



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.

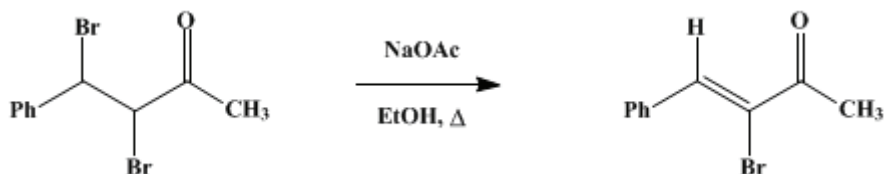
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.125 (1955); Vol. 27, p.9 (1947).

α -BROMOBENZALACETONE

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



Submitted by Norman H. Cromwell, Donald J. Cram, and Chas. E. Harris.
Checked by R. L. Shriner and William O. Foye.

1. Procedure

Warning: Precautions must be taken to avoid contact with α -bromobenzalacetone since it is a skin irritant (Note 1).

In a 500-ml. round-bottomed flask fitted with a reflux condenser are placed 100 g. (0.33 mole) of benzalacetone dibromide (p. 105), 30 g. (0.37 mole) of anhydrous sodium acetate, and 250 ml. of 95% ethanol, and the mixture is refluxed vigorously for 4 hours in the absence of direct sunlight. The precipitate of sodium bromide is removed by filtration, and the alcohol is removed from the filtrate by distillation under reduced pressure (Note 2). The residual salt-oil mixture is extracted with two 50-ml. portions of ether, and the ether solution is transferred to a 250-ml. separatory funnel (Caution! (Note 1)).

The ether solution is washed thoroughly six times with 25-ml. portions of saturated sodium chloride solution and twice with 25-ml. portions of 5% sodium bicarbonate solution (Note 3). The ether layer is allowed to dry over anhydrous sodium sulfate at room temperature for 24 hours. The ether is removed by distillation, and the residual oil is distilled from a Claisen flask under reduced pressure, using an oil bath. A yield of 47–54 g. (64–73%) of a pale yellow oil, boiling at 114–117°/1 mm. (Note 4), is obtained. On cooling, the oil crystallizes; m.p. 30–31°. The product is stored in a dark bottle in the ice chest (Note 5) and (Note 6).

2. Notes

1. α -Bromobenzalacetone or its solutions cause the formation of red spots on the skin. After several days these form large red blisters that are painful and take several days to heal. The affected parts should be treated with a mixture of peanut-oil and glycerol containing a little ammonia.
2. The reduced pressure produced by a water pump is satisfactory. The flask is warmed with a hot water bath (40–50°).
3. It is necessary that the product be entirely free from acetic acid before it is distilled in order to obtain the yields stated.
4. Boiling points at other pressures are: 136–138°/4 mm.; 150–151°/10 mm.
5. When stored in this manner the product is quite stable and darkens only slightly after 9 months.
6. The analogous α -bromobenzalacetophenone may be prepared by a similar procedure. In a 1-l. three-necked round-bottomed flask fitted with a mercury-sealed stirrer and a reflux condenser are placed 150 g. (0.41 mole) of benzalacetophenone dibromide,¹ 41 g. (0.50 mole) of anhydrous sodium acetate, and 250 ml. of 95% ethanol. The mixture is stirred and refluxed for 5 hours and then worked up in the same manner as described above for α -bromobenzalacetone. Distillation gives a yield of 100–110 g. (85–94%) of a pale yellow oil, boiling at 170–173°/1 mm. On cooling, the oil crystallizes and melts at 42–44°. This product should also be stored in a dark bottle in the ice chest, but it is more stable and darkens less on standing than the analogous α -bromobenzalacetone. This product is less irritating to the skin than α -bromobenzalacetone (Note 1).

3. Discussion

α -Bromobenzalacetone has been prepared from benzalacetone dibromide by heating with alcoholic potassium hydroxide² or with sodium acetate³ solutions. α -Bromobenzalacetophenone is prepared by a similar procedure from benzalacetophenone dibromide.⁴

References and Notes

1. *Org. Syntheses Coll. Vol. 1*, 205 (1941).
 2. Watson, *J. Chem. Soc.*, **85**, 464 (1904).
 3. Cromwell and Cram, *J. Am. Chem. Soc.*, **65**, 305 (1943).
 4. Wislicenus, *Ann.*, **308**, 226 (1899); Cromwell, *J. Am. Chem. Soc.*, **62**, 2899 (1940).
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Appendix

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

ethanol (64-17-5)

acetic acid (64-19-7)

ammonia (7664-41-7)

ether (60-29-7)

sodium acetate (127-09-3)

glycerol (56-81-5)

sodium bicarbonate (144-55-8)

sodium chloride (7647-14-5)

sodium bromide (7647-15-6)

sodium sulfate (7757-82-6)

potassium hydroxide (1310-58-3)

Benzalacetophenone dibromide (611-91-6)

Benzalacetone dibromide (6310-44-7)

α -Bromobenzalacetone

3-Buten-2-one, 3-bromo-4-phenyl- (31207-17-7)

α -bromobenzalacetophenone (6935-75-7)

