



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.

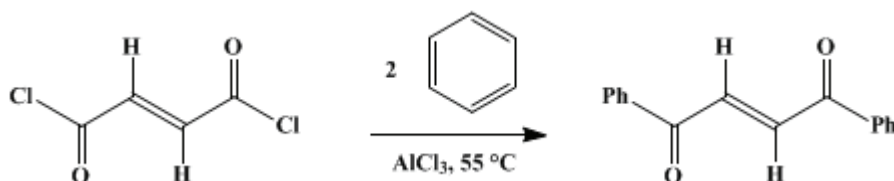
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.248 (1955); Vol. 20, p.29 (1940).

***trans*-DIBENZOYLETHYLENE**

[2-Butene-1,4-dione, 1,4-diphenyl-]



Submitted by R. E. Lutz

Checked by C. F. H. Allen and F. P. Pingert.

1. Procedure

Eighteen hundred milliliters of [benzene](#) ([Note 1](#)) and 350 g. of finely ground anhydrous [aluminum chloride](#) (2.6 moles) ([Note 2](#)) are placed in a 3-l. three-necked flask, fitted with a mechanical stirrer, a dropping funnel ([Note 3](#)) containing 153 g. (1 mole) of [fumaryl chloride](#) ([p. 422](#)), and a reflux condenser ([Note 4](#)). A trap for absorbing hydrogen chloride is attached to the condenser.

The mixture is well stirred and heated externally by hot water (50–60°) ([Note 5](#)), the water removed, and the [fumaryl chloride](#) admitted at a *brisk* rate, moderated only enough to avoid a too rapid evolution of [hydrogen chloride](#); this requires 15–25 minutes ([Note 6](#)) and ([Note 7](#)). The mixture turns dark red and soon reaches the boiling point; [hydrogen chloride](#) is rapidly given off. The mixture is then refluxed gently for 10 minutes with stirring.

The pasty red mixture is then poured portionwise upon 4 kg. of cracked ice to which has been added 75 ml. of concentrated [hydrochloric acid](#), the reaction mixture being thoroughly stirred before each pouring so that the aluminum chloride complex does not settle out and become concentrated at the bottom of the flask. The residue in the flask is decomposed by adding some of the ice and water. After standing 20–30 minutes, very hot water ([Note 8](#)) is added to melt any ice or frozen [benzene](#) and raise the temperature generally. The bulk of the aqueous layer is discarded by drawing it off with a glass tube connected to a suction flask. The [benzene](#) layer is next washed at least four times with hot water ([Note 8](#)) and ([Note 9](#)). Finally the warm [benzene](#) layer is transferred to a large separatory funnel, any crusts of [dibenzoyl ethylene](#) adhering to the various pieces of apparatus are dissolved in hot [benzene](#), and the solutions combined; the small water layer is separated and discarded ([Note 10](#)). The hot [benzene](#) layer is then filtered, either by gravity using a large glass funnel or by suction on a Büchner funnel, into a 3-l. round-bottomed flask. After a few porcelain chips have been added, the bulk of the solvent is distilled, using a steam or boiling water bath. Most of the residual solvent is removed under diminished pressure, using a water pump, and heating until the syrupy liquid begins to crystallize suddenly ([Note 11](#)). At this point, the heating and suction are discontinued and 125 ml. of 95% [ethanol](#) is added rapidly, stirring with a wooden paddle to break up any lumps. The flask is cooled a few minutes under the tap, and the bright yellow product is collected on a 127-mm. Büchner funnel. The solid is triturated on the funnel with cold [ethanol](#) for 10 minutes to remove adhering mother liquor, and sucked as dry as possible. The yield is 186–197 g. (78–83%) ([Note 11](#)), and the melting point is 109–110° ([Note 12](#)) and ([Note 13](#)).

2. Notes

1. The checkers used thiophene-free [benzene](#), m.p. 5°; it gave a product of better quality than the commercial hydrocarbon. A large excess is used to facilitate stirring.
2. Resublimed [aluminum chloride](#) is suitable; it requires no further grinding. The excess over the required 2 moles assures a complete reaction and a product of good color.
3. A dropping funnel is preferred to the ordinary separatory funnel, since the rate of addition of the [fumaryl chloride](#) is important.

