[CONTRIBUTION FROM THE GOLD DUST CORPORATION RESEARCH LABORATORY]

Preparation of *m*-Fluorobenzotrifluoride

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Swarts[1] prepared fluorobenzene, *m*-difluorobenzene[2] as well as a number of fluorinated derivatives of benzene and its homologs.[2] *m*-Difluorobenzene has a lower boiling point than fluorobenzene; also benzotrifluoride has a lower boiling point than toluene. The author thought it of interest to extend the number of fluorinated aromatics for the purpose of studying the influence of fluorine atoms on the boiling points of aromatic hydrocarbons. Preparation of the first compound in the series contemplated, *m*-fluorobenzotrifluoride, is given below.

Benzotrichloride was converted to the trifluoride by antimony trifluoride. This was nitrated, reduced, diazotized, converted to the complex borofluoride and finally to the desired *m*-fluorobenzotrifluoride.

Experimental Part

Benzotrifluoride was prepared in 75.5% yield using a modified procedure of Swarts.[2] A ratio of 2:1 benzotrichloride to antimony trifluoride was used instead of a 5:1 ratio. The distillate was made alkaline with sodium hydroxide and steam distilled, thus eliminating cumbersome washings with hydrochloric and tartaric acids.

m-Nitrobenzotrifluoride was prepared in 89.5% yield using Swarts'[2] procedure.

The nitro compound was reduced to the amine in 87.5% yield using Swarts'[2] procedure with the following modification: after the reaction was over all of the alcohol and some of the hydrochloric acid was distilled off. The residue was made alkaline with sodium hydroxide and steam distilled.

Preparation of *m*-Benzotrifluoride Diazonium Fluoborate.—Modified Balz and Schiemann[3] procedure was used. To 157 g. of *m*-aminobenzotrifluoride, 184 cc. of concentrated hydrochloric acid and 100 cc. of water were added. The mixture was cooled internally with dry ice; 70.4 g. of sodium nitrate in 200 cc. of water was slowly added, keeping the reaction mixture at between −10 and −5°. Addition takes forty-five minutes. The solution was filtered and poured into a cold solution of 78 g. of boric acid in 195 g. of 52% commercial hydrofluoric acid. The reaction was carried in a copper beaker. The mass was stirred for fifteen minutes and filtered through a Buchner funnel. It was washed first with alcohol, then with ether and dried in a vacuum desiccator; yield of the salt was 194 g. or 78.5% theoretical.

Thermal Decomposition of *m*-Benzotrifluoride Diazonium Fluoborate.—The following apparatus was employed. A three-necked 500-cc. flask was attached through its central neck to a distilling tube which leads to a downward condenser attached to a series of three U-tubes immersed in a mixture of gasoline and dry ice. The second and the third tube had glass beads on the bottom. The third tube was attached to three wash bottles in series containing 20% caustic solution. The third wash bottle was attached to a water pump. One of the necks of the three-necked flask was used to introduce, from time to time, small amounts of the diazonium salt, while air dried by sulfuric acid was passed through the other neck.

The flask was heated on a sand-bath. The salt was added in approximately 2-g. portions. The decomposition was very rapid; the gases formed were swept by the continuous current of dry air (drawn by the water pump). The liquid condensed primarily in the first U-tube, a few cc., however, was caught by the glass beads in the second and even in the third tube. The liquid was red due to some impurity. It was made alkaline with a caustic solution, steam distilled, taken up in ether, dried with calcium chloride, filtered and fractionated: b. p. 99.5–100.5° at 762 mm. uncorr., yield on the basis of salt, 92% of the theoretical; $d_{25.4}$ 1.2891; n_{D}^{25} 1.390. Fluorine was determined by the method of Vaughn and Nieuwland.[4]

Anal. Calcd. for $C_7H_4F_4$: F, 46.34. Found: F, 46.32.

Summary

1. Improvements on some of the procedures of Swarts have been developed.

2. A new type of apparatus for the decomposition of diazonium fluoroborates and the use of dry ice as an internal cooling agent in diazotization have been described.

3. *m*-Fluorobenzotrifluoride has been prepared.

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(1) Swarts, *Rec. trav. chim.*, **27**, 120 (1908).

(2) Swarts, *Bull. acad. roy. sci. Belg.*, **113**, 241–278 (1913); **35**, 375–420 (1898); *Rec. trav. chim.*, **35**, 155–165 (1915); **33**, 263–280, 299–300 (1914).

(3) Balz and Schiemann, *Ber.*, **60**, 1186–1190 (1927).

(4) Vaughn and Nieuwland, *Ind. Eng. Chem.*, *Anal. Ed.*, **3**, 274–275 (1931).