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Sodium Hypochlorite/Dowex 1X8-200: an Effective Oxidant for the Oxidation of Aromatic Amines to Quinones†

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Polymer supported hypochlorite ion is a useful oxidant for the oxidation of aromatic amines to the corresponding quinones.

Organic reactions on supported reagents have received recently considerable attention from synthetic chemists because of their high efficiency, environmental safety and convenient work up procedures.[1–3] Polymer supported reagents have emerged as a complementary approach to *solid* phase organic synthesis.[4,5] Reagents supported on insoluble polymers are particularly convenient for solving many problems in organic chemistry.[6–8]

Sodium hypochlorite is a readily available and inexpensive oxidant and has been used for the oxidation of variety of compounds.[9] Unfortunately, the traditional NaClO oxidation methods in this transformation are limited by the very low solubility of NaClO in most organic solvents. In order to overcome this limitation, milder NaClO oxidation methods such as oxidation under phase transfer catalyst have been developed.[10,11] However these methods possess disadvantages, *e.g.*, long reaction times, high temperatures and use of expensive polar aprotic solvents.

We have now found that it is possible to obtain in a simple way a polymer supported ClO^- reagent for the oxidation of aromatic amines to quinones utilizing a commercial anion exchanger resin.

Oxidation of aromatic amines to quinones is an important reaction in organic chemistry and a variety of oxidizing reagents such as potassium dichromate,[12] potassium nitrosodisulfonate,[13] ferric chloride,[14] sodium nitrate,[15] silver oxide and lead dioxide,[16] lead tetraacetate[17] and hydrogen peroxide[18] have been developed. Most of the reported reagents require vigorous conditions,[12,13,15] some require tedious work up,[17] give low yields[15,16] or long reaction times.[14,19]

We report here the use of hypochlorite ion on Dowex 1X8-200 as an inexpensive alternative for oxidation of aromatic amines with total selectivity to the corresponding quinones. Table 1 lists a variety of aromatic amines oxidized with supported ClO^- on Dowex 1X8-200 anion exchanger resin to the corresponding quinones.

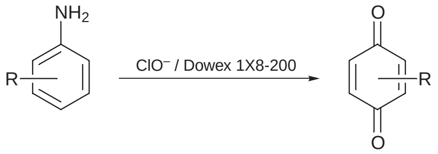
Experimental

All melting points are uncorrected. IR spectra were recorded (KBr) on an FT-IR Unicam Mattson 1000 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker AC-80 (80 MHz) spectrometer in $CDCl_3$ and chemical shifts are indicated in δ. Chemicals were purchased from Merck, Aldrich and Riedel AG and were used without further purification. All products are known compounds and were identified by their mp, IR and ^{1}H NMR spectroscopic properties. All yields refer to isolated products.

Preparation of ClO^- Supported on an Anion Exchanger Resin.—To prepare the reagent, 55 g of the chloride form of Dowex 1X8-200, a macroreticular anion exchanger resin containing quaternary ammonium group, was added under stirring to a 200 ml solution of 1.85 M NaOCl. Chloride ions were readily displaced and the ClO^- form of the resin was qualitatively obtained in 2 h. The resin was then successively rinsed with water, acetone and absolute ethanol and finally dried *in vacuo* at 65 °C for 5 h. The capacity of the resin was determined by stirring 1.0 g of the resin overnight with 20 ml of 2 M aqueous potassium hydroxide, filtering off and titrating iodometrically. In the obtained hypochlorite solution, the determined average capacity of the dried resin was 2.2 mmol ClO^- g^{-1} of resin.

Oxidation of Aromatic Amines into Quinones: General Procedure.—Aromatic amine (2 mmol) and the dry ClO^- form of the resin (1.5 g) were refluxed in 25 ml of dry tetrahydrofuran under vigorous stirring for 30 min, then the reaction mixture was filtered through a sintered glass and the filtrate concentrated and worked up

Table 1 Oxidation of aromatic amines to quinones



Amine	Product	Mmol substrate: g resin	Solvent	Reaction time/min	Yield(%)
Aniline	1,4-Benzoquinone	1:1.5	Tetrahydrofuran	30	88
2-Toluidine	2-Methyl-5-benzoquinone	1:2	Tetrahydrofuran	30	93
3-Chloroaniline	2-Chloro-1,4-benzoquinone	1 : 1.8	Tetrahydrofuran	45	85
1,2-Phenylenediamine	1,2-Benzoquinone	1:2	Dichloromethane	150	95
2-Aminophenol	1,2-Benzoquinone	1:2	Ethyl acetate	150	91
4-Aminophenol	1,4-Benzoquinone	1 : 2	1,2-Dimethoxyethane	45	97
2-Toluidine	2-Methyl-1,4-benzoquinone	1:1.5	Tetrahydrofuran	30	95
1-Aminonaphthalene	1,4-Naphthoquinone	1:1.8	1,2-Dimethoxyethane	45	90
1-Amino-2-naphthole	1,2-Naphthoquinone	1:2	1,2-Dimethoxyethane	150	89
1-Amino-4-naphthole	1,4-Naphthoquinone	1 : 2	1,2-Dimethoxyethane	85	93

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with 1 M hydrochloric acid. Flash chromatography (hexane–ethyl acetate 8 : 2 v/v. gave the corresponding quinone.

(i) 1,4-*Benzoquinone*: yellow solid, mp 114–116 °C (lit.[20] 115–117 °C), IR(KBr) 3060, 1680, 1658, 1600, 1570, 1510 cm^{-1}, δ_H ($CDCl_3$) 6.8(s).

(ii) 1,2-*Benzoquinone*: red–purple solid, decomposed at 60 °C (lit.[20] 60–70 °C), IR(KBr) 3050, 2910, 1748, 1688, 1670, 1410, 1292 cm^{-1}.

(iii) 2-*Methyl*-1,2-*benzoquinone*: yellow–purple solid, mp 67–69 °C (lit.[20] 115–117 °C), IR(KBr), 3333, 3030, 1672, 1610, 1447, 1351, 1300 cm^{-1}, δ_H ($CDCl_3$) 2.1(s), 6.6–6.8(m).

(iv) 2-*Chloro*-1,4-*benzoquinone*: yellow–red solid, mp 55–57 °C (lit.[20] 57 °C), IR(KBr) 3050, 1691, 1662, 1590, 1370, 1330, 1290 cm^{-1}, δ_H ($CDCl_3$) 6.9(s), 6.4–6.8(m).

(v) 1,2-*Naphthoquinone*: yellow-red solid, mp 146–148 °C (lit.[20] 146 °C), IR(KBr) 3027, 1669, 1610, 1591, 1560, 1450, 1412 cm^{-1}.

(vi) 1,4-*Naphthoquinone*: yellow solid, mp 127 °C (lit.[20] 128.5 °C), IR(KBr) 3030, 1675, 1610, 1590, 1610, 1485, 1330, 1320 cm^{-1}, δ_H ($CDCl_3$) 7.0(s), 7.7–8.2(m).

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