



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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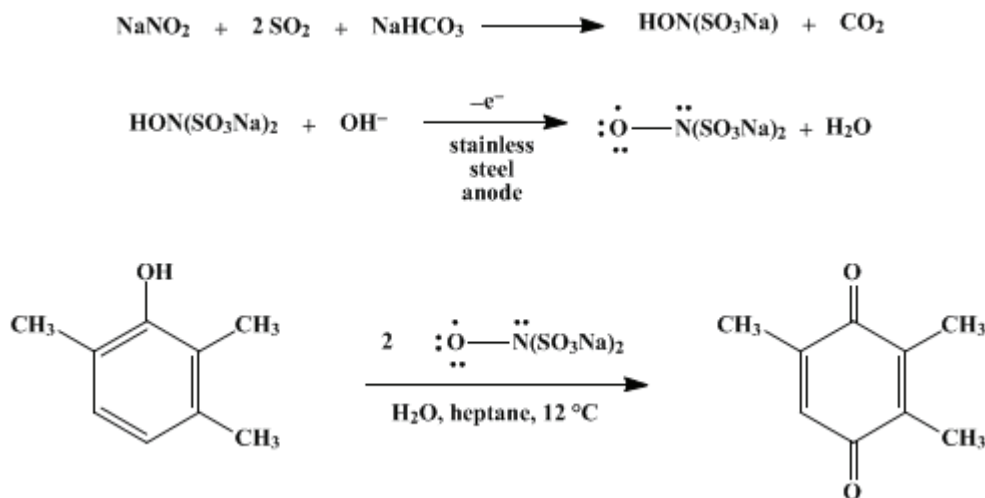
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OXIDATION WITH THE NITROSODISULFONATE RADICAL. I. PREPARATION AND USE OF DISODIUM NITROSODISULFONATE: TRIMETHYL-*p*-BENZOQUINONE

[Nitrosodisulfonic acid, disodium salt and 2,5-Cyclohexadiene-1,4-dione, 2,3,5-trimethyl-]



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1. Procedure

A. *Disodium nitrosodisulfonate*. A 1-l., resin kettle equipped with a mechanical stirrer, a thermometer, a gas-inlet tube suspended about 0.5 cm. above the bottom of the vessel, and an ice-cooling bath is charged with 15.0 g. (0.217 mole) of sodium nitrite (Note 1), 16.8 g. (0.200 mole) of sodium hydrogen carbonate (Note 1), and 400 g. of ice. Sulfur dioxide (25.6 g., 0.400 mole, (Note 2)) is passed into the cold, initially heterogeneous mixture with stirring over a period of 40 minutes. Near the end of the sulfur dioxide addition, the light brown color of the reaction mixture fades almost completely. The resulting colorless to pale-yellow solution of disodium hydroxylaminedisulfonate (Note 3), which has an approximate pH of 4, is stirred for 10 minutes before 59.5 g. (0.480 mole) of sodium carbonate monohydrate (Note 1) is added, giving a solution of pH 11. The gas-inlet tube is removed from the reaction vessel and replaced with a rectangular anode constructed from a 3.5 cm. by 4.7 cm. piece of stainless-steel mesh (about 16 mesh/cm.²) with a stainless-steel wire as an electrical lead. The cathode is a cylindrical coil formed from a 1.5-mm. by 40-cm. piece of stainless-steel wire suspended in a 5-cm. by 10-cm. porous porcelain thimble filled with aqueous 10% sodium carbonate. The porcelain thimble containing the cathode is suspended in the reaction vessel so that the liquid levels in the anode and cathode compartments are the same. The cathode-anode resistance of the electrolysis cell should be in the range of 5–10 ohms. While the reaction solution is continuously stirred and maintained at a temperature of 12° with an ice bath, the electrolysis is started by applying a sufficient potential (approximately 10 volts, (Note 4)) to the anode and cathode leads, giving a cell current of 2.0 amp. As the electrolysis proceeds, the potential applied to the cell is adjusted to maintain a cell current of 2.0 amp. The formation of the nitrosodisulfonate radical is evidenced by the appearance of a deep purple color (Note 5). The electrolysis is continued with stirring and cooling until quantitative measurement of the optical density of the reaction solution (Note 5), indicates the concentration of disodium nitrosodisulfonate to be 0.42–0.47 M (84–94% yield). The typical reaction time is 4 hours; the amount of electricity passed through the cell totals approximately 28,800 coulombs or 8 amp-hours (theoretically, 19,300 coulombs or 5.4 amp-hours). This solution of the nitrosodisulfonate radical is

removed from the anode compartment of the electrolysis cell and used directly in the next step (Note 6).

