



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.

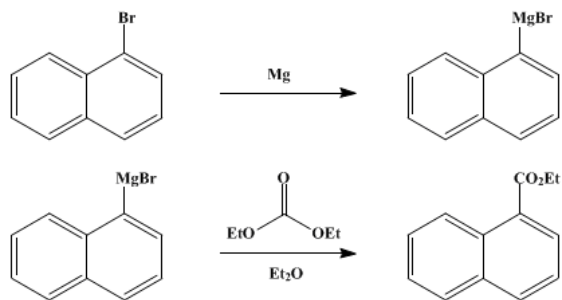
In some articles in *Organic Syntheses*, chemical-specific hazards are highlighted in red "Caution Notes" within a procedure. It is important to recognize that the absence of a caution note does not imply that no significant hazards are associated with the chemicals involved in that procedure. Prior 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.

ETHYL α -NAPHTHOATE

[1-Naphthoic acid, ethyl ester]



Submitted by Frank C. Whitmore and D. J. Loder.
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1. Procedure

A solution of α -naphthylmagnesium bromide is prepared from 24.3 g. (1 gram atom) of magnesium and 207 g. (1 mole) of α -bromonaphthalene by the procedure given on p. 425 (Note 1), but using a large separatory funnel and a 3-l. three-necked flask. The Grignard reagent is transferred to the separatory funnel, and 177 g. (1.5 moles) of ethyl carbonate (Note 2) and 100 cc. of absolute ether are placed in the flask. Stirring is begun, and the α -naphthylmagnesium bromide is added as rapidly as the refluxing of the solution permits. Stirring is continued for a half hour after the addition is finished, and the reaction mixture is then left to stand overnight.

Hydrolysis is effected by pouring the reaction mixture, with shaking, into a 5-l. flask containing 1.2–1.5 kg. of cracked ice. The basic magnesium bromide is dissolved by adding gradually 145 cc. of cold 30 per cent sulfuric acid (30 cc. of concentrated acid and 120 cc. of water). The organic layer is separated and the aqueous layer extracted with 100 cc. of ether. The combined ether solutions are concentrated by distilling the solvent from a steam bath until the volume of the residue is about 400 cc. The residue is washed with two 40-cc. portions of 5 per cent sodium carbonate solution (Note 3) and dried with 20 g. of anhydrous calcium chloride. The calcium chloride is removed by filtration and the ether is distilled from a steam bath. The residue is then transferred to a 500-cc. distilling flask and distilled; the fraction boiling from 287° to 307° is collected as crude ethyl α -naphthoate. The crude product is redistilled from a 250-cc. modified Claisen flask. The yield of pure ester, boiling at 143–144.5°/3 mm., is 136–147 g. (68–73 per cent of the theoretical amount) (Note 4).

2. Notes

1. If benzene is not added to the reagent, α -naphthylmagnesium bromide precipitates and a separatory funnel of wide bore must be used to prevent clogging during the addition of the reagent to the ester.
2. Two hundred cubic centimeters of commercial ethyl carbonate is washed with 40 cc. of 10 per cent sodium carbonate solution, then with 40 cc. of saturated calcium chloride, and finally with 60 cc. of water. After standing for two hours over 10 g. of calcium chloride, the ester is distilled and the fraction boiling at 125–126° is collected. Ethyl carbonate should not be allowed to stand over anhydrous calcium chloride for more than a day, for the ester combines with the salt.
3. By acidification of the sodium carbonate solution there is obtained 2–3 g. of α -naphthoic acid.
4. This preparation has been run satisfactorily using five times the amounts of materials specified above.

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3. Discussion

Ethyl α -naphthoate has been prepared by treating α -naphthoyl chloride with absolute ethyl alcohol,¹ by heating a mixture of α -naphthoic acid and ethyl alcohol in the presence of sulfuric acid,² and by the procedure described above.³

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 602

References and Notes

1. Hofmann, Ber. **1**, 42 (1868).
2. Perkin, J. Chem. Soc. **69**, 1178 (1896).
3. Loder and Whitmore, J. Am. Chem. Soc. **57**, 2727 (1935).

Appendix

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

ethyl alcohol (64-17-5)

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

Benzene (71-43-2)

ether (60-29-7)

magnesium (7439-95-4)

sodium carbonate (497-19-8)

α -Bromonaphthalene (90-11-9)

ethyl carbonate

Ethyl α -naphthoate,

1-Naphthoic acid, ethyl ester (3007-97-4)

α -naphthylmagnesium bromide

α -Naphthoic acid (86-55-5)

α -naphthoyl chloride (879-18-5)

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