



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](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.

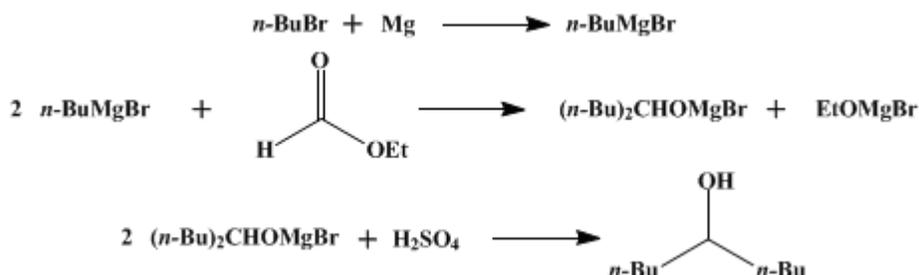
The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries 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.*

*Organic Syntheses, Coll. Vol. 2, p.179 (1943); Vol. 15, p.11 (1935).*

## DI-*n*-BUTYLCARBINOL

### [5-Nonanol]



Submitted by G. H. Coleman and David Craig.

Checked by John R. Johnson and H. B. Stevenson.

### 1. Procedure

In a 3-l. three-necked, round-bottomed flask, fitted with a 500-cc. separatory funnel, a liquid-sealed mechanical stirrer, and a reflux condenser, are placed 36.5 g. (1.5 gram atoms) of [magnesium turnings](#) and 500 cc. of absolute [ether](#). A solution of 206 g. (1.5 moles) of [n-butyl bromide](#) ([Org. Syn. Coll. Vol. I, 1941, 28, 37](#)) in 250 cc. of absolute [ether](#) is placed in the separatory funnel. The stirrer is started, and 10–15 cc. of the bromide solution is allowed to flow into the flask from the funnel; the reaction generally begins within a few minutes ([Note 1](#)). As soon as refluxing is vigorous, the flask is surrounded by ice and water and the rate of addition of the bromide is adjusted so that moderate refluxing occurs. After all the solution has been added (thirty to forty minutes), the cooling bath is removed. Stirring is continued for fifteen minutes longer, after which only a small residue of unreacted [magnesium](#) remains.

The flask is cooled in an ice bath and a solution of 55.5 g. (0.75 mole) of pure [ethyl formate](#) ([Note 2](#)) in 100 cc. of absolute [ether](#) is placed in the separatory funnel. The stirrer is started and the [ethyl formate](#) solution is added at such a rate that the ether refluxes gently. This addition requires about one-half hour. The cooling bath is then removed and stirring is continued for ten minutes.

With vigorous stirring ([Note 3](#)), 100 cc. of water is added through the separatory funnel at such a rate that rapid refluxing occurs. Following this, a cold solution of 85 g. (46 cc., 0.85 mole) of concentrated [sulfuric acid](#) in 400 cc. of water is added. After the addition of the acid, the two layers become practically clear. A large part of the ethereal layer is decanted into a 1-l. round-bottomed flask, and the remainder, together with the aqueous layer, is transferred to a separatory funnel. The solid remaining in the flask is washed with two 25-cc. portions of [ether](#), which are added to the material in the separatory funnel. The ethereal layer is separated and combined with the decanted portion. The flask is fitted with an efficient fractionating column, and the [ether](#) is distilled from a steam bath until the temperature of the vapor reaches about 50°. To the residual impure carbinol ([Note 4](#)) is added 75 cc. of 15 per cent aqueous [potassium hydroxide](#) solution and the flask is fitted with a reflux condenser. The mixture is boiled vigorously under reflux for three hours, after which the purified carbinol is removed by steam distillation, the volume in the flask being kept at 250–300 cc. The distillate is collected in a separatory funnel so that the lower aqueous layer can be drawn off periodically. The distillation is complete when about 1.5 l. of water has been collected.

The upper layer of [di-n-butylcarbinol](#) is separated and allowed to stand over 10 g. of anhydrous [potassium carbonate](#) for one hour. The liquid is decanted into a 500-cc. Claisen flask, and the residual [potassium carbonate](#) is washed with three 10-cc. portions of dry [ether](#), which are added to the material in the distilling flask. After removing a small fraction of low-boiling material, there is obtained 90–92 g. (83–85 per cent of the theoretical amount) of pure [di-n-butylcarbinol](#), b.p. 97–98°/20 mm. ([Note 5](#)).

## 2. Notes

1. The reaction between the ethereal solution of *n*-butyl bromide and the magnesium generally starts without any assistance; if necessary, a small amount of a previously prepared Grignard reagent or a crystal of iodine may be used to start the reaction.
2. It is best to use freshly distilled ethyl formate, which may be purified in the following way: To 100 g. of commercial ethyl formate is added 15 g. of anhydrous potassium carbonate, and the mixture is allowed to stand for one hour with occasional shaking. The ester is decanted into a dry 200-cc. flask, and 5 g. of phosphorus pentoxide is added. The flask is provided with an efficient fractionating column, and the ethyl formate is distilled into a receiver protected from atmospheric moisture. A fraction boiling at 53–54° was used in this preparation.
3. During the addition of the water it is necessary to stir efficiently so that the solid which is produced will be precipitated in a finely divided form and not in large aggregates.
4. The formic ester of di-*n*-butylcarbinol is present as an impurity in the crude product and is hydrolyzed by refluxing with potassium hydroxide solution.
5. Di-*n*-butylcarbinol can be distilled at atmospheric pressure without appreciable decomposition (b.p. 193–194°/743 mm.) but it is preferable to distil under diminished pressure. The following boiling points were observed under various pressures: 97°/20 mm., 104°/30 mm., 109°/40 mm., 117°/60 mm., 130°/100 mm.

## 3. Discussion

Di-*n*-butylcarbinol has been prepared by the action of *n*-butylmagnesium bromide upon *n*-valeraldehyde<sup>1</sup> and upon ethyl formate.<sup>1, 2</sup> It has also been obtained by the catalytic hydrogenation of di-*n*-butyl ketone in the presence of platinum.<sup>3</sup>

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 5
- Org. Syn. Coll. Vol. 4, 210
- Org. Syn. Coll. Vol. 9, 510

---

## References and Notes

1. Malengreau, Bull. acad. roy. Belg. cl. sci. **1906**, 802 [C. A. **1**, 1970 (1907)].
2. Dillon and Lucas, J. Am. Chem. Soc. **50**, 1713 (1928).
3. Vavon and Ivanoff, Compt. rend. **177**, 453 (1923).

---

## Appendix

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

potassium carbonate (584-08-7)

sulfuric acid (7664-93-9)

ether (60-29-7)

magnesium,  
magnesium turnings (7439-95-4)

n-butyl bromide (109-65-9)

platinum (7440-06-4)

iodine (7553-56-2)

potassium hydroxide (1310-58-3)

ethyl formate (109-94-4)

n-butyilmagnesium bromide (693-03-8)

5-Nonanol,  
DI-n-BUTYLCARBINOL (623-93-8)

di-n-butyl ketone (502-56-7)

phosphorus pentoxide (1314-56-3)

n-valeraldehyde (110-62-3)