



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.

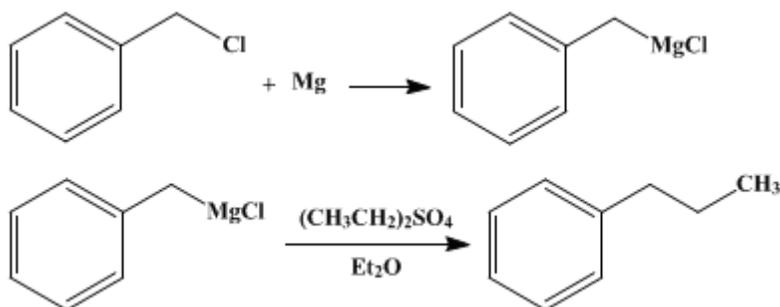
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.471 (1941); Vol. 4, p.59 (1925).

***n*-PROPYLBENZENE**

[Benzene, propyl-]



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1. Procedure

In a dry 3-l. flask, fitted with a mercury-sealed stirrer, a 500-cc. dropping funnel, and a condenser provided at its upper end with a drying tube containing a mixture of calcium chloride and soda-lime (Note 1), is placed 48.6 g. (2 atoms) of magnesium turnings. There are then added 200 cc. of dry ether, a small crystal of iodine, and about 25 cc. of a solution of 253 g. (230 cc., 2 moles) of freshly distilled benzyl chloride in 1 l. of dry ether. If the reaction does not start at once, the flask is partially immersed in a bath containing water heated to about 40°. As soon as the ether begins to boil, and reaction sets in, the bath is removed and stirring is commenced. The remainder of the benzyl chloride in ether can be added during the course of one-half hour if the reaction is regulated by cooling the greater part of the flask by immersion in ice water (Note 2). The reaction will continue for about fifteen minutes after all the benzyl chloride has been added, and then the mixture is refluxed gently for about fifteen minutes.

To the stirred benzylmagnesium chloride is then added 616 g. (522 cc., 4 moles) of freshly distilled diethyl sulfate (Note 3). The addition of diethyl sulfate is so regulated that gentle refluxing takes place throughout the reaction. Once reaction is started with a few cubic centimeters of diethyl sulfate, it is necessary to cool the reaction flask by ice water in order to complete addition within about one hour. When all the ester has been added, stirring is continued with gentle boiling for fifteen minutes (Note 4).

The cooled mixture is next poured, with stirring, upon a mixture of 1 kg. of crushed ice, 1 l. of water, and 200 cc. of concentrated hydrochloric acid. After stirring a few minutes to dissolve the sludge, the major part of the water layer is siphoned off and the ethereal solution is separated. The water layer is washed once with about 50 cc. of ether, and this washing is added to the ethereal solution of *n*-propylbenzene. The ether is removed by distillation from a water or steam bath through a fractionating column. The residue is poured into 1 l. of 10 per cent sodium hydroxide solution in about 50 per cent alcohol, and this mixture is refluxed for one hour (Note 5). After the *n*-propylbenzene is thrown out by the addition of a large volume of water, the hydrocarbon is separated, combined with an ether extract of the aqueous layer, dried by standing over 10–15 g. of solid potassium hydroxide, and fractionally distilled through an efficient column. The yield of *n*-propylbenzene, distilling at 155–160°, is 165–180 g. (70–75 per cent of the theoretical amount).

2. Notes

1. The function of the calcium chloride and soda-lime is to absorb any moisture and carbon dioxide which might diffuse into the reaction flask. The deleterious effect of another constituent of the atmosphere, oxygen, may be decreased by first sweeping out the flask with dry nitrogen or hydrogen. The initial use of a dry inert atmosphere may also be supplemented by the use of a trap¹ to exclude the air, particularly in those operations requiring extensive periods.

2. **Benzylmagnesium chloride** is one of a group of Grignard reagents which can be prepared in satisfactory yields by the rapid addition of the halide to **magnesium** in **ether**.²
3. If the **diethyl sulfate** is dark in color it should be washed, prior to distillation, with ice water and then with a **sodium bicarbonate** solution until all free acid is removed.
4. At the end of this time a negative color test shows that the Grignard reagent has been used up.
5. The solution is refluxed with alcoholic alkali to decompose any unaltered **diethyl sulfate**.

3. Discussion

n-Propylbenzene can be prepared by the action of **sodium** on **propylbromide** and **bromobenzene**;³ by the action of **diethylzinc**⁴ or **ethylmagnesium bromide**⁵ on **benzyl chloride**; by the action of **diethyl sulfate**⁶ or **ethyl *p*-toluenesulfonate**⁷ on **benzylmagnesium chloride**; and by the reduction of **ethyl phenyl ketone**,⁸ **methyl benzyl ketone**,⁸ or **propenylbenzene**.⁹ Propylbenzene can also be obtained from **benzene** by a variety of alkylation processes: With **cyclopropane** and **aluminum chloride**¹⁰ or **hydrogen fluoride**;¹¹ with **propylene** and **phosphorus pentoxide**;¹² with **propyl bromide** and **aluminum chloride**;¹³ and with **propyl alcohol** and **aluminum chloride**¹⁴ or **sulfuric acid**.¹⁵

This preparation is referenced from:

- **Org. Syn. Coll. Vol. 2, 47**
- **Org. Syn. Coll. Vol. 4, 605**

References and Notes

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Appendix

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

ester

soda-lime

hydrocarbon

alcohol (64-17-5)

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

ether (60-29-7)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

sodium bicarbonate (144-55-8)

magnesium,
magnesium turnings (7439-95-4)

propylene (115-07-1)

propylbromide,
Propyl bromide (106-94-5)

oxygen (7782-44-7)

nitrogen (7727-37-9)

carbon dioxide (124-38-9)

hydrogen fluoride (7664-39-3)

iodine (7553-56-2)

aluminum chloride (3495-54-3)

potassium hydroxide (1310-58-3)

sodium (13966-32-0)

benzyl chloride (100-44-7)

bromobenzene (108-86-1)

propyl alcohol (71-23-8)

benzylmagnesium chloride (6921-34-2)

Benzene, propyl-,
Propylbenzene,

n-PROPYLBENZENE (103-65-1)

diethyl sulfate (64-67-5)

diethylzinc (557-20-0)

ethylmagnesium bromide (925-90-6)

ethyl phenyl ketone (93-55-0)

Methyl benzyl ketone (103-79-7)

propenylbenzene

cyclopropane (75-19-4)

phosphorus pentoxide (1314-56-3)

ethyl p-toluenesulfonate (80-40-0)