B. *Trimethyl-p-benzoquinone*. The aqueous solution containing approximately 0.17 mole of *disodium nitrosodisulfonate* is placed in a 1-l., round-bottomed flask fitted with a mechanical stirrer, a thermometer, and an ice bath. A solution of 10.0 g. (0.0734 mole) of *2,3,6-trimethylphenol* (Note 7) in 100 ml. of *heptane* is added to the reaction flask, and the resulting mixture is stirred vigorously for 4 hours with continuous cooling, maintaining the reaction temperature below 12°. The yellow *heptane* layer is separated, and the brown aqueous phase is extracted with two 100-ml. portions of *heptane*. The combined *heptane* solutions are quickly (Note 8) washed with three 50-ml. portions of cold (0–5°), 4 *M* aqueous *sodium hydroxide*, followed by two 100-ml. portions of saturated aqueous *sodium chloride*. The organic solution is dried over anhydrous *magnesium sulfate* and concentrated at 40° with a rotary evaporator, yielding 10.0–10.9 g. (91–99%) of crude *trimethyl-p-benzoquinone* as a yellow liquid, which crystallizes when cooled below room temperature. Further purification may be accomplished by distillation under reduced pressure, yielding 8.5–8.7 g. (77–79%) of the quinone, b.p. 53° (0.4 mm.), which crystallizes on standing as yellow needles, m.p. 28–29.5° (Note 9).

2. Notes

1. Reagent grades of these inorganic reagents were employed.
2. *Sulfur dioxide* was purchased from Matheson Gas Products. It is convenient to use *sulfur dioxide* contained in a lecture bottle so that the small cylinder can be mounted on a balance allowing continuous measurement of the weight of *sulfur dioxide* added.
3. The following alternative procedure may be used to prepare a solution of *disodium hydroxylaminedisulfonate*. *Sodium nitrite* (15 g., 0.22 mole) and 41.6 g. (0.400 mole) of *sodium bisulfite* are added to 250 g. of ice. With stirring, 22.5 ml. (0.393 mole) of *acetic acid* is added in one portion, and the mixture is stirred for 90 minutes in an ice bath. At the end of the stirring period the reaction solution is pH 5 and a potassium iodide-starch test is negative. A solution of 50 g. (0.47 mole) of *sodium carbonate* in water (total volume 250 ml.) is added. This buffered solution of *disodium hydroxylaminedisulfonate* may be used for electrolytic oxidation.
4. Since accurate control of the anode potential is not required in this oxidation, a variety of direct current sources may be employed, provided they are able to supply continuously a current of about 2 amp. at a potential of about 12 volts. One of the simplest direct current sources is an unfiltered rectifier of the type used to charge automobile batteries.
5. In 1 *M* aqueous *potassium hydroxide* solution, the nitrosodisulfonate radical has a maximum in the visible at 544 nm (ϵ 14.5).
6. The submitters report that approximately half of the nitrosodisulfonate radical had decomposed after the solution was stored at 0° for 2 weeks. They report the following procedure for the isolation of Fremy's salt (*dipotassium nitrosodisulfonate*).

Caution! Fremy's salt may decompose spontaneously in the solid state.²

To the cold (12°), purple solution of *disodium nitrosodisulfonate* was added, dropwise and with stirring, a solution of 37.3 g. (0.501 mole) of *potassium chloride* in 100 ml. of water. The resulting mixture, from which the orange-yellow *dipotassium nitrosodisulfonate* crystals precipitated, was allowed to stand overnight in the refrigerator, and the crystals were filtered with suction and washed with 100 ml. of 1 *M* aqueous *potassium-hydroxide*. The damp crystals weighed 55 g. A 1-g. aliquot of the wet material was dried at room temperature in a desiccator over Drierite, leaving 0.76 g. of orange crystals (72% yield based on *sodium nitrite*). On two occasions small samples of dried material decomposed spontaneously. *It is again stressed that if the electrolyzed solution is not used directly, any isolated Fremy's salt should be stored as a slurry in 0.5 M potassium carbonate at 0°.*

7. Crude *2,3,6-trimethylphenol*, purchased from Aldrich Chemical Company, Inc., was purified by recrystallization from either *hexane* or *chlorobenzene*, m.p. 62–63°.

