced from $Na_2Cr_2O_7{\cdot}2H_2O$ (165 g, 0.5534 mol), 105 mL of 96% H_2SO_4, and 235 mL of H_2O. Addition required approximately 2.5 h. After the addition, the reaction mixture was allowed to stir for at least 24 h. The reaction mixture was washed with ether (4 × 200 mL), and the combined ether extracts were washed with saturated $NaHCO_3$ solution (2 × 100 mL) and with water (200 mL). The ether layer was dried over $MgSO_4$ and concentrated in vacuo to yield 2,6-dimethylbenzoquinone: 28.1 g (84%); mp 44–46 °C (lit. mp 45–47 °C); ^1H NMR ($CDCl_3$) 6.55 (s, 2), 2.00 (s, 6); mass spectrum, *m/e* 136.

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Registry No. **1**, 576-26-1; **2**, 527-61-7; **3**, 95-87-4; **4**, 137-18-8; **5**, 128-39-2; **6**, 719-22-2; **7**, 527-35-5; **8**, 527-17-3; **9**, 89-83-8; **10**, 490-91-5; **11**, 526-75-0; **12**, 526-86-3; 2-methoxyphenol, 90-05-1.

Reaction of Activated Aryl and Heteroaryl Halides with Hexamethylphosphoramide[1]

John T. Gupton,* John P. Idoux,* Graeme Baker,
Cesar Colon, A. Donald Crews, Cindy D. Jurss, and
Richard C. Rampi

*Department of Chemistry, University of Central Florida,
Orlando, Florida 32816*

Received October 25, 1982

The use of hexamethylphosphoramide (HMPA) to effect N,N-dimethylation of an aromatic substrate via aromatic nucleophilic substitution has captured the interest of several groups of workers.[1-4] For example, the reaction of HMPA with substituted nitro-[1-3] and cyanobenzenes[1,3] and the reaction of HMPA with several activated haloheteroaryl compounds[4] have been reported. Because of the synthetic usefulness demonstrated by these various reports, we have extended our investigation[1] of the aromatic nucleophilic substitution reaction of HMPA and report here our findings of the effect of various aryl and heteroaryl activating groups as well as the effect of various leaving groups. The activated aryl and heteroaryl substrates that we have studied to date are reported in Tables I and II, respectively.

As indicated in entries **a**–**h** in Table I, the nitro and cyano groups are very effective in activating the benzene ring toward reaction with HMPA. Ortho or para substitution appears to be necessary to make such transformations synthetically useful. Electron-releasing groups appear to deactivate this reaction as exemplified by the higher reaction temperature and longer reaction time required for the conversion of 1-chloro-4-methyl-2-nitrobenzene (entry **e**, Table I) to 2-nitro-4-methyl-*N*,*N*-dimethylaniline.

Another group that effects such a transformation is the trifluoromethyl (entry **i**, Table I), albeit in low yield. The reaction is, however, very clean and the starting material can be easily separated from the product by acid extrac-

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