



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.

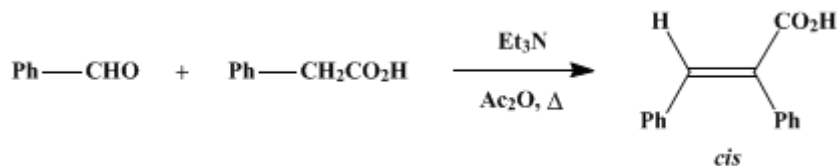
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 4, p.777 (1963); Vol. 33, p.70 (1953).

α -PHENYLCINNAMIC ACID

[Acrylic acid, 2,3-diphenyl-]



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Checked by T. L. Cairns and J. C. Lorenz.

1. Procedure

In a 500-ml. round-bottomed flask are placed 40.5 ml. (42.4 g., 0.40 mole) of freshly purified benzaldehyde (Note 1), 54.6 g. (0.40 mole) of phenylacetic acid,² 40 ml. of anhydrous triethylamine (Note 2), and 80 ml. of acetic anhydride (Note 3). The mixture is boiled gently under reflux for 5 hours. After the heating period is over, the 500-ml. flask containing the reaction mixture is incorporated into a steam-distillation apparatus (Note 4). The reaction mixture is distilled with steam until the distillate coming over is no longer cloudy, and then about 50 ml. more of the distillate is collected. The distillate can be discarded. The aqueous residue is cooled, and the solution is then separated from the solid by decantation. The solid is dissolved in 500 ml. of hot 95% ethanol, and 500 ml. of water, including the solution originally decanted from the crude solid, is added to the hot solution. The mixture is heated to boiling, and 2 g. of decolorizing carbon is added. The hot solution is filtered, and the filtrate is immediately acidified to Congo red with 6*N* hydrochloric acid. The solution is cooled, and the resulting crystals are removed from the mixture by filtration. The yield of crude α -phenylcinnamic acid (m.p. around 161–165°) is 60–67 g. The product is purified by crystallization from aqueous ethanol (Note 5). The over-all yield of purified product, m.p. 172–173°, is 48–53 g. (54–59%). The product is the isomer with the two phenyl groups *cis* to each other since decarboxylation yields *cis*-stilbene³ (see p. 857).

2. Notes

1. Benzaldehyde, suitable for this synthesis, is purified in the following way. A 60-g. (58-ml.) sample is washed with two 20-ml. portions of 10% sodium carbonate and then with water. It is then dried over 5–10 g. of anhydrous magnesium sulfate. A few small crystals of hydroquinone or catechol are added with the drying agent. The dry benzaldehyde is decanted through a cotton plug into a Claisen flask; it is distilled under reduced pressure, preferably below 30 mm.
2. Sharples anhydrous grade triethylamine was used without further purification.
3. The acetic anhydride is carefully fractionated; the 137–139° fraction is collected.
4. A simple steam-distillation apparatus such as that given by Fieser⁴ is entirely satisfactory. It is usually necessary to heat the distillation flask with a steam bath or a small flame in order to minimize the accumulation of excess water in the flask.
5. The submitters used 5 ml. of 95% ethanol and 5 ml. of water per gram of crude product for recrystallization. The checkers found use of 3:2 ethanol:water by volume more convenient.

3. Discussion

α -Phenylcinnamic acid has been prepared by the distillation of benzylmandelic acid,⁵ by the condensation of phenylacetyl chloride⁶ or phenylacetic acid⁷ with benzaldehyde in the presence of triethylamine; by the reaction of sodium or potassium phenylacetate with benzaldehyde in acetic anhydride;^{8,9,10,11} and by the treatment of ethyl α -bromo- α,β -diphenylpropionate with potassium hydroxide.¹² The most convenient synthesis appears to be that described above.^{13,14,15}

This preparation is referenced from:

References and Notes

1. State University of Iowa, Iowa City, Iowa.
 2. *Org. Syntheses Coll. Vol.* **1**, 436 (1941).
 3. Taylor and Crawford, *J. Chem. Soc.*, **1934**, 1130.
 4. Fieser, *Experiments in Organic Chemistry*, 3rd ed., p. 150, D. C. Heath and Company, Boston, 1955.
 5. Malkin and Robinson, *J. Chem. Soc.*, **127**, 376 (1925).
 6. Katoh, *Science Repts. Tokyo Bunrika Daigaku*, **2**, 257 (1935).
 7. Ishikawa and Tukeuchi, *Science Repts. Tokyo Bunrika Daigaku*, **A3**, 231 (1939); Zimmerman and Ahramjian, *J. Am. Chem. Soc.*, **81**, 2086 (1959); Riemschneider and Kampf, *Monatsh.*, **90**, 518 (1959).
 8. Oglialoro, *Gazz. chim. ital.*, **8**, 429 (1887).
 9. Bakunin, *Gazz. chim. ital.*, **31 II**, 77 (1901).
 10. Posner, *J. prakt. Chem.*, [2] **82**, 437 (1910).
 11. Johnson, in Adams, *Organic Reactions*, Vol. 1, p. 252, John Wiley & Sons, New York, 1942.
 12. D'yakonov and Vinogradova, *Zhur. Obshchei Khim.*, **23**, 244 (1953) [*C. A.*, **48**, 3318 (1954)].
 13. Buckles and Hausman, *J. Am. Chem. Soc.*, **70**, 415 (1948).
 14. Buckles, *J. Chem. Educ.*, **27**, 210 (1950).
 15. Buckles, Bellis, and Coder, *J. Am. Chem. Soc.*, **73**, 4972 (1951).
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Appendix

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

sodium or potassium phenylacetate

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

acetic anhydride (108-24-7)

hydroquinone (123-31-9)

sodium carbonate (497-19-8)

benzaldehyde (100-52-7)

decolorizing carbon (7782-42-5)

potassium hydroxide (1310-58-3)

Phenylacetic acid (103-82-2)

Catechol (120-80-9)

magnesium sulfate (7487-88-9)

phenylacetyl chloride (103-80-0)

triethylamine (121-44-8)

α -Phenylcinnamic acid,
Acrylic acid, 2,3-diphenyl- (3368-16-9)

benzylmandelic acid

ethyl α -bromo- α,β -diphenylpropionate

cis-Stilbene (645-49-8)