



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.

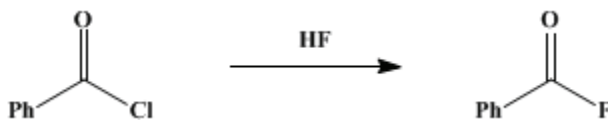
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These paragraphs were added in September 2014. The statements above do not supersede any specific hazard caution notes and safety instructions included in the procedure.

Organic Syntheses, Coll. Vol. 5, p.66 (1973); Vol. 45, p.3 (1965).

BENZOYL FLUORIDE



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1. Procedure

Caution! Anhydrous hydrogen fluoride is toxic and in contact with skin can cause serious burns. This preparation should be carried out in a well-ventilated hood. Rubber gloves and safety goggles should be worn by the operator. In case of contact with hydrogen fluoride wash the affected skin area immediately with copious amounts of water, and apply a calcium gluconate paste (Note 1).

Hydrogen fluoride (50 g., 2.5 moles) is distilled from the cylinder through a polyethylene tube into a 250-ml. polyethylene transfer bottle which has been previously weighed and calibrated. A vent is provided during this process by inserting a large-gauge hypodermic needle through the bottle cap. No provision against atmospheric moisture is necessary. The bottle is cooled in a dry ice-acetone bath, and 45–50 ml. of liquid hydrogen fluoride is collected. The amount of liquid obtained can be determined by weight difference; however, since an excess of hydrogen fluoride is employed, the exact weight need not be determined. The time required for collection of the hydrogen fluoride can be appreciably shortened by placing the cylinder in a pan of warm water.

The reaction itself is carried out in a 1-l. polyolefin bottle (Note 2) or fused silica flask (Note 3) fitted with an inlet tube (Note 4) leading to the bottom of the reaction vessel and a reflux condenser which is connected to a hydrogen chloride absorber or which leads directly to the hood. A condenser suitable for work with anhydrous hydrogen fluoride can easily be prepared from a glass-jacketed polyolefin, Teflon[®], silica, or copper tube (Note 5).

Benzoyl chloride (281 g., 2.0 moles) is placed in the reaction vessel, and the hydrogen fluoride gas is then introduced by its distillation from the transfer bottle through the inlet tube. Prior to this distillation the hypodermic needle is closed off by a metal cap. The hydrogen fluoride is added over a period of approximately 1 hour. Generally, external cooling is not needed, as the evaporating hydrogen chloride cools the reaction mixture. When the addition is completed, the reaction mixture is warmed to 30–40° and kept at this temperature for 1 hour. The mixture is then washed in an ordinary glass separatory funnel (Note 6) with 500 ml. of ice water in which 12.5 g. (0.2 mole) of boric acid is dissolved (Note 7). The organic layer is quickly separated, and to it are added 10 g. of anhydrous sodium fluoride and 10 g. of anhydrous sodium sulfate (Note 7). The mixture is allowed to stand for 30 minutes and is then filtered and distilled through a short Vigreux column. The yield of benzoyl fluoride b.p. 159–161°, n_D^{20} 1.4988 (Note 8), is 187–200 g. (75–80%).

2. Notes

1. An alternative treatment which has been used with good results at Rohm and Haas Company is, after thoroughly washing the exposed area with tap water, to soak the burned area in an ice-cold 0.2% solution of Hyamine 1622 (a product of Rohm and Haas Company) in 70% aqueous ethanol for 1 hour. It has also been stated that soaking the affected area with ice and water for 1 hour is almost as effective.²
2. Polyolefin bottles of suitable size are commercially available. One inconvenience occasionally observed with bottles which have not previously been in contact with hydrogen fluoride is the formation of a slight pink color in the reaction mixture, possibly due to the plasticizers. This coloration does not affect either the yields or the purity of the product, however, because the color is generally eliminated

after the product is washed and treated with [sodium fluoride](#).

3. No color problem exists when fused silica equipment, preferably with normal joints lubricated with a fluorinated grease, is used.

