



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.

Organic Syntheses, Coll. Vol. 1, p.205 (1941); Vol. 8, p.60 (1928).

DIBENZOYLMETHANE

[1,3-Propanedione, 1,3-diphenyl-]



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1. Procedure

In a 2-l. three-necked, round-bottomed flask, fitted with a stirrer, reflux condenser, and dropping funnel, are placed 184 g. (0.5 mole) of [benzalacetophenone dibromide](#) ([Note 1](#)) and 165 cc. of [methyl alcohol](#) ([Note 2](#)). A solution of [sodium methoxide](#), previously prepared ([Note 3](#)) from 23 g. (1 atom) of [sodium](#) and 230 cc. of absolute [methyl alcohol](#) (p. 249), is added rapidly to the stirred solution, and the mixture is then refluxed for one hour.

Sufficient concentrated [hydrochloric acid](#) (about 8 cc.) is added to neutralize the mixture, and then an additional 4 cc. After refluxing for five minutes ([Note 4](#)), 160 cc. of cold water is added, and the flask is cooled by ice water. The cooling and rapid stirring induce the formation of small crystals which are separated by filtration and washed once with 50 cc. of cold 50 per cent [methyl alcohol](#) and then with water until free of acid. The yield of crude, air-dried, [dibenzoylmethane](#) is 83–89 g. (74–80 per cent of the theoretical amount). The crude product is very pure but, if desired, may be recrystallized from 150 cc. of hot [methyl alcohol](#). The first crop, obtained by cooling to 0°, weighs 74–80 g. (66–71 per cent of the theoretical amount) and melts at 77–78° ([Note 5](#)). Partial evaporation of the solvent yields 3–5 g. of less pure product ([Note 6](#)).

2. Notes

1. The yield depends somewhat upon the quality of the dibromide. The product which gave the results described in the procedure was prepared by dissolving 208 g. (1 mole) of [benzalacetophenone](#) (p. 78) in 600 cc. of [carbon tetrachloride](#) or [carbon disulfide](#), cooling the solution in an ice bath, and adding with stirring 160 g. (51.2 cc., 1 mole) of [bromine](#). After the reaction was complete, the dibromide was filtered off and washed with two 250-cc. portions of hot [alcohol](#). The product obtained in this way melted at 156–157° and weighed about 310 g.
2. Pure [methyl alcohol](#) is essential. Synthetic [methyl alcohol](#) of 99 per cent purity is satisfactory. [Methyl alcohol](#) from wood distillation must be made absolute, by heating with quicklime or by some other means.
3. The time required for the preparation of the [sodium methoxide](#) solution is significantly reduced if all the [sodium](#), cut in small pieces (about 1 cm. or less), is placed in a flask which is attached to a reflux condenser and immersed in cold water, and the alcohol added slowly through the condenser. When the initial vigorous reaction moderates, the cooling bath can be removed. The time required is about one-half hour.
4. Prolonged heating with mineral acids should be avoided because of extensive hydrolysis to [benzoic acid](#) and [acetophenone](#).
5. In one experiment, the checkers first obtained a product of needle-like crystals which melted at 71–72°. On standing overnight, the pure compound melting at 77–78° formed.
6. If, instead of partial evaporation to obtain the second crop of product, the mother liquor is thrown into water and the resulting oil taken up in [ether](#), and the ether solution shaken with a saturated aqueous solution of [copper acetate](#), about 8 g. of the light green copper derivative is obtained. When this copper salt of dibenzoylmethane is suspended in a solution of 20 cc. of concentrated [sulfuric acid](#) and 80 cc. of

water and shaken intermittently with 70 cc. of ether, solution takes place and the separated ether layer after drying over calcium chloride and evaporating to dryness under reduced pressure yields about 6 g. of dibenzoylmethane melting at 77–78°.

3. Discussion

Dibenzoylmethane can be prepared by the hydrolysis of dibenzoylacetic acid;¹ by the slow spontaneous decomposition of acetyl dibenzoylmethane;² by the action of metallic sodium,³ sodium ethoxide,³ sodium methoxide,⁴ alcoholic potash,⁴ or sodamide⁵ on mixtures of acetophenone and ethyl benzoate; by the action of alcoholic potash,⁶ sodium methoxide,⁷ or sodium ethoxide⁸ on benzalacetophenone dibromide; by the action of sodamide on acetophenone and ethyl benzoate in ether;⁹ and by the action of sodium ethoxide on certain alkyl benzoates.¹⁰

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 244
- Org. Syn. Coll. Vol. 3, 125
- Org. Syn. Coll. Vol. 3, 251

References and Notes

1. Baeyer and Perkin, Ber. **16**, 2134 (1883); Perkin, J. Chem. Soc. **47**, 250 (1885).
2. Claisen, Ann. **291**, 83 (1896).
3. Claisen, Ann. **291**, 52 (1896).
4. Bülow and von Sicherer, Ber. **34**, 2372 (1901).
5. Claisen, Ber. **38**, 696 (1905).
6. Wislicenus, Ann. **308**, 219 (1899); Abell, J. Chem. Soc. **101**, 1002 (1912).
7. Pond, Maxwell and Norman, J. Am. Chem. Soc. **21**, 964 (1899).
8. Sluiter, Rec. trav. chim. **24**, 368 (1905).
9. Vila, Anales Soc. españ. fis quim. **27**, 668 (1929) [C. A. **24**, 358 (1930)].
10. Magnani and McElvain, J. Am. Chem. Soc. **60**, 813 (1938); Org. Syn. **20**, 32 (1940).

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

dibromide

copper derivative

copper salt of dibenzoylmethane

alcoholic potash

alcohol (64-17-5)

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)
methyl alcohol (67-56-1)
ether (60-29-7)
bromine (7726-95-6)
carbon tetrachloride (56-23-5)
Benzoic acid (65-85-0)
Benzalacetophenone (94-41-7)
Acetophenone (98-86-2)
sodium methoxide (124-41-4)
sodium,
metallic sodium (13966-32-0)
sodium ethoxide (141-52-6)
carbon disulfide (75-15-0)
Dibenzoylmethane,
1,3-Propanedione, 1,3-diphenyl- (120-46-7)
Benzalacetophenone dibromide (611-91-6)
copper acetate (142-71-2)
dibenzoylacetic acid
acetyl dibenzoylmethane
ethyl benzoate (93-89-0)
sodamide (7782-92-5)