a small amount of insoluble polymer was formed during polymerization. The insoluble product may be originated from the cross-linking by the activated allyl protons of polymer. The inherent viscosities were in the range of 0.07-0.12 dl/g. These low viscosities indicate that the poly(PPB) had a relatively low molecular weight.

The resulting poly(PPB) was also hygroscopic as like with that of monomer PPB. The IR spectrum of poly(PPB) showed neither the acetylenic carbon-carbon stretching frequency (2125 cm^{-1}) nor the acetylenic $\equiv$C-H stretching frequency (3225 cm^{-1}). Instead the carbon-carbon double bond stretching frequency in the polymer backbone was observed at 1627 cm^{-1} with the characteristic peaks of pyridine moiety. The UV-visible spectrum of poly(PPB) exhibited the characteristic broad absorption peak (up to 600 nm) which is originated from the $\pi{\rightarrow}\pi^*$ transition of the conjugated polyene. ^{1}H-NMR spectrum of poly(PPB) showed the pyridyl and vinyl protons at 6.8-10.1 ppm and the methylene protons at about 5.3 ppm. The ^{13}C-NMR spectrum of poly(PPB) did not show the acetylenic carbon peaks (63, 82 ppm), instead the carbon-carbon double bond and pyridyl peaks in the polymer were observed at 121-147 ppm.

In conclusion, a new conjugated polyelectrolyte having pyridine moiety was synthesized in a moderate yield by palladium and platinum chlorides. A more description of poly (PPB) and other derivatives on electrical and gas permeation properties will be discussed elsewhere.

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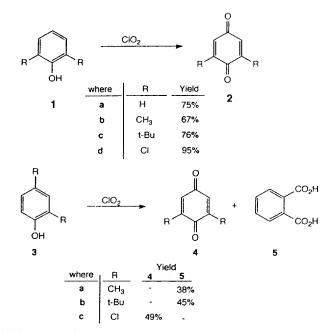
Oxidation of Phenols and Naphthols with Chlorine Dioxide

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Quinones are versatile starting materials in the synthesis
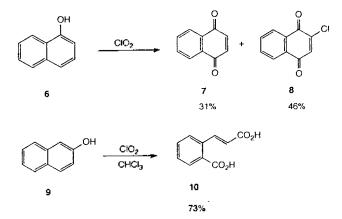

Scheme 1. Oxidation of phenols with chlorine dioxide.

of many important natural products and are particularly useful as dienophiles in Diels-Alder reactions. Quinones may be produced in high yield by the oxidation of phenols and aromatic amines with Fremy's salt[1] or various oxidants[2]. Even though o-arylhydroxylamines are easily oxidized to the corresponding quinones, preparation of o-hydroxyamines meet a difficulty of contamination of side products. As a consequence, many o-arylhydroxylamines are not always readily available as starting materials.

On the other hand aromatic phenols are readily available and are usually quite inexpensive. However the two best reagents (*i.e.*, Fremy's salt and thallium nitrate) for the oxidation of these substrates are relatively expensive and those oxidants are only soluble in aqueous or semiaqueous solution. Even though some successful attempts[3] to oxidize hydrophobic phenols to quinones with Fremy's salt in a two-phase ether-water mixture using phase transfer catalysts are reported, most oxidations are only carried out in aqueous solution.

We report here a simple method for the oxidation of phenols and naphthols to the corresponding quinones and the various interesting products such as phthalic acid and 2-carboxycinnamic acid by chlorine dioxide. Chlorine dioxide has been used as a germicide for drinking water,[4] and has found extensive use in the destruction[5] of certain chemicals including phenols, but has not been studied extensively on the oxidation of phenols and naphthols. Chlorine dioxide is a yellow gas radical which is produced[6] by the reaction of aqueous potassium persulfate and aqueous sodium chlorite. Air or nitrogen passed through the solution to carry the generated chlorine dioxide to the point of use. Oxidations are carried out in organic solvents[7] such as chloroform and THF as well as semiaqueous solution. pH effects on the oxidation are investigated using buffer in semiaqueous solution.

