Organic Syntheses

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). 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.

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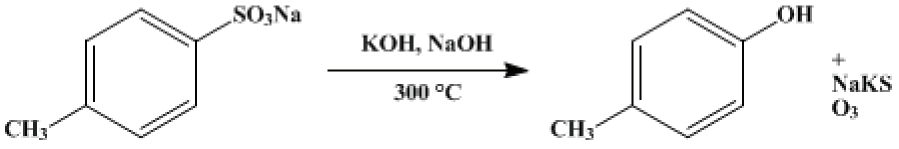
p-CRESOL



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1. Procedure

One kilogram of technical sodium hydroxide and .400 g. of technical potassium hydroxide (Note 1) are melted together in a cast-iron flat-bottomed kettle, 18 cm. in depth and 18 cm. in diameter. The fused mass is well stirred by means of a piece of iron pipe closed at one end, containing a thermometer; the hand is protected by a rubber glove wrapped with a cloth. The temperature of the fused mass is allowed to fall to 230°, and 150 g. (0.73 mole) of technical sodium *p*-toluenesulfonate (Note 2) is stirred in. The temperature is now slowly raised while 450 g. (2.2 moles) more of sodium *p*-toluenesulfonate is added slowly, the additions being made whenever the melt becomes sufficiently thin to stir in the solid. When all has been added, the temperature should be about 270°; the addition requires about thirty minutes. The temperature is now raised to 300°, with occasional stirring. At this point there is a layer of heavy froth on the surface of the thin melt, and as the temperature rises this is stirred in, the whole melt becoming frothy and showing a tendency to foam over. On continuing to raise the temperature, the foaming suddenly disappears at about 330°; the melt becomes dark and evolution of hydrogen sets in. The mixture is now thin and of uniform consistency; it is poured at once into an iron tray and allowed to cool.

The solidified product is dissolved in 6-7 l. of water in a 12-l. flask, and a solution of concentrated (95 per cent) sulfuric acid (about 880 cc.) in about 2 l. of water is added until the liquor has a distinct odor of sulfur dioxide. The heat of neutralization is sufficient to cause the solution to boil; it is at once distilled in a current of steam (Note 3) until a sample of the distillate gives only a slight precipitate with bromine water. The distillate (about 6–7 l.) is saturated with salt and the oil separated. The watery solution may be again distilled with steam in order to recover the small amount of cresol in solution. The oil is at once distilled under reduced pressure, and the fraction which boils at 95–96° /15 mm. is collected. The forerun is freed of water and redistilled, yielding a further quantity. On cooling, the product solidifies to a white, crystalline mass melting at 31° (Note 4). The yield is 200–230 g. (63–72 per cent of the theoretical amount based on sodium *p*-toluenesulfonate of 95 per cent purity).

2. Notes

1. Fusion with sodium hydroxide alone yields no cresol, the fused sodium hydroxide appearing to have no solvent action on the sodium *p*-toluenesulfonate. On the other hand, potassium hydroxide works entirely satisfactorily, as do mixtures of sodium hydroxide and potassium hydroxide containing not less than 28 per cent of potassium hydroxide. In the above directions the minimum amount of potassium hydroxide is indicated.
2. Technical sodium *p*-toluenesulfonate is, as a rule, of about 95 per cent purity; it contains about 2 per cent of sodium chloride and some moisture. Attempts to prepare a *p*-cresol of higher melting point by fusion of recrystallized sodium *p*-toluenesulfonate (which should presumably contain no isomers) have failed; it has been found impossible to raise the melting point above 31.4°.
3. Since distillation in a current of steam in a laboratory is apt to be a tedious process when only the regular form of Liebig condenser is employed, much time can be saved by the use of the apparatus described on p. 479.
4. Traces of isomeric cresols can be removed by treatment with quinone chloroimide.[1]

3. Discussion

p-Cresol can be prepared from diazotized *p*-toluidine,[2] and by the fusion of *p*-toluenesulfonic acid with potassium hydroxide.[3]

References and Notes

1. Gibbs, J. Am. Chem. Soc. **49**, 839 (1927).
2. Kekulé, Jahresber. 458 (1866); Körner, Z. Chem. 326 (1868).
3. Wurtz, Ann. **144**, 122 (1867); **156**, 258 (1870); Engelhardt and Latschinov, Z. Chem. 618 (1869).

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

bromine water

cresols

sulfuric acid (7664-93-9)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

sodium chloride (7647-14-5)

sulfur dioxide (7446-09-5)

potassium hydroxide (1310-58-3)

cresol (95-48-7)

quinone chloroimide

p-toluidine (106-49-0)

p-toluenesulfonic acid (104-15-4)

p-CRESOL (106-44-5)

sodium p-toluenesulfonate (657-84-1)