



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.

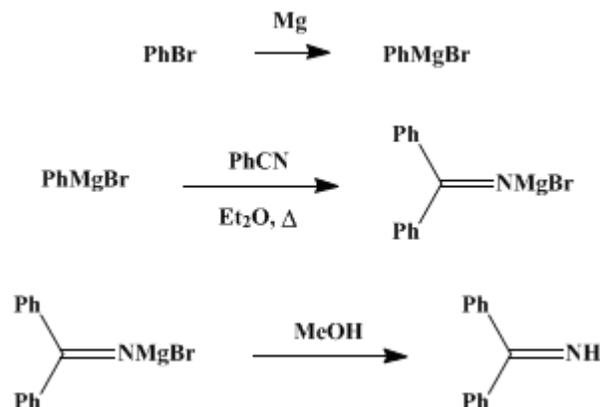
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 5, p.520 (1973); Vol. 44, p.51 (1964).*

## DIPHENYL KETIMINE

### [Diphenylmethylenimine]



Submitted by P. L. Pickard<sup>1</sup> and T. L. Tolbert<sup>2</sup>.

Checked by C. L. Dickinson, H. D. Hartzler, and B. C. McKusick.

### 1. Procedure

The apparatus consists of a 1-l. three-necked flask equipped with a mechanical stirrer, a 250-ml. dropping funnel, and a Friedrichs reflux condenser fitted with a calcium chloride drying tube. Magnesium turnings (13.4 g., 0.55 g. atom) and 200 ml. of anhydrous diethyl ether are put in the flask (Note 1). Slow stirring is started, and 4 ml. of bromobenzene (Note 2) is added from the funnel. After reaction has started (Note 3), the stirring rate is increased, and moderate reflux is maintained by addition of 80.5 g. of bromobenzene (making a total of 86 g. or 0.55 mole) in 100 ml. of ether. The solution is refluxed for 30–45 minutes after the addition and is cooled to room temperature. Stirring is continued while a solution of 51.5 g. (0.50 mole) of benzonitrile (Note 2) in 100 ml. of ether is added slowly enough (Note 4) to maintain only a gentle reflux. On completion of the addition, the reaction mixture of pale-yellow liquid and white solid is refluxed with stirring for 4–6 hours. The stirred mixture is cooled to room temperature, and the Grignard-nitrile complex is decomposed by cautious addition of 120 ml. (3 moles) of anhydrous methanol (Note 5).

On completion of the methanol addition, the mixture is stirred for 30 minutes and filtered. Low-boiling material is stripped from the filtrate, and the residue is distilled through a 45-cm. Vigreux column at reduced pressure. There is a fore-run, b.p. 120–127° (3.5 mm.), that weighs about 5 g. Then 55–73 g. (61–81%) of diphenyl ketimine is collected at 127–128° (3.5 mm.) or 151–152° (8 mm.);  $n_D^{20}$  1.6180–1.6191 (Note 6). The product should be stored under nitrogen to prevent yellowing.

### 2. Notes

1. Freshly opened commercial (Baker and Adamson) anhydrous ether is suitable. The checkers found it more convenient to use commercial phenylmagnesium bromide than to prepare it. They obtained 80 g. (88%) of the ketimine by charging the flask with 175 ml. (0.525 mole) of 3*N* phenylmagnesium bromide (Arapahoe Chemicals, Boulder, Colorado), then adding 51.5 g. of benzonitrile as described.
2. Both bromobenzene and benzonitrile (white label grade, Eastman Kodak Company) were distilled before use.
3. If the reaction does not start spontaneously, a crystal of iodine may be added and the mixture may be warmed.
4. Care should be taken to prevent a buildup of unreacted nitrile that could result in uncontrolled reaction.
5. The methanol should be added as fast as possible. A quantity of gummy material will form as the

decomposition progresses, but with continued addition of [methanol](#) it will be rapidly converted to crystalline [methoxymagnesium bromide](#).

6. Gas chromatographic analysis of the product from three consecutive preparations showed less than 0.1% impurity. Similar results were obtained on 0.005-ml. samples in an F. and M. 202 Temperature Programed Gas Chromatograph using two columns: a 12-foot column of 10% HiVac grease and 5% Marlex-50 on 100–140 mesh Gas Chrom A, at a constant temperature of 275°, with a [helium](#) flow rate of 120 ml. per minute; and a 20-foot column of 20% GE-SE 30 on 100–140 mesh Gas Chrom A, programed at 3.3° per minute from 250° to 300°, with a [helium](#) flow rate of 120 ml. per minute.

### 3. Discussion

This procedure is a modification of the method employed by Moureu and Mignonac,<sup>3</sup> who first reported the preparation of ketimines via Grignard-nitrile complexes. The use of [methanol](#) in the decomposition step results in higher yields and extends the method to the less stable ketimines.<sup>4</sup> The preparation of [diphenyl ketimine](#) by the thermal decomposition of [benzophenone oxime](#) has been described in *Organic Syntheses*.<sup>5</sup>

### 4. Merits of the Preparation

The procedure is general and is often the best way to make ketimines.

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### References and Notes

1. Celanese Chemical Company, Clarkwood, Texas.
2. Chemstrand Research Center, Inc., Durham, North Carolina.
3. C. Moureu and G. Mignonac, *Compt. Rend.*, **156**, 1801 (1913).
4. P. L. Pickard and T. L. Tolbert, *J. Org. Chem.*, **26**, 4886 (1961).
5. A. Lachman, *Org. Syntheses*, Coll. Vol. **2**, 234 (1943).

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### Appendix

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

[methanol](#) (67-56-1)

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

[benzotrile](#) (100-47-0)

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

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

[iodine](#) (7553-56-2)

[bromobenzene](#) (108-86-1)

[Phenylmagnesium bromide](#) (100-58-3)

[Benzophenone oxime](#) (574-66-3)

Diphenylmethylenimine,  
Diphenyl ketimine (1013-88-3)

helium (7440-59-7)

methoxymagnesium bromide