



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.

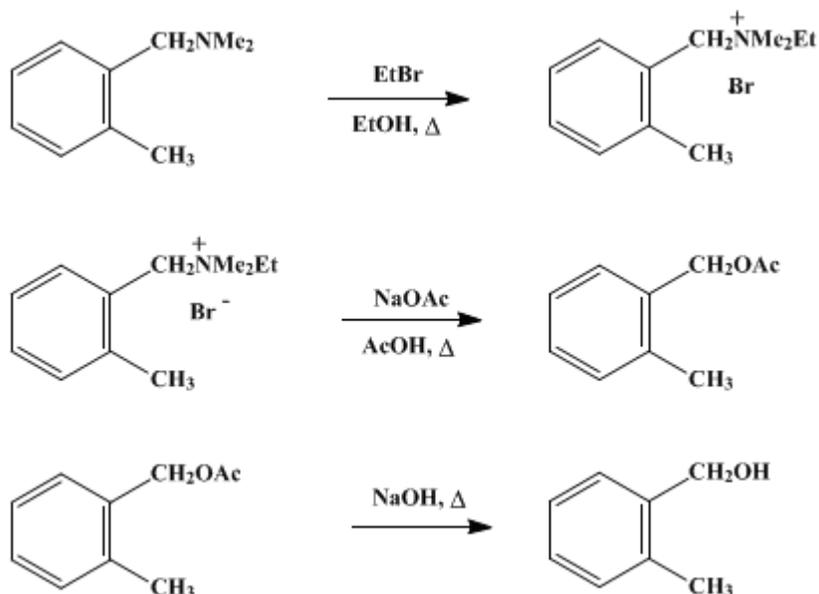
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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***o*-METHYLBENZYL ALCOHOL**

[Benzyl alcohol, *o*-methyl-]



Submitted by W. R. Brasen and C. R. Hauser¹.

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1. Procedure

A. *o*-Methylbenzyl acetate. A solution of 29.8 g. (0.20 mole) of 2-methylbenzyl dimethylamine (p.585) and 32.7 g. (0.30 mole) of ethyl bromide in 40 ml. of absolute ethanol is placed in a 500-ml. round-bottomed flask fitted with a reflux condenser capped with a calcium chloride drying tube. The solution is heated under reflux on the steam bath for 1 hour; then an additional 10.8 g. (0.10 mole) of ethyl bromide is added and the heating continued for an additional 3 hours. The solvent and residual ethyl bromide are removed to reduced pressure (water aspirator) while the flask is heated in a water bath kept at about 60° (Note 1). The oily residue is treated with about 300 ml. of absolute ether, and on scratching crystallization is induced. The product is collected on a Büchner funnel, washed with two 50-ml. portions of anhydrous ether, and dried in a vacuum desiccator. The yield of colorless 2-methylbenzylethyl dimethylammonium bromide is 47.5–49.0 g. (92–95%) (Note 2). It is hygroscopic and should therefore not be exposed to moist air.

In a 500-ml. round-bottomed flask, fitted with a reflux condenser capped with a calcium chloride drying tube, are placed 38.7 g. (0.15 mole) of the quaternary ammonium bromide (Note 3) described above, 24.6 g. (0.3 mole) of fused sodium acetate, and 100 ml. of glacial acetic acid. The mixture is boiled under reflux for 24 hours (Note 4) and then allowed to cool. It is transferred to a large beaker (Note 5), 250 ml. of water is added, and the acid is partially neutralized by the addition of 84 g. of solid sodium bicarbonate. The mixture is extracted with three 75-ml. portions of ether, and the combined ether solutions are washed with two or more 50-ml. portions of saturated sodium bicarbonate solution until all the acetic acid has been removed. The ether layer is then washed with 50 ml. of saturated sodium chloride solution and dried over anhydrous sodium sulfate. The ether is removed by distillation, and the residue is distilled under reduced pressure. The yield of colorless liquid acetate, b.p. 119–121°/15 mm. or 129–131°/31 mm., is 21.6–22.4 g. (88–91%), n_D^{25} 1.5041–1.5045 (Note 6).

