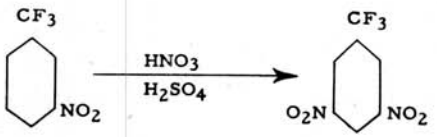
SOME FACTORS IN THE SYNTHESIS OF 3, 5-DINITROBENZOTRIFLUORIDE*

O. F. WILLIAMS AND G. C. FINGER
State Geological Survey, Urbana, Illinois

The synthesis of certain symmetrical aromatic fluorine compounds under investigation in this laboratory necessitated the development of a large-scale laboratory preparation of 3, 5-dinitrobenzotrifluoride.



Adaptation of the original synthesis by Finger and Reed[1] of this dinitro compound to a large-scale laboratory preparation required further investigation to determine optimum yield conditions.

The synthesis of 3, 5-dinitrobenzotrifluoride involves the nitration of *m*-nitrobenzotrifluoride with a fuming nitric and sulfuric acid mixture. The nitro group entering the aromatic nucleus is directed to the meta position common to both the $-CF_3$ group and the original nitro group. The difficulty involved in nitrating *m*-dinitrobenzotrifluoride may be predicted when a comparison is made with *m*-nitrobenzene, as both compounds contain two meta directing groups in the 1,3 positions. The nitration of *m*-dinitrobenzene is extremely difficult; therefore, it would be expected that nitration of *m*-nitrobenzotrifluoride would also be difficult. This theoretical analogy was verified experimentally as it was necessary to use a fuming nitric-sulfuric acid mixture at a temperature of about 100°C. in order to obtain a satisfactory yield of 3,5-dinitrobenzotrifluoride.

To develop a standard procedure for a large-scale laboratory preparation of 3,5-dinitrobenzotrifluoride which would produce a maximum yield of product, consistent with economical use of both time and materials, required a study of the effects on the dinitro yield by the following conditions: (1) concentration and volume of sulfuric and nitric acid used in nitration; and (2) time and temperature of nitration.

An investigation of the effects of the conditions given above on the yield of 3,5-dinitrobenzotrifluoride was conducted by performing a series of nitrations in which the conditions were varied from run to run. The yield of dinitrobenzotrifluoride as affected by various concentrations and volumes of acids used are shown in Tables 1 and 2.

From the data obtained, indications are that fuming sulfuric acid (30 percent free SO_3) and fuming nitric acid (sp. gr. 1.49-1.5), a nitration temperature of 100°C., and a heating period of three hours produced better yields of 3,5-dinitrobenzotrifluoride. Nitration temperatures higher than 100°C., and heating periods longer than 3 hours were found to effect only negligible increases in the yield.

The crude 3,5-dinitrobenzotrifluoride, washed free of acid with dilute alkali, is still contaminated with small amounts of isomers and unreacted *m*-nitrobenzotrifluoride which make imperative an efficient purification process. Fractional crystallization of the crude product from methanol gave a pure product but

* Published with the approval of the Chief, Illinois State Geological Survey.

TABLE 1.—YIELDS OF 3,5-DINITROBENZOTRIFLUORIDE AS AFFECTED BY DIFFERENT ACID CONCENTRATIONS

Reagent	Concentration	Average Yield of 3, 5-Dinitrobenzotrifluoride
Fuming H_2SO_4	15% SO_3	35 Percent
Fuming H_2SO_4	25% SO_3	40 Percent
Fuming H_2SO_4	30% SO_3	45 Percent*
Fuming H_2SO_4	60% SO_3	40 Percent
Fuming HNO_3	Sp. gr. 1.49-5	45 Percent*
Red fuming HNO_3	.....	40 Percent

* Procedure was standardized on these concentrations.

TABLE 2.—YIELD OF 3,5-DINITROBENZOTRIFLUORIDE VS. VOLUME OF REAGENTS

Acid	Volume Ratio Acid: C_6H_4 (CF_3) (NO_2) 1, 3	Percent Yield of C_6H_3 (CF_3) $(NO_2)_2$ 1, 3, 5
H_2SO_4 (30% free SO_3)	5:1	41
H_2SO_4 (30% free SO_3)	3.6:1*	45
HNO_3 (Sp. gr. 1.99-1.5)	1.8:1	41
HNO_3 (Sp. gr. 1.49-1.5)	6.4:1*	51

* Procedure standardized on these ratios.

low recovery, due to the additional solubility effect of the unreacted *m*-nitrobenzotrifluoride. Purification by steam distillation was found to be impractical because the dinitro compound is slightly steam distillable. Fractional distillation under diminished pressure followed by recrystallization of the dinitro from methanol proved to be the most efficient method for purifying the crude dinitro product.

EXPERIMENTAL

Nitrations were carried out in a 5-liter three-necked (standard joints) round-bottomed flask submerged in a water bath containing a coil of copper tubing with connections so arranged as to permit circulation through the coil of either low or high pressure steam, tap water, or a cold brine solution. The flask was equipped with a Claisen adapter to which was attached a dropping funnel and a reflux condenser, a thermometer, and a mercury-sealed stirrer coupled to the shaft of a one-half h.p. motor.

m-Nitrobenzotrifluoride was added to the stirred fuming nitric and sulfuric acid mixture maintaining the nitration temperature at 100° C. throughout the addition and the subsequent two-hour heating period. The efficient heat transfer system previously described makes possible precise temperature control at 100° C. of the nitration reaction which is exothermic.

A modification of the above experimental procedure involves a nitration of benzotrifluoride with the spent acid to produce enough *m*-nitrobenzotrifluoride for a subsequent large-scale dinitrobenzotrifluoride preparation. This modification is advantageous from the standpoint of more efficient utilization of materials but has the disadvantage of increasing the dinitro production time.

SUMMARY

A study was made of the nitration of *m*-nitrobenzotrifluoride to determine the conditions most favorable for obtaining good yields of 3,5-dinitrobenzotrifluoride. From the results thus obtained, a large-scale laboratory method of preparation of 3, 5-dinitrobenzotrifluoride was developed.

BIBLIOGRAPHY

1. FINGER AND REED. J. Am. Chem. Soc. *66*, 1972-1974 (1944).