



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.

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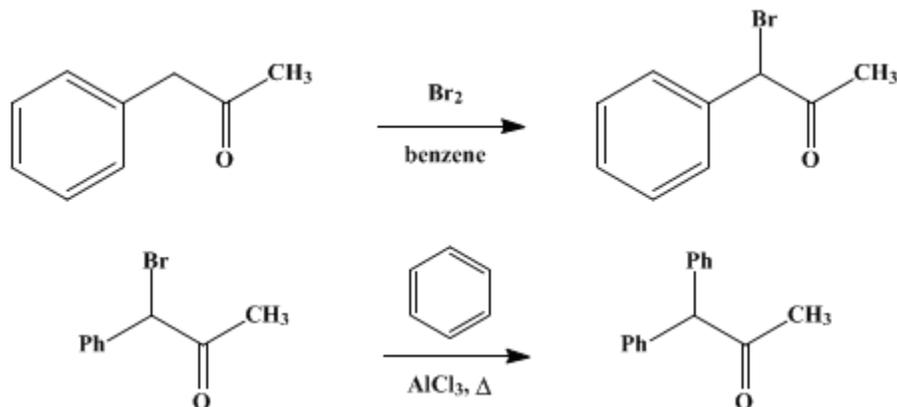
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*These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.*

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## **$\alpha,\alpha$ -DIPHENYLACETONE**

### **[2-Propanone, 1,1-diphenyl-]**



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### **1. Procedure**

A.  *$\alpha$ -Bromo- $\alpha$ -phenylacetone*. A 1-l. three-necked flask is equipped with a sealed stirrer (Note 1), a dropping funnel, and a water-cooled reflux condenser provided with a short inverted U-tube on the open end; the equipment is assembled in the hood. In the flask are placed 200 ml. of dry, thiophene-free benzene (Note 2) and 37 g. (36.89 ml., 0.276 mole) of phenylacetone (Note 3). The stirrer is started, and 45 g. (14.42 ml., 0.28 mole) of reagent bromine is added dropwise during a period of 1 hour. The reaction mixture first becomes cloudy but changes to a clear orange-red solution by the time all the bromine is added. After the addition of bromine is complete, a rapid stream of dry nitrogen or carbon dioxide is passed through the solution by means of an inlet tube which now replaces the dropping funnel. The hydrogen bromide issuing from the inverted U-tube at the top of the condenser may be trapped in water in an Erlenmeyer flask or other container adjusted so that the water surface is about 1 cm. below the outlet of the tube. The reaction is complete when no more hydrogen bromide fumes can be detected in the gas issuing from the condenser. This operation requires 3–6 hours. During this period the reaction mixture becomes yellow to green. The benzene solution of  $\alpha$ -bromo- $\alpha$ -phenylacetone is then transferred to a dry 500-ml. separatory funnel (Note 4).

B.  *$\alpha,\alpha$ -Diphenylacetone* (Note 5). The reaction flask used in A is again equipped as it was originally, and in it are placed 75 g. (0.56 mole) of anhydrous aluminum chloride (Note 6) and 150 ml. of dry benzene (Note 2). The stirrer is started, and the flask is heated by means of a steam bath so that the benzene boils gently. The benzene solution of  $\alpha$ -bromo- $\alpha$ -phenylacetone (Part A) is added dropwise from the separatory funnel to the boiling mixture over a period of 1 hour. After the addition is complete, the almost black reaction mixture is heated to boiling for an additional hour, then cooled and poured with stirring onto 500 g. of crushed ice and 100 ml. of concentrated hydrochloric acid contained in a 2-l. beaker. The deeply colored benzene solution gradually becomes orange-yellow. When the ice has melted, the benzene layer is separated and the aqueous layer is extracted with three 50-ml. portions of ether. The combined ether and benzene solution is washed with 100 ml. of water and then with 100 ml. of saturated sodium bicarbonate solution. After the solution has been dried for at least 1 hour over 60 g. of anhydrous sodium sulfate, the solvents are evaporated on a steam bath until the solution no longer boils. The dark residue is transferred to a 250-ml. Claisen flask equipped for reduced-pressure distillation and having a receiver fused to the side arm (Note 7). The residual benzene is first distilled at 19–20 mm. while the flask is being heated on a steam bath. The steam bath is replaced by an oil or metal bath which is gradually heated to 190°. A small fore-run of yellow oil which darkens rapidly is collected. It is removed from the receiver by siphoning and rinsing with acetone. The bath is allowed to

cool to 100–120°, the system is evacuated with an oil pump (Note 8), and the diphenylacetone is distilled. The bulk of the material boils at 142–148°/2–3 mm. The distillate may solidify in the receiver (Note 9). The crude product is triturated with just sufficient petroleum ether (b.p. 35–60°) to moisten it, cooled in an ice-water bath, collected on a filter, and washed on the filter with small amounts of petroleum ether at 0–5° until nearly colorless. The amount of petroleum ether used up to this point should not exceed 50 ml. The product is then crystallized from petroleum ether using 8 ml. of solvent per gram of crude, dry solid. The hot solution is allowed to stand at room temperature until crystallization begins, and then at 0–5° for 16 hours (Note 10). The crystals are collected by filtration and dried in air at room temperature. The yield of nearly colorless product melting at 60–61° (Note 11) is 31–33 g. (53–57%).

