



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.

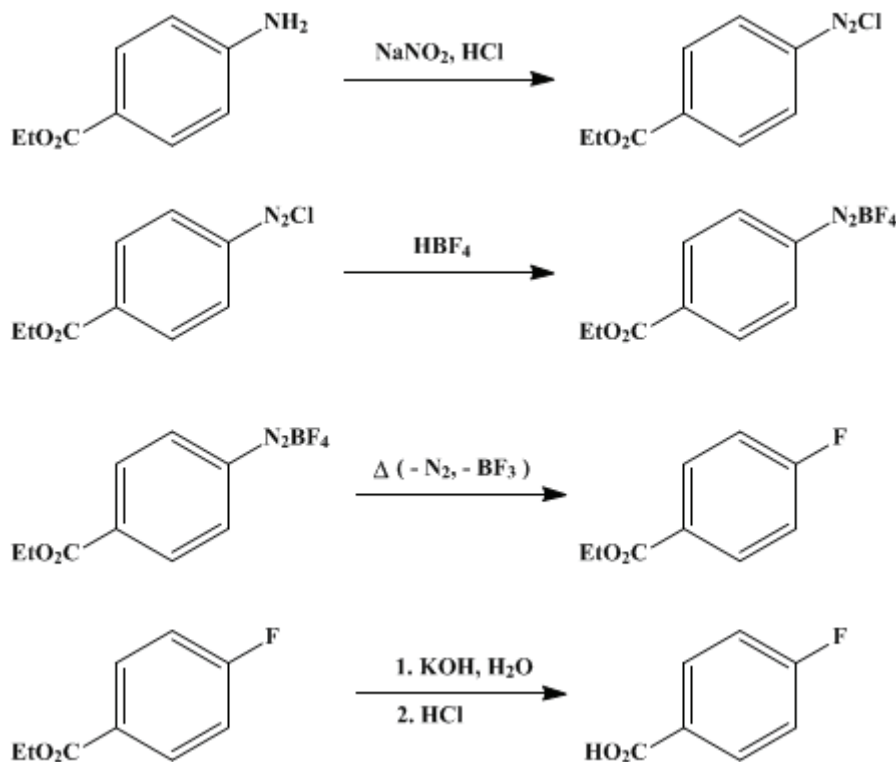
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

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p-FLUOROBENZOIC ACID

[Benzoic acid, *p*-fluoro-]



Submitted by G. Schiemann and W. Winkelmüller.

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1. Procedure

In a 5-l. round-bottomed flask are placed 165 g. (1 mole) of ethyl *p*-aminobenzoate (Note 1), 300 cc. of water, and 204 cc. (2.5 moles) of concentrated hydrochloric acid (sp. gr. 1.19). This mixture is warmed on a steam bath for an hour with occasional shaking. The flask containing the resulting white paste of *p*-carbethoxyaniline hydrochloride is placed in an ice-salt bath and cooled to 0° . The mixture is stirred mechanically, and a solution of 72.6 g. (1 mole) of 95 per cent sodium nitrite in a minimum quantity of water is run in slowly while the temperature is kept below 7° . The diazotization is complete when a faint positive test for nitrous acid with starch-iodide paper persists for ten minutes.

While the diazotization is in process, 68 g. (1.1 moles) of boric acid is dissolved in 133 g. (4 moles) of 60 per cent hydrofluoric acid (Note 2) in a beaker coated with paraffin-wax. The temperature is kept below 25° during the addition to avoid melting the paraffin-wax, and, after the addition, the solution is chilled in an ice-water bath.

The ice-cold fluoboric acid solution is added rather rapidly, with stirring, to the diazonium solution while the temperature is kept below 10° . A thick paste of *p*-carbethoxybenzenediazonium fluoborate precipitates; stirring is continued for twenty to thirty minutes. The solid is filtered on an 18.5-cm. Büchner funnel and washed consecutively with 300 cc. of cold water, 300 cc. of commercial methyl alcohol, and 200 cc. of commercial ether; it is sucked as dry as possible between washings. The fluoborate is then dried over concentrated sulfuric acid (sp. gr. 1.84) in a vacuum desiccator (Note 3). The yield of the dried fluoborate is 198–205 g. (75–78 per cent of the theoretical amount); the decomposition point is $93\text{--}94^\circ$.

The thermal decomposition may be conveniently carried out in a 2-l. distilling flask. A second distilling flask of 1-l. capacity is connected directly to the side arm of the first to serve as a receiver. Attached to the side arm of the receiver is a rubber tube arranged to lead the escaping gases over 2 l. of water in a 5-l. round-bottomed flask. The boron trifluoride dissolves in the water, and the other gases are led into a good hood (Note 4). The *p*-carbethoxybenzenediazonium fluoborate is placed in the decomposition flask and heated at its upper edge with a Bunsen flame. When the white fumes of boron trifluoride commence to appear, the flame is removed and the decomposition is permitted to proceed spontaneously. The heat is applied as necessary, and finally the flask is strongly heated to complete the decomposition and melt the solid. Some of the ethyl ester, b.p. 105–106°/25 mm., of *p*-fluorobenzoic acid is collected in the receiver, where it is carried by the gases, but the larger part is left in the decomposition flask. The ester is washed from the decomposition flask and the receiver with ether, and the ether is distilled from a steam bath. The residue is refluxed for one hour on a steam bath with a solution of 56 g. (1 mole) of potassium hydroxide in 80 cc. of 95 per cent ethyl alcohol and 120 cc. of water. The solution is then filtered while still hot. The *p*-fluorobenzoic acid is precipitated by adding concentrated hydrochloric acid to the hot filtrate until the mixture is acid to Congo paper. After the mixture has cooled, the solid is filtered and allowed to dry. For purification, the *p*-fluorobenzoic acid is dissolved in a hot solution of 40 g. of potassium carbonate in 400 cc. of water; the solution is treated with Norite and filtered hot. Hydrochloric acid is added with stirring to precipitate the fluorobenzoic acid, which is then cooled, filtered, and dried.

