



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.

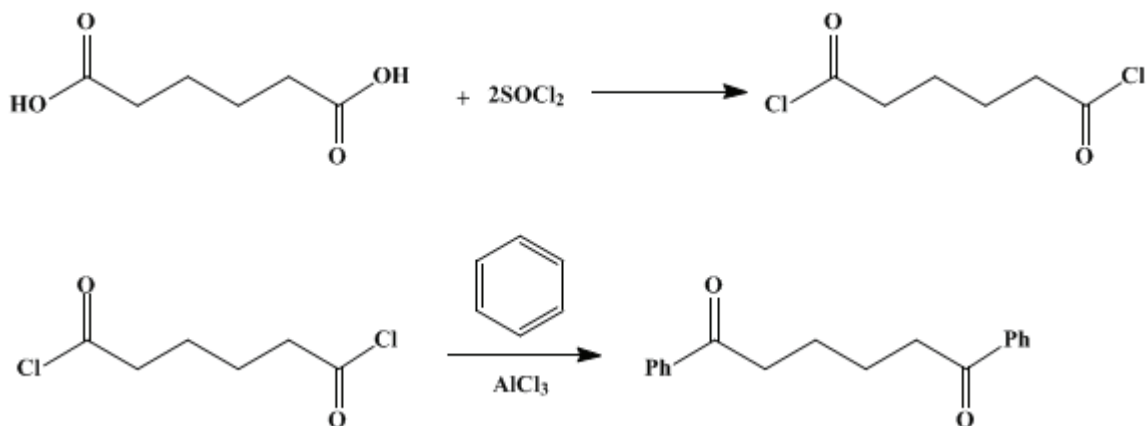
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.169 (1943); Vol. 13, p.32 (1933).

1,4-DIBENZOYL BUTANE

[1,6-Hexanedione, 1,6-diphenyl-]



Submitted by Reynold C. Fuson and Joseph T. Walker.

Checked by W. H. Carothers and W. L. McEwen.

1. Procedure

One mole (146 g.) of **adipic acid** (*Org. Syn. Coll. Vol. I, 1941, 18*), previously dried over **sulfuric acid** in a vacuum, is placed in a 1-l. round-bottomed flask equipped with a condenser, and 357 g. (217 cc., 3 moles) of **thionyl chloride** is added at once. The mixture is heated gently on a water bath held at a temperature of 50–60°. After about four hours, solution is complete and evolution of **hydrogen chloride** has ceased. The flask is now connected to a downward condenser and heated under diminished pressure by a water bath to remove any excess **thionyl chloride**. The light yellow residue of **adipyl chloride** is ready for use.

A mixture of 300 g. (2.25 moles) of anhydrous **aluminum chloride** and 1.5 l. (17 moles) of **benzene** (dried over **sodium** and distilled) is placed in a 3-l. three-necked flask equipped with a mercury-sealed stirrer, a reflux condenser, and a dropping funnel. The reaction mixture is cooled in an ice bath, and, with rapid stirring, the **adipyl chloride** is added through the dropping funnel at an *even rate* during the course of forty-five minutes (*Note 1*). The reaction mixture darkens slowly but does not become black. After the **adipyl chloride** has been added, the ice bath is removed and stirring is continued for two hours at room temperature (*Note 2*).

The solution is then poured slowly, with constant stirring, into a mixture of 1 kg. of cracked ice and 200 cc. of concentrated **hydrochloric acid** in a 5-l. flask. There should be a small quantity of ice remaining after decomposition is complete. When the ice has melted, the mixture of water, precipitated **dibenzoylbutane**, and **benzene** is divided into two equal portions, and 1–1.25 l. of **benzene** is added to each. The solid is dissolved by shaking and gentle warming on the steam bath; the **benzene** layers are separated and washed, first with an equal volume of dilute **sodium carbonate** solution, and then with water.

The **benzene** solution is placed in a 5-l. flask, and 3–3.5 l. of **benzene** is removed by distillation. The residual liquid is set aside and allowed to cool. The **dibenzoylbutane** which crystallizes after several hours is filtered; it melts at 104–107° (*Note 3*). An equal volume of **ether** is added to the light brown filtrate, and a second crop of crystals is obtained (*Note 4*).

The yield of crude product is 199–216 g. (75–81 per cent of the theoretical amount). The material may be recrystallized by dissolving it in 1 l. of hot 95 per cent **ethyl alcohol**. Upon cooling, crystals which melt at 106–107° separate. The yield of recrystallized product is 190–210 g.

2. Notes

1. It is very important to keep the reaction mixture cold during the addition of the acid chloride; otherwise there will be charring which will lead to a discolored product.
2. If the reaction mixture is allowed to stand at this point the yield is materially decreased.
3. The melting point and color of the crude product seem to be influenced by the quality of the [aluminum chloride](#). The checkers used a very pure [aluminum chloride](#) and found that the color of the reaction mixture was never darker than a bright orange, that the crude product was always colorless, and that the crude product always melted at 106–108°. If a less pure [aluminum chloride](#) is used the crude product is sometimes brown. This color may be completely removed by washing with a few cubic centimeters of cold [ether](#), in which the diketone is only slightly soluble.
4. The checkers found that only 5–6 g. of material was precipitated by the addition of [ether](#). For this reason it seems scarcely worth while to carry out this part of the procedure.

3. Discussion

Dibenzoylbutane has been prepared by the action of [aluminum chloride](#) on a mixture of [benzene](#) and [adipyl chloride](#)¹ or [benzene](#) and polymeric [adipic anhydride](#).² It has also been obtained from [adiponitrile](#) and [phenylmagnesium bromide](#),³ and as a by-product in the action of [zinc](#) on [\$\alpha,\beta\$ -dibromopropiophenone](#)⁴ and [\$\alpha,\alpha'\$ -dibromodibenzoylbutane](#).⁵ Melting points between 102°¹ and 112°⁴ have been recorded for the diketone.

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 6, 401](#)

References and Notes

1. Etaix, *Ann. chim. phys.* (7) **9**, 372 (1896).
2. Hill, *J. Am. Chem. Soc.* **54**, 4105 (1932).
3. Compère, *Bull. soc. chim. Belg.* **44**, 523 (1935).
4. Kohler, *Am. Chem. J.* **42**, 384 (1909).
5. Fuson and Farlow, *J. Am. Chem. Soc.* **56**, 1593 (1934).

Appendix

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

[ethyl alcohol](#) (64-17-5)

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

[hydrogen chloride](#),
[hydrochloric acid](#) (7647-01-0)

[Benzene](#) (71-43-2)

[ether](#) (60-29-7)

[thionyl chloride](#) (7719-09-7)

Adipic acid (124-04-9)

sodium carbonate (497-19-8)

aluminum chloride (3495-54-3)

zinc (7440-66-6)

sodium (13966-32-0)

Phenylmagnesium bromide (100-58-3)

1,4-Dibenzoylbutane,
1,6-Hexanedione, 1,6-diphenyl- (3375-38-0)

adipyl chloride (111-50-2)

dibenzoylbutane

adipic anhydride

adiponitrile (111-69-3)

α,β -dibromopropiophenone

α,α' -dibromodibenzoylbutane