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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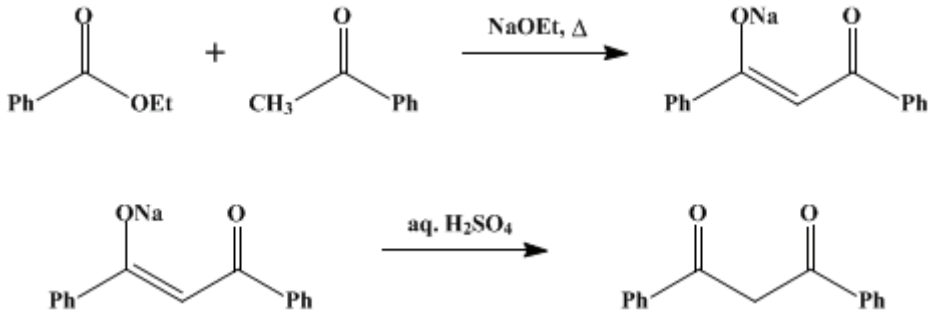
Organic Syntheses, Coll. Vol. 3, p.251 (1955); Vol. 20, p.32 (1940).

DIBENZOYLMETHANE

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



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1. Procedure

In a dry 2-l. three-necked flask are placed 600 g. (4 moles) of freshly distilled ethyl benzoate and 60 g. (0.5 mole) of freshly distilled acetophenone (Note 1). The flask is fitted with a mercury-sealed stirrer which must be rugged enough to stir the reaction mixture even after it becomes very viscous (Note 2). A condenser for downward distillation is attached to one of the necks, and a 500-ml. filter flask is used as the receiver. This receiver is connected to a water pump through a suction flask carrying a two-holed rubber stopper, one hole of which is left open. The reaction flask is heated in an oil bath kept at 150–160°, and, after the mixture is hot, 44 g. (0.65 mole) of sodium ethoxide (Note 3) is added through the third arm of the flask in 1- to 2-g. portions. The ethoxide addition can be conveniently accomplished with a spoon shaped to enter the arm of the flask or by placing a very short-stemmed large funnel in the third neck and pushing the ethoxide through the funnel with a small glass rod or wire spatula. The reaction mixture becomes orange immediately; ethanol distils after the first few additions, and thereafter the evolution of ethanol is quite vigorous. The additions are made as rapidly as evolution of the ethanol permits. During the ethoxide addition a gentle stream of air is kept passing through the flask by means of a water pump attached to the receiver in order to prevent the ethanol vapor from rising in the third arm of the flask and interfering with the addition (Note 4).

After all the ethoxide has been added (20–30 minutes) the gelatinous reaction mixture is stirred until no more distillate comes over (15–30 minutes). The weight of this distillate amounts to 38–45 g. (Note 5).

The oil bath is removed, and, with the stirring maintained, the reaction mixture is cooled to room temperature by running cold water over the flask. Then 150 ml. of water is added to dissolve the reaction mass, and both layers of the mixture are transferred to a separatory funnel. An ice-cold solution of 25 ml. of concentrated sulfuric acid in 200 ml. of water is added, and the mixture is shaken vigorously. The ester layer is separated and washed with 200 ml. of water; it is then shaken with successive 200-ml. portions of 5% sodium bicarbonate solution until the evolution of carbon dioxide ceases, after which it is washed with 200 ml. of water. The bicarbonate solution is separated and extracted with 100 ml. of ether (Note 6). The ether extract, after washing with 50 ml. of water, is combined with the ester layer and the resulting ethereal solution dried with 40 g. of calcium chloride. The ether is removed by distillation from a water bath, and the excess ethyl benzoate is removed by distillation under reduced pressure. The recovered ester, b.p. 80–83°/8 mm., amounts to 475–490 g. After the ester is removed the temperature of the oil bath is slowly raised to 180–185° while the system is maintained under 8 mm. pressure. A small amount of liquid distilling higher than the ester is thus removed. When no more distillate comes over at this temperature, the remaining oil, while still warm, is poured into a 500-ml. Erlenmeyer flask and allowed to crystallize. This crude dibenzoylmethane weighs

92–108 g. and is usually brown. It is recrystallized by dissolving in 150 ml. of hot methanol, adding 1 g. of Norit, filtering, and cooling the filtrate to 0° (Note 7). The yield of yellow crystals of dibenzoylmethane, m.p. 77–78° (Note 8), thus obtained is 70–80 g. (62–71% based on the acetophenone).

2. Notes

1. The apparatus and all reagents must be carefully dried.
2. A thick glass rod stirrer bent to fit around the inside of the flask works well. The mixture is too viscous to be stirred with a Hershberg stirrer.
3. The sodium ethoxide should be freshly prepared according to the directions under acetylacetone (p. 16). It must be kept in a tightly stoppered bottle and handled quickly.
4. The water flow through the pump is so regulated that no appreciable vacuum is allowed to build up in the reaction flask when the side arm through which the ethoxide is added is closed.
5. The amount of this distillate depends somewhat upon the rate of flow of air through the apparatus. If an appreciable vacuum builds up, this distillate may contain some acetophenone.
6. By acidification of the aqueous bicarbonate layer, 20–25 g. of benzoic acid may be obtained.
7. If the product is still dark colored, it may be purified by recrystallization from 400 ml. of 90% methanol and the color removed with Norit. In either method of crystallization 4–6 g. of inferior product may be obtained from the mother liquor.
8. Occasionally crystals melting at 71–72° may be obtained which upon standing change to the higher-melting form.

3. Discussion

In addition to the methods listed in *Org. Syntheses* Coll. Vol. **1**, 205 (1941), dibenzoylmethane has been prepared by the action of sodium amide[1] and lithium amide[2] on acetophenone and ethyl benzoate, by the action of sodium ethoxide on certain alkyl benzoates,[3] by the reaction of ethyl benzoate and sodium acetylbenzoylmethane,[4] and by the hydrolysis of N-(1,3-dimethylbutyl) acetophenone imide.[5]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 244

References and Notes

1. Levine, Conroy, Adams, and Hauser, *J. Am. Chem. Soc.*, **67**, 1510 (1945).
2. Zellars and Levine, *J. Org. Chem.*, **13**, 160 (1948).
3. Magnani and McElvain, *J. Am. Chem. Soc.*, **60**, 813 (1938).
4. McElvain and Weber, *J. Am. Chem. Soc.*, **63**, 2192 (1941).
5. Haury, Cerrito, and Ballard, U. S. pat. 2,418,173 [*C. A.*, **41**, 4510 (1947)].

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

sodium acetylbenzoylmethane

ethanol (64-17-5)

calcium chloride (10043-52-4)

sulfuric acid (7664-93-9)

methanol (67-56-1)

ether (60-29-7)

sodium bicarbonate (144-55-8)

Benzoic acid (65-85-0)

carbon dioxide (124-38-9)

Acetophenone (98-86-2)

sodium ethoxide (141-52-6)

Dibenzoylmethane,
1,3-Propanedione, 1,3-diphenyl- (120-46-7)

ethyl benzoate (93-89-0)

sodium amide (7782-92-5)

Acetylacetone (123-54-6)

lithium amide (7782-89-0)

N-(1,3-dimethylbutyl) acetophenone imide