4. The inlet tube can be either polyolefin, Teflon[®], fused silica, or [copper](#).

5. Silica or [copper](#) gives much better heat transfer than do plastic tubes. The checkers found, however, that the use of a condenser was superfluous and that substitution of a simple polyethylene tube long enough to vent the off-gas away from the operator and apparatus was quite satisfactory.

6. Although some slight etching can take place, at this stage glass equipment is entirely safe, and no contamination of the product occurs.

7. The crude product contains [hydrogen fluoride](#) which is removed by the addition of [boric acid](#) to the wash water ($\text{H}_3\text{BO}_3 + 4\text{HF} \rightarrow \text{HBF}_4 + 3\text{H}_2\text{O}$). The [sodium fluoride](#) disposes of any [hydrogen fluoride](#) remaining in the [benzoyl fluoride](#) ($\text{NaF} + \text{HF} \rightarrow \text{NaHF}_2$).

8. [Benzoyl fluoride](#) is a potent lachrymator and is undoubtedly toxic. It is advisable to rinse all glassware with [acetone](#) followed by 10% aqueous [ammonia](#) before removing the glassware from the hood.

3. Discussion

[Benzoyl fluoride](#) can also be prepared by the reaction of anhydrous [hydrogen fluoride](#)^{3,4,5} or [potassium fluoride](#)⁶ with [benzoic anhydride](#) and by the halogen exchange of [benzoyl chloride](#) with alkali fluorides, such as [NaF](#),⁷ [KF](#),⁶ [KHF₂](#),⁸ [Na₂SiF₆](#),⁹ or various other metal fluorides.¹⁰

4. Merits of the Preparation

The described procedure, first applied by Colson and Fredenhagen,^{3,4} is useful for the preparation of a wide variety of acyl fluorides.⁵ The yields are normally 80–90%. Some examples of acyl fluorides prepared are listed in Table I. [Benzoyl fluoride](#) can also be employed as a convenient source of acyl fluoride by reaction with [acetic acid](#).¹¹

TABLE I

| Product | B.P., °C. |
|----------------------------|-------------|
| Propionyl fluoride | 43 |
| <i>n</i> -Butyryl fluoride | 69 |
| Isobutyryl fluoride | 61 |
| Valeryl fluoride | 90 |
| Isovaleryl fluoride | 81 |
| Caproyl fluoride | 122 |
| Heptanoyl fluoride | 40 (15 mm.) |
| Octanoyl fluoride | 62 (15 mm.) |
| Pelargonyl fluoride | 81 (15 mm.) |
| Decanoyl fluoride | 92 (15 mm.) |
| Fluoroacetyl fluoride | 54 |
| Chloroacetyl fluoride | 77 |
| Dichloroacetyl fluoride | 85 |
| Trichloroacetyl fluoride | 67 |
| Bromoacetyl fluoride | 104 |
| Phthaloyl fluoride | 84 (15 mm.) |
| Phenylacetyl fluoride | 85 (15 mm.) |

This preparation is referenced from:

- [Org. Syn. Coll. Vol. 5, 332](#)
- [Org. Syn. Coll. Vol. 6, 628](#)

References and Notes

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Appendix

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

KF

KHF₂

Na₂SiF₆

ethanol (64-17-5)

hydrogen chloride (7647-01-0)

acetic acid (64-19-7)

ammonia (7664-41-7)

sodium sulfate (7757-82-6)

hydrogen fluoride (7664-39-3)

copper (7440-50-8)

acetone (67-64-1)

benzoyl chloride (98-88-4)

Benzoic anhydride (93-97-0)

boric acid (10043-35-3)

sodium fluoride,
NaF (7681-49-4)

potassium fluoride (7789-23-3)

Benzoyl fluoride (455-32-3)

calcium gluconate

Propionyl fluoride

Isobutyryl fluoride

Valeryl fluoride

Isovaleryl fluoride

Caproyl fluoride

Heptanoyl fluoride

Octanoyl fluoride

Pelargonyl fluoride (463-18-3)

Decanoyl fluoride

Fluoroacetyl fluoride

Chloroacetyl fluoride

Dichloroacetyl fluoride

Trichloroacetyl fluoride

Bromoacetyl fluoride

Phthaloyl fluoride

Phenylacetyl fluoride

n-Butyryl fluoride