4. A wide-bore condenser permits a more rapid reaction, favoring an increased yield and better product.
5. If the mixture is not heated before the **fumaryl chloride** is added the reaction is slow, and when the temperature finally rises the accumulated chloride and intermediates react so vigorously that frothing and boiling over occur.
6. If for any reason stirring is interrupted, the *addition of fumaryl chloride must be stopped immediately*, and the stirrer started again *very cautiously*.
7. The product and yield are better with the shorter time of addition.
8. Very hot water is desirable; unless the **benzene** layer is really warm (50–60°), the separation into layers is poor and the product does not readily dissolve. For the same reasons, hot water is used in the subsequent washings.
9. The first and second wash waters should be acidulated with 25 ml. of concentrated **hydrochloric acid**; this facilitates the formation of layers.
10. If the water used has been hot enough to keep the **benzene** really warm (50–60°), there are no crusty deposits.
11. Ordinarily there is but 8 g. in the second crop; however, in the event that not enough solvent has been removed, there may be a larger amount, with a correspondingly smaller first crop. The total yield is 194–205 g. (82–86%). If the first crop weighs over 190 g., it is not economical to work up the mother liquor.
12. In some runs, the product sinters slightly at 106°, but the melting point is unaltered.
13. Lower-melting material, whatever its source, can be recrystallized from 95% **ethanol**, using 3 ml. per gram.

3. Discussion

trans-Dibenzoylethylene has been prepared by the present method,¹ by heating **dibenzoylmalic acid**,² by condensing **benzoylformaldehyde** and **acetophenone**,³ and by the Friedel-Crafts reaction on **benzoylacrylyl chloride**.⁴ Analogs may be prepared using other aromatics such as **mesitylene**,^{1,4,5,6} with **carbon disulfide** as the solvent, and also using other acid chlorides such as **mesaconyl chloride**,⁷ **dibromofumaryl chloride**,⁸ and **dimethylfumaryl chloride**.⁹

A mixture of stereoisomers has been prepared by the action of alcoholic **potassium hydroxide** on **phenacyl chloride**.¹⁰

References and Notes

1. Conant and Lutz, *J. Am. Chem. Soc.*, **45**, 1305 (1923); Oddy, *J. Am. Chem. Soc.*, **45**, 2159 (1923).
2. Paal and Schulze, *Ber.*, **33**, 3798 (1900).
3. Smedley, *J. Chem. Soc.*, **95**, 219 (1909).
4. Lutz, *J. Am. Chem. Soc.*, **52**, 3432 (1930).
5. Conant and Lutz, *J. Am. Chem. Soc.*, **47**, 891 (1925).
6. Weygand and Lanzendorf, *J. prakt. Chem.*, **151**, 209 (1938).
7. Lutz and Taylor, *J. Am. Chem. Soc.*, **55**, 1177 (1933).
8. Lutz, *J. Am. Chem. Soc.*, **52**, 3421 (1930).
9. Lutz and Taylor, *J. Am. Chem. Soc.*, **55**, 1599 (1933).
10. Bogoslovskii, *J. Gen. Chem. U.S.S.R.*, **14**, 993 (1944) [*C. A.*, **39**, 4600 (1945)].

Appendix

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

aluminum chloride complex

ethanol (64-17-5)

hydrogen chloride,
hydrochloric acid (7647-01-0)

Benzene (71-43-2)

Acetophenone (98-86-2)

aluminum chloride (3495-54-3)

potassium hydroxide (1310-58-3)

benzoylformaldehyde (1074-12-0)

carbon disulfide (75-15-0)

Mesitylene (108-67-8)

phenacyl chloride (532-27-4)

2-Butene-1,4-dione, 1,4-diphenyl-

Fumaryl chloride (627-63-4)

dibenzoylethylene,
trans-Dibenzoylethylene

dibenzoylmalic acid

benzoylacrylyl chloride

mesaconyl chloride

dibromofumaryl chloride

dimethylfumaryl chloride