



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.

In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior to performing a reaction, a thorough risk assessment should be carried out that includes a review of the potential hazards associated with each chemical and experimental operation on the scale that is planned for the procedure. Guidelines for carrying out a risk assessment and for analyzing the hazards associated with chemicals can be found in Chapter 4 of Prudent Practices.

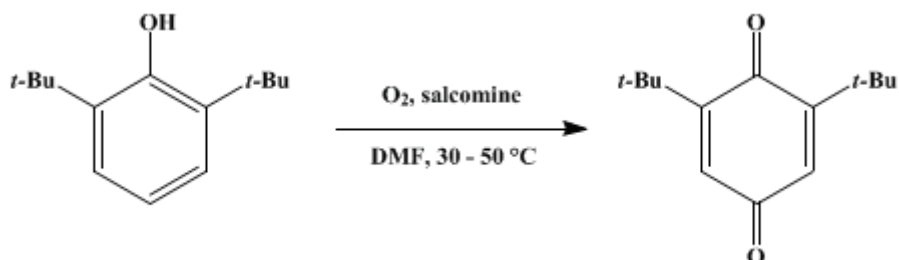
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

*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.*

*Organic Syntheses, Coll. Vol. 6, p.412 (1988); Vol. 57, p.78 (1977).*

**OXIDATION WITH BIS(SALICYLIDENE)  
ETHYLENEDIIMINOCOBALT(II) (SALCOMINE): 2,6-DI-*tert*-  
BUTYL-*p*-BENZOQUINONE**

[2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-]



Submitted by C. R. H. I. De Jonge<sup>1</sup>, H. J. Hageman, G. Hoentjen, and W. J. Mijs.  
Checked by K. Balasubramanian, Robert K. Boeckman, and Carl R. Johnson.

### 1. Procedure

A 200-ml., three-necked flask equipped with a mechanical stirrer, a thermometer, and a gas-inlet tube is charged with 41.2 g. (0.200 mole) of 2,6-di-*tert*-butylphenol (Note 1) in 75 ml. of *N,N*-dimethylformamide (Note 2) and 2.5 g. (0.0075 mole) of salcomine (Note 3). With stirring, oxygen is introduced at such a rate that the temperature does not exceed 50°. This is continued for 4 hours, and at the end of the reaction the temperature drops to about 25°. The reaction mixture is then poured onto 500 g. of crushed ice and 15 ml. of 4 *N* hydrochloric acid. A yellow-brown precipitate is formed, collected by suction filtration, and washed on the filter with three 50-ml. portions of 1 *N* hydrochloric acid, with three 100-ml. portions of water, and twice with 25-ml. portions of cold ethanol. Drying under reduced pressure at 50° for 3 hours gives 43 g. of crude 2,6-di-*tert*-butyl *p*-benzoquinone as a dark-yellow crystalline solid. Recrystallization from ethanol gives 36.5 g. (83%) of pure 2,6-di-*tert*-butyl-*p*-benzoquinone, m.p. 65–66° (Note 4), (Note 5).

### 2. Notes

1. 2,6-Di-*tert*-butylphenol purchased from Aldrich Chemical Company, Inc., was used.
2. When chloroform or methanol is used as the solvent for the oxidation of phenols, other products, originating from coupling of aryloxy radicals, e.g., polyphenylene ethers and/or diphenoquinones, are also formed.<sup>2</sup>
3. Bis(salicylidene)ethylenediiminocobalt(II) can be prepared according to the procedure described in *Inorg. Synth.*<sup>3</sup>
4. 2,6-Di-*tert*-butyl-*p*-benzoquinone should be stored in a brown bottle.
5. The product has the following spectral properties; IR (CHCl<sub>3</sub>) cm.<sup>-1</sup>: 1652, 1597; <sup>1</sup>H NMR (CDCl<sub>3</sub>), δ 1.33, 6.56.

### 3. Discussion

Various 2,6-disubstituted *p*-benzoquinones have been prepared by oxidation of the corresponding 2,6-disubstituted phenols with potassium nitrosodisulfonate<sup>4,5</sup> or lead dioxide in formic acid.<sup>6</sup> Oxidative coupling of 2,6-disubstituted phenols to poly-2,6-disubstituted phenylene ethers followed by treatment of the polymers in acetic acid with lead dioxide is reported<sup>7</sup> to give low yields of the corresponding 2,6-disubstituted *p*-benzoquinones.

Salcomine is a useful catalyst for the selective oxygenation of 2,6-disubstituted phenols to the corresponding *p*-benzoquinones when *N,N*-dimethylformamide is used as the solvent; laborious

procedures are avoided and high yields of pure *p*-benzoquinones are obtained. Following the procedure described above, the authors have prepared 2,6-diphenyl-*p*-benzoquinone (m.p. 134–135°, yield 86%) and 2,6-dimethoxy-*p*-benzoquinone (m.p. 252°, yield 91%) from the appropriate phenols.

---

## References and Notes

1. Organic and Polymer Chemistry Department, Akzo Corporate Research Laboratories, Arnhem, The Netherlands.
  2. H. M. van Dort and H. J. Geursen, *Recl. Travl. Chim. Pays-Bas*, **86**, 520 (1967).
  3. H. Diehl and C. C. Hack, *Inorg. Synth.*, **3**, 196 (1950).
  4. H. J. Teuber and W. Rau, *Chem. Ber.*, **86**, 1036 (1953).
  5. H. J. Teuber and O. Glosauer, *Chem. Ber.*, **98**, 2643 (1965).
  6. C. R. H. I. de Jonge, H. M. van Dort, and L. Vollbracht, *Tetrahedron Lett.*, 1881, (1970).
  7. H. Finkbeiner and A. T. Toothaker, *J. Org. Chem.*, **33**, 4347 (1968).
- 

## Appendix

### Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

BIS(SALICYLIDENE)ETHYLENEDIIMINOCOBALT(II) (SALCOMINE)

salcomine

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

acetic acid (64-19-7)

methanol (67-56-1)

chloroform (67-66-3)

oxygen (7782-44-7)

formic acid (64-18-6)

N,N-dimethylformamide (68-12-2)

Bis(salicylidene)ethylenediiminocobalt(II)

2,5-Cyclohexadiene-1,4-dione, 2,6-bis(1,1-dimethylethyl)-,  
2,6-Di-tert-butyl-*p*-benzoquinone,  
2,6-di-tert-butyl *p*-benzoquinone (719-22-2)

potassium nitrosodisulfonate

2,6-di-tert-butylphenol (128-39-2)

lead dioxide

2,6-diphenyl-p-benzoquinone

2,6-dimethoxy-p-benzoquinone

Copyright © 1921-2005, Organic Syntheses, Inc. All Rights Reserved