B. *o*-Methylbenzyl alcohol. A solution of 5 g. (0.12 mole) of sodium hydroxide in 50 ml. of water is added to a solution of 16.4 g. (0.1 mole) of 2-methylbenzyl acetate (prepared as described above, part

A) in 50 ml. of [methanol](#) contained in a 250-ml. round-bottomed flask fitted with a reflux condenser. The mixture is boiled under reflux for 2 hours, cooled, diluted with 50 ml. of water, and extracted with three 75-ml. portions of [ether](#). The combined [ether](#) solutions are washed with 50 ml. of water and 50 ml. of saturated [sodium chloride](#) solution and dried over anhydrous [sodium sulfate](#). The solvent is removed by distillation, finally at reduced pressure to remove the last traces of [methyl alcohol](#), and the residue is dissolved in 50 ml. of boiling 30–60° petroleum ether. The colorless crystals obtained on cooling, finally in the ice bath, are collected by suction filtration, washed with a few milliliters of cold petroleum ether, and air-dried. Concentration of the mother liquors to 6–7 ml. and cooling gives an additional crop. The total yield of product melting between 33–34° and 35–36° is 11.6–11.8 g. (95–97%) ([Note 7](#)).

2. Notes

1. A capillary ebullition tube is used to prevent bumping.
2. [2,3-Dimethylbenzylethyldimethylammonium bromide](#) can be prepared similarly in comparable yield. The salts are suitable for use in the displacement reaction without purification.
3. The ethobromides are preferable to methiodides in this reaction, because the former salts are more soluble in glacial [acetic acid](#) and do not liberate halogen as do the iodides.
4. The [sodium acetate](#) dissolves as the mixture reaches reflux temperature, but a small amount of solid (perhaps [sodium bromide](#)) remains undissolved throughout the heating.
5. Considerable foaming may occur during the neutralization, and material may be lost if the process is carried out in a small narrow-mouthed vessel.
6. The submitters have used the same procedure for the preparation of [2,3-dimethylbenzyl acetate](#) from the corresponding quaternary salt ([Note 2](#)). The yield of material b.p. 127–129°/9 mm. was 94%.
7. Hydrolysis of [2,3-dimethylbenzyl acetate](#) ([Note 6](#)) by this procedure gave [2,3-dimethylbenzyl alcohol](#), m.p. 65–66°, in 96% yield.

3. Discussion

The vicinal methylbenzyl alcohols have been prepared in general by the abnormal reaction of the appropriately substituted Grignard reagent with [formaldehyde](#).² The present method is preferred over the former because it yields purer products than the Grignard approach.

[o-Methylbenzyl alcohol](#) also has been prepared by the [lithium aluminum hydride](#) reduction of [o-toluic acid](#)³ or [ethyl o-toluate](#),⁴ and by the hydrolysis of [o-xylyl bromide](#).⁴

References and Notes

1. Duke University, Durham, North Carolina. Work supported by the Office of Ordnance Research.
2. Reichstein, Cohen, Ruth, and Meldahl, *Helv. Chim. Acta*, **19**, 412 (1936); Siegel, Boyer, and Jay, *J. Am. Chem. Soc.*, **73**, 3237 (1951).
3. Daub and Castle, *J. Org. Chem.*, **19**, 1571 (1954).
4. Dev, *J. Indian Chem. Soc.*, **32**, 403 (1955).

Appendix

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

petroleum ether

[ethanol](#) (64-17-5)

acetic acid (64-19-7)

methyl alcohol,
methanol (67-56-1)

ether (60-29-7)

sodium acetate (127-09-3)

sodium hydroxide (1310-73-2)

formaldehyde (50-00-0)

sodium bicarbonate (144-55-8)

sodium chloride (7647-14-5)

ammonium bromide (12124-97-9)

sodium bromide (7647-15-6)

Ethyl bromide (74-96-4)

sodium sulfate (7757-82-6)

lithium aluminum hydride (16853-85-3)

2,3-dimethylbenzyl alcohol (13651-14-4)

2-Methylbenzyl dimethylamine (4525-48-8)

2-methylbenzylethyldimethylammonium bromide

2-methylbenzyl acetate,
o-Methylbenzyl acetate (17373-93-2)

2,3-Dimethylbenzylethyldimethylammonium bromide

2,3-dimethylbenzyl acetate

o-Toluic acid (118-90-1)

o-Methylbenzyl alcohol,
Benzyl alcohol, o-methyl- (89-95-2)

ethyl o-toluate (87-24-1)

o-xylol bromide (576-23-8)