Organic Syntheses

A Publication
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for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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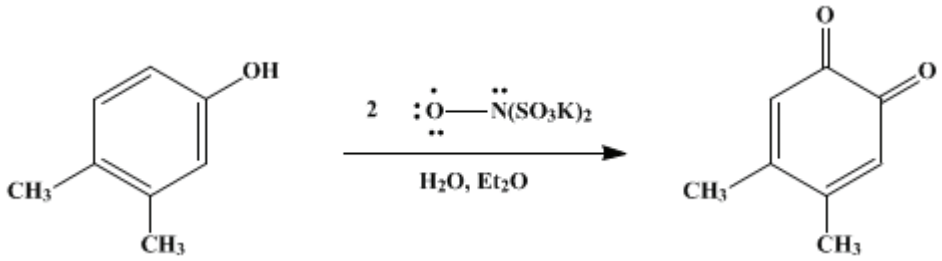
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.052.0088

Organic Syntheses, Coll. Vol. 6, p.480 (1988); Vol. 52, p.88 (1972).

USE OF DIPOTASSIUM NITROSODISULFONATE (FREMY'S SALT): 4,5-DIMETHYL-*o*-BENZOQUINONE

[3,5-Cyclohexadiene-1,2-dione, 4,5-dimethyl-]



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1. Procedure

A solution of 15 g. of sodium dihydrogen phosphate (Note 1) in 5 l. of distilled water is placed in a 6-l. separatory funnel. To this solution is added 90 g. (0.33 mole) of dipotassium nitrosodisulfonate (Fremy's salt) (Note 2). The mixture is shaken to dissolve the inorganic radical. A solution of 16 g. (0.13 mole) of 3,4-dimethylphenol (Note 3) in 350 ml. of diethyl ether is added quickly to the purple solution. As the mixture is shaken vigorously for 20 minutes (Note 4), the color of the solution changes to red-brown. The *o*-quinone thus formed is extracted in three portions with 1.2 l. of chloroform. The combined organic layers are dried over anhydrous sodium sulfate (Note 5), filtered, and evaporated under reduced pressure at 20–23° (Note 6). The residual, somewhat oily, red-brown crystals are slurried twice with 15 ml.-portions of ice-cold ether and collected on a filter. The dark-red crystals, after air drying, weigh 8.7–8.9 g. (49–50%), m.p. 105–107° (Note 7).

2. Notes

1. Monobasic sodium phosphate, $NaH_2PO_4 \cdot H_2O$, obtained from Merck & Co., Inc., was used. This buffer was found to be satisfactory for this reaction.
2. Fremy's salt may be purchased from Aldrich Chemical Company, Inc., or from Matheson, Coleman and Bell. The Fremy's salt used by the checker was prepared electrolytically.[2]
3. 3,4-Dimethylphenol was obtained from Eastman Organic Chemicals, m.p. 63–65°.
4. An efficient stirrer may be substituted for the shaking.
5. The drying was accomplished in about 5 minutes.
6. Higher temperatures may accelerate dimerization of the product.
7. The product is reported to melt at 102°.[3] This material has ^{1}H NMR peaks ($CDCl_3$) at δ 2.14 and 6.19 with relative intensities of 3 : 1. The IR spectrum ($CHCl_3$) shows the strongest absorption at 1670 cm^{-1} accompanied, among others, by four more bands at 1390, 1280, 1005, and 835 cm^{-1}. The product has UV maxima, nm (ε), ($CHCl_3$) at 260 (2600), 400 (1120), and 572 (288). It is reported that the material undergoes slow Diels-Alder dimerization.[4]

3. Discussion

o-Quinones exemplify a very important and reactive class of compounds for general organic synthesis. In the past they have been prepared from catechol derivatives by silver oxide dehydrogenation.[3] The unique oxidizing properties of Fremy's salt allow a number of readily available phenols to be converted to *o*-quinones in excellent yield.[4] The scope of this oxidation, the Teuber reaction, is the subject of numerous papers[5] which have been reviewed recently.[6]

References and Notes

1. H.-J. Teuber, Institut für Organische Chemie der Universität, Frankfurt/Main.
2. P. A. Wehrli and F. L. Pigott, *Inorg. Chem.*, **9**, 2614 (1970).
3. R. Willstätter and F. Müller, *Ber. Dtsch. Chem. Ges.*, **44**, 2171 (1911).
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5. H.-J. Teuber and S. Benz, *Chem. Ber.*, **100**, 2918 (1967) and earlier papers.
6. H. Zimmer, D. C. Lankin and S. W. Horgan, *Chem. Rev.*, **71**, 229 (1971).

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

DIPOTASSIUM NITROSODISULFONATE (FREMY'S SALT)

Fremy's salt

ether,
diethyl ether (60-29-7)

chloroform (67-66-3)

silver oxide (20667-12-3)

sodium sulfate (7757-82-6)

3,4-dimethylphenol (95-65-8)

sodium dihydrogen phosphate (7558-80-7)

DIPOTASSIUM NITROSODISULFONATE

3,5-Cyclohexadiene-1,2-dione, 4,5-dimethyl-,
4,5-Dimethyl-o-benzoquinone (4370-50-7)

sodium phosphate (7601-54-9)