



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.

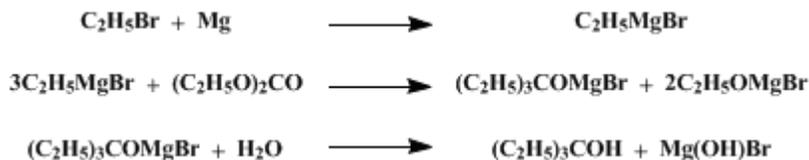
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.602 (1943); Vol. 11, p.98 (1931).

TRIETHYL CARBINOL

[3-Pentanol, 3-ethyl-]



Submitted by W. W. Moyer and C. S. Marvel.

Checked by Frank C. Whitmore and D. J. Loder.

1. Procedure

In a 3-l. three-necked flask, fitted with a mechanical stirrer, a 500-cc. separatory funnel, and an efficient reflux condenser to which a calcium chloride tube is attached, are placed 107 g. (4.4 gram atoms) of [magnesium turnings](#) and 800 cc. of anhydrous [ether](#). The reaction is started by adding 5 cc. (7 g., 0.06 mole) of [ethyl bromide](#) ([Note 1](#)) without stirring. The stirrer is started, and a solution of 480 g. (4.4 moles) of [ethyl bromide](#) in 1 l. of anhydrous [ether](#) is added as rapidly as the refluxing of the [ether](#) allows. The addition requires about two hours ([Note 2](#)). The reaction is practically complete when all the halide has been added, but stirring should be continued for fifteen minutes longer.

A solution of 156 g. (1.32 moles) of [ethyl carbonate](#) ([Note 3](#)) in 200 cc. of [ether](#) is added to the Grignard reagent, with rapid stirring, over a period of approximately three hours. The reaction is vigorous, and the [ether](#) refluxes continually. After all the [diethyl carbonate](#) has been added, the flask is heated on a water bath and stirring is continued for another hour.

The reaction mixture is hydrolyzed by pouring it, with frequent shaking, into a 5-l. round-bottomed flask containing 1.5 kg. of cracked ice and a solution of 300 g. of [ammonium chloride](#) in 600 cc. of water. The [ether](#) layer is separated in a large separatory funnel, and the aqueous residue is extracted with two 500-cc. portions of [ether](#) ([Note 4](#)).

The [ether](#) is distilled from the combined extracts, and the crude [triethyl carbinol](#) is dried with 10 g. of anhydrous [potassium carbonate](#). The alcohol is then distilled at atmospheric pressure, and the portion (80–90 g.) boiling at 139–142° is collected. The low-boiling distillate is treated with 5 g. of anhydrous [potassium carbonate](#), filtered, and redistilled, whereby another portion (about 25 g.) of [triethyl carbinol](#) boiling at 139–142° is obtained. The process is repeated once, or twice if necessary, and an additional 20 g. is collected ([Note 5](#)). The total yield is 125–135 g. (82–88 per cent of the theoretical amount) ([Note 6](#)). [Triethyl carbinol](#) is a viscous liquid with a penetrating, camphor-like odor.

2. Notes

1. The [ethyl bromide](#) used in this preparation was dried over [calcium chloride](#) and then distilled from [phosphorus pentoxide](#). The fraction boiling at 38–39° was collected. Directions for preparing [ethyl bromide](#) are given in *Org. Syn. Coll. Vol. I, 1941, 29, 36*.
2. The time of addition may be decreased by cooling the flask externally. A towel is folded in a narrow strip and wrapped about the flask above the [ether](#) line, and cracked ice is packed on top of the flask. This arrangement allows the [ether](#) vapor to be condensed without appreciable cooling of the reaction mixture.
3. The commercial "99 per cent" ester was used. It was purified according to the description given in [Note 2 on p. 283](#) above.
4. The [ether](#) used for extraction may be obtained by distilling the [ether](#) from the [triethyl carbinol](#) solution.
5. In checking this preparation the first drying was allowed to continue for fifteen hours. The first

fractionation of the carbinol yielded 122 g., the second 10 g., and the third yielded none.

6. The preparation of homologous trialkyl carbinols by use of the Grignard reagent and ethyl carbonate was found to be very satisfactory. The following compounds were prepared: tri-*n*-propyl carbinol (b.p. 89–92°/20 mm.) in 75 per cent yield; tri-*n*-butyl carbinol (b.p. 129–131/20 mm.) in 84 per cent yield; tri-*n*-amyl carbinol (b.p. 160–164°/19 mm.) in 75 per cent yield; and tri-*n*-heptyl carbinol (b.p. 195–200°/6 mm.) in 72 per cent yield.

3. Discussion

Triethyl carbinol has been prepared by the action of zinc on a mixture of ethyl iodide and diethyl ketone;¹ by the action of magnesium on ethyl bromide in diethyl ketone solution;² by the action of sodium and ethyl bromide on diethyl ketone or ethyl propionate;³ as a by-product in the reaction between ethylmagnesium bromide and carbon oxysulfide;⁴ and by the action of ethylmagnesium bromide on ethyl propionate,⁵ ethyl chloroformate,⁶ ethyl cyanoformate,⁷ or ethyl carbonate.⁸

References and Notes

1. Barataeff and Saytzeff, *J. prakt. Chem.* (2) **34**, 463 (1886).
2. Davies and Kipping, *J. Chem. Soc.* **99**, 298 (1911).
3. Morton and Stevens *J. Am. Chem. Soc.* **53**, 2247 (1931).
4. Weigert, *Ber.* **36**, 1009 (1903).
5. Schreiner, *J. prakt. Chem.* (2) **82**, 295 (1910); Böeseken and Wildschut, *Rec. trav. chim.* **51**, 169 (1932).
6. Mazurewitsch, *J. Russ. Phys.-Chem. Soc.* **42**, 1582 (1910) (*Chem. Zentr.* **1911**, I, 1500).
7. Bruylants, *Bull. soc. chim. Belg.* **33**, 529 (1924).
8. Whitmore and Badertscher, *J. Am. Chem. Soc.* **55**, 1560 (1933).

Appendix

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

carbon oxysulfide

Grignard reagent

calcium chloride (10043-52-4)

potassium carbonate (584-08-7)

ether (60-29-7)

ammonium chloride (12125-02-9)

magnesium,
magnesium turnings (7439-95-4)

Ethyl bromide (74-96-4)

zinc (7440-66-6)

sodium (13966-32-0)

ethyl chloroformate (541-41-3)

ethylmagnesium bromide (925-90-6)

Ethyl iodide (75-03-6)

ethyl carbonate

ethyl propionate (105-37-3)

ethyl cyanoformate (623-49-4)

TRIETHYL CARBINOL,
3-Pentanol, 3-ethyl- (597-49-9)

diethyl carbonate (105-58-8)

diethyl ketone (96-22-0)

phosphorus pentoxide (1314-56-3)

tri-n-propyl carbinol (2198-72-3)

tri-n-butyl carbinol (597-93-3)

tri-n-amyl carbinol

tri-n-heptyl carbinol