



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.

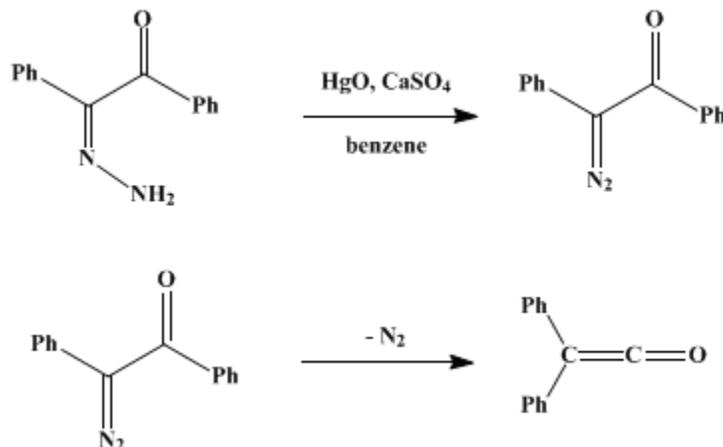
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.356 (1955); Vol. 20, p.47 (1940).

DIPHENYLKETENE

[Ketene, diphenyl-]



Submitted by Lee Irvin Smith and H. H. Hoehn.
Checked by Nathan L. Drake and Jonathan Williams.

1. Procedure

Fifty-six grams (0.25 mole) of [benzil monohydrazone](#) [*Org. Syntheses*, **15**, 62 (1935)] ([Note 1](#)) is mixed in a mortar with 81 g. (0.38 mole) of yellow [mercuric oxide](#) and 35 g. of anhydrous [calcium sulfate](#) ([Note 2](#)). The mixture is introduced into a 1-l. three-necked flask fitted with a stirrer, a condenser, and a thermometer. The flask is placed in a water bath, 200 ml. of dry thiophene-free [benzene](#) is added, and the suspension is stirred at 25–35° (thermometer in solution) for 4 hours ([Note 3](#)) and ([Note 4](#)). The reaction mixture is filtered through a fine-grained filter paper, with slight suction, and the residue is washed with dry [benzene](#) until the washings are colorless.

The [benzene](#) solution of the diazo compound is poured into a separatory funnel protected with a drying tube and connected to a 125-ml. Claisen distilling flask provided with a condenser set for downward distillation and arranged so that it can be heated in a bath of Wood's metal. The temperature of the metal bath being maintained at 100–110°, the [benzene](#) solution is dropped slowly into the hot flask. Under these conditions, the [benzene](#) is removed by distillation and the diazo compound is transformed into [diphenylketene](#). The residue is distilled under reduced pressure in an atmosphere of [nitrogen](#), and the fraction boiling at 115–125° at 3–4 mm. ([Note 5](#)) is collected. The yield is 31 g. (64%) of a product which, on redistillation, yields 28 g. of [diphenylketene](#) boiling at 119–121° at 3.5 mm. (58%).

[Diphenylketene](#) is best stored in an atmosphere of [nitrogen](#); the addition of a small crystal of [hydroquinone](#) serves to inhibit polymerization ([Note 6](#)).

2. Notes

1. [Benzil monohydrazone](#) can also be obtained in practically quantitative yield using [hydrazine hydrate](#), a method first suggested by Curtius and Thun.¹ [Hydrazine hydrate](#) (45 g., 0.75 mole, of an 85% solution of [hydrazine hydrate](#) in water) is slowly dropped into a hot solution of [benzil](#) (158 g., 0.75 mole) in alcohol (300 ml.) with stirring. The product begins to separate from the hot solution after three-fourths of the [hydrazine hydrate](#) has been added. The solution is heated under reflux for 5 minutes after all the [hydrazine hydrate](#) has been added. The flask is then cooled to 0°, and the hydrazone is filtered off and washed twice on the funnel with 100-ml. portions of cold [ethanol](#). The product melts at 149–151° with decomposition.

2. Anhydrous [calcium sulfate](#) removes the water formed in the oxidation.
3. Considerable heat is generated at the beginning of the reaction, and ice must be used in the water bath to keep the temperature within the prescribed limits. After 10–15 minutes the ice is removed, and the temperature is maintained at 25–35° by the water bath.
4. Best results are obtained when the reaction mixture is stirred for 4 hours.
5. A viscous red residue always remains in the distilling flask, necessitating superheating to remove the last traces of [diphenylketene](#).
6. According to the submitters, the preparation has been carried out using twice the quantities of material throughout with no loss in yield of [diphenylketene](#).

3. Discussion

[Diphenylketene](#) has been prepared by action of [tripropylamine](#) on [diphenylacetyl chloride](#),² by treating [diphenylchloroacetyl chloride](#) with granulated [zinc](#),³ and by the action of [quinoline](#) on [diphenylacetyl chloride](#).⁴ It is most conveniently prepared by heating phenylbenzoyldiazomethane—a method first described by Schroeter⁵ and later used by Staudinger.⁶

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 2, 496](#)
- [Org. Syn. Coll. Vol. 6, 392](#)
- [Org. Syn. Coll. Vol. 6, 549](#)

References and Notes

1. Curtius and Thun, *J. prakt. Chem.*, (2) **44**, 176 (1891).
2. Staudinger, *Ber.*, **44**, 1619 (1911).
3. Staudinger, *Ber.*, **38**, 1735 (1905).
4. Staudinger, *Ber.*, **40**, 1148 (1907).
5. Schroeter, *Ber.*, **42**, 2346 (1909).
6. Staudinger, *Ber.*, **44**, 1623 (1911).

Appendix

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

[ethanol](#) (64-17-5)

[Benzene](#) (71-43-2)

[hydroquinone](#) (123-31-9)

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

[mercuric oxide](#) (21908-53-2)

[calcium sulfate](#) (7778-18-9)

[Benzil](#) (134-81-6)

zinc (7440-66-6)

hydrazine hydrate (7803-57-8)

Quinoline (91-22-5)

Benzil monohydrazone (5344-88-7)

Diphenylacetyl chloride (1871-76-7)

Diphenylketene,
Ketene, diphenyl- (525-06-4)

tripropylamine (102-69-2)

diphenylchloroacetyl chloride (2902-98-9)