2,6-Disubstituted phenols such as 2,6-dimethyl, 2,6-di-*tert*-butyl, and 2,6-dichlorophenol as well as phenol as shown in Scheme 1 are oxidized into the corresponding quinones

Scheme 2. Oxidation of naphthols with chlorine dioxide.

Table 1. % Yield of the Oxidation Products with ClO_2 in Various Solvents

Products	DMF	THF	CHCl₃	Acetone	Acetone/Buffer (pH)*			
					4.2	7.1	9.3	10.3
2a	35%	40%	—ᵃ	15%	44%	70%	75%	63%
2b	32%	35%	—ᵃ	—ᵃ	36%	63%	67%	30%
2c	18%	21%	30%	—ᵃ	58%	72%	76%	68%
2d	—ᵃ	35%	—ᵃ	38%	91%	95%	72%	50%
4c	—ᵃ	—ᵃ	—ᵃ	—ᵇ	—ᵃ	49%	40%	—ᵃ
5a	—ᶜ	—ᶜ	—ᶜ	—ᶜ	38%	30%	42%	—ᵃ
5b	—ᶜ	—ᶜ	—ᶜ	—ᶜ	45%	41%	40%	—ᵃ
7	12%	17%	20%	22%	9%	11%	31%	—ᵃ
8	27%	31%	28%	37%	46%	35%	35%	—ᵃ
10	—ᵃ	—ᵈ	73%	—ᵃ	—ᵈ	—ᵈ	—ᵈ	—ᵈ

ᵃNot tried. ᵇMixtures of 4c and uncharacterized products. ᶜMixtures of trace amounts of 3,5-dialkylated-o-benzoquinone, quinone dimers and uncharacterized products. ᵈDid not detect oxidized products.

*Commercial products used, pH indicate pH of buffer solution, acetone to buffer=1:1 (v/v), every reaction carried out under the ice bath.

with the treatment of chlorine dioxide in acetone-buffer solution under the ice bath. 2,6-Dichlorophenols are most easily oxidized as a 2,6-dichloro-p-benzoquinone in 95% yield. 2,6-Dimethylphenol, 2,6-di-tert-butylphenol and phenol gave a moderate yield in about 70%. But 2,4-disubstituted phenols produced a variety of several products including phthalic acid, 2,6-disubstituted para benzoquinone and several uncharacterized substances. For example, the treatment of 2,4-dimethyl-, and 2,4-di-tert-butylphenol with chlorine dioxide produced unidentified yellow materials and a phthalic acid. Mechanistic pathway for the formation of phthalic acid from 2,4-dialkyl phenols has not been speculated at this point but obviously oxidation as well as rearrangement did occur during the reaction period. Phthalic acid was obtained in about 40% yield from the oxidation of 2,4-dimethylphenol as well as 2,4-di-tert-butylphenol. Treatment of 2,4-dichlorophenol with chlorine dioxide produced 2,6-dichloro-p-benzoquinone in about 50% yield instead of 2,4-dichloro-o-benzoquinone. Chlorine rearrangement or chlorine cleavage followed by chlorination[8] might occur during the reaction process but not known at this moment.

Naphthols were treated with chlorine dioxide under the similar reaction conditions applied for phenol oxidation in Scheme 2. 1-Naphthols produced two products such as 31% of 1,4-naphthoquinone, and 46% of 2-chloro-1,4-naphthoquinone. Chlorinated naphthoquinone indicate that chlorination might be followed after oxidation of naphthol. But variation of reaction condition such as reaction time and the amount of chlorine dioxide did not much change the ratio of the reaction products, suggesting that chlorination as well as oxidation might occur simultaneously. On the other hand treatment of 2-naphthol with chlorine dioxide in chloroform yielded a clean ring cleaved 2-carboxycinnamic acid in 73% yield. 2-Carboxycinnamic acid has been prepared by the oxidation of 2-naphthol with peracetic acid[9] and 1,2-naphthoquinone with perbenzoic acid[10] followed by acid hydrolysis, but the present method could be one of the easiest way preparing a 2-carboxycinnamic acid without contamination with various naphthoquinones.

