



A Publication  
of Reliable Methods  
for the Preparation  
of Organic Compounds

## Working with Hazardous Chemicals

The procedures in *Organic Syntheses* are intended for use only by persons with proper training in experimental organic chemistry. All hazardous materials should be handled using the standard procedures for work with chemicals described in references such as "Prudent Practices in the Laboratory" (The National Academies Press, Washington, D.C., 2011; the full text can be accessed free of charge at [http://www.nap.edu/catalog.php?record\\_id=12654](http://www.nap.edu/catalog.php?record_id=12654)). All chemical waste should be disposed of in accordance with local regulations. For general guidelines for the management of chemical waste, see Chapter 8 of Prudent Practices.

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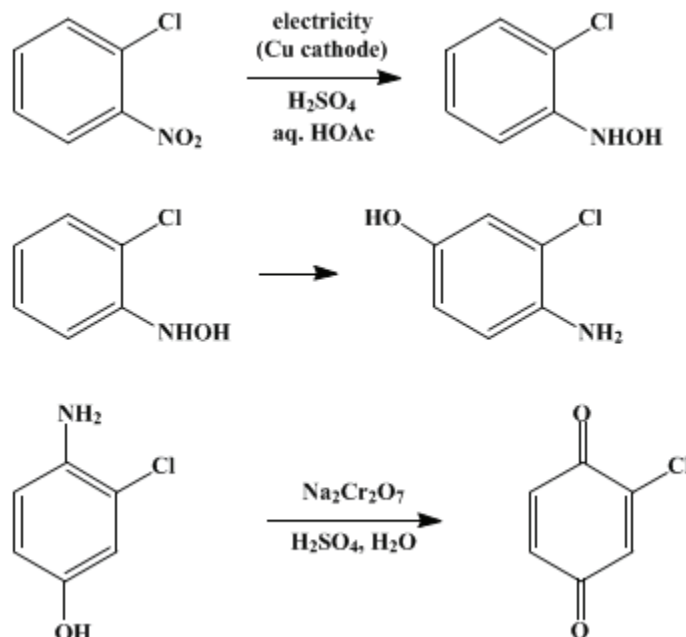
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

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## CHLORO-*p*-BENZOQUINONE

[*p*-Benzoquinone, chloro-]



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Checked by N. J. Leonard and R. W. Fulmer.

### 1. Procedure

A. *Apparatus.* The reduction is carried out in a 400-ml. beaker. The anode, a cylinder of sheet lead 3 in. in height and 2.25 in. in diameter, rests on the bottom of the beaker. Clamped inside the anode and extending almost to the bottom of the beaker is the catholyte chamber, a porous cup (Note 1) 5 in. deep and 1.75 in. in diameter. Clamped securely inside the cup and about 0.25 in. above its inside bottom surface is the cathode, a cylinder of 25-gauge sheet copper 6 in. long and 1.25 in. in diameter. It is provided with a row of seven vertical slots 0.25 in. wide and 1.25 in. long, evenly spaced around its circumference; the lower ends of the slots are about 2.5 in. from the bottom of the cathode (Note 2). Both electrodes are provided with binding posts for connection to the circuit. A stirrer is constructed with two double propeller blades attached to the shaft, one about 1.5 in. above the other, at a pitch that will direct the flow of liquid downward. The mechanically driven stirrer is set to run deep inside the cathode (Note 3).

The current may be drawn from a commercially available battery charger (Note 4) or from a storage battery, each capable of operating at about 6 volts. Experiment has shown that the considerable ripple in the output of the charger has no adverse effect on the reduction. A transformer in the input to the charger, or a variable resistance in the battery circuit, and a 0–3 ampere range d.c. ammeter complete the apparatus.

B. *Reduction of *o*-chloronitrobenzene.* The stirrer is set in position carefully inside the cathode, which is clamped in place at the top. The porous cup, previously impregnated with the electrolyte, is charged with 11.5 g. (0.073 mole) of *o*-chloronitrobenzene (Note 5) and about 80 ml. of a mixture of acetic acid (70 ml.), concentrated sulfuric acid (22 ml.), and water (8 ml.) (Note 6). The cup is then clamped securely in position, and the beaker containing the anode is supported just clear of the bottom of the porous cup and filled with the same solution of aqueous sulfuric and acetic acids to the same level as the liquid inside the cup. The stirrer is started, the current turned on, and the system observed for a

few minutes until the current has become stable. It is then adjusted at some convenient value no greater than 2 amperes.

