



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](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.

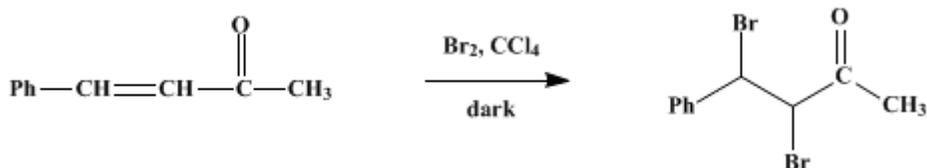
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

*Organic Syntheses, Coll. Vol. 3, p.105 (1955); Vol. 27, p.5 (1947).*

## BENZALACETONE DIBROMIDE

### [2-Butanone, 3,4-dibromo-4-phenyl-]



Submitted by Norman H. Cromwell and Richard Benson.  
Checked by R. L. Shriner and William O. Foye.

### 1. Procedure

In a 1-l. three-necked round-bottomed flask fitted with an efficient mechanical stirrer, a thermometer, and a 125-ml. dropping funnel are placed 100 g. (0.68 mole) of pure, redistilled benzalacetone<sup>1</sup> and 300 ml. of carbon tetrachloride. The reaction flask is immersed in an ice-water bath to maintain the reaction mixture between 10° and 20°. With stirring, a cooled solution of 109.5 g. (34.2 ml., 0.68 mole) of bromine in 60 ml. of carbon tetrachloride is run through the dropping funnel as rapidly as the color is destroyed (Note 1). During this addition the reaction flask should be shielded from direct sunlight (Note 2).

After all the bromine has been added, stirring is continued for 4–5 minutes longer and the dibromide is collected by filtration on an 11-cm. Büchner funnel, using suction. The product is washed with 100 ml. of warm 75% ethanol (Note 3). The crude product is purified by dissolving in the minimum amount of boiling methanol (800–1000 ml.) and cooling the solution in an ice bath for 4 hours. The product is collected by filtration and dried in a vacuum desiccator in the absence of light for 24 hours. The yield amounts to 110–120 g. (52–57%) of white needles which melt at 124–125° (Note 4).

### 2. Notes

1. Until a considerable amount of the dibromide has precipitated, the bromine solution may be run into the reaction mixture as fast as the color is discharged, within the temperature limits of 10–20°. As the mixture becomes thick with the precipitated bromide it is necessary to reduce the speed of the addition of the bromine solution considerably.
2. Strong sunlight seems to favor the substitution of the available  $\alpha$ -hydrogen as evidenced by the strong evolution of hydrogen bromide.
3. If the crude product is dried it is found to melt at 114–117° and to weigh 138–144 g. This is probably a mixture of the two racemic forms.
4. Evaporation and subsequent cooling of the filtrate give a second crop of white crystals, about 15 g., melting at 112–115°. This may be the lower-melting racemate.

### 3. Discussion

Benzalacetone dibromide has been prepared by the addition of bromine to a solution of benzalacetone in chloroform,<sup>2</sup> in carbon disulfide,<sup>3</sup> and in carbon tetrachloride;<sup>4</sup> and by the reaction of benzalacetone with N-bromosuccinimide.<sup>5</sup>

This preparation is referenced from:

- *Org. Syn. Coll. Vol. 3, 125*

## References and Notes

1. *Org. Syntheses Coll. Vol. 1*, 77 (1941).
  2. Claisen and Claparede, *Ber.*, **14**, 2463 (1881).
  3. Watson, *J. Chem. Soc.*, **85**, 464 (1904).
  4. Cromwell, *J. Am. Chem. Soc.*, **62**, 3471 (1940).
  5. Southwick, Pursglove, and Numerof, *J. Am. Chem. Soc.*, **72**, 1600 (1950).
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### Appendix Chemical Abstracts Nomenclature (Collective Index Number); (Registry Number)

$\alpha$ -hydrogen

ethanol (64-17-5)

methanol (67-56-1)

chloroform (67-66-3)

hydrogen bromide (10035-10-6)

bromine (7726-95-6)

carbon tetrachloride (56-23-5)

Benzalacetone (122-57-6)

carbon disulfide (75-15-0)

Benzalacetone dibromide,  
2-Butanone, 3,4-dibromo-4-phenyl- (6310-44-7)

N-bromosuccinimide (128-08-5)