



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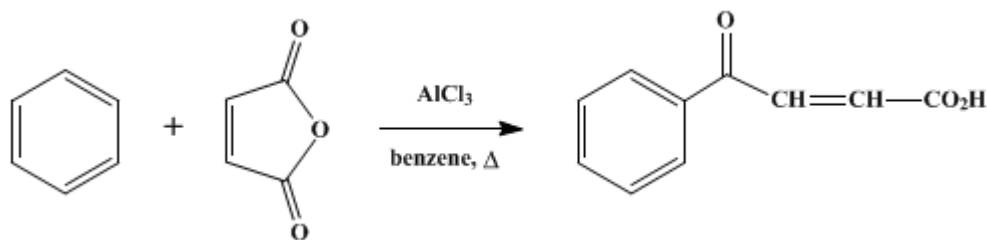
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 3, p.109 (1955); Vol. 29, p.11 (1949).

β -BENZOYLACRYLIC ACID

[Acrylic acid, β -benzoyl-]



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1. Procedure

In a 1-l. three-necked round-bottomed flask fitted with a mercury-sealed stirrer and a reflux condenser are placed 34 g. (0.347 mole) of [maleic anhydride \(Note 1\)](#) and 175 g. (200 ml., 2.24 moles) of dry, thiophene-free [benzene](#). Stirring is started, and, when the [maleic anhydride](#) has dissolved, 100 g. (0.75 mole) of anhydrous reagent grade [aluminum chloride](#) powder is added in 6–8 portions through the third neck of the flask at a rate so that the [benzene](#) refluxes moderately. The addition requires about 20 minutes. The mixture is then heated under reflux on a steam bath and stirred for 1 hour. The reaction flask is cooled thoroughly in an ice bath, a 250-ml. dropping funnel is attached to the third neck, and the mixture is hydrolyzed by adding 200 ml. of water with stirring and cooling (the first 50 ml. during 15–20 minutes and the balance in about 10 minutes), followed by 50 ml. of concentrated [hydrochloric acid \(Note 2\)](#). Stirring is continued for an additional 40 minutes, during which time it may be necessary to use a spatula to scrape adhering particles of the red-brown [aluminum chloride](#) addition compound from the walls of the flask.

The hydrolyzed mixture is transferred to a 1-l. Claisen flask, the transfer of material being completed by rinsing with about 50 ml. of warm water. The flask is heated in a water bath at 50–60°, and the [benzene](#) and some water are distilled at 20–30 mm. pressure ([Note 3](#)). While the residue is still molten, it is transferred to a 1-l. beaker, and the flask is rinsed with 50 ml. of warm water. After standing at 0–5° for 1 hour, the yellow solid is collected on a suction filter and washed with a solution of 25 ml. of concentrated [hydrochloric acid](#) in 100 ml. of water and then with 100 ml. of water. The washing is done most efficiently by suspending the solid in the wash liquid, cooling to 0–5° with stirring, and then filtering with suction. The preparation should not be interrupted before this point ([Note 3](#)), at which stage the crude acid may be air-dried overnight at room temperature if desired. The crude product is dissolved in a solution of 40 g. of anhydrous [sodium carbonate](#) in 250 ml. of water by warming to 40–50° ([Note 4](#)), 2 g. of Celite or other filter aid is added, and the solution is filtered with suction while warm. After the filter has been washed with two 30-ml. portions of warm water, 2 g. of Norit is added to the combined filtrates and the mixture is heated at 40–50° for 10–15 minutes with frequent stirring, then filtered with suction. The clear, yellow filtrate is transferred to a 1-l. beaker and cooled to 5–10°, and 70 ml. of concentrated [hydrochloric acid](#) is added dropwise with stirring. Efficient cooling and stirring are necessary to avoid the precipitation of the acid as an oil. After being cooled to 0–5°, the mixture is filtered with suction; the solid is washed with two 50-ml. portions of cold water and then is dried at 50° for 12–36 hours to give 56–63 g. of light-yellow anhydrous [\$\beta\$ -benzoylacrylic acid](#), m.p. 90–93° ([Note 5](#)). The crude acid may be crystallized from [benzene](#), using 12–15 ml. of [benzene](#) per 5 g. of acid and cooling at 5–10° ([Note 6](#)) to give 44–47 g. of [\$\beta\$ -benzoylacrylic acid](#), m.p. 94–96° ([Note 7](#)). Concentration of the filtrate to one-fourth to one-fifth of its original volume gives an additional 3–6 g., melting in the range 92–96°. The total yield is 49–52 g. (80–85%) ([Note 8](#)).

