



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.

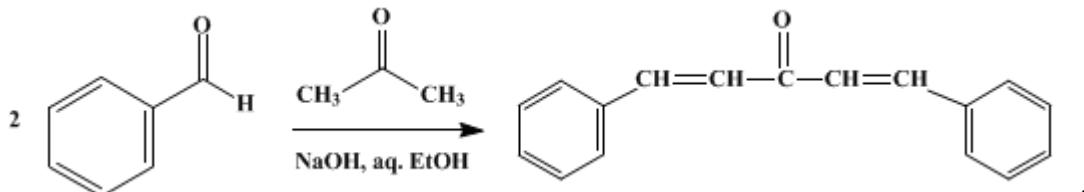
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.167 (1943); Vol. 12, p.22 (1932).

DIBENZALACETONE

[3.6/r gpvcf lgp/5/qpg.'3.7/f krj gp{ n]



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1. Procedure

A cooled solution of 100 g. of sodium hydroxide in 1 l. of water and 800 cc. of alcohol (Note 1) is "placed" in a 2-l. wide-mouthed glass jar which is surrounded with water and fitted with a mechanical stirrer. The solution "is kept at "about 20"-25° and "stirred "vigorously (Note 2) "while "one-half of a mixture of 106 g. (1 mole) of benzaldehyde and 29 g. (0.5 mole) of acetone is added (Note 3). In about two or three minutes a yellow cloud forms which soon becomes a "flocculent "precipitate. After "fifteen minutes the rest "of "the mixed reagents is added, and the container is rinsed "with "a "little "alcohol "which" is "added" to "the mixture. Vigorous "stirring is "continued "for "one-half hour longer, "and "the "mush is then filtered with suction on a large Büchner funnel. The product is thoroughly washed "with distilled water (Note 4) "and "then dried "at room "temperature "to "constant "weight. "The yield" is 105"-110 g. (90-94 "per cent of "the "theoretical amount) (Note 5) of a product which melts at 104-107°.

The crude dibenzalacetone may be recrystallized from hot ethyl acetate, "using 100 cc." of "solvent "for each 40 g. of material. The recovery in this purification is about 80 percent; the purified product melts at 110-111°.

2. Notes

1. Sufficient alcohol is used to dissolve the benzaldehyde rapidly and to retain the benzalacetone in solution until it has had time to react with the second molecule of aldehyde. Lower concentrations of "base slow up the formation of the dibenzalacetone and thus favor side reactions which yield a sticky product. Higher concentrations of base give added difficulty in washing. These concentrations were suggested by, "and are approximately the same as, those used in the preparation of benzalacetophenone described in *Org. Syn. Coll. Vol. I, 1941, 78*.
2. Only temperatures between 20 and 25° were tried; it was assumed that a change of temperature would have the same effect that it has in the preparation of benzalacetophenone mentioned above. Stirring is essential, as it makes considerable difference in the uniformity of the product.
3. The benzaldehyde was u.s.p. quality which had been washed with sodium carbonate solution and distilled. Commercial c.p. acetone was used. The theoretical quantities are used, since an excess of benzaldehyde results in a sticky product while an excess of acetone favors the production of dibenzalacetone. The mixture is prepared before addition in order to ensure additions of equivalent quantities.
4. Since the product is practically insoluble in water, large amounts can be used in the washing. Sodium compounds are probably the chief impurities. The dried product contains some sodium carbonate which results from the failure to remove the sodium hydroxide completely. There remain also the impurities insoluble in water. However, the product is pure enough for use in most reactions.
5. If the mush is allowed to stand several hours, chilled, and filtered cold, a slightly larger yield is obtained, but this is not worth while. The filtrate may be used as a medium for a second run in which about 93 per cent of the theoretical yield is obtained. The melting point of the second product is slightly lower.

3. Discussion

Dibenzalacetone has been prepared by condensing **benzaldehyde** with **acetone** using as condensing agents dry **hydrogen chloride**,¹ 10 per cent **sodium hydroxide** solution,² and glacial **acetic acid** with **sulfuric acid**.³ It has also been obtained by condensing **benzalacetone** with **benzaldehyde** in the presence of dilute **sodium hydroxide**.⁴ Straus and Ecker⁵ were the first to record the use of **ethyl acetate** for crystallization.

References and Notes

1. Claisen and Claparède, Ber. **14**, 350 (1881).
2. Schmidt, ibid. **14**, 1460 (1881); Claisen, ibid. **14**, 2470 (1881); Straus and Caspari, ibid. **40**, 2698 (1907).
3. Claisen and Claparède, ibid. **14**, 2460 (1881).
4. Claisen and Ponder, Ann. **223**, 141 (1884).
5. Straus and Ecker, Ber. **39**, 2988 (1906).

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

alcohol (64-17-5)

sulfuric acid (7664-93-9)

hydrogen chloride (7647-01-0)

acetic acid (64-19-7)

ethyl acetate (141-78-6)

sodium hydroxide (1310-73-2)

sodium carbonate (497-19-8)

Benzalacetophenone (94-41-7)

benzaldehyde (100-52-7)

acetone (67-64-1)

Benzalacetone (122-57-6)

Dibenzalacetone,
1,4-pentadien-3-one, 1,5-diphenyl (35225-79-7)