



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.

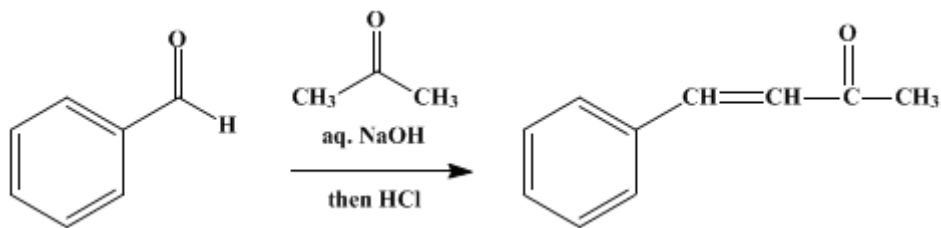
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 1, p.77 (1941); Vol. 3, p.17 (1923).

BENZALACETONE

[3-Buten-2-one, 4-phenyl-]



Submitted by N. L. Drake and P. Allen, Jr.

Checked by C. S. Marvel and A. W. Sloan.

1. Procedure

In a 2-l. bottle equipped with a mechanical stirrer are mixed 635 g. (800 cc., 11.0 moles) of u. s. p. acetone (Note 1) and (Note 2), 420 g. (400 cc., 4.0 moles) of freshly distilled benzaldehyde boiling at 178–180° (shaken with dilute sodium carbonate just before distillation), and 400 cc. of water. To this mixture, 100 cc. of 10 per cent aqueous sodium hydroxide is slowly added from a dropping funnel (Note 3), while the solution is stirred, and cooled by a water bath. The rate of addition of the alkali is so regulated that the temperature remains between 25–31°. This requires from one-half to one hour. The mixture is now stirred for two and one-quarter hours at room temperature (Note 4). At the end of this time dilute hydrochloric acid is added until the mixture is acid to litmus. The two layers which form are separated in a separatory funnel. The lower aqueous layer is extracted with 100 cc. of benzene, and the benzene solution added to the yellow oil which formed the upper layer in the first separation. This benzene solution is shaken with 100 cc. of water and separated.

The benzene is then removed by distilling from a steam bath, and the residue distilled under reduced pressure (Note 5), any water which condenses with the forerun being separated (Note 6). A special distilling flask with a fractionating side arm (p. 130) is best employed. The material which distils at 148–160° /25 mm., 133–143° /16 mm., or 120–130° /7 mm. weighs 430–470 g.; it solidifies to a crystalline mass on standing, and is pure enough for all practical purposes. On redistillation there is obtained 375–450 g. (65–78 per cent of the theoretical amount) of material boiling at 137–142° /16 mm. or 123–128° /8 mm., which solidifies on standing to crystals which melt at 40–42° (Note 7) and (Note 8).

2. Notes

1. Benzalacetone acts as an irritant, and care should be taken to prevent it from coming in contact with the skin.
2. A large excess of acetone is taken, so as to diminish the formation of dibenzalacetone.
3. If the sodium hydroxide is added too rapidly and without cooling, the mixture darkens and the yield is lowered. The rate of addition is best determined by watching the temperature of the reaction mixture.
4. Instead of stirring the mixture after the addition of the sodium hydroxide, the bottle may be securely stoppered and shaken on a shaking machine for the same length of time.
5. The lower the pressure used in the distillation the less decomposition occurs, and the less residue is left in the distilling flask. This residue contains some dibenzalacetone.
6. The first few cubic centimeters of the distillate have a greenish color, but the rest is light yellow. For this reason it is desirable to collect the first of the distillate separately, if a very light colored product is desired.
7. On exposure to air benzalacetone gradually turns brown, especially if it is slightly impure. Pure material can be kept for months in an ordinary stoppered bottle without changing color.
8. By a like procedure in which benzaldehyde is replaced by an equivalent quantity (540 g.) of

anisaldehyde, anisalacetone (b.p. 180–185° /18 mm., m.p. 72–74°) has been obtained in a yield of 83 per cent of the theoretical amount. The distillation residue, on recrystallization from ethyl acetate, yields 18 g. of dianisalacetone (m.p. 128–129°).

3. Discussion

Benzalacetone can be prepared by condensing benzaldehyde and acetone by means of dilute alkali¹ and from benzaldehyde and diketene.²

This preparation is referenced from:

- Org. Syn. Coll. Vol. 3, 105

References and Notes

1. Claisen and Ponder, Ann. **223**, 139 (1884); Vorländer, Ann. **294**, 275 (footnote) (1897); Claisen, Ber. **14**, 2468 (1881); Lewinsohn, Perfumery Essent. Oil Record, **15**, 118 (1924) [C. A. **18**, 2222 (1924)].
 2. Carbide and Carbon Chemicals Corp., U. S. pat. 2,108,427 [C. A. **32**, 2956 (1938)]; Hurd and Roe, J. Am. Chem. Soc. **61**, 3355 (1939).
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Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

ethyl acetate (141-78-6)

sodium hydroxide (1310-73-2)

sodium carbonate (497-19-8)

benzaldehyde (100-52-7)

acetone (67-64-1)

Benzalacetone,
3-Buten-2-one, 4-phenyl- (122-57-6)

Dibenzalacetone (35225-79-7)

Anisalacetone (943-88-4)

dianisalacetone (2051-07-2)

diketene (674-82-8)

anisaldehyde (123-11-5)

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