



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.

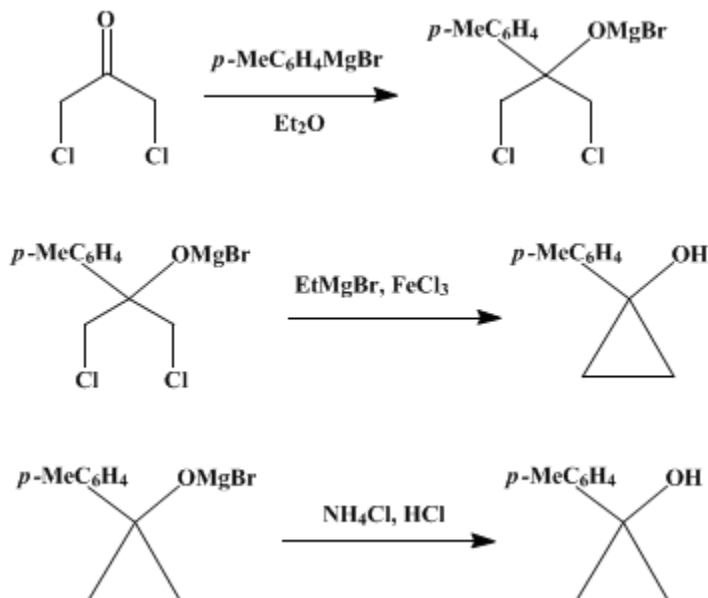
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The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures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

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## 1-*p*-TOLYLCYCLOPROPANOL



Submitted by C. H. DePuy and R. A. Klein<sup>1</sup>.  
Checked by O. Aniline and K. B. Wiberg.

### 1. Procedure

In a dry 3-l. three-necked, round-bottomed flask fitted with an efficient reflux condenser, a stirrer, a Y-tube holding a 1-l. and a 250-ml. addition funnel, and protected from moisture by calcium chloride tubes is placed 5.76 g. (0.237 mole) of magnesium turnings barely covered by anhydrous ether. *p*-Bromotoluene (40 drops) and ethyl bromide (20 drops) are added, and the reaction starts immediately. *p*-Bromotoluene (35.0 g., 0.205 mole) in 200 ml. of anhydrous ether is added at such a rate that reflux is maintained. To the resultant solution of *p*-methylphenylmagnesium bromide is added, over a 1-hour period, a solution of 25.4 g. (0.200 mole) of dichloroacetone in 200 ml. of anhydrous ether.

At the same time, in a separate 2-l. three-necked, round-bottomed flask equipped with reflux condenser, stirrer, and addition funnel, ethylmagnesium bromide is prepared from 128.6 g. (1.18 moles) of ethyl bromide and 30 g. (1.23 moles) of magnesium in 800 ml. of anhydrous ether. When the reaction is complete, the addition funnel is replaced by a rubber stopper containing a short glass tube, and the reflux condenser is replaced by an exit tube lightly plugged with a small amount of glass wool. The Grignard reagent solution is forced, under mild nitrogen pressure, through the glass wool plug into the 1-l. addition funnel (Note 1). In the 250-ml. addition funnel is placed a filtered solution of 2.5 g. (0.0154 mole) of anhydrous ferric chloride in 200 ml. of anhydrous ether. Stirring is resumed, and the two solutions are simultaneously added to the dichloroacetone-*p*-methylphenylmagnesium bromide solution over a 2-hour period (Note 2). Stirring is continued for an additional 14 hours under dry nitrogen.

The reaction mixture is added to a slurry of 1500 g. of ice and 600 ml. of 2*N* hydrochloric acid saturated with ammonium chloride. The ether layer is separated, and the aqueous layer is extracted three times with 200-ml. portions of ether. The combined organic layers are washed with three 200-ml. portions of water until a neutral reaction is obtained with litmus and the wash water is free of chloride. The solution is dried over anhydrous magnesium sulfate and stored in a refrigerator. After evaporation of the ether, the residue is distilled at a low pressure through a short Vigreux column (Note 3). The fraction, b.p. 70–78° (0.4 mm.) (oil bath 100–135°), is collected to give 15–17 g. (51–57%) of the crude carbinol which crystallizes upon standing in an ice box. The product is recrystallized from pentane (4 g. per g. of alcohol) in an ice-salt mixture to give the pure alcohol, m.p. 38–39°.

## 2. Notes

1. Since the ethyl Grignard reagent is used in large excess, no special precautions need to be taken in the transfer to prevent the loss of small amounts.
2. Large volumes of gas are generated, primarily [ethane](#) and [ethylene](#), from the disproportionation of the ethyl radicals produced in the reaction of [ethylmagnesium bromide](#) with [ferric chloride](#). The reaction should be carried out in an efficient hood, or else a tube should be run from the top of the reflux condenser to a hood.
3. 1-Arylcyclopropanols readily rearrange to propiophenones under the influence of acids and bases. In carrying out the distillation, care must be taken that the apparatus is clean and neutral.

## 3. Discussion

The method is that of DePuy and co-workers.<sup>2</sup> No other syntheses of 1-arylcyclopropanols have been reported.

## 4. Merits of the Preparation

The procedure can be adapted to the preparation, in comparable yield, of a variety of 1-substituted cyclopropanols, alkyl as well as aryl.

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## References and Notes

1. Department of Chemistry, University of Colorado, Boulder, Colorado.
  2. C. H. DePuy, G. M. Dappen, K. L. Eilers, and R. A. Klein, *J. Org. Chem.*, **29**, 2813 (1964).
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## Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

[hydrochloric acid](#) (7647-01-0)

[ether](#) (60-29-7)

[ammonium chloride](#) (12125-02-9)

[magnesium](#) (7439-95-4)

[Ethyl bromide](#) (74-96-4)

[nitrogen](#) (7727-37-9)

[ethylene](#) (9002-88-4)

[ferric chloride](#) (7705-08-0)

[dichloroacetone](#) (513-88-2)

[Pentane](#) (109-66-0)

ethylmagnesium bromide (925-90-6)

magnesium sulfate (7487-88-9)

ethane (74-84-0)

p-Bromotoluene (106-38-7)

p-methylphenylmagnesium bromide (4294-57-9)

1-p-Tolylcyclopropanol (40122-37-0)