



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.

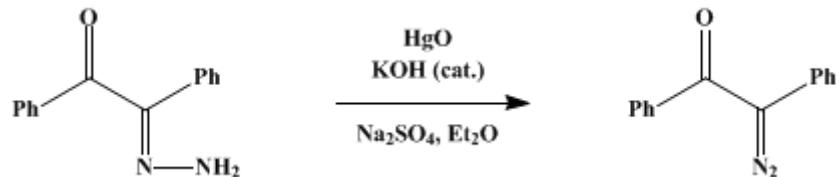
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.496 (1943); Vol. 15, p.62 (1935).

PHENYLBENZOYLDIAZOMETHANE

[Acetophenone, α -diazo- α -phenyl-]



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1. Procedure

Thirty grams (0.134 mole) of **benzil hydrazone** (Note 1) is mixed in a mortar with 60 g. (0.28 mole) of yellow **mercuric oxide** and 15 g. of anhydrous **sodium sulfate** (Note 2). The mixture is introduced into a 500-cc. glass-stoppered bottle and covered with 200 cc. of absolute **ether** (Note 3). Four cubic centimeters of a cold, saturated solution of alcoholic **potassium hydroxide** is added to catalyze the reaction (Note 4), and the mixture is shaken for ten to fifteen minutes. The solution is filtered by gravity through a fine paper, and the residue is washed several times with **ether** until the liquid is only slightly colored. The combined ethereal extracts are evaporated to dryness at the pressure of the water pump by heating the flask in a water bath to a temperature not greater than 40° (Note 5). The yellow, crystalline material is dried on a porous plate and recrystallized from anhydrous **ether**. The yield of azibenzil which melts at about 79° with decomposition is 26–28 g. (87–94 per cent of the theoretical amount) (Note 6).

2. Notes

1. Benzil hydrazone¹ may be prepared as follows:² A mixture of 52 g. (0.4 mole) of **hydrazine sulfate** (*Org. Syn. Coll. Vol. I, 1941, 309*), 110 g. (0.8 mole) of **sodium acetate**, and 250 g. of water is boiled five minutes, cooled to about 50°, and 225 cc. of **methyl alcohol** added. The precipitated **sodium sulfate** is filtered and washed with a little alcohol.

A hot solution of 50 g. (0.24 mole) of **benzil** (*Org. Syn. Coll. Vol. I, 1941, 87*) in 75 cc. of **methyl alcohol** is prepared, and the above solution, heated to 60°, is added. Most of the **benzil hydrazone** separates immediately, but the yield is increased by refluxing for half an hour. The hydrazone is filtered from the cold solution and washed with a little **ether** to remove the yellow color. The yield is 50.5 g. (94 per cent of the theoretical amount), melting at 147–151° with decomposition.

Directions for preparing **benzil hydrazone** from **benzil** and **hydrazine hydrate** are given in *Org. Syn. 20, 48*.

2. The **sodium sulfate** absorbs the water formed during the reaction.
3. By using **ether**, instead of **benzene** or petroleum ether as specified in the older methods, the evaporation of the solvent after the reaction is facilitated.
4. Without this catalyst the oxidation may require several hours and the results may vary considerably, depending largely upon the quality of the **mercuric oxide**.
5. The material may explode if the evaporation is carried out at atmospheric pressure on the steam bath.
6. This procedure may be used also for the preparation of **diazofluorene**.³

3. Discussion

Phenylbenzoyldiazomethane, azibenzil, has been prepared by the oxidation of **benzil hydrazone** with **mercuric oxide**,⁴ using **benzene** or petroleum ether as the solvent, and without the catalyst here specified.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 356
 - Org. Syn. Coll. Vol. 6, 392
 - Org. Syn. Coll. Vol. 6, 840
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References and Notes

1. Curtius and Thun, J. prakt. Chem. (2) **44**, 176 (1891).
 2. Private communication from C. F. H. Allen.
 3. Staudinger and Kupfer, Ber. **44**, 2207 (1911); Staudinger and Gaule, ibid. **49**, 1955 (1916).
 4. Curtius and Thun, J. prakt. Chem. (2) **44**, 182 (1891).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

petroleum ether

azibenzil

Benzene (71-43-2)

methyl alcohol (67-56-1)

ether (60-29-7)

sodium acetate (127-09-3)

sodium sulfate (7757-82-6)

mercuric oxide (21908-53-2)

Benzil (134-81-6)

potassium hydroxide (1310-58-3)

hydrazine hydrate (7803-57-8)

Hydrazine sulfate (10034-93-2)

Phenylbenzoyldiazomethane,
Acetophenone, α -diazo- α -phenyl- (3469-17-8)

Benzil hydrazone (5344-88-7)

diazofluorene