8. This extraction with aqueous *sodium hydroxide* removes phenolic by-products and starting material and must be performed quickly because *p*-quinones are unstable with strong bases.

9. The product has IR absorption (CHCl_3) at 1645 (conjugated C=O) and 1619 cm^{-1} (C=C) with UV maxima (95% $\text{C}_2\text{H}_5\text{OH}$) nm (ϵ) at 256 (16,700), 341 (3880), and 430 (shoulder, 30). The material has ^1H NMR peaks (CDCl_3) at 1.9–2.2 (partially resolved m, 9H, 3CH_3) and 6.5–6.7 (m, 1H, CH), with the following abundant peaks in its mass spectrum: *m/e* (rel. int.), 150 (100, M^+), 122 (24), 121 (14), 107

(30), 79 (18), 68 (20), 54 (14), 40 (18), and 39 (16).

3. Discussion

The nitrosodisulfonate salts, particularly the dipotassium salt (Freymy's salt), are useful reagents for the selective oxidation of phenols and aromatic amines to quinones (the Teuber reaction).^{3,4} [Dipotassium nitrosodisulfonate](#), commercially available, has been prepared by the oxidation of a hydroxylaminedisulfonate salt with [potassium permanganate](#),^{3,5,4} with [lead dioxide](#),⁶ or by electrolysis.^{2,7} The present procedure illustrates the electrolytic oxidation, forming an alkaline, aqueous solution of the relatively soluble [disodium nitrosodisulfonate](#) and avoids a preliminary filtration, which is required to remove [manganese dioxide](#) formed when [potassium permanganate](#) is used as the oxidant.^{3,5,4}

Solutions of nitrosodisulfonate salts are most stable in weakly alkaline solutions (pH 10) and decompose rapidly when the solution is acidic or strongly alkaline.³ [Dipotassium nitrosodisulfonate](#) has been reported to decompose spontaneously,^{2,3} suggesting that procedures involving the use of substantial quantities of the dry solid salt may be hazardous. In the present procedure, separation and use of the solid salt is avoided since the [disodium nitrosodisulfonate](#) is formed and used in aqueous solution. In this procedure, two moles of the preformed nitrosodisulfonate salt are consumed in the oxidation of one mole of the phenol to the benzoquinone derivative.³ The submitters report that only one molar equivalent of the nitrosodisulfonate salt is required if the electrochemical oxidation is carried out in a [heptane](#) solution of the phenol.

[Trimethyl-*p*-benzoquinone](#) has been prepared by the oxidation of [2,3,5-trimethyl-1,4-benzenediamine](#) with [iron\(III\) chloride](#)⁸ and by the oxidation of [2,3,5-trimethylphenol](#) with [dipotassium nitrosodisulfonate](#).⁹

References and Notes

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Appendix

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

Drierite

[potassium carbonate](#) (584-08-7)

[acetic acid](#) (64-19-7)

[sodium hydroxide](#) (1310-73-2)

[sodium hydrogen carbonate](#) (144-55-8)

potassium permanganate (7722-64-7)

sodium chloride (7647-14-5)

sodium carbonate (497-19-8)

sulfur dioxide (7446-09-5)

sodium nitrite (7632-00-0)

sodium bisulfite (7631-90-5)

chlorobenzene (108-90-7)

potassium hydroxide,
potassium-hydroxide (1310-58-3)

manganese dioxide (1313-13-9)

iron(III) chloride (7705-08-0)

disodium hydroxylaminedisulfonate

potassium chloride (7447-40-7)

magnesium sulfate (7487-88-9)

heptane (142-82-5)

hexane (110-54-3)

sodium carbonate monohydrate (5968-11-6)

2,3,6-trimethylphenol (2416-94-6)

DIPOTASSIUM NITROSODISULFONATE

Disodium nitrosodisulfonate,
Nitrosodisulfonic acid, disodium salt

2,5-Cyclohexadiene-1,4-dione, 2,3,5-trimethyl-,
Trimethyl-p-benzoquinone (935-92-2)

2,3,5-trimethyl-1,4-benzenediamine

2,3,5-trimethylphenol (697-82-5)

lead dioxide