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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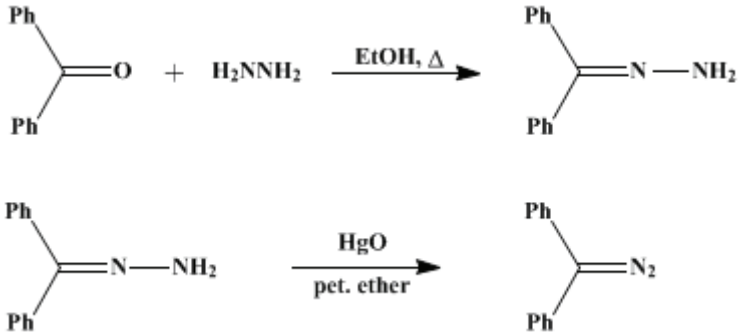
Organic Syntheses, Coll. Vol. 3, p.351 (1955); Vol. 24, p.53 (1944).

DIPHENYLDIAZOMETHANE

[Methane, diazodiphenyl-]



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1. Procedure

In a pressure bottle are placed 19.6 g. (0.1 mole) of benzophenone hydrazone (Note 1), 22 g. (0.1 mole) of yellow oxide of mercury, and 100 ml. of petroleum ether (b.p. 30–60°). The bottle is closed, wrapped in a wet towel, and shaken mechanically at room temperature for 6 hours. The mixture is then filtered to remove mercury and any benzophenone azine (Note 2), and the filtrate is evaporated to dryness under reduced pressure at room temperature. The crystalline residue of diphenyldiazomethane melts when its temperature reaches that of the room (Note 3), but it is difficult to purify and this product is pure enough for all practical purposes. The material weighs 17.3–18.6 g. (89–96%). The product should be used immediately (Note 4).

2. Notes

1. Benzophenone hydrazone is most readily prepared from benzophenone (40 g., 0.22 mole) in 150 ml. of absolute ethanol with 41.2 g. (0.824 mole) of 100% hydrazine; the mixture is heated under reflux for 10 hours. On cooling in ice, colorless benzophenone hydrazone separates. The yield is 37.5 g. (87%), m.p. 97–98°. If anhydrous hydrazine is not available, it may be prepared by the method described in *Org. Syntheses*, **24**, 53 (1944).
2. This ketazine is insoluble in petroleum ether.
3. The reported melting point of diphenyldiazomethane is 29–30°, but this melting point is shown only after the substance has been recrystallized from petroleum ether.
4. On standing, diphenyldiazomethane decomposes to yield benzophenone azine. In one of the checkers' runs the product was stored at room temperature; after 2 days, crystals of the azine were visible. The product at this stage was assayed by treatment with benzoic acid; addition of 6.8 g. of the diazo compound in a thin stream to a solution of 17 g. of benzoic acid in 90 ml. of ether, and, after 30 minutes, extraction of the excess benzoic acid with dilute sodium hydroxide followed by distillation of the ether gave 7.4 g. (75%) of crude benzohydryl benzoate melting at 83–85°. In the same procedure the freshly prepared diazo compound gave a quantitative yield of the crude ester.

3. Discussion

Diphenyldiazomethane has been prepared only by oxidation of benzophenone hydrazone.[1] The procedure given above is that of Staudinger, Anthes, and Pfenninger, with minor changes.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 6, 392
- Org. Syn. Coll. Vol. 7, 438

References and Notes

1. Staudinger, Anthes, and Pfenninger, *Ber.*, **49**, 1932 (1916)

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

petroleum ether

oxide of mercury

benzohydryl benzoate

ethanol (64-17-5)

ether (60-29-7)

sodium hydroxide (1310-73-2)

Benzoic acid (65-85-0)

mercury (7439-97-6)

Benzophenone (119-61-9)

hydrazine (302-01-2)

Diphenyldiazomethane (883-40-9)

Methane, diazodiphenyl-

benzophenone hydrazone (5350-57-2)

benzophenone azine (983-79-9)