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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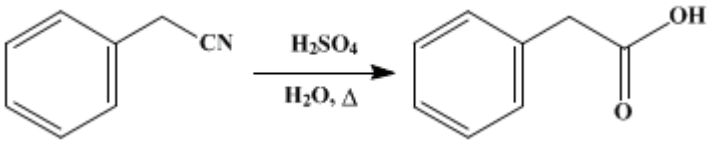
Organic Syntheses, Coll. Vol. 1, p.436 (1941); Vol. 2, p.63 (1922).

PHENYLACETIC ACID

[α-Toluic acid]



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1. Procedure

In a 5-l. round-bottom flask, fitted with a mechanical stirrer and reflux condenser, are mixed 1150 cc. of water, 840 cc. of commercial sulfuric acid (Note 1) and 700 g. (6 moles) of benzyl cyanide (p. 107). The mixture is heated under a reflux condenser and stirred for three hours (Note 2), cooled slightly, and then poured into 2 l. of cold water. The mixture should be stirred so that a solid cake is not formed; the phenylacetic acid is then filtered off. This crude material is melted under water and washed by decantation several times with hot water. These washings, on cooling, deposit a small amount of phenylacetic acid which is filtered off and added to the main portion of material. The last of the hot water is poured off from the material while it is still molten, and it is then transferred to a 2-l. Claisen distilling flask and distilled under reduced pressure. A small amount of water comes over first and is rejected; about 20 cc., containing an appreciable amount of benzyl cyanide, then distils. This fraction is used in the next run. The distillate boiling at 176–189°/50 mm. is collected separately and solidifies on standing. It is practically pure phenylacetic acid, m.p. 76–76.5°, and weighs 630 g. (77.5 per cent of the theoretical amount) (Note 3). As the fraction which is returned to the second run of material contains a considerable portion of phenylacetic acid, the yield actually amounts to at least 80 per cent.

For the preparation of small quantities of phenylacetic acid, it is convenient to use the modified method given in (Note 3).

2. Notes

1. The standard directions for the preparation of phenylacetic acid specify that the benzyl cyanide is treated with dilute sulfuric acid prepared by adding three volumes of sulfuric acid to two volumes of water. The reaction, however, goes so vigorously that it is always necessary to have a trap for collecting the benzyl cyanide which is blown out of the apparatus. The use of the more dilute acid, as described in the above directions, is more satisfactory.
The odor of phenylacetic acid is disagreeable and persistent.
2. The phenylacetic acid may also be made by boiling under a reflux condenser for eight to fifteen hours, without a stirrer, but this method is not nearly so satisfactory as that described in the procedure.
3. The following modified procedure can be used for the preparation of small quantities of the acid. One hundred grams of benzyl cyanide is added to a mixture containing 100 cc. of water, 100 cc. of concentrated sulfuric acid, and 100 cc. of glacial acetic acid. After this has been heated for forty-five minutes under a reflux condenser, the hydrolysis is practically complete. The reaction mixture is then poured into water, and the phenylacetic acid is isolated in the usual manner.

3. Discussion

The standard method for the preparation of phenylacetic acid is the hydrolysis of benzyl cyanide with either alkali[1] or acid.[2] The acid hydrolysis runs by far the more smoothly and so was the only one studied. Phenylacetic acid can also be prepared by the carbonation of benzylmagnesium chloride[3] and by the catalytic reduction of mandelic acid.[4]

This preparation is referenced from:

- Org. Syn. Coll. Vol. 1, 107
- Org. Syn. Coll. Vol. 2, 61
- Org. Syn. Coll. Vol. 2, 156
- Org. Syn. Coll. Vol. 2, 229
- Org. Syn. Coll. Vol. 2, 389
- Org. Syn. Coll. Vol. 4, 760
- Org. Syn. Coll. Vol. 4, 777

References and Notes

1. Cannizzaro, Ann. **96**, 247 (1855); Mann, Ber. **14**, 1465 (1881); Bodroux, Compt. rend. **151**, 236 (1910).
2. Staedel, Ber. **19**, 1950 (1886).
3. Austin and Johnson, J. Am. Chem. Soc. **54**, 655 (1932).
4. Zelinsky, Packendorff, and Leder-Packendorff, Ber. **67**, 301 (1934).

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

sulfuric acid (7664-93-9)

acetic acid (64-19-7)

Mandelic acid (90-64-2)

α-Toluic acid (65-85-0)

Benzyl cyanide (140-29-4)

Phenylacetic acid (103-82-2)

benzylmagnesium chloride (6921-34-2)