[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

THE PREPARATION OF QUINONES FROM *p*-AMINOPHENOLS OBTAINED BY ELECTROLYTIC REDUCTION OF AROMATIC NITRO COMPOUNDS

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A previous publication (1) from this laboratory has presented the development of a method for the preparation of *p*-quinones which involves oxidation of aminophenols prepared by electrolytic reduction of aromatic nitro compounds. The preparation of chloroquinone from *o*-chloronitrobenzene was studied for development of the method. The present report is concerned with evaluation of the scope of the method by its extension to several types of quinones. Satisfactory results have been obtained with 1-nitronaphthalene and with a series of aromatic nitro compounds in which the aromatic ring is substituted with low molecular weight alkyl groups or chlorine atoms. Methoxyquinone has been prepared in low yield, but about as satisfactorily as by other methods.

The reductions were carried out essentially as described in the previous publication (1). A cylindrical copper cathode of simple construction was employed, working in a catholyte composed of 75% sulfuric acid diluted with acetic acid. It was found that this electrolyte is a good solvent for most nitro compounds; of the materials used, only 2,5-dichloronitrobenzene and 1-nitronaphthalene were not completely in solution at the concentrations employed. The homogeneity of the catholyte, with the accompanying ease of maintaining a high concentration of nitro compound at the cathode surface, is undoubtedly responsible in part for the success of the method, for the concentration of reducible material is a major factor in maintaining the desired cathode potential. Another significant feature which contributes to the usefulness of the method is the fact that the aminophenols are always in acid solution so that their instability in neutral and alkaline solution is avoided.

When acetic acid was removed from the catholytes by continuous ether extraction, the extracts were always deeply colored, but in only two of the systems studied (6-chloro-2-nitrotoluene and 2,5-dichloronitrobenzene) was it found that sufficient aminophenol was extracted into the ether to warrant recovery.

The optimum temperature for oxidation (*Cf.* Table I) depends upon the stabilities of the various aminophenols and quinones. Stabilization of an aminophenol by halogen has been reported in the preceding paper (1); also it has been previously observed in this laboratory (2) that attempted nitric acid oxidation of 3,4,6-trichloro-*o*-cresol yields 3,4-dichloro-6-nitro-*o*-cresol instead of the quinone whose formation would result from loss of the halogen atom *para* to the hydroxyl group. In some instances, the yield of quinone is lowered seriously by use of an improper temperature for oxidation, and methoxyquinone is rather unstable to the oxidizing medium, even at 0°.

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The isolation procedure found satisfactory for chloroquinone (1) was used without modification for the alkylquinones studied and for 3-chlorotoluquinone. 2,5-Dichloroquinone proves not to steam-distill at a reasonable rate [in contrast with the dichlorotoluquinones (2)]; however, sublimation of the crude material yielded almost pure quinone directly. This same technique was also useful for the isolation of 1,4-naphthoquinone; the procedure described by Fieser (3) was also satisfactory. A sublimer of simple construction that easily handles 10-gram quantities of these quinones has been described (4).

TABLE I

PREPARATION OF *p*-BENZOQUINONES

NITRO COMPOUND	OXID'N TEMP., °C.	QUINONE	YIELD[a], %	MELTING POINTS, °C.		
				crude	cryst.	lit.
NITROBENZENE	5–10	*p*-Benzoquinone	74	110–112	114.6–115.6	116[c]
2-Ethyl-	5–10	Ethylquinone	68	34–36	36.8– 37.6	37[d]
2-Methyl-	5–10	Toluquinone	72	63–66	67.6– 68.4	68–69[e]
3-Methyl-	5–10	Toluquinone	72	63–66	67.6– 68.4	68–69
3-Chloro-2-methyl-	15–20	3-Chlorotoluquinone	65	51–55	54.5– 55.5	54.9–55.8[f]
2-Chloro-	25–35	Chloroquinone	54	53–55	55.5– 56.3	57[g]
3-Chloro-	25–35	Chloroquinone	54	53–55	55.5– 56.3	57
2,5-Dichloro-	55–60	2,5-Dichloroquinone	50[b]	159–160	159.3–160.2	158[g]
2-Methoxy-	0–5	Methoxyquinone	24	144–145	144.6–145.2	144–145[h]
3-Methoxy-	0–5	Methoxyquinone	24	144–145	144.6–145.2	144–145
1-Nitronaphthalene	90	1,4-Naphthoquinone	44[b]	122–124	124.0–124.6	124–125[k]

[a] Pure quinones, crystallized from ethanol (85–90% recovery) except methoxyquinone (benzene-hexane). [b] Sublimed prior to crystallization. [c] Fieser, *Experiments in Organic Chemistry*, 2nd ed., D. C. Heath and Co., New York, 1941, p. 229. [d] Clemmensen, *Ber.*, **47**, 56 (1914). [e] Smith and Irwin, *J. Am. Chem. Soc.*, **63**, 1036 (1941). [f] Cason, Allen, and Goodwin, *J. Org. Chem.*, **13**, 403 (1948). [g] Conant and Fieser, *J. Am. Chem. Soc.*, **45**, 2201 (1923). [h] Dimroth, Eber and Wehr, *Ann.*, **446**, 147 (1926). [k] Fieser, *Org. Syntheses*, Coll. Vol. I, 383 (1941).