The temperature will rise slowly and should be maintained at 30–45° throughout the reduction, with cooling as necessary. The system requires no attention while in operation except for occasional inspection and possibly the addition of a few milliliters of 90% [acetic acid](#) to maintain the surface of the catholyte at the desired level ([Note 7](#)).

C. *Oxidation of 4-amino-3-chlorophenol*. When the reduction is complete ([Note 8](#)), the system is disassembled, the catholyte poured into a flask, and the apparatus rinsed with hot water into the same flask. The combined catholyte and washings are extracted with [ether](#) in a continuous-type liquid-liquid extractor to remove the [acetic acid](#) almost completely ([Note 9](#)). The residual aqueous acid solution of the aminophenol ([Note 10](#)) is made up to 4*N* in [sulfuric acid](#) by adding 20 ml. of concentrated [sulfuric acid](#) and diluting with water to 400 ml.

At room temperature there is added in one portion a solution of 11 g. (0.037 mole, 50% excess over the theoretical amount) of [sodium dichromate dihydrate](#) in 20 ml. of water. A rise in temperature of some 6–7° will be observed; it is desirable to moderate the temperature by external cooling if it should rise above 35°.

After the mixture has been allowed to stand at room temperature for at least an hour ([Note 11](#)), a few grams of clean sand is added and the dark red mixture is filtered with suction. The filtrate is extracted with [ether](#) (100 ml., then 4–5 portions of about 30 ml. each), and each extract is used in turn to extract the filter cake.

The [ether](#) extracts are combined; the [ether](#) is removed by distillation ([Note 12](#)), and the dark red tarry residue subjected to steam distillation. Some 40–50 ml. of distillate is collected after solid quinone no longer appears in the condenser (total volume about 150 ml.).

There is obtained by filtration 5.0–5.5 g. (48–53%) of yellow chloro-*p*-quinone of m.p. 53–55°; [ether](#) extraction of the filtrate yields a further 1.0 g., which brings the total yield to 58–63% ([Note 12](#)) and ([Note 13](#)). Crystallization from a small volume of aqueous [ethanol](#) (85–90%) raises the melting point to 55–56°.

## 2. Notes

1. A Norton dense grade Alundum extraction thimble has been found suitable. Deposition of [silicic acid](#) in the interstices of the cup to decrease transfer of material is desirable. This is accomplished by soaking the cup for an hour in 20% water glass, draining off the excess, and then keeping the cup totally immersed for 3 hours in 20% aqueous [sulfuric acid](#).<sup>2</sup> Finally, the cup is stored completely immersed in the electrolyte.
2. This cathode design, with the stirring described, is regarded as preferable to the combination used by Lukens<sup>3</sup> and much simpler in construction. It provides better dispersion of the organic material, a feature which is particularly necessary if these reductions are carried out in aqueous solution ([Note 6](#)).
3. Very rapid and efficient stirring is required to strip the intermediate [o-chlorophenylhydroxylamine](#) from the cathode so that the acid-catalyzed rearrangement to [4-amino-3-chlorophenol](#) may occur rather than reduction of the substituted hydroxylamine to [o-chloroaniline](#).
4. A Battery Booster, type 6-AC-4, manufactured by P. R. Mallory and Company, Inc., Indianapolis, Indiana, gave good service.
5. Material equivalent to Eastman Kodak Company white label grade was used. It has been found that the same results are obtained using [m-chloronitrobenzene](#). Likewise, either *o*- or *m*-nitrotoluene may be used in the preparation of [toluquinone](#) ([Note 13](#)).
6. The submitter states that lower yields of quinones (50–65%) are obtained by using as the electrolyte 75% by weight aqueous [sulfuric acid](#). The catholyte at the end of the reduction is diluted to about 500 ml. (4*N* in [sulfuric acid](#)) and oxidized directly. The low solubility of the nitro compounds in the aqueous acid makes exceedingly efficient stirring a necessity, and the cell must be maintained at 50–60° during the reduction to keep the nitro compound molten and so promote the formation of a fine emulsion. Solid [aminophenol sulfate](#) sometimes crystallizes near the end of the reduction, and evolution of [hydrogen](#)

near the end of the run may force the pasty material out the top of the porous cup. In general, these difficulties are more troublesome than the continuous extraction necessitated by the use of [acetic acid](#) in the catholyte.

7. In operation, a flood of electrolyte should be observable pouring over the lower ends of the slots in the cathode.

8. Complete reduction of the nitro compound is assured by the use of about 1.2 equivalents of current (9.4 ampere-hours), but a larger excess of current is no disadvantage.

