Oxidation of Halophenols and Highly Substituted Phenols with Lead(IV) Acetate

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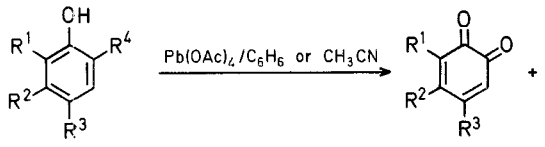
A complex mixture of products is obtained upon oxidation of phenols with lead(IV) acetate[1,2,3]. Very rarely can the method be utilized for synthetic purposes when phenols are substrates. In connection with an extended study on the pathways of aromatic oxidation[4-8], we became interested in optimization of reaction conditions in order to obtain good yields of products. We have restricted ourselves to halophenols and highly substituted phenols to minimize the formation of polymeric and oligomeric products.

We find that the product distribution (in contrast to literature reports[3]) is solvent dependent. In a less polar medium such as benzene, the product formed is predominantly *ortho*. In acetonitrile, although the predominant product is still *ortho*, the disparity between isomer distribution is narrowed (Table); clearly, the reaction of phenols with lead(IV) acetate takes place by at least two independent pathways. The results are given in the Table.



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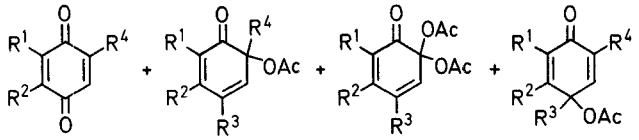

3 4 5 6

R^1, R^2, R^3, R^4 = Cl, Br, alkyl
or R^1 R^2 = —CH—CH—CH=CH—;

Reactions observed:
R^2, R^4 = Cl or Br, **1→2+3;**
R^3, R^4 = alkyl, **1→4;**
R^3 = H, R^4 = alkyl, **1→3+4;**
R^3 = alkyl, R^4 = H, **1→5+6.**

Oxidation of 2,4-Dichloro-1-naphthol (1b); Typical, Small-Scale Procedure:

A solution of 2,4-dichloro-1-naphthol (**1b**; 426 mg, 2 mmol) in benzene (25 ml) is mixed with lead(IV) acetate (1.77 g, 4 mmol). The heterogeneous solution is stirred with exclusion of atmospheric moisture for 10 h at room temperature. The reaction mixture is then poured into water (100 ml) and extracted with ether (2 × 100 ml). The ether extracts are dried with anhydrous sodium sulphate and the solvent evaporated. The products are separated by T.L.C. of the residue on silica gel, using 1:2 chloroform/hexane to give *4-chloro-1,2-naphthoquinone* **(2b);** yield: 305 mg (84%); m.p. 132–134 °C; R_f: 12, and *2-chloro-1,4-naphthoquinone* **(3b);** yield: 43 mg (11%); m.p. 117 °C; R_f: 11.

Oxidation of 2,4-Dibromo-1-naphthol (1a); Typical Procedure:

A solution of 2,4-dibromo-1-naphthol (**1a**; 5 g, ~17 mmol) in benzene (100 ml) is added to lead(IV) acetate (14.6 g, 33.2 mmol). The heterogeneous mixture is stirred with exclusion of atmospheric

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Table. Oxidation of Phenols with Lead(IV) Acetate using Benzene or Acetonitrile as Solvent