The location of the methyl group or the chlorine atom either *ortho* or *meta* to the nitro group appears to have no significant effect on the rates of either reduction or rearrangement of the arylhydroxylamines. Differences in the course of the reactions or in the quinone yields could not be detected. In anticipation of the preparation of alkylquinones from mixtures of *ortho* and *para* nitroalkylbenzenes, a mixture of equal parts of *o*- and *p*-nitrotoluenes was used in one experiment. The presence of the *p*-isomer had no adverse effect on the yield of quinone from the *o*-isomer.

Methoxyquinone was obtained with relative difficulty. When the oxidation was carried out at 5–10° and the mixture allowed to stand at room temperature for an hour before isolation of the quinone only dark, tarry materials were obtained. The difficulty was traced to instability of methoxyquinone to aqueous acid, which appears not to have been reported previously (5). A sample of this

quinone, prepared by the diazonium coupling procedure (6), was transformed into a purple solid by standing for 15 minutes at room temperature in contact with 4 *N* sulfuric acid. For the preparation, best results were obtained by continuous extraction with benzene immediately after oxidation at 0–5°, while the extraction flask was kept in an ice-bath. This procedure gave excellent quinone, although in only 25% yield. It is probable that during the required four-hour extraction much of the quinone undergoes decomposition in the acid medium.

Complete investigation of the isolation of the aminophenols was not carried out; however, by reducing in a vacuum the volumes of the aqueous acid solutions remaining after removal of acetic acid, crystalline aminophenol sulfates were obtained, probably a mixture (7) of the normal and acid salts. Several samples were converted to the quinones in yields (over-all from nitro compounds) similar to those recorded in Table I.

EXPERIMENTAL

All melting points, reported in Table I, are corrected.

The reduction procedure was the same as that previously described as optimum (Ref. 1, cathode "g" and reduction procedure "4"). Any variations in the procedures for oxidation and isolation are described below.

p-Benzoquinone. The aqueous acid solution of the aminophenol, after removal of acetic acid, was oxidized at 5–10° by the slow addition of 11.4 g. (1.5 equiv.) of sodium dichromate dihydrate in 20 ml. of water. After it had stood for two hours at room temperature, the mixture was worked up as described previously (1).

Toluquinone, ethylquinone, and chloroquinone were prepared by the same sequence of procedures described for *p*-benzoquinone, except that chloroquinone was obtained by oxidation at 25–35°.

3-Chlorotoluquinone. The ether extract of the catholyte, containing the acetic acid and a small amount of the aminophenol, was subjected to vacuum-distillation. After most of the solvent had been removed the dark residue was extracted twice with warm 25-ml. portions of 2 *N* sulfuric acid. These extracts were combined with the aqueous solution of the aminophenol, the acid concentration was adjusted to 4 *N*, and the mixture handled as described above for *p*-benzoquinone, except that the oxidation was conducted at 15–20°.

2,5-Dichloroquinone. Since some of the nitro compound tends to crystallize on the walls of the porous cup during the reduction, it was washed into the stirred catholyte occasionally with hot 90% acetic acid.

Appreciable amounts of dichloroaminophenol were extracted into the ether along with the acetic acid. This material was recovered by extraction with 1 *N* sodium hydroxide (two 50-ml. portions) of the dark residue from the distillation in a vacuum of most of the ether and acetic acid. The alkaline aminophenol solution was treated with Norit, filtered, and made slightly acid with 6 *N* sulfuric acid. The resultant suspension of aminophenol was added to the original aqueous acid solution of the aminophenol. After the acid concentration had been adjusted to 4 *N* the mixture was heated to boiling, filtered from a little suspended solid, and oxidized at 55–60° by the addition in one portion of 11.4 g. (1.5 equivalents) of sodium dichromate dihydrate in 20 ml. of water. The crude quinone, which precipitated rapidly as a tan-colored solid, was filtered from the cooled mixture, dried, and sublimed at 20 mm. pressure and 140°. Crystallization of the yellow sublimate from ethanol gave 95% recovery of pure quinone.