When 85 g. (0.32 mole) of *p*-carbethoxybenzenediazonium fluoborate is thus decomposed, there is obtained 38–40 g. of *p*-fluorobenzoic acid (84–89 per cent of the theoretical amount based on the fluoborate; 63–69 per cent based on the ester of *p*-aminobenzoic acid). The melting point of the purified acid is 186°. The crude acid melts at 183–184°.

2. Notes

1. Ethyl *p*-aminobenzoate can be prepared by reduction of the corresponding nitro compound as described in *Org. Syn. Coll. Vol. I*, 1941, 240, or by esterification of *p*-aminobenzoic acid: 274 g. (2 moles) of *p*-aminobenzoic acid is added to 1.4 kg. of ethyl alcohol which has been saturated with dry hydrogen chloride. The reaction mixture is refluxed for twenty-four hours, poured into water, neutralized with sodium carbonate, and the insoluble ester is separated by filtration. The yield is 80 per cent of the theoretical amount.

2. *Hydrofluoric acid causes extremely painful burns. Exposed parts of the body must be protected when working with this material. Compare Note 3, p. 297.*

For preparing the fluoboric acid a lead jar may be conveniently used instead of the beaker lined with paraffin-wax. By using a lead stirrer of the usual shape, mechanical stirring may be substituted. The stirrer should be thrust through a hole in a lead cover of sufficient size to prevent spattering of the hydrofluoric acid.

Forty per cent fluoboric acid is now available commercially; 200 g. of the commercial product may be used in the procedure above.

3. It is very important that the fluoborate be dry. If this solid is wet, the decomposition is very violent, tar is formed, and the yield is lowered.

4. A simpler apparatus for the decomposition is a 2-l. round-bottomed short-necked flask connected by means of a wide (2-cm.) bent tube to a 1-l. flask containing 500 cc. of water. The gases from the second flask are led to a good hood.

3. Discussion

p-Fluorobenzoic acid has been prepared by the oxidation of *p*-fluorotoluene with chromic acid in dilute sulfuric acid at 160°;¹ by the oxidation of *p*-fluorotoluene with potassium permanganate;² by the electrolytic oxidation of *p*-fluorotoluene;³ by heating *p*-carboxybenzenediazonium chloride with fuming hydrofluoric acid;⁴ by the oxidation of *p*-fluorobenzaldehyde;⁵ by the oxidation of *p,p'*-difluorostilbene with potassium permanganate;⁶ by the oxidation of 4,4'-difluorobiphenyl with nitric acid;⁷ and by the oxidation of 4,4'-difluorobiphenyl with chromic acid.⁸ The above method is adapted from that of Balz and Schiemann.⁹

References and Notes

1. Wallach, Ann. **235**, 263 (1886).
 2. Slothouwer, Rec. trav. chim. **33**, 324 (1914); Holleman, *ibid.* **25**, 332 (1906); Holleman and Slothouwer, Proc. K. Akad. Wetensch. Amsterdam **19**, 497, 500 (1910) (Chem. Zentr. **1911**, I, 74); Koopal, Rec. trav. chim. **34**, 152 (1915); Meyer and Hub, Monatsh. **31**, 933 (1910).
 3. Fichter and Rosenzweig, Helv. Chim. Acta **16**, 1154 (1933).
 4. Schmitt and Gehren, J. prakt. Chem. (2) **1**, 394 (1870); Paterno and Oliveri, Gazz. chim. ital. **12**, 87 (1882).
 5. Rinkes, Chem. Weekblad **16**, 206 (1919).
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 7. v. Hove, Bull. acad. roy. Belg. [5] **12**, 801 (1926) (Chem. Zentr. **1927**, I, 884).
 8. Schiemann and Roselius, Ber. **62**, 1813 (1929).
 9. Balz and Schiemann, *ibid.* **60**, 1186 (1927).
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Appendix

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

fluoboric acid

ethyl alcohol (64-17-5)

potassium carbonate (584-08-7)

sulfuric acid (7664-93-9)

hydrogen chloride,
hydrochloric acid (7647-01-0)

methyl alcohol (67-56-1)

ether (60-29-7)

nitric acid (7697-37-2)

potassium permanganate (7722-64-7)

sodium carbonate (497-19-8)

sodium nitrite (7632-00-0)

nitrous acid (7782-77-6)

hydrofluoric acid (7664-39-3)

Norite (7782-42-5)

potassium hydroxide (1310-58-3)

chromic acid (7738-94-5)

boric acid (10043-35-3)

boron trifluoride (7637-07-2)

fluorobenzoic acid (445-29-4)

Ethyl p-aminobenzoate (94-09-7)

4,4'-DIFLUOROBIPHENYL (398-23-2)

p-aminobenzoic acid,
ester of p-aminobenzoic acid (150-13-0)

p-Fluorobenzoic acid,
Benzoic acid, p-fluoro- (456-22-4)

p-carbethoxyaniline hydrochloride

p-Carbethoxybenzenediazonium fluoborate

p-fluorotoluene (352-32-9)

p-carboxybenzenediazonium chloride

p-fluorobenzaldehyde (459-57-4)

p,p'-difluorostilbene