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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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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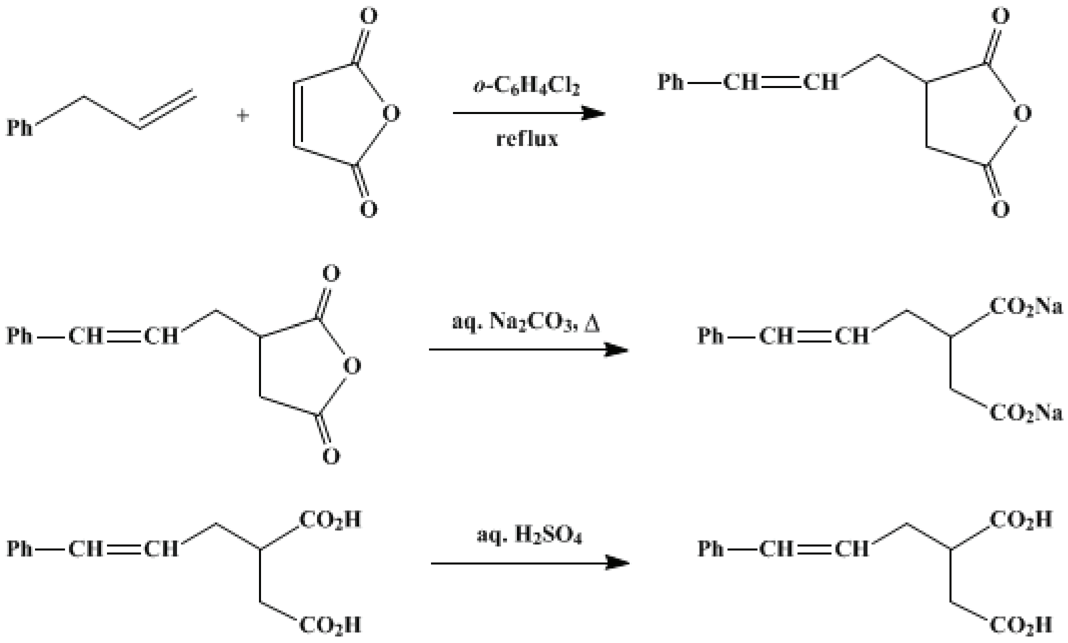
γ-PHENYLALLYLSUCCINIC ACID

[Succinic acid, cinnamyl-]



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1. Procedure

A mixture of 35.4 g. (0.3 mole) of allylbenzene, 29.4 g. (0.3 mole) of maleic anhydride, and 50 ml. of *o*-dichlorobenzene (Note 1) in a 200-ml. round-bottomed flask is heated under reflux for 22 hours under an air condenser. While the orange mixture cools to 50°, the flask is equipped for vacuum distillation. At a bath temperature below 130°, the solvent and unreacted starting materials are removed by vacuum distillation with a water pump. The boiling range is 66–72°/23 mm. The viscous residue is poured while hot into a 125-ml. sausage flask (Note 2), and the transfer is completed with small amounts of acetone. After removal of the acetone by vacuum distillation with a water pump, the product is distilled, b.p. 199–206°/2 mm. (bath temperature 220–270°), to give 27–35 g. (42–54%) of a pale yellow liquid which solidifies readily (Note 3).

The product is melted in the receiver and poured into 100 ml. of benzene. An additional 25 ml. of hot benzene is used to rinse the receiver. The benzene solution is brought to boiling, filtered, and diluted with approximately 100 ml. of petroleum ether (60–75°) until faintly turbid. It is reheated to boiling, allowed to cool, and finally refrigerated for 4 hours. The white crystals are collected on a Büchner funnel, washed with two 25-ml. portions of cold 1:1 benzene-petroleum ether, pressed dry, and airdried. The yield of anhydride melting at 103–105° is 24–31 g. (37–48%) (Note 4).

The anhydride is readily hydrolyzed by boiling a mixture of 21.6 g. (0.1 mole) of anhydride, 22.0 g. (0.207 mole) of anhydrous sodium carbonate, and 250 ml. of water for 2 hours on a hot plate. The pale yellow solution is cooled and extracted with 100 ml. of isopropyl ether (Note 5). The ether extract is washed with 50 ml. of water, and the combined water layers are acidified to Congo red by the slow addition of 10% sulfuric acid. The acid separates as an oil which quickly solidifies on cooling and stirring. It is collected on a Büchner funnel, washed with cold water, pressed dry on the funnel, and finally air-dried. The yield is 22 g. (94% based on the anhydride), m.p. 140–143°. The acid is conveniently recrystallized from acetonitrile (Note 6), using 5 ml. per gram of crude acid. The recovery of pure acid having a melting point of 142–143° is 85% (Note 7).

2. Notes

1. Allylbenzene can be prepared from phenylmagnesium bromide and allyl bromide.[2] The maleic anhydride used was Eastman Kodak Company white label grade. Slightly higher yields are obtained if it is freshly distilled at 25 mm. Commercial *o*-dichlorobenzene should be distilled before use.
2. A suitable flask is prepared from a 525-ml. distilling flask by replacing the narrow side arm with a 150-mm. length of 10-mm. tubing. The side arm of a second flask is cut off to 25 mm., and the two flasks are connected by inserting the 10-mm. side arm into the bulb of the second flask.

A few boiling stones or sticks are added to the first flask containing the material to be distilled, a rubber stopper bearing a thermometer is inserted, and vacuum is applied to the shortened side arm of the receiver.

3. A Wood's metal bath is convenient as a high-temperature heat source.
4. Once-crystallized anhydride is sufficiently pure for conversion to the acid. A second recrystallization gives pure material, m.p. 106.0–106.5°.
5. Ethyl ether may be used. The aqueous layers must then be heated to boiling and cooled before acidification; otherwise the acid is slow to crystallize.
6. Acetonitrile is most convenient, but ethanol, aqueous acetic acid, or aqueous dioxane may be used.
7. The acid is partially dehydrated near its melting point. The reported melting point was observed by immersing the capillary at 140° and heating at 2° per minute.

3. Discussion

γ-Phenylallylsuccinic anhydride and the derived acid have been prepared by heating maleic anhydride with excess allylbenzene in an autoclave at 170–175° for 24 hours.[3] The above procedure is more convenient since an autoclave is unnecessary.

References and Notes

1. University of Michigan, Ann Arbor, Michigan.
2. Hershberg, *Helv. Chim. Acta*, **17**, 351 (1934).
3. Alder, Pascher, and Schmitz, *Ber.*, **76**, 27 (1943).

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

petroleum ether

benzene-petroleum ether

ethanol (64-17-5)

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

Benzene (71-43-2)

ether,

ethyl ether (60-29-7)

acetonitrile (75-05-8)

sodium carbonate (497-19-8)

Allyl bromide (106-95-6)

acetone (67-64-1)

Phenylmagnesium bromide (100-58-3)

dioxane (123-91-1)

isopropyl ether (108-20-3)

maleic anhydride (108-31-6)

γ-Phenylallylsuccinic acid,
Succinic acid, cinnamyl- (5671-91-0)

allylbenzene (300-57-2)

γ-Phenylallylsuccinic anhydride (7508-06-7)

o-dichlorobenzene (95-50-1)