



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.

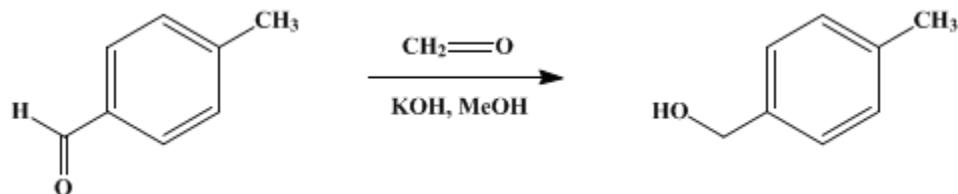
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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***p*-TOLYL CARBINOL**

[Benzyl alcohol, *p*-methyl-]



Submitted by David Davidson and Marvin Weiss.
Checked by Reynold C. Fuson and E. A. Cleveland.

1. Procedure

The apparatus consists of a 3-l. three-necked flask fitted with a mercury-sealed mechanical stirrer, a reflux condenser, a dropping funnel, and a thermometer which reaches almost to the bottom of the flask. Five hundred grams of **potassium hydroxide** pellets (85 per cent **potassium hydroxide**) (7.6 moles) and 750 cc. of commercial absolute **methyl alcohol** (free from **acetone**) are placed in the flask, and stirring is begun. The bulk of the alkali dissolves in a few minutes, with the evolution of heat. The flask is now surrounded by an ample cold-water bath, and, when the internal temperature drops to 60°, addition of a mixture of 360 g. (353 cc., 3 moles) of ***p*-tolualdehyde** (Note 1), 300 cc. of **formalin** (3.9 moles) (Note 2), and 300 cc. of absolute **methyl alcohol** is begun at such a rate that the internal temperature remains at 60–70°. This addition requires about fifteen minutes. The internal temperature is then maintained at 60–70° for three hours, after which the reflux condenser is replaced by a downward condenser and the **methyl alcohol** distilled with the aid of a brine bath until the internal temperature reaches 101°. Nine hundred cubic centimeters of cold water is then added to the warm residue, and the mixture is cooled. The resulting two layers are separated at once (Note 3), and the aqueous layer is extracted with three 200-cc. portions of **benzene**. The combined oil and extracts are washed with five or six 50-cc. portions of water (Note 4), and the combined washings extracted with 50 cc. of **benzene**, the **benzene** layer being added to the washed extract. The **benzene** solution is cleared by shaking it with a few grams of anhydrous **sodium sulfate** and is then distilled under diminished pressure. After removal of the **benzene**, 331 g. (90 per cent of the theoretical amount) of ***p*-tolyl carbinol** (b.p. 116–118°/20 mm.) is obtained; the product solidifies in the receiver to a mass of oil-drenched crystals melting at 54–55°. Recrystallization from an equal weight of commercial **heptane** (b.p. 90–100°) gives an 80 per cent recovery of long needles which melt at 61°. A further 8 per cent is recoverable by concentration of the mother liquor (Note 5) and (Note 6).

2. Notes

1. A technical grade of ***p*-tolualdehyde**, obtained from Fritzsche Brothers, New York, New York, was found satisfactory. Directions for preparing ***p*-tolualdehyde** are given on p. 583.
2. The **formaldehyde** content of the solution is determined by analysis (p. 611).
3. The upper layer solidifies if allowed to stand.
4. This washing removes **potassium *p*-toluate**, which causes difficulty in the distillation of the product if allowed to remain.
5. The final residue from the mother liquor is an oil which does not solidify in a freezing mixture and which appears to be a mixture of *p*- and *m*-tolyl carbinols. Only a trace of **phthalic acid** (phenolphthalein test) was obtained by oxidizing this oil with permanganate; the portion of the oil which was more readily soluble in water yielded a **phenylurethan** which depressed the melting point of the **phenylurethan** of either ***p*-tolyl carbinol** or **benzyl alcohol**.
6. Under the same conditions, **benzaldehyde** yielded 80 per cent of **benzyl alcohol** and **piperonal** 86 per cent of **piperonyl alcohol**.

3. Discussion

p-Tolyl carbinol has been prepared from *p*-tolualdehyde by the action of alcoholic potassium hydroxide,¹ by electrolytic reduction,² and by the reducing action of the Grignard reagent,³ as well as from *p*-toluic acid by electrolytic reduction.⁴ The procedure described is an adaptation of a general method for reducing aromatic aldehydes to the corresponding alcohols.⁵

References and Notes

1. Cannizzaro, Ann. **124**, 252 (1862).
2. Law, J. Chem. Soc. **91**, 755 (1907).
3. Oddo, Gazz. chim. ital. **41** (I) 285 (1911).
4. Mettler, Ber. **39**, 2933 (1906).
5. Davidson and Bogert, J. Am. Chem. Soc. **57**, 905 (1935).

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

p- and m-tolyl carbinols

Benzene (71-43-2)

methyl alcohol (67-56-1)

formaldehyde,
formalin (50-00-0)

sodium sulfate (7757-82-6)

benzaldehyde (100-52-7)

acetone (67-64-1)

potassium hydroxide (1310-58-3)

Benzyl alcohol (100-51-6)

phthalic acid (88-99-3)

piperonal (120-57-0)

heptane (142-82-5)

phenylurethan (101-99-5)

Piperonyl alcohol (495-76-1)

p-Toluic acid (99-94-5)

p-Tolualdehyde (104-87-0)

p-TOLYL CARBINOL,
Benzyl alcohol, p-methyl- (589-18-4)

potassium p-toluate

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