Organic Syntheses

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.

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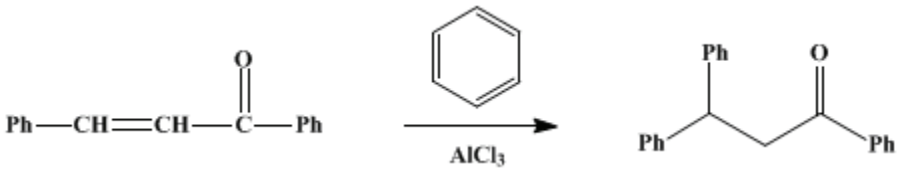
β,β-DIPHENYLPROPIOPHENONE

[Propiophenone, β,β-diphenyl-]



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1. Procedure

In a 3-l. round-bottomed, three-necked flask fitted with a liquid-sealed mechanical stirrer, a thermometer, and a 500-cc. separatory funnel are placed 1.7 l. of dry benzene and 160 g. (1.2 moles) of powdered, anhydrous aluminum chloride (Note 1). The mixture is cooled to 10° by means of an ice-water bath and maintained at 10–20° during the addition of a solution of 120 g. (0.58 mole) of benzalacetophenone (Note 2) in 300 cc. of dry benzene. This addition requires about thirty minutes. The cooling bath is then removed and stirring continued at room temperature until all the dense, yellow precipitate formed at first has gone into solution (Note 3). The reaction is complete after stirring for an additional hour.

The bulk of the brown-colored benzene solution is decanted into a cold mixture of 100 cc. of concentrated hydrochloric acid and 1.5 l. of water in a 5-l. round-bottomed flask. The remainder is filtered on a Büchner funnel, and the lumps of aluminum chloride are washed with two 100-cc. portions of benzene. The filtrates are added to the main solution and the whole is washed thoroughly with the dilute acid. If the layers do not separate readily the mixture is filtered with gentle suction and the water separated by siphoning. The solution is washed twice with 1.5-l. portions of water and filtered again if necessary.

The clear, light yellow benzene solution is subjected to rapid steam distillation (Note 4) in the same 5-l. flask, and when no more benzene passes over the flask is cooled under the tap with shaking. The residual oil solidifies to light brown pellets. These are collected, separated from water as much as possible, and dissolved in 2250 cc. of boiling alcohol. Five grams of decolorizing carbon is added; the hot solution is filtered with suction and allowed to cool. The best results are obtained if the alcoholic solution is stirred slowly with a mechanical stirrer while cooling to room temperature. Stirring is stopped when the mixture becomes semi-solid, and the mass is then allowed to stand for twenty-four hours. The fine, colorless needles are filtered on a 15-cm. Büchner funnel and pressed as dry as possible. The yield of thoroughly air-dried, colorless material melting at 91–92° (Note 5) amounts to 125–140 g. (76–85 per cent of the theoretical amount) (Note 6).

2. Notes

1. Trial runs demonstrated that one mole of benzalacetophenone required at least two moles of anhydrous aluminum chloride to complete the reaction at room temperature. When less aluminum chloride was used the yellow addition product failed to dissolve entirely even after stirring for twenty-four hours, and the yield was decreased.
2. The benzalacetophenone (Org. Syn. Coll. Vol. I, **1941**, 78) must be quite pure (m.p. 55–56°) and, in particular, free from benzaldehyde.
3. A change in appearance of the mixture is very noticeable at the end of the reaction. The yellow color rapidly gives way to a dark brown. A perfectly clear solution is not produced as the aluminum chloride remains in suspension.
4. If the benzene solution is steam-distilled directly from the acid mixture the crude product is darker in

color, more difficult to crystallize, and less pure after crystallization.
5. The melting point of β,β-diphenylpropiophenone is given in the literature[1], [2], [3] as 96°. The product melting at 91–92° was recrystallized to constant melting point from alcohol and from ligroin, but the melting point remained at 92° (corr.). The oxime and the monobromoketone prepared according to Kohler[3] were found to melt at 133° (corr.) and 166° (corr.), respectively.
6. An additional 12–16 g. of less pure product, melting at 88–91°, may be obtained by concentrating the mother liquor to 400 cc.

3. Discussion

β,β-Diphenylpropiophenone has been prepared from benzalacetophenone with phenylmagnesium bromide,[1] and a number of other phenylmetallic compounds;[2] by the condensation of benzalacetophenone and benzene with concentrated sulfuric acid[3] or with aluminum chloride,[4] and by the action of aluminum chloride on a mixture of benzene and the hydrochloride of benzalacetophenone.[4] The procedure described here is essentially that of Vorländer and Friedberg.[4]

References and Notes

1. Kohler, Am. Chem. J. **29**, 352 (1903).
2. Gilman and Kirby, J. Am. Chem. Soc. **63**, 2047 (1941).
3. Kohler, Am. Chem. J. **31**, 642 (1904).
4. Vorländer and Friedberg, Ber. **56**, 1144 (1923).

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

ligroin

hydrochloride of benzalacetophenone

alcohol (64-17-5)

sulfuric acid (7664-93-9)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

Benzalacetophenone (94-41-7)

benzaldehyde (100-52-7)

decolorizing carbon (7782-42-5)

aluminum chloride (3495-54-3)

Phenylmagnesium bromide (100-58-3)

β,β-Diphenylpropiophenone,

Propiophenone, β,β-diphenyl- (606-86-0)