



A Publication
of Reliable Methods
for the Preparation
of Organic Compounds

Working with Hazardous Chemicals

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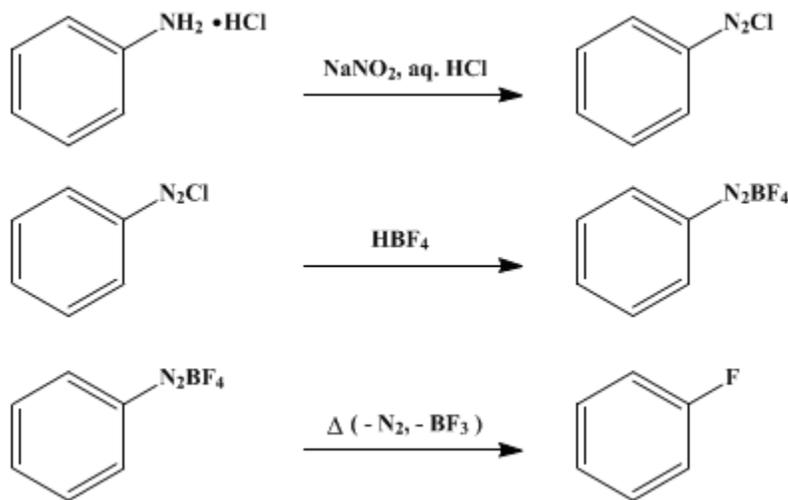
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 2, p.295 (1943); Vol. 13, p.46 (1933).

FLUOROBENZENE

[Benzene, fluoro-]



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1. Procedure

A mixture of 1350 cc. of water and 1650 cc. (20 moles) of concentrated hydrochloric acid (sp. gr. 1.19) is placed in a 30 by 30 cm. glass jar or a 40-l. crock and stirred mechanically (Note 1) while strongly cooled by an ice-salt mixture. Two thousand and seventy-five grams (16 moles) of aniline hydrochloride (Note 2) and a solution of 1.2 kg. (17 moles) of sodium nitrite in 1.5 l. of water are made ready. When the temperature of the acid has reached 5° or below, about one-third of the aniline hydrochloride is added to it, and diazotization is begun by the slow addition of the nitrite solution, the temperature being held below 7° . Additional aniline hydrochloride is added from time to time in such amounts that an excess of crystals is always present. The entire amount may be added by the time that half of the nitrite has been added. The diazotization is stopped when a positive test for free nitrous acid is obtained with potassium iodide starch paper. This should require nearly all the nitrite solution.

Fluoboric acid is made concurrently with the diazotization by the addition, in small amounts, of 1 kg. (16.2 moles) of boric acid (u.s.p. crystals) to 2150 g. (65 moles) of 60 per cent hydrofluoric acid (Note 3). The addition is carried out in two 3-l. flasks coated with wax (Note 4) which are shaken and kept cold by immersion in iced water. The temperature of the acid should not be allowed to rise above $20\text{--}25^\circ$.

The ice-cold solution of fluoboric acid is then poured into the diazonium solution, which has been cooled below 0° . The temperature should remain under 10° during the addition, which is carried out fairly rapidly. Powerful stirring is required to agitate the thick magma at this stage (Note 1). After twenty to thirty minutes' stirring, the brown-colored mass is filtered with suction, using two 24-cm. Büchner funnels. The yellowish crystalline solid is washed with about 800 cc. of iced water, with the same volume of methyl alcohol, and with about 900 cc. of commercial ethyl ether. The solid should be sucked as free as possible from liquid after each washing. This washing is important, since it improves the stability of the product (Note 5).

The light-brown, fluffy salt is spread out on absorbent paper overnight in a current of air (a table placed near a hood is effective), and is then placed in a 12-l. flask (Note 6). This is connected by a wide bent tube through a long, wide condenser to three 2-l. Erlenmeyer flasks arranged in series and immersed in ice-salt mixtures. The last flask is fitted with an exit tube leading to a good hood, to carry

off the voluminous fumes of boron fluoride, or to an absorption system containing ice and water or soda solution (Note 7). The solid is heated gently at one point near its surface with a small flame until decomposition begins. The flame is then withdrawn and the reaction allowed to continue spontaneously as long as it will. If the reaction becomes too vigorous, it may be necessary to cool the flask by rubbing it with a piece of ice (Note 8). The mixture is heated cautiously from time to time, as may be necessary to keep the reaction going. At the last it should be heated vigorously until no more fumes of boron fluoride are evolved. The last traces of fluorobenzene may be removed from the reaction flask by applying a slight suction to the receiving flask.

The combined distillate is separated from any phenol which may have settled out. It is washed four or five times with 10 per cent sodium hydroxide solution until the washings are almost colorless and then once with water (Note 9). It is dried by shaking with crushed calcium chloride, and then distilled from a 2-l. flask through a short column at a fairly rapid rate. The first runnings may contain a little water and can be further dried. The product is a colorless liquid with an odor resembling that of benzene. The yield of fluorobenzene boiling at 84–85° is 780–870 g. (51–57 per cent of the theoretical amount) (Note 10).