Most phenol oxidants such as Fremy's salt and thallium nitrate are only soluble in aqueous or semiaqueous solution, but chlorine dioxide can be soluble in both aqueous and organic solvents such as acetone, chloroform, and even hexane. For example 2-naphthol oxidation to 2-carboxycinnamic

acid was conducted in chloroform, on the other hand, 2,6-disubstituted phenols were oxidized in acetone/buffer mixture. Table 1 summarized the % yield of the oxidation products in the various solvents. Phenols were oxidized most effectively with chlorine dioxide under the acetone-buffer solution. On the other hand, 2-naphthol was oxidized in chloroform to 2-carboxycinnamic acid but in the aqueous solution any oxidized products were not obtained. Yield of the products may vary depending on the pH of buffer but the best results were obtained under the neutral pH. Organic solvents have been used most successfully on the oxidation of hydrophobic phenols such as "calixarene" to calixquinone with chlorine dioxide[6].

Experimental

Generation of Chlorine Dioxide. Chlorine dioxide was produced by mixing of 100 ml of 4% aqueous potassium persulfate and 50 ml of 16% aqueous sodium chlorite into a 250 ml 3-neck flask. Air or nitrogen passed through this solution carried the generated chlorine dioxide to the point of use. When a pure solution of chlorine dioxide was to be prepared the gas stream was passed for about a half hour through a tube into a dark bottle filled solvent well chilled in an ice bath to minimize the loss of chlorine dioxide to the atmosphere.

Oxidation of Phenol. To a solution of 0.30 g of phenol in 10 ml acetone and 10 ml of pH 9.3 buffer, chlorine dioxide was passed through under the ice bath. After 1 h 100 ml of water added and extracted with chloroform. Evaporation of chloroform left a reddish oil which was purified by the column chromatography (eluent, chloroform : hexane = 1 : 1) to give 0.26 g (75%) of yellow p-benzoquinone 2a. mp. 111-113°C (lit. 114.5°C)[11]. ¹H-NMR (CDCl₃) δ6.95 (s, 4H, ArH), IR (KBr) 1650, 1595 cm⁻¹.

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Oxidation of 2,6-Dimethylphenol. 2,6-Dimethyl-*p*-benzoquinone **2b** was prepared in 63% yield following the above reaction procedure in acetone and pH 7.1 buffer. mp. 69-72°C (lit. 70-71°C)[12]. ^{1}H-NMR (CDCl₃) δ 6.55 (s, 2H, ArH), 2.05 (s, 6H, CH₃), IR (KBr) 1651, 1614 cm⁻¹.

Oxidation of 2,6-Di-*tert*-Butylphenol. 2,6-Di-*tert*-butyl-*p*-benzoquinone **2c** was prepared in 76% yield following the above precedure in acetone and pH 9.3 buffer. mp. 64-66°C (lit. 65-66°C)[12]. ^{1}H-NMR (CDCl₃) δ 6.50 (s, 2H, ArH), 1.25 (s, 18H, CH₃), IR (KBr) 1655, 1599 cm⁻¹.

Oxidation of 2,6-Dichlorophenol. To a solution of 0.30 g of 2,6-dichlorophenol in 10 m*l* acetone and 10 m*l* of pH 7.1 buffer, chlorine dioxide was passed through under the ice bath. The reaction was completed in 1.5 hr by the TLC. 100 m*l* of water added to the reaction mixture to facilitate the crystallization. The bright yellow needle product (0.3 g, 95% yield) was collected by the filtration. mp. 124-125°C (lit. 120-121°C)[13]. ^{1}H-NMR of **2d** (CDCl₃) δ 7.01 (s, 2H, vinyl proton from quinone). IR (KBr) 1701, 1649 cm⁻¹. Mass (EI) 176.

