Organic Syntheses

A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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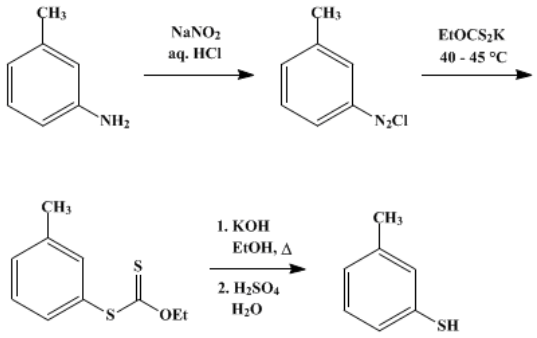
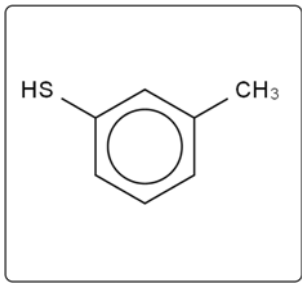
m-THIOCRESOL

[*m*-Toluenethiol; *m*-tolyl mercaptan]





Submitted by D. S. Tarbell and D. K. Fukushima.
Checked by C. F. H. Allen and John R. Byers, Jr..

1. Procedure

All the steps in this preparation, including sealing the product in bottles or ampoules, should be carried out under a good hood. Care should be exercised to avoid contact with m-thiocresol or its solutions since it is a skin irritant.

See the discussion in Org. Synth. 1973, Coll. Vol. 5, 1050 with regard to potential hazards associated with this procedure.

In a 1-l. flask, equipped with a mechanical stirrer and thermometer for reading low temperatures, and immersed in an ice bath, are placed 150 ml. of concentrated hydrochloric acid (sp. gr. 1.18) and 150 g. of crushed ice. The stirrer is started, and 80 g. (0.75 mole) of *m*-toluidine (b.p. 92–93°/15 mm.) is slowly added. The mixture is cooled to 0°, and a cold solution of 55 g. (0.8 mole) of sodium nitrite in 125 ml. of water is slowly added, the temperature being kept below 4°.

In a 2-l. flask equipped with a thermometer, dropping funnel, and stirrer is placed a solution of 140 g. of potassium ethyl xanthate (Note 1) in 180 ml. of water. This mixture is warmed to 40–45° and kept in that range during the slow addition of the cold diazonium solution (Note 2); about 2 hours is required (Note 3). After an additional 30 minutes at this temperature to ensure complete decomposition of the intermediate compound, the red, oily *m*-tolyl ethyl xanthate is separated and the aqueous layer is extracted twice, using 100-ml. portions of ether. The combined oil and extracts are washed once with 100 ml. of 10% sodium hydroxide solution (Note 4) and then with several portions of water until the washings are neutral to litmus. The ether solution is dried over 25 g. of anhydrous calcium chloride, and the ether is removed by distillation. The crude residual *m*-tolyl ethyl xanthate is dissolved in 500 ml. of 95% ethanol, the solution brought to boiling, and the source of heat removed. To this hot solution is added slowly 175 g. of potassium hydroxide pellets so that the solution keeps boiling, and the mixture is refluxed until a sample is completely soluble in water (about 8 hours). Approximately 400 ml. of ethanol is then removed by distillation on a steam bath, and the residue is taken up in the minimum of water (about 500 ml.). The aqueous solution is extracted with three 100-ml. portions of ether, the extract being discarded. The aqueous solution is now made strongly acid to Congo red paper, using 6 *N* sulfuric acid (Note 5) (625–650 ml.). The acidified solution is placed in a 3-l. flask, 2 g. of zinc dust is added, and the *m*-thiocresol is distilled with steam. The lower layer of the *m*-thiocresol is separated; the aqueous layer is extracted with three 100-ml. portions of ether, the extracts being added to the oil. After drying with 50 g. of Drierite, the ether is removed by distillation, and the oily residue is distilled under reduced pressure. The yield of colorless *m*-thiocresol, b.p. 90–93°/25 mm., is 59–69 g. (63–75%) (Note 6) and (Note 7). It is best preserved in sealed glass bottles because of its disagreeable odor.

2. Notes

1. Eastman Kodak Company technical potassium ethyl xanthate was used.
2. The diazonium solution is left in the ice bath, and only 10- to 15-ml. portions are placed in the dropping funnel at one time.
3. Many diazonium solutions have been reported to react explosively with solutions of metallic polysulfides even at low temperatures.[1,2] A violent reaction with xanthates is mentioned only in one report.[3] Neither the authors nor the checkers observed any unusual reactivity during this preparation or with the procedure given for dithiosalicylic acid.[4] On a large scale (100 moles of *m*-toluidine) flashes of light have been occasionally observed (private communication, L. J. Roll).
4. This wash serves to remove any *m*-cresol present.
5. This acidification liberates carbon oxysulfide, which has a very disagreeable odor.
6. The refractive index is n_D^{25} 1.568–1.571.
7. Other boiling points are 195°/760 mm.; 120°/100 mm.; 107°/50 mm.

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3. Discussion

The only practical laboratory procedure for preparing *m*-thiocresol is by the alkaline hydrolysis of *m*-tolyl ethyl xanthate, obtained from *m*-toluenediazonium chloride and potassium ethyl xanthate.[3,5] The procedure described is essentially that of Bourgeois.[5]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 5, 1050

References and Notes

1. Nawiasky, Ebersole, and Werner, *Chem. Eng. News*, **23**, 1247 (1945).
2. Hodgson, *Chemistry & Industry*, **1945**, 362.
3. Leuckart, *J. prakt. Chem.*, [2] **41**, 189 (1890).
4. *Org. Syntheses* Coll. Vol. **2**, 580 (1943).
5. Bourgeois, *Rec. trav. chim.*, **18**, 447 (1899).

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

carbon oxysulfide

Drierite

ethanol (64-17-5)

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

ether (60-29-7)

sodium hydroxide (1310-73-2)

sodium nitrite (7632-00-0)

potassium hydroxide (1310-58-3)

zinc (7440-66-6)

potassium ethyl xanthate (140-89-6)

m-Thiocresol,
m-Toluenethiol,
m-tolyl mercaptan (108-40-7)

m-toluidine (108-44-1)

m-tolyl ethyl xanthate

m-cresol (108-39-4)

m-toluenediazonium chloride