## 2. Notes

1. A rubber tubing seal is satisfactory. The submitters used an all-glass seal made from a 5-ml. glass syringe.
2. The benzene was reagent grade and was dried by distilling until no more water collected in the condenser. The undistilled portion was used directly.
3. Phenylacetone was obtained from the Swope Oil Company, Philadelphia, Pennsylvania. On attempted distillation of this material as received, the checkers observed considerable water in the forerun. The distillation was interrupted, the material was dried over anhydrous sodium sulfate and redistilled at atmospheric pressure, but small amounts of water still appeared in the condensate, indicating possible decomposition. The fraction boiling at 214–214.8° (uncor.)/ 756 mm. was used.
4. The transfer may be carried out easily by admitting dry nitrogen or air under pressure continuously to the flask and allowing the benzene solution to be blown out of the flask through the glass tube previously used for introducing nitrogen or carbon dioxide.
5. Once Part B is started, it should be continued without interruption until the Friedel-Crafts reaction product is decomposed.
6. Baker and Adamson reagent grade powdered aluminum chloride was used.
7. Diphenylacetone may solidify in the side arm, in which event it may become necessary to melt it by heating with a small flame.
8. It is necessary to protect the pump by means of a sodium hydroxide tower since hydrogen halide may be evolved during the distillation. The checkers, in addition, used a Dry Ice trap.
9. The checkers transferred the distillate to another container before solidification occurred.
10. The checkers found that the small additional amount (approximately 5 g.) of product obtained by cooling to –25° is more highly colored and considerably less pure than that obtained at 0–5°.
11. A labile form of  $\alpha,\alpha$ -diphenylacetone, melting at 46°, is described in the literature.<sup>1,2</sup>

## 3. Discussion

$\alpha,\alpha$ -Diphenylacetone has been prepared by the oxidation of 1,1-diphenyl-2-propanol;<sup>1</sup> by the action of dilute mineral acid on 1,1-diphenyl-1,2-propanediol,<sup>1,2</sup> 1,1-diphenyl-1-hydroxy-2-ethoxypropane,<sup>3</sup> 1,1-diphenyl-1-hydroxy-2-aminopropane,<sup>4</sup> 1,1-diphenyl-2-ethoxy-1-propene,<sup>5</sup> and 2,2-diphenyl-3-methylethylenimine;<sup>6</sup> by the distillation at atmospheric pressure of 1,1-diphenyl-2-methylethylene oxide;<sup>7</sup> by the reaction of benzene with  $\alpha$ -phenyl- $\alpha$ -chloro- (or bromo-) acetone;<sup>8,9</sup> by acetylation of potassium *t*-butyl diphenylacetate, followed by hydrolysis<sup>10</sup> and by the rearrangement of  $\alpha$ -methyldeoxybenzoin in the presence of zinc chloride.<sup>11</sup> The present method is adapted from the procedure of Ruggli, Dahn, and Wegmann.<sup>8</sup>

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## References and Notes

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4. Thomas and Bettziechi, *Z. physiol. Chem.*, **140**, 265 (1924).

5. Bardan, *Bull. soc. chim. France*, **49**, 1875 (1931).
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  7. Levy and Lagrave, *Compt. rend.*, **180**, 1032 (1925); *Ann. chim.*, (10) **8**, 365 (1927).
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  10. Yost and Hauser, *J. Am. Chem. Soc.*, **69**, 2325 (1947).
  11. Zaleskaya, *Zhur. Obschei Khim.*, **18**, 1168 (1948) [*C. A.*, **43**, 1754 (1949)].
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**Appendix**  
**Chemical Abstracts Nomenclature (Collective Index Number);**  
**(Registry Number)**

petroleum ether

$\alpha$ -phenyl- $\alpha$ -chloro- (or bromo-) acetone

$\alpha$ -methyldesoxybenzoin

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

ether (60-29-7)

hydrogen (1333-74-0)

sodium hydroxide (1310-73-2)

sodium bicarbonate (144-55-8)

hydrogen bromide (10035-10-6)

bromine (7726-95-6)

sodium sulfate (7757-82-6)

nitrogen (7727-37-9)

carbon dioxide (124-38-9)

acetone (67-64-1)

aluminum chloride (3495-54-3)

zinc chloride (7646-85-7)

phenylacetone (103-79-7)

$\alpha,\alpha$ -Diphenylacetone,

2-Propanone, 1,1-diphenyl-,  
diphenylacetone (781-35-1)

$\alpha$ -bromo- $\alpha$ -phenylacetone (23022-83-5)

1,1-diphenyl-2-propanol (29338-49-6)

1,1-diphenyl-1,2-propanediol

1,1-diphenyl-1-hydroxy-2-ethoxypropane

1,1-diphenyl-1-hydroxy-2-aminopropane

1,1-diphenyl-2-ethoxy-1-propene

2,2-diphenyl-3-methylethylenimine

1,1-diphenyl-2-methylethylene oxide

potassium t-butyl diphenylacetate