Organic Syntheses

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.

The procedures described in *Organic Syntheses* are provided as published and are conducted at one's own risk. *Organic Syntheses, Inc.*, its Editors, and its Board of Directors do not warrant or guarantee the safety of individuals using these procedures and hereby disclaim any liability for any injuries or damages claimed to have resulted from or related in any way to the procedures herein.

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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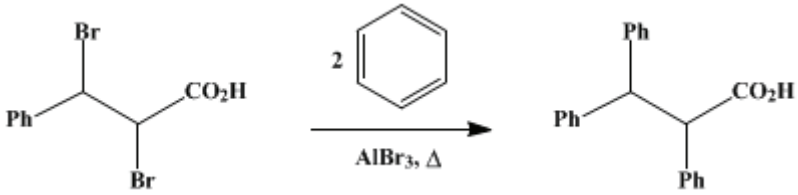
α,β,β-TRIPHENYLPROPIONIC ACID

[Propionic acid, 2,3,3-triphenyl-]



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1. Procedure

A 5-l. three-necked flask is fitted with a mechanical rubber-sleeved stirrer, a dropping funnel, and a reflux condenser capped with a calcium chloride tube leading to a gas-absorption trap.[2] The system is flame-dried, and the flask is charged with 308 g. (1 mole) of α,β-dibromohydrocinnamic acid (Note 1) and 800 ml. of dried (by distillation) thiophene-free benzene. While the α,β-dibromohydrocinnamic acid is maintained in suspension by stirring (Note 2), a freshly prepared solution of 294 g. (1.1 moles) of anhydrous aluminum bromide (Note 3) in 400 ml. of anhydrous thiophene-free benzene is added from the dropping funnel over a period of 30 minutes. The clear orange-to-red solution is then heated under reflux with stirring for 4 hours.

The mixture is cooled to room temperature and maintained there with the aid of a cooling bath while 500 ml. of concentrated hydrochloric acid is added slowly from the dropping funnel. The mixture should be stirred vigorously during this addition, which requires about 30 minutes and is accompanied by copious evolution of hydrogen bromide (Note 4) and separation of the α,β,β-triphenylpropionic acid as a thick white slurry. Stirring is continued for an additional 30 minutes, 2 l. of water is added, and the product is separated by suction filtration. The waxy filter cake is washed with two 250-ml. portions of water, then dried overnight at room temperature and finally at 75° (Note 5). The crude, almost colorless α,β,β-triphenylpropionic acid amounts to 287–302 g. (95–100% yield), m.p. 215–218°. Recrystallization by dissolution in 3 l. of isopropyl alcohol (Note 6), followed by concentration of the filtered solution to 1.5 l. before cooling, yields 200–236 g. (66–78%) of colorless needles, m.p. 220–221°.

2. Notes

1. α,β-Dibromohydrocinnamic acid is conveniently prepared by the method of Reimer.[3] The checkers employed the following procedure. To a gently boiling solution of 296 g. (2 moles) of cinnamic acid in 2 l. of C.P. carbon tetrachloride contained in a 5-l. three-necked flask fitted with a reflux condenser, a dropping funnel, and a mechanical stirrer is added slowly (1.5 hours) with stirring 320 g. (2 moles) of bromine dissolved in 200 ml. of carbon tetrachloride. After 25–50% of the bromine is added, the α,β-dibromohydrocinnamic acid begins to precipitate with evolution of heat. Stirring and heating are continued for an additional 30 minutes after all the bromine is added. The mixture is cooled to room temperature; the product is separated by suction filtration and is washed with a small amount of cold carbon tetrachloride. The air-dried product amounts to 558–580 g. (91–94% yield) of colorless crystals, m.p. 197–198° to 202–204°.
2. If a solution instead of suspension is used, troublesome gel formation may occur during the aluminum bromide addition.
3. Colorless, crystalline, anhydrous aluminum bromide supplied by the Westvaco Chemical Division, Food Machinery and Chemical Corporation, New York, New York, was used. When dissolved in dry benzene at room temperature with mechanical stirring, a perfectly clear yellow solution results, if the reagents are of high purity.
4. If stirring is not sufficiently vigorous of if the temperature is too low, the evolution of hydrogen

bromide may be delayed and then may begin abruptly and be difficult to control.
5. If the wet product is introduced directly into the drying oven it may darken slightly.
6. If the solution is appreciably colored it may be treated with decolorizing carbon at this point. Toluene or dilute ethanol may also be used for the recrystallization, but these solvents are less satisfactory.

3. Discussion

α,β,β-Triphenylpropionic acid has been prepared by the alkaline hydrolysis of the addition product of phenylmagnesium bromide and methyl α-phenylcinnamate;[4] by the reaction of α-phenylcinnamic acid with benzene in the presence of aluminum chloride;[5] by the reaction of α,β-dibromohydrocinnamic acid with benzene in the presence of aluminum bromide or ferric chloride;[6] by the reaction of phenylacetic acid with benzhydryl chloride in the presence of sodamide;[7] and by the reduction of 2,3,3-triphenylacrylonitrile with benzyl alcohol and alkali, followed by hydrolysis of the crude product.[8] The procedure described here is a modification of the method of Earl and Wilson.[6]

References and Notes

1. G. D. Searle and Company, Chicago, Illinois.
2. *Org. Syntheses Coll. Vol.* **2**, 4 (1943).
3. Reimer, *J. Am. Chem. Soc.*, **64**, 2510 (1942).
4. Kohler and Heritage, *Am. Chem. J.*, **33**, 156 (1905).
5. Eijkman, *Chem. Weekblad*, **5**, 655 (1908) (*Chem. Zentr.*, **1908 II**, 1100).
6. Earl and Wilson, *J. Proc. Roy. Soc. N. S. Wales*, **65**, 178 (1932) [*C. A.*, **26**, 2976 (1932)].
7. Hauser and Chambers, *J. Am. Chem. Soc.*, **78**, 4996 (1957).
8. Avramoff and Sprinzak, *J. Am. Chem. Soc.*, **80**, 493 (1958).

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

ethanol (64-17-5)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

hydrogen bromide (10035-10-6)

bromine (7726-95-6)

carbon tetrachloride (56-23-5)

decolorizing carbon (7782-42-5)

aluminum chloride (3495-54-3)

toluene (108-88-3)

isopropyl alcohol (67-63-0)

Benzyl alcohol (100-51-6)

Phenylacetic acid (103-82-2)

ferric chloride (7705-08-0)

Phenylmagnesium bromide (100-58-3)

cinnamic acid (621-82-9)

aluminum bromide

sodamide (7782-92-5)

2,3,3-triphenylacrylonitrile (6304-33-2)

α-Phenylcinnamic acid (3368-16-9)

benzhydryl chloride (90-99-3)

α,β,β-Triphenylpropionic acid,
Propionic acid, 2,3,3-triphenyl- (53663-24-4)

methyl α-phenylcinnamate

α,β-dibromohydrocinnamic acid (6286-30-2)