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.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

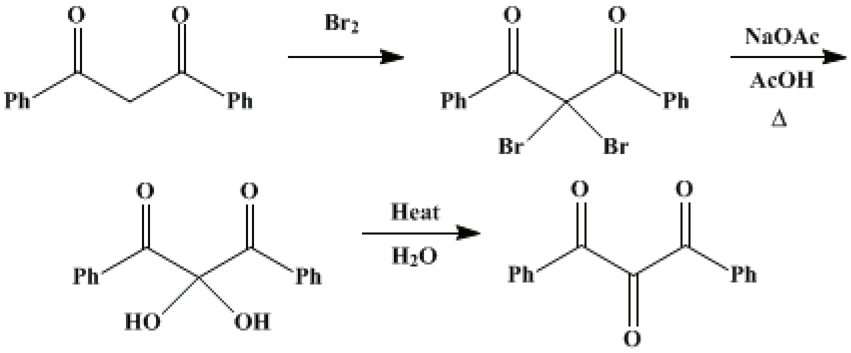
These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

DOI:10.15227/orgsyn.013.0038

Organic Syntheses, Coll. Vol. 2, p.244 (1943); Vol. 13, p.38 (1933).

DIPHENYL TRIKETONE

[Propanetrione, diphenyl-]



Submitted by Lucius A. Bigelow and Roy S. Hanslick.
Checked by W. W. Hartman and Lloyd A. Smith.

1. Procedure

(*A*) *Dibenzoyldibromomethane*.—In a 1-l. three-necked flask, equipped with a mechanical stirrer, a dropping funnel, and a thermometer, are placed 56 g. (0.25 mole) of dibenzoylmethane (Org. Syn. Coll. Vol. I, **1941**, 205; Org. Syn. **20**, 32) and 14 cc. of chloroform. The flask is surrounded by an ice bath, the stirrer is started, and a solution of 28.5 cc. (88 g., 0.55 mole) of dry bromine (Note 1) in 230 cc. of chloroform is added slowly from the dropping funnel during a period of about thirty minutes. The temperature of the mixture should not exceed 15° during the bromination; the hydrogen bromide evolved is continuously removed by aspirating a gentle stream of air over the surface of the solution. After all the bromine has been added, stirring is continued for about fifteen minutes. The solution is then transferred to a distilling flask, and the solvent is completely removed under diminished pressure at room temperature (Note 2). The slightly colored residue is crystallized from 125 cc. of hot 95 per cent ethyl alcohol. The dibenzoyldibromomethane is obtained in the form of white crystals melting at 94–95°. The yield is 72.4 g. (76 per cent of the theoretical amount) (Note 3).

(*B*) *Diphenyl Triketone Hydrate*.—A solution of 34.3 g. (0.42 mole) of fused sodium acetate in 142 cc. of hot glacial acetic acid is prepared in a 1-l. round-bottomed flask; 72.4 g. (0.19 mole) of dibenzoyldibromomethane is added, and the mixture is refluxed until the precipitation of sodium bromide ceases (one and one-half to two hours). The mixture is then cooled to room temperature and diluted with 150–200 cc. of water with constant shaking to dissolve the inorganic salt and to precipitate the triketone hydrate, which separates as a white, curdy mass (Note 4). This is separated by filtration, washed well with water, and dried in an oven at 60°. The melting point varies from 65 to 90°, depending upon the extent of dehydration that occurs during the drying operation. The yield is 41.5 g. (86 per cent of the theoretical amount based on the dibenzoyldibromomethane).

(*C*) *Diphenyl Triketone*.—The 41.5 g. (0.16 mole) of triketone hydrate is distilled in vacuum from a Claisen flask heated by means of a sand bath. A distilling flask is used as a receiver, and no condenser is necessary. The neck of the receiving flask must be warmed, however, to prevent clogging of the apparatus by crystallization of the distillate. The anhydrous triketone distils at 174–176°/2 mm. as a reddish oil that solidifies to a light yellow, crystalline mass. This is dissolved in 70 cc. of hot ligroin (b.p. 90–120°); it separates on cooling in light yellow needles which melt at 68–70°. The yield is 35 g. (91 per cent of the theoretical amount based on the triketone hydrate; 59 per cent based on the dibenzoylmethane) (Note 5).

2. Notes

1. The bromine should be dried by washing it with concentrated sulfuric acid.
2. If the solvent is removed by heat at ordinary pressure, there is a decrease both in the yield and the purity of the product.
3. If the recrystallization is omitted, a lower yield of the triketone hydrate is obtained.
4. If the hydrate separates in part in an oily condition, it may be dissolved in a small amount of glacial acetic acid and reprecipitated with an equal volume of water.
5. The triketone is hygroscopic and must be kept in a vacuum desiccator or sealed tube.

3. Discussion

The two general methods for the preparation of diphenyltriketone involve the treatment of dibenzoylmethane with bromine[1] and with oxides of nitrogen.[2] De Neufville and v. Pechmann, who originated the first method, recommended[1] conversion of the diketone to dibenzoylbromomethane and transformation of this to the acetate and then to dibenzoylbromocarbinol acetate which was split to the triketone. This sequence has been used with success by Kohler and Erickson[3] to prepare the triketone in good yields, but the present method, mentioned but not described by De Neufville and v. Pechmann,[1] is simpler and more direct.

References and Notes

1. De Neufville and v. Pechmann, Ber. **23**, 3375, 3379 (1890).
2. Wieland and Bloch, ibid. **37**, 1524, 1531 (1904).
3. Kohler and Erickson, J. Am. Chem. Soc. **53**, 2308 (1931).

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

oxides of nitrogen

ligroin

ethyl alcohol (64-17-5)

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

sodium acetate (127-09-3)

chloroform (67-66-3)

hydrogen bromide (10035-10-6)

bromine (7726-95-6)

sodium bromide (7647-15-6)

Dibenzoylmethane (120-46-7)

DIPHENYL TRIKETONE,
Propanetrione, diphenyl-,
Diphenyltriketone (643-75-4)

Dibenzoyldibromomethane (16619-55-9)

Diphenyl Triketone Hydrate

triketone hydrate

dibenzoylbromomethane

dibenzoylbromocarbinol acetate