Oxidation of 2,4-Dimethylphenol. To a solution of 0.24 g of 2,4-dimethylphenol in 30 m*l* of acteone and pH 4.2 buffer, chlorine dioxide was passed through under the ice bath. After 30 min 100 m*l* of water was added and extracted with chloroform. Solvents was removed by the rotary evaporator to leave yellow oil which was triturated with hexane to yield 0.10 g (38%) of white crystal of phthalic acid **5**. The yellow product was separated by the column chromatography but failed to identify. mp. of **5**; 205-206°C dec. (lit. 210°C dec)[14]. ^{1}H-NMR of **5** (DMSO-d₆) δ 12.0-14.0 (br.s, 2H, OH), 7.54-7.68 (m, 4H, ArH), IR of **5** (KBr) 3000, 2654, 2526, 1691, 1585 cm⁻¹. Mass of **5** (EI) 166.

Oxidation of 2,4-Di-*tert*-Butylphenol. Following the reaction sequence described above, 45% of phthalic acid was prepared by the treatment of 2,4-di-*tert*-butylphenol with chlorine dioxide.

Oxidation of 2,4-Dichlorophenol. To a solution of 0.30 g of 2,4-dichlorophenol in 30 m*l* of acetone and 30 m*l* of pH 7.1 buffer, chlorine dioxide was passed through under the ice bath for 1 h. Following the usual work-up procedure 0.16 g (49%) of bright needle (which was identified as 2,6-dichloro-*p*-benzoquinone) was obtained after the column chromatography (eluent, chloroform : hexane=7 : 3).

Oxidant of 1-Naphthol. To a solution of 0.30 g of 1-naphthol in 40 m*l* acetone, chlorine dioxide was passed through under the ice bath for 1.5 h. Evaporated the solvents and the residue was purified by the column chromatography (eluent, chloroform : hexane=4 : 6) to yield 0.12 g (37%) of 2-chloro-1,4-naphthoquinone **8** and 0.07 g (22%) of 1,4-naphthoquinone **7**. mp. of **7**; 126-128°C (lit. 124-125°C)[11]. ^{1}H-NMR of **7** (CDCl₃) δ 8.02 and 7.75 (m, 4H, ArH from aromatic), 6.95 (s, 2H, vinyl proton from quinone). IR of **7** (KBr) 1660, 1600 cm⁻¹. Mass spectrum of **7** (EI) 158. mp. of **8**; 114-116°C (lit. 112-115°C)[14]. ^{1}H-NMR of **8** (CDCl₃) δ 8.18, 8.10 and 7.80 (m, 4H, ArH from aromatic), 7.24 (s, 1H, vinyl proton from quinone). IR of **8** (KBr) 1670 and 1600 cm⁻¹. Mass spectrum of **8** (EI) 192.

Oxidation of 2-Naphthol. To a solution of 0.30 g of 2-naphthol in 20 m*l* chloroform, chlorine dioxide was passed through under the ice bath for 1 h. The white precipitate formed was collected by the suction filtration to yield 0.16

g (73%) of 2-carboxycinnamic acid **10** exclusively. mp. 213-215°C (lit. 217-219°C)[9]. ^{1}H-NMR (DMSO-d₆) δ 12.8 (s, 2H, OH), 8.35 and 6.45 (pair of d, 2H, -CH=CH-), 7.90 (d, 1H, ArH), 7.85 (d, 1H, ArH), 7.65 (t, 1H, ArH), 7.55 (t, 1H, ArH). ^{13}C-NMR (DMSO-d₆) δ 168.01 and 167.28 (-CO₂H), 142.46, 134.76, 132.04, 130.89, 130.22, 129.62, 127.65, and 121.23 (ArH and vinyl carbons). IR (KBr) 2997, 1683, 1626, 1278 cm⁻¹. Mass spectrum (EI) 192.

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Photoaddition of *p*-Quinones to 1,4-Diethynyl-benzenes

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Quinones are an important class of compounds in organic synthesis, in industry, and in Nature.[1] Due to their various