9. It has been found satisfactory to continue the extraction for 30 minutes after the volume of the aqueous phase no longer decreases visibly. Saturated aqueous [sodium bicarbonate](#) washes may be used to effect removal of the [acetic acid](#) from [ether](#) solutions of alkyl quinones. The cascade distribution apparatus devised by Kies and Davis<sup>4</sup> is useful for this purpose. As halogenated quinones have been found to be unstable to bicarbonate, the [acetic acid](#) must be removed before oxidation of the corresponding aminophenols.

10. It has been found that the sulfates of the aminophenols may be obtained in yields about the same as those recorded for the quinones by concentrating the aqueous catholytes under reduced pressure after removal of the [acetic acid](#).

11. It is recommended that the oxidation mixture be stored in a refrigerator if more than 6–8 hours must elapse before the work-up is completed.

12. Prolonged heating after removal of the [ether](#) may lead to sublimation of the product, with resulting lower yield.

13. Essentially the same procedure, with alteration only in the temperature during the oxidation, is stated by the submitter to be satisfactory for the preparation of several other *p*-benzoquinones. For [p-benzoquinone](#) itself and for [toluquinone](#) (both in 80% yield) the oxidation is best carried out at 5–10°; for [3-chlorotoluquinone](#) (70% yield), at 15–20°; for [2,5-dichloroquinone](#) (50% yield), at 55–60°. In the last case, some of the weakly basic aminophenol is [ether](#) extracted along with the [acetic acid](#); it may be recovered by distilling most of the [ether](#) and [acetic acid](#) under reduced pressure, extracting the dark residue with two 25-ml. portions of 1*N* [sodium hydroxide](#), and making the alkaline extract neutral or slightly acid with [sulfuric acid](#). Normal oxidation is carried out after combining this suspension of aminophenol with the original aqueous solution.

The low vapor pressure of [2,5-dichloroquinone](#) precludes the use of steam distillation; however, the quinone precipitates directly from the oxidation mixture as a tan solid and may be purified readily by sublimation, followed by crystallization from [ethanol](#). An excellent sublimation apparatus that will easily handle 10-g. quantities of this quinone has been described.<sup>5</sup>

This method has given only 25% yield of [methoxyquinone](#) which is highly sensitive to acid and requires a special isolation procedure.<sup>6</sup>

### 3. Discussion

The present method is the result of a study by Cason, Harman, Goodwin, and Allen.<sup>6,7</sup> The sequence of electrolytic reduction followed by oxidation has been used for the preparation of [5-bromotoluquinone](#),<sup>8</sup> [5-chlorotoluquinone](#),<sup>9</sup> and [3-chlorotoluquinone](#).<sup>10</sup> The preparation of an intermediate [p-aminophenol](#) from the corresponding aromatic nitro compound by electrolytic reduction is a useful general method.<sup>11,12,13,14,15,16,17,18</sup> Chloro-*p*-quinone has been prepared by acid dichromate oxidation of [chlorohydroquinone](#)<sup>19,20,21,22</sup> or [2-chloro-4-aminophenol](#).<sup>23,24</sup> It has been shown that pure chloro-*p*-quinone is obtained only with some difficulty when [chlorohydroquinone](#) is used.<sup>7</sup> [Potassium bromate](#) also has been used to oxidize [chlorohydroquinone](#) to chloro-*p*-quinone.<sup>25</sup>

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### References and Notes

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**Appendix**  
**Chemical Abstracts Nomenclature (Collective Index Number);**  
**(Registry Number)**

o- or m-nitrotoluene

ethanol (64-17-5)

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

ether (60-29-7)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

sodium bicarbonate (144-55-8)

potassium bromate (7758-01-2)

m-Chloronitrobenzene (121-73-3)

o-chloronitrobenzene (88-73-3)

p-benzoquinone (106-51-4)

sodium dichromate dihydrate (10588-01-9)

4-amino-3-chlorophenol

silicic acid (7699-41-4)

toluquinone

aminophenol sulfate

3-chlorotoluquinone

2,5-dichloroquinone

methoxyquinone

5-bromotoluquinone

5-chlorotoluquinone

chlorohydroquinone (615-67-8)

2-chloro-4-aminophenol (3964-52-1)

chlorohydroquinine

p-aminophenol (123-30-8)

o-chloroaniline (95-51-2)

Chloro-p-benzoquinone,  
p-Benzoquinone, chloro- (695-99-8)

o-chlorophenylhydroxylamine