2. Notes

1. A good grade of commercial maleic anhydride was used, m.p. 52–54°.
2. When β -benzoylacrylic acid is heated with dilute hydrochloric acid, β -benzoyllactic acid is formed, which makes the purification of the product very difficult.¹ For this reason the mixture is well cooled during hydrolysis and the hydrochloric acid is not added until the heat of the exothermic hydrolysis has been dissipated.
3. The benzene solution of β -benzoylacrylic acid is concentrated under reduced pressure to avoid overheating, and the crude product is separated from aqueous hydrochloric acid without long standing in order to minimize the possibility of forming β -benzoyllactic acid (Note 2).
4. Heating a mixture of β -benzoylacrylic acid and excess sodium carbonate causes hydrolysis to acetophenone and other products, which decreases the yield and interferes with purification of the product.^{2,3}
5. Before drying, the product is the monohydrate, m.p. 64–65° when pure. It is dried until it reaches constant weight and has the melting point of the anhydrous acid.
6. The benzene solution should not be boiled longer than necessary to dissolve the acid, because prolonged heating discolors the product.
7. The evidence indicates that this is the *trans* form of β -benzoylacrylic acid.^{4,5,6} Inhalation of β -benzoylacrylic acid dust should be avoided because of its sternutatory action.
8. It has been reported (E. L. Ringwald, private communication) that this reaction may be carried out on a large scale (170 g. of maleic anhydride, 1 kg. of dry benzene, and 1 kg. of aluminum chloride). After the first addition of 500 g. of aluminum chloride, the remaining material is added in 100-g. portions. The mixture is heated with stirring at 55–60° for 1 hour. The complex is decomposed by pouring into ice and concentrated hydrochloric acid. The crude air-dried product, separated by filtration, is combined with the residue obtained by removal of the solvent. The combined crude products are recrystallized from benzene-hexane. The yield is 252 g. (m.p. 95–96°) of first crop, and 15 g. (m.p. 90–94°) of second crop, a total yield of 87%.

3. Discussion

β -Benzoylacrylic acid has been prepared by the condensation of acetophenone and chloral to 1,1,1-trichloro-2-hydroxy-3-benzoylpropane, followed by hydrolysis to the corresponding acid and dehydration;⁷ by the action of iodine, potassium iodide, and sodium carbonate on γ -phenylisocrotonic acid;⁸ by bromination of β -benzoylpropionic acid and subsequent dehydrohalogenation;¹ by the action of phenylzinc chloride on maleic anhydride;⁹ and by the condensation of the acid chloride of ethyl hydrogen maleate with benzene in the presence of aluminum chloride, followed by hydrolysis.¹⁰ The present method is based on the work of von Pechmann and others.^{2,11,12}

References and Notes

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 6. Lutz and Scott, *J. Org. Chem.*, **13**, 284 (1948).
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Appendix

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

acid chloride of ethyl hydrogen maleate

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

sodium carbonate (497-19-8)

potassium iodide (7681-11-0)

iodine (7553-56-2)

Acetophenone (98-86-2)

aluminum chloride (3495-54-3)

β -Benzoylpropionic acid (2051-95-8)

β -Benzoylacrylic acid,
Acrylic acid, β -benzoyl- (583-06-2)

chloral (75-87-6)

maleic anhydride (108-31-6)

β -benzoyllactic acid

1,1,1-trichloro-2-hydroxy-3-benzoylpropane

γ -phenylisocrotonic acid

phenylzinc chloride

hexane (110-54-3)