Organic Syntheses

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.

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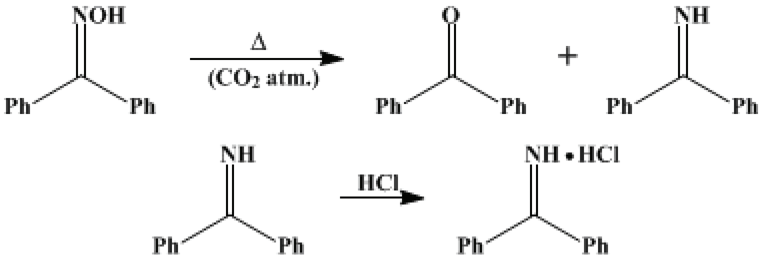
DIPHENYLMETHANE IMINE HYDROCHLORIDE

[Benzohydrylideneimine, hydrochloride]



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1. Procedure

A piece of glass tubing 80 cm. long and 2 cm. in internal diameter is sealed at one end and loosely packed with 49 g. (0.25 mole) of benzophenone oxime (p. 70). The tube is supported in a nearly horizontal position, dipping slightly toward the closed end, and connected to a small filter flask by means of rubber stoppers and a piece of glass tubing bent at a right angle. The system is evacuated by means of a water pump, and dry carbon dioxide is admitted; the system is re-evacuated and carbon dioxide is admitted again. The oxime is then heated with a free flame, beginning at the upper end and heating at one spot until decomposition takes place before heating a further portion (Note 1). When all the oxime has been decomposed, the mixture which has collected at the closed end of the tube (Note 2) is heated strongly for a short time to complete the decomposition, and allowed to cool. Suction is again applied to the tube, and the condensed water is driven out by gently warming the tube. The liquid is then transferred to a small distilling flask and distilled at a pressure of about 20 mm. The distillate, consisting of a mixture of benzophenone and diphenylmethane imine, is dissolved in 400 cc. of ligroin (60–90°), and the imine hydrochloride is precipitated by bubbling in dry hydrogen chloride. The salt is filtered with suction (Note 3), washed with a little ligroin, dried, and preserved in a dry atmosphere (Note 4). It sublimes without decomposition at 230–250° (Note 5). The yield is 16–18 g. (59–66 per cent of theoretical amount) (Note 6).

2. Notes

1. When the heating is carefully done, no material is carried out of the tube with the gases.
2. Care should be taken to prevent any drops of water that have condensed in the cool portion of the tube from running back and mixing with the liquid that is being heated.
3. Benzophenone may be recovered from the filtrate.
4. In moist air the hydrochloride is changed to a mixture of benzophenone and ammonium chloride. The free base on standing in air gives off ammonia and gradually deposits crystals of benzophenone.
5. The imine salt can be converted into the free base by the method of Hantzsch and Kraft, which involves treating a solution of the salt in chloroform with dry ammonia.
6. The yield depends greatly on the quality of the benzophenone oxime. If this contains moisture or has been exposed to moist air, especially in a closed space, for any length of time, the yield is markedly decreased.

3. Discussion

Diphenylmethane imine (or its hydrochloride) has been obtained by heating diphenyldichloromethane with urethane at 130°;[1] by the action of ammonia on diphenyldibromomethane;[2] by treating benzophenonechloroimide with phosphorus pentachloride in ether solution,[3] or dry hydrogen chloride in ligroin solution;[4] by the action of phenylmagnesium bromide on N-bromobenzamide,[2] benzonitrile,[5] cyanogen bromide,[6] cyanogen chloride,[7] and alkyl thiocyanates.[8] It has also been obtained by passing a mixture of ammonia and benzophenone vapor over thorium oxide at 380–390°;[9] by the catalytic reduction of benzophenone oxime using hydrogen and a nickel catalyst in absolute alcohol solution at ordinary temperature and pressure;[10] by passing a mixture of hydrogen and benzophenone oxime vapor over reduced copper at 200°;[11] and by the action of sodium ethoxide on N-monochlorodiphenylmethylamine in alcoholic solution.[12] The method described here has been previously published by Lachman.[13]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 70
- Org. Syn. Coll. Vol. 5, 520

References and Notes

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13. Lachman, ibid. **46**, 1477 (1924).

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

ligroin

Benzohydrylideneimine, hydrochloride

Diphenylmethane imine (or its hydrochloride)

benzophenonechloroimide

alcohol (64-17-5)

hydrogen chloride (7647-01-0)

ammonia (7664-41-7)

ether (60-29-7)

ammonium chloride (12125-02-9)

hydrogen (1333-74-0)

benzonitrile (100-47-0)

phosphorus pentachloride (10026-13-8)

chloroform (67-66-3)

carbon dioxide (124-38-9)

thorium oxide

copper (7440-50-8)

nickel (7440-02-0)

Benzophenone (119-61-9)

diphenyldichloromethane (2051-90-3)

sodium ethoxide (141-52-6)

Phenylmagnesium bromide (100-58-3)

Benzophenone oxime (574-66-3)

diphenylmethane imine hydrochloride (5319-67-5)

Cyanogen bromide (506-68-3)

diphenylmethane imine (1013-88-3)

urethane (51-79-6)

diphenyldibromomethane

N-bromobenzamide

cyanogen chloride (506-77-4)

N-monochlorodiphenylmethylamine