

ammonium nitrate at 190°C in a dry atmosphere for 40 minutes.

Yield = 1.5g

References:

1. A. VOGEL, *Practical Organic Chemistry*, p. 306, 3d ed., Longmans Green, London, 1957.
2. *Org. Syntheses*, coll. vol. 2:103 (1943).
3. B:112; J:367; I, vol. 1:77ff; *Ibid.*, vol. 2:136ff.
4. FRIERSON AND BROWNE, *J. Am. Chem. Soc.*, 56:2384 (1934).
5. DENNIS AND BROWNE, *Ibid.*, 26:577 (1904).

B. COMPOUND ANION

23. Ammonium Fluoroborate *

(I)



Sixty milliliters of concentrated sulfuric acid are mixed with 100 ml of water in an ordinary beaker and 24g of boric acid are dissolved in the warm solution by further heating. The solution is cooled slightly and then 60g of ammonium fluoride are added to the liquid in small portions with continuous stirring. Mechanical stirring is preferable. No appreciable amounts of hydrogen fluoride should be lost through volatilization during the addition. When all the fluoride has been added, the reaction is completed by heating for one-half hour on the steam bath, cooling in ice, filtering by suction, and draining well. The product is washed with about 50ml of acetone to remove acid.

Yield = 38–40g

The crude salt is generally satisfactory for most purposes, but it may be purified by dissolving it in 50ml of hot water containing 4ml of concentrated ammonia, heating to precipitate any silica, then filtering and evaporating.

(II)



Thirty-one grams of boric acid are weighed into a 250ml beaker and covered with 57g of ammonium hydrogen fluo-

ride. The mixture is stirred at room temperature until a clear liquid is obtained and then heated slowly on a hot plate or low flame. Slight gas evolution begins at 105°C and is fairly vigorous at 110°C. The mixture is maintained at 115–120°C stirring constantly with a thermometer. When the residue begins to solidify the thermometer is replaced with a clean iron rod. Stirring is continued until the opalescent product turns white and scarcely clings to the rod any longer. The temperature is about 125°C at the end of the reaction. The product is transferred to a watch glass and the remaining ammonia and water is driven off by heating in an oven at 140°C.

Yield = 52g

The product is recrystallized from 75ml of water and 6ml of ammonia as in (I).

COGNATE PREPARATIONS

23 a. Potassium Fluoroborate *



Under the hood, 6.2g of boric acid are dissolved in 25g of ice-cold 40% hydrofluoric acid (prepared by mixing 80ml of 50% acid with 20ml of water) in a plastic vessel, and the solution of fluoroboric acid is allowed to stand for 6 hours at room temperature to complete formation of the complex acid. The latter is then recooled and 6.9g of anhydrous potassium carbonate (or the equivalent amount of the bicarbonate or hydroxide) is added in small portions; much frothing accompanies the addition. The product precipitates immediately; the quantity of product suspended in water is deceptive, as many highly fluorinated salts have indices of refraction close to that of water itself. After being cooled in ice, the seemingly opalescent solution gives a 90% yield of white product which is dried *in vacuo*.

Potassium fluoroborate is also produced by dissolving 10g ammonium salt in ten times its weight of water and precipitating with 10g of potassium chloride in 40ml of water.

23 b. Sodium Fluoroborate is prepared similarly, using 5.3g of anhydrous sodium carbonate or its equivalent.