



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.

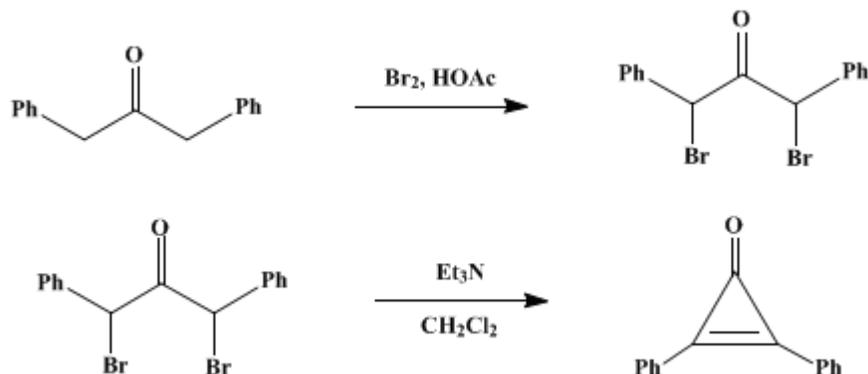
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.514 (1973); Vol. 47, p.62 (1967).

DIPHENYLCYCLOPROPENONE



Submitted by R. Breslow and J. Posner¹.

Checked by E. J. Corey and M. F. Semmelhack.

1. Procedure

Caution! See (Note 1).

A. *α,α' -Dibromodibenzyl ketone*. To a solution of 70 g. (0.33 mole) of commercial *dibenzyl ketone* in 250 ml. of glacial *acetic acid* in a 2-l. one-necked flask fitted with a magnetic stirrer a solution of 110 g. (0.67 mole) of *bromine* in 500 ml. of *acetic acid* is added through a dropping funnel over a 15-minute period. After addition is complete, the mixture is stirred for an additional 5 minutes and is then poured into 1 l. of water. Solid *sodium sulfite* is added in small portions until the initial yellow color of the solution is discharged, and the mixture is allowed to stand for 1 hour. The slightly yellow *dibromoketone* is then collected by filtration and air-dried. Recrystallization from 1 l. of ligroin yields 97 g. of white needles, m.p. 79–87°; an additional 11 g., m.p. 79–83°, is obtained by concentrating the mother liquors, and the two crops are combined (Note 1).

B. *Diphenylcyclopropenone*. A solution of 100 ml. of *triethylamine* (Note 2) in 250 ml. of *methylene chloride* is magnetically stirred in a 2-l. one-necked flask while 108 g. (0.29 mole) of the above *dibromoketone* in 500 ml. of *methylene chloride* is added dropwise over 1 hour. The mixture is stirred for an additional 30 minutes and then extracted with two 150-ml. portions of 3*N* *hydrochloric acid*; the aqueous extracts are discarded. The red organic solution is transferred to a 2-l. Erlenmeyer flask and cooled in an ice bath. While this solution is swirled, a cold solution of 50 ml. of concentrated *sulfuric acid* in 25 ml. of water is slowly added. A slightly pink precipitate of *diphenylcyclopropenone bisulfate* gradually separates (Note 3). This is collected on a sintered-glass funnel and washed with two 100-ml. portions of *methylene chloride*. The solid is then returned to the flask (Note 4) along with 250 ml. of *methylene chloride* and 500 ml. of water, and 5 g. of solid *sodium carbonate* is added in small portions. The organic layers is collected and the aqueous solution extracted with two 150-ml. portions of *methylene chloride*. The combined organic layers are dried over *magnesium sulfate* and evaporated to dryness. The impure *diphenylcyclopropenone* is recrystallized by repeated extraction with boiling *cyclohexane* (total 1.5 l.), the solution being decanted in each case from a reddish oily impurity. On cooling, the solution deposits 29 g. of white crystals, and an additional 1 g. can be obtained by concentrating the mother liquors to 150 ml. The combined 30 g., m.p. 119–120°, represents an overall yield of 44% based on *dibenzylketone*.

2. Notes

1. Care should be taken to prevent either the *dibromoketone* or the *cyclopropenone* from coming into contact with the skin, as allergic reactions have been observed in several cases. The use of gloves is

recommended especially for the [bromoketone](#). The latter product has a wide melting range because it is a mixture of the *meso*- and *d,l*-compounds.

2. For best results the commercial [triethylamine](#) (Matheson, b.p. 89–90°) should be purified to remove primary and secondary amines and water, either by distillation from [acetic anhydride](#) and then from [barium oxide](#), or by reaction with [phenylisocyanate](#).^{2,3}

3. If the white solid fails to separate after 15–30 minutes, concentrated [sulfuric acid](#) is added in 4-ml. portions to the cooled solution with swirling until the white solid appears.

4. Since some of the white solid adheres to the walls of the flask, it is convenient to use the same flask for the neutralization after rinsing it with [methylene chloride](#).

3. Discussion

[Diphenylcyclopropenone](#) has also been prepared by the action of [phenylchlorocarbene](#) on [phenylketene acetal](#)⁴ and by the reaction of dihalocarbene with [diphenylacetylene](#).⁵ The present procedure⁶ is the most convenient on a preparative scale.

4. Merits of the Preparation

[Diphenylcyclopropenone](#) is the first stable molecule prepared which has a carbonyl group in a three-membered ring. In a very real sense the compound has aromatic character and is fairly stable.⁴ An interesting cycloaddition reaction of enamines with [diphenylcyclopropenone](#) has been reported.⁷

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 6, 991](#)
- [Org. Syn. Coll. Vol. 7, 319](#)

References and Notes

1. Department of Chemistry, Columbia University, New York, New York 10027.
2. A. Weissberger, "Technique of Organic Chemistry," Vol. VII, 2nd ed., Interscience Publishers Inc., New York, 1955, p. 445.
3. J. C. Sauer, *Org. Syntheses, Coll. Vol. 4*, 561 (1963).
4. R. Breslow, R. Haynie, and J. Mirra, *J. Am. Chem. Soc.*, **81**, 247 (1959).
5. M. E. Volpin, Yu. D. Koreshkov, and D. N. Kursanov, *Izv. Akad. Nauk SSSR*, 560 (1959).
6. R. Breslow, J. Posner, and A. Krebs, *J. Am. Chem. Soc.*, **85**, 234 (1963).
7. J. Ciabattini and G. A. Berchtold, *J. Org. Chem.*, **31**, 1336 (1966).

Appendix

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

[sulfuric acid](#) (7664-93-9)

[hydrochloric acid](#) (7647-01-0)

[acetic acid](#) (64-19-7)

[acetic anhydride](#) (108-24-7)

[sodium sulfite](#) (7757-83-7)

sodium carbonate (497-19-8)
bromine (7726-95-6)
barium oxide
cyclohexane (110-82-7)
methylene chloride (75-09-2)
phenylisocyanate (103-71-9)
magnesium sulfate (7487-88-9)
dibenzyl ketone,
dibenzylketone (102-04-5)
Diphenylacetylene (501-65-5)
dibromoketone,
bromoketone (593-95-3)
triethylamine (121-44-8)
Diphenylcyclopropanone (886-38-4)
diphenylcyclopropanone bisulfate
cyclopropanone (2961-80-0)
phenylchlorocarbene
phenylketene acetal
 α,α' -Dibromodibenzyl ketone (958-79-2)