1,4-Naphthoquinone. As was the case with the dichloronitro compound, crystallized nitronaphthalene was occasionally washed off the walls of the porous cup, during the reduction, with hot 90% acetic acid. After acetic acid had been extracted from the catholyte as usual the aminophenol solution, which contained some crystalline solid, was diluted to 500

ml. and 10 ml. of concentrated sulfuric acid was added. After this mixture had been boiled for a half hour, at which time most of the solid had dissolved, Norit was added and the mixture filtered hot. The hot solution was immediately poured into an agitated solution of 14.5 g. (2 equiv.) of sodium dichromate dihydrate in 50 ml. of water. As the mixture was allowed to cool with occasional shaking the tacky precipitate changed to a dark granular solid. The dry solid (11.2 g.) was sublimed at 20 mm. and 140° to yield 5.3 g. (46%, over-all) of clean yellow quinone of m.p. 122–124°. Crystallization from ethanol gave 5.1 g. (96% recovery) of pure quinone.

Methoxyquinone. (*a*). After reduction, acetic acid was removed from the catholyte as usual, then the aminophenol solution was cooled to 0° and oxidized with 1.5 equiv. of oxidant as the temperature was kept below 5°. As soon as addition of the oxidant was complete the mixture was placed in the continuous extractor and cooled in an ice-bath during the benzene extraction. After the dark brown extract had been concentrated to about 150 ml. by distillation of the benzene through a 12-inch Vigreux type column, it was passed through a 2 × 15 cm. column containing 20 g. of a mixture of equal parts by weight of Supercel and Norit. The column retained the quinone, which was eluted with benzene to give a clear orange solution. After most of the benzene had been distilled through the Vigreux column an equal volume (20 ml.) of hexane was added to the hot solution. Orange-yellow methoxyquinone (2.6 g.) crystallized from the solution which was cooled in ice. Pure quinone (2.4 g.) was obtained by crystallization from benzene-hexane. Various other methods of isolation failed to yield significant amounts of pure quinone.

(*b*). 3-Methoxy-4-hydroxyazobenzene-4′-sulfonic acid was prepared from 58.3 g. (0.47 mole) of guaiacol by the diazonium coupling procedure as detailed by Smith and co-workers (6). The alkaline solution of the azo dye, after it had been kept overnight to ensure completion of the coupling reaction, was acidified strongly by the addition of one liter of concentrated hydrochloric acid. The slurry of azo dye was filtered after it had been cooled in ice, and the red-brown solid was crystallized from 2500 ml. of water slightly acidified with hydrochloric acid. There was obtained 121.5 g. (79%, calc'd as the monohydrate) of fine dark green irridescent crystals which showed no m.p. but darkened and became opaque at 168°.

The azo dye (16.3 g., 0.05 mole) was dissolved in 110 ml. of 1 *N* sodium hydroxide, and at 70° there was added portionwise during five minutes 21.0 g. (1.2 equiv.) of sodium hydrosulfite. The resulting amber solution (*p*H 7.2) was heated one-half hour on the steam-bath, then cooled in ice for two hours. The light brown crystalline solid was collected and crystallized from about 80 ml. of boiling water containing a little hydrosulfite. There resulted 2.5 g. (36%) of nearly white crystals of 2-methoxy-4-aminophenol, m.p. 165–170° (dec.). Another crystallization from water gave material of m.p. 175–177° (dec.) literature (7), m.p. 176–177° (dec.). Some samples could be purified only after an initial crystallization from toluene (200 ml. per g.).

A solution of 2.15 g. (0.007 mole, 1.5 equiv.) of sodium dichromate dihydrate in 5 ml. of water was added dropwise at 5–10° to a solution of 2.0 g. (0.014 mole) of the aminophenol in 30 ml. of 4 *N* sulfuric acid. The solution was extracted continuously with benzene as described in Method "*a*" above, and the extract was passed through a Supercel-Norit column to yield 1.3 g. of methoxyquinone. An additional crystallization from benzene-hexane gave 1.1 g. (55%) of pure methoxyquinone.

SUMMARY

Satisfactory extension is reported of a previously developed sequence for the preparation of *p*-benzoquinones. The procedure, which involves electrolytic reduction of an aromatic nitro compound, followed by oxidation of the aminophenol, is also satisfactory for preparation of 1,4-naphthoquinone from 1-nitronaphthalene. The general utility, convenience of manipulation, and over-all yields of the method appear to compare favorably with those of any other syn-

thetic approach to *p*-quinones. Preparation of methoxyquinone, by both the electrolytic method and the diazonium coupling procedure, is complicated by the high water-solubility of the quinone, and its instability in acid medium.

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