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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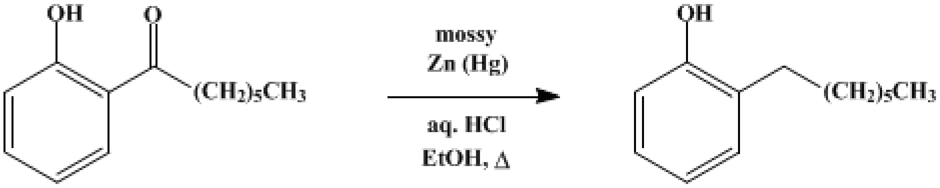
Organic Syntheses, Coll. Vol. 3, p.444 (1955); Vol. 20, p.57 (1940).

o-*n*-HEPTYLPHENOL

[Phenol, *o*-*n*-heptyl-]



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1. Procedure

In a 1-l. three-necked flask fitted with a stirrer (Note 1) and a reflux condenser is placed 200 g. of amalgamated mossy zinc (Note 2). A mixture of 200 ml. of water and 200 ml. of concentrated hydrochloric acid is added and then a solution of 60 g. of *o*-heptanoyl phenol (Note 3) in 100 ml. of ethanol. The mixture is agitated vigorously and refluxed until reduction is complete (Note 4).

To the mixture is added 120 ml. of toluene, stirring being continued for a few minutes. The toluene solution is separated from the aqueous solution and washed three times with water. The solution is filtered from suspended matter, and the toluene is distilled from a Claisen flask until a thermometer in the liquid reads 170° (Note 5). The residue is then distilled under reduced pressure, the portion boiling at 118–123° at 1 mm. being collected (Note 6). The yield of colorless *o*-*n*-heptylphenol is 45–47 g. (81–86%) (Note 7).

2. Notes

1. The stirrer should be as large and substantial as the flask will accommodate, since the rate of reduction depends greatly on complete emulsification of the oil.
2. The zinc is amalgamated in the reaction flask by covering it with a solution of 4 g. of mercuric chloride in 300 ml. of water. Occasional agitation during 30 minutes is sufficient for amalgamation. The solution is poured off, and the zinc is rinsed once with water.
3. *o*-Heptanoyl phenol may be prepared by the method of Miller and Hartung [*Org. Syntheses* Coll. Vol. **2**, 543 (1943)]. The checkers found that, by keeping the mixture of *ortho* and *para* isomers in a cool place overnight, most of the *para* isomer crystallized and could be separated by filtration. The *ortho* isomer is then obtained by fractional vacuum distillation, repeated two or three times. *o*-Heptanoylphenol boils at 135–140°/3 mm.; *p*-heptanoyl phenol boils at 200–207°/4 mm.
4. The reduction requires at least 8 hours and may take twice that long. For testing completeness of reduction, 0.1 ml. of the oil is withdrawn and dissolved in 2 ml. of ethanol; to the solution is added 2–4 drops of a 10% solution of ferric chloride in ethanol. A deep red or reddish brown color is produced by the ketone; a light brownish yellow color indicates completion of the reduction. A standard solution containing 0.5 g. of the ketone per liter of ethanol is used for comparison, 2 ml. of this being treated with a few drops of the ferric chloride solution. Since the *para* acylphenols usually do not give a pronounced color with ferric chloride, at least 8 hours should be allowed for their reduction.
5. Drying of the toluene extract is unnecessary, since the water is carried over during the removal of the toluene. If necessary, the toluene may be returned once to the flask to effect complete removal of the water.
6. The residue from the distillation is usually less than 5 g. and may be discarded.
7. Other ketones may be reduced by this same procedure. The submitters report that the following have been reduced with yields of 70–90%: *o*- and *p*-butyryl phenols, *o*- and *p*-valeryl phenols, *o*- and *p*-caproyl phenols, *o*- and *p*-heptanoyl phenols, *o*- and *p*-octanoyl phenols, *o*- and *p*-pelargonyl phenols, *o*- and *p*-undecylyl phenols. The same procedure applies to acyl resorcinols and acyl chlororesorcinols.

Caproyl and octanoyl resorcinols reduce to the corresponding alkyl derivatives in yields of 70–80%. Butyryl, valeryl, caproyl, heptanoyl, and octanoyl chlororesorcinols reduce to the corresponding alkyl chlororesorcinols in yields of 60–75%.

3. Discussion

Primary alkyl phenols have been prepared by the reduction of acyl phenols;[1] by the demethylation of the corresponding ethers;[1,2] by the diazotization of the corresponding amines;[3] and by the alkali fusion of sulfonates.[4] Alkyl resorcinols have been prepared by the reduction of acyl resorcinols.[1,5,6] Alkyl chlororesorcinols have been prepared from the corresponding acyl chlororesorcinols by reduction.[7]

References and Notes

1. Johnson and Hodge, *J. Am. Chem. Soc.*, **35**, 1014 (1913); Coulthard, Marshall, and Pyman, *J. Chem. Soc.*, **1930**, 280.
2. Klages, *Ber.*, **32**, 1438 (1899).
3. *Org. Syntheses* Coll. Vol. **1**, 128, 407 (1941).
4. Ullmann, *Enzykolpädie der technischen Chemie*, Vol. **9**, p. 35, Urban and Schwarzenberg, Berlin, 1921.
5. Johnson and Lane, *J. Am. Chem. Soc.*, **43**, 348 (1921).
6. Dohme, Cox, and Miller, *J. Am. Chem. Soc.*, **48**, 1688 (1926).
7. Read, Reddish, and Burlingame, *J. Am. Chem. Soc.*, **56**, 1377 (1934).

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

butyryl phenols

o- and p-valeryl phenols

o- and p-caproyl phenols

o- and p-heptanoyl phenols

o- and p-octanoyl phenols

o- and p-pelargonyl phenols

o- and p-undecylyl phenols

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

toluene (108-88-3)

zinc (7440-66-6)

mercuric chloride (7487-94-7)

ferric chloride (7705-08-0)

o-n-HEPTYLPHENOL,
Phenol, o-n-heptyl- (5284-22-0)

o-heptanoyl phenol,
o-Heptanoylphenol

p-heptanoyl phenol