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](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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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. This washing removes potassium \( p \)-toluate, which causes difficulty in the distillation of the product if allowed to stand.
4. Under the same conditions, benzaldehyde yielded 80 per cent of benzyl alcohol and piperonal 86 per cent of piperylnyl 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.\(^5\)

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**References and Notes**


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**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