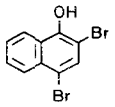
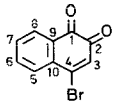
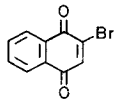
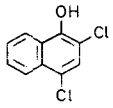
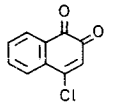
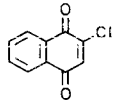
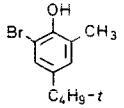
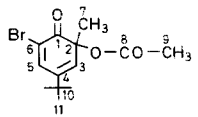
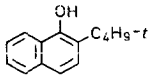
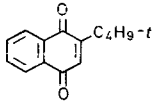
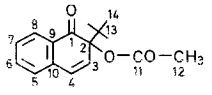
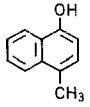
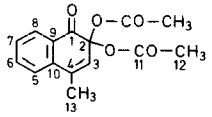
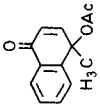
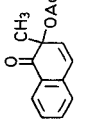
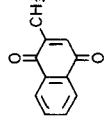
Substrate		Products[a]		Yield [%] in C_6H_6	Yield [%] in CH_3CN	m.p. [°C]	Molecular formula[b] or Lit. m.p. [°C]	I.R. (nujol) ν [cm^{-1}]	^{1}H-N.M.R. ($CDCl_3$) δ [ppm]	^{13}C-N.M.R. ($CDCl_3$) δ [ppm]
1a		**2a**		81	60	136–138°	150°[9]	1680, 1665	7.0 (s, 1H); 7.4–8.2 (m, 4H)	129.7 (dd, C-6); 130.7 (dd, C-7); 131.9 (dd, C-5); 132.1 (s + dd, C-10 + C-3); 133.5 (s, C-9); 135.8 (dd, C-8); 145.4 (s, C-4); 179.1 (s, C-1, 2)
		3a		12	34	129°	130°[10]	—	—	—
1b		**2a**		84	63	135–136°	132–136°[11]	—	—	—
		3a		11	27	117°	117°[12]	—	—	—
1c		**4c**		90	49	117–118°	$C_{13}H_{17}BrO_3$ (301.1)	1735, 1690	1.15 (s, 9H); 1.4 (s, 3H); 2.08 (s, 3H); 5.91 (d, 1H, J = 2.6 Hz); 7.5 (d, 1H, J = 2.6 Hz)	20.3 (q, C-9); 24.2 (q, C-7); 28.8 (q, C-11); 34.1 (s, C-10); 79.1 (s, C-2); 122.9 (s, C-6); 133.1 (d, C-3); 142.4 (s, C-4); 143.3 (d, C-5); 169.1 (s, C-8); 191.6 (s, C-1)
1d		**3d**		62	70	77°	76–77°[13]	—	—	—
		4d		20	14	125°	$C_{16}H_{18}O_3$ (258.3)	1735, 1680	0.95 (s, 9H); 2.06 (s, 3H); 5.97 (d, 1H, J = 10 Hz); 6.65 (d, 1H, J = 10 Hz); 7.1–7.5 (m, 3H); 7.93 (dd, 1H)	20.6 (q, C-12); 24.6 (q, C-14); 39.4 (s, C-13); 84.8 (s, C-2); 126.5 (dd, C-5); 127.5 (d + dd, C-3, 6); 128.2 (dd, C-7); 131.8 (s, C-10); 133.2 (dd, C-8); 134.1 (d, C-4); 137.5 (s, C-9); 169.7 (s, C-11); 196 (s, C-1)
1e		**5e**		52	21	170–171°	$C_{15}H_{14}O_5$ (274.3)	1750, 1692	2.08 (s, 6H); 2.25 (d, 3H); 5.98 (q, 1H); 7.4–7.7 (m, 3H); 8.09 (dd, 1H)	19.5 (q, C-13); 20.5 (q, C-12); 93.7 (C-2); 122.9 (d, C-3); 125.2 (dd, C-5); 126.8 (dd, C-6); 128.9 (dd, C-7); 130.5 (s, C-10); 133.9 (dd, C-8); 136.0 (s, C-4); 138.0 (s, C-9); 168.2 (s, C-11); 188.7 (s, C-1)

Table. (Continued)

Substrate	Products[a]	Yield [%] in C_6H_6	Yield [%] in CH_3CN	m.p. [°C]	Molecular formula[b] or Lit. m.p. [°C]	I.R. (nujol) ν [cm^{-1}]	^{1}H-N.M.R. ($CDCl_3$) δ [ppm]	^{13}C-N.M.R. ($CDCl_3$) δ [ppm]
	6e 	40	70	95–96°	$C_{13}H_{12}O_3$ (216.2)	1740, 1670	1.68 (s, 3H); 2.06 (s, 3H); 6.3 (d, 1H, J = 12 Hz); 6.9 (d, 1H, J = 12 Hz); 7.2–7.6 (m, 3H); 8.1 (dd, 1H)	21.3 (q, C-12); 30.5 (q, C-13); 74.9 (s, C-4); 124.0 (dd, C-5); 127.0 (dd, C-6); 127.5 (d, C-3); 128.0 (dd, C-7); 130.2 (s, C-10); 133.2 (dd, C-8); 145.0 (s, C-9); 150.2 (d, C-2); 169.1 (s, C-11); 184.0 (s, C-1)
	**4f** 	88	74	semi-solid	$C_{13}H_{12}O_3$ (216.2)	1740, 1690	1.4 (s, 3H); 2.05 (s, 3H); 5.99 (d, 1H, J = 10 Hz); 6.55 (d, 1H, J = 10 Hz); 7.2–7.5 (m, 3H); 8.03 (dd, 1H)	20.8 (q, C-12); 24.4 (q, C-13); 78.6 (s, 2H); 125.7 (dd, C-5); 127.6 (dd, 6H); 128.0 (d, C-3); 128.4 (dd, C-7); 130.0 (s, C-10); 135.2 (dd, C-8); 135.6 (d, C-4); 138.0 (s, C-9); 170.8 (s, C-11); 197.8 (s, C-1)
	3f 	3	16	104°	105–107°[14]	—	—	—

[a] The products were identified by N.M.R., I.R., and mass spectra, and isolated by preparative T.L.C. (silica gel, chloroform/hexane, 1:2). The new compounds were crystallised from benzene/hexane.

[b] The microanalyses were in satisfactory agreement with the calculated values (C ±0.43, H ±0.34); exception: **4f**, C −0.53%.

moisture for 10 h at room temperature, then filtered, and the residue washed with ether (2 × 50 ml). The combined filtrate and washings are treated with water (150 ml), and extracted with ether (2 × 150 ml). The ether extract is dried with sodium sulphate and the solvent evaporated. The products are separated by column chromatography (150 cm × 40 mm) on silica gel (160 g), using 1:2 chloroform/hexane as eluent. The first yellow-coloured fraction (80 ml) is evaporated and the residue recrystallised from ethanol to give *2-bromo-1,4-naphthoquinone* **(3a)**; yield: 0.48 g (12%); m.p. 129–130 °C. The second fraction (600 ml) is evaporated and the residue recrystallised from benzene/hexane to give *4-bromo-1,2-naphthoquinone* **(2a)** as red crystals; yield: 3.2 g (81%); m.p. 136–138 °C.

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