2. Notes

1. A slow-speed, paddle stirrer with several blades is preferable because of the large amount of suspended matter present at several times in the process. A stirrer of wood or metal protected with acid-proof paint is satisfactory, although the paint does not last well. Rubber-covered stirrers may also be used.
2. A technical grade of aniline hydrochloride is used. Technical sodium nitrite, hydrochloric acid, and hydrofluoric acid are also employed. Aniline (1485 g.) and hydrochloric acid (3 l.) without any added water can be used in place of the aniline hydrochloride, water, and acid. The separation of aniline hydrochloride in a hard cake on the side of the jar, however, leads to difficulty in cooling and stirring.
3. A corresponding amount of 48 per cent or of 52 per cent hydrofluoric acid may also be used. The quantities given represent an excess of fluoboric acid. A larger excess may be taken but does not appreciably influence the yield. Fluoboric acid (40 per cent) is now a commercial product. Hydrofluoric acid in contact with the skin produces extremely painful burns. It is therefore necessary to use every precaution to protect exposed parts of the body, especially the hands and eyes. Long acid-resisting rubber gloves and rubber goggles should be worn. If one is burned by the acid, the burned surface, which has become white, is held under running water until the natural color returns. Prompt application of a paste made from magnesium oxide and glycerin is said to be helpful in preventing burns from becoming serious [Fredenhagen and Wellmann, *Angew. Chem.* **45**, 537 (1932)].
4. The fluoboric acid may be more conveniently prepared in a lead jar with mechanical stirring. Such a jar can be readily made from sheet lead by bending to shape and soldering. A piece of iron rod fitted into some narrow lead pipe and having a strip of lead soldered on at the bottom makes an effective stirrer, and a wooden lid covered on the under side with a sheet of lead may serve as a cover. The solder is slowly attacked by the acid and can be protected with an acid-proof grease. The fluoboric acid is siphoned from the jar by means of a rubber tube.
5. The presence of moisture affects the stability of benzenediazonium fluoborate. The moist product, if allowed to stand packed together, may undergo spontaneous decomposition. In damp weather, when spread out on paper, it becomes dark and slowly decomposes. The same result is observed if it is not sufficiently washed.
6. The decomposition may also be carried out in two batches from 5-l. flasks. It is more easily controlled in this way.
7. On account of the large volume of gas evolved, all connections should be made with wide tubing.
8. Normally the decomposition proceeds smoothly under the intermittent heating. If the salt is moist, however, the reaction proceeds more rapidly, and, unless the flask is cooled, it may pass beyond control (see (Note 5)).
9. Since the density of fluorobenzene is about 1.025, it is important that the right strength of caustic soda solution be used in order to effect clean separation of the two layers. Before washing with water, the caustic soda should be completely removed.
10. Preparations have been successfully carried out with two times and three times the quantities here

stated and with almost proportionate yields. A large stoneware filter in addition to the lead pot (Note 4) is then desirable to handle the larger quantities of material.

3. Discussion

The method for the preparation of fluorobenzene described above is adapted from that of Balz and Schiemann.¹ It is recommended that benzenediazonium fluoborate be precipitated from a solution whose total hydrogen-ion concentration does not exceed 1 mole per liter.² The diazonium fluoborate has also been prepared from aniline hydrochloride and nitrosyl borofluoride.³

Fluorobenzene has also been prepared in 50 per cent yield from benzene diazopiperidide and hydrofluoric acid,⁴ although the reaction is said to proceed violently and cannot be used with quantities greater than 10–15 g. of piperidide. Other methods depend on the formation of benzenediazonium fluoride and its decomposition into fluorobenzene when heated.^{5, 6, 7} The claim of Valentiner and Schwarz⁵ that this reaction proceeds in aqueous solution could not be substantiated by the submitter.

This preparation is referenced from:

- Org. Syn. Coll. Vol. 2, 188
- Org. Syn. Coll. Vol. 2, 225
- Org. Syn. Coll. Vol. 2, 299
- Org. Syn. Coll. Vol. 5, 133
- Org. Syn. Coll. Vol. 5, 1135

References and Notes

1. Balz and Schiemann, Ber. **60**, 1188 (1927).
2. E. I. du Pont de Nemours and Company, U. S. pat. 1,916,327 [C. A. **27**, 4539 (1933)].
3. Voznesenskii and Kurskii, J. Gen. Chem. (U.S.S.R.) **8**, 524 (1938) [C. A. **32**, 8379 (1938)].
4. Wallach, Ann. **235**, 258 (1886); Wallach and Heusler, *ibid.* **243**, 219 (1888).
5. Valentiner and Schwarz, Ger. pat. 96,153 [Frdl. **5**, 910 (1897–1900); Chem. Zentr. **1898**, I, 1224].
6. Holleman and Beekman, Rec. trav. chim. **23**, 225 (1904).
7. Swarts, *ibid.* **27**, 120 (1908).

Appendix

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

caustic soda

nitrosyl borofluoride

fluoboric acid

large stoneware filter

benzene diazopiperidide

piperidide

calcium chloride (10043-52-4)

hydrochloric acid (7647-01-0)

Benzene (71-43-2)

methyl alcohol (67-56-1)

ethyl ether (60-29-7)

aniline (62-53-3)

sodium hydroxide (1310-73-2)

glycerin (56-81-5)

phenol (108-95-2)

potassium iodide (7681-11-0)

aniline hydrochloride (142-04-1)

sodium nitrite (7632-00-0)

nitrous acid (7782-77-6)

hydrofluoric acid (7664-39-3)

boric acid (10043-35-3)

Fluorobenzene,
Benzene, fluoro- (462-06-6)

magnesium oxide

benzenediazonium fluoborate

benzenediazonium fluoride

boron fluoride (7637-07-2)