The Mono-Nitration of Benzotrifluoride*

G. C. Finger, N. H. Nachtrieb and F. H. Reed

State Geological Survey, Urbana, Illinois

Benzotrifluoride ($C_6H_5CF_3$) and its derivatives show promise of becoming commercially significant, due to their unusual properties. The $-CF_3$ side chain, in contrast to its chlorine analog, $-CCl_3$, is remarkably stable to most chemical reagents. Benzotrifluoride is readily prepared from benzotrichloride and anhydrous antimony trifluoride, usually with heat and pressure.[1]

The most common approach to the synthesis of benzotrifluoride derivatives is through the meta nitro compound and is illustrated by the following equation:

$$C_6H_5CF_3 + HNO_3 \rightarrow CF_3 \cdot C_6H_4 \cdot NO_2\ (1,3) + H_2O$$

Swarts,[2] in 1898, obtained a 89 per cent yield by nitrating benzotrifluoride with a large excess (approximately 500 per cent) of fuming nitric acid. The reaction was run at 0°C and then finished off at reflux temperature. Aelony[3] reported a yield of 89.5 per cent using the same method. Booth[1] modified the procedure slightly and reported a 96 per cent yield with a mixture of one part of fuming nitric (sp. gr. 1.5) acid and 1.5 parts of concentrated sulfuric acid. The latter procedure is very indefinite, as no supplementary information was given to clarify it; the high yield may have been based on the crude product. The status of this nitration obviously is (1) that fuming nitric acid is used in large excess, (2) the addition of sulfuric acid increases the yield, (3) the nitro compound is very stable, and (4) the high yields indicate the absence of higher nitration products. Swarts,[4] in a very careful study, also showed that 99 per cent of the nitration was the meta derivative, which shows that the $-CF_3$ group is one of most powerful meta directing groups known.

With the above facts in mind, a study was made to determine the factors which influence the yield, so as to evolve a more simple and economical procedure. The experiments were divided into classes, (1) nitration by a nitric acid—sulfuric acid mixture, and (2) nitration by solid sodium nitrate in the presence of sulfuric acid. The factors of temperature, concentration of reagents, relative amounts of reactants, and time were studied.

Experimental

The nitrations were run on 0.5 or 1.0 mol quantities of benzotrifluoride (b.p. 99-100°C.) in a 500 cc. three-necked flask, equipped with a mercury-sealed or a closely fitted shaft stirrer, a thermometer, and, in the case of the nitric acid method, a separatory funnel. The concentrated sulfuric acid was the ordinary c.p. acid (95.5-97 per cent). Agitation was vigorous enough in all cases to obtain intimate contact of all reactants. At the end, the nitration mixture was poured over ice; the crude nitro compound separated as a heavy pale yellow to cream colored oil. The oil was washed once again with water, then twice with approximately two per cent sodium carbonate or sodium hydroxide solution, giving a yellow to orange aqueous layer, and finally with water. The washings were all extracted with ether and the combined ether extracts treated in the same way as was the crude nitro product. The crude product and ether extracts were separately dried over anhydrous magnesium sulfate.

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The magnesium sulfate was removed by suction filtration. The dried ether extracts were evaporated on a steam cone and the residue was then combined with the main fraction. All distillations were made by using a Claisen flask-air condenser set up with an oil bath for heating; the pure fraction was taken at 200-203°C.

The material which remained after removal of the main fraction from all experiments was combined. Vacuum distillation of this residue showed that it consisted almost entirely of the mono nitro compound. Therefore, the yields may actually be somewhat higher than listed.

a. Nitric acid-sulfuric acid mixture

The literature, as well as preliminary work, appears to indicate that the addition of concentrated sulfuric acid to the nitric acid favors an increased yield; consequently all of the experiments were made with a nitric acid-sulfuric acid mixture. Since only a mononitrate can be formed, the benzotrifluoride was added dropwise to the nitric-sulfuric acid mixture with occasional cooling to hold the temperature between 30 to 35°C. The experiments are tabulated in Table I.

TABLE I—YIELDS OF $CF_3.C_6H_4.NO_2$ 1,3

(Nitric acid-Sulfuric acid Method)

Sp. Gr. HNO_3	Per cent excess HNO_3	Moles of H_2SO_4	Mol ratio $\frac{H_2O‡}{H_2SO_4}$	Yield of $CF_3.C_6H_4.NO_2$ (1,3) in grams			
				Theor.	Crude	Pure	% (Pure)
1.42–1.425	10	0.75	2.05	95.5	78.3	40.3	42.2
1.42–1.425	10	1.05	1.5	95.5	90.0	73.8	77.2
1.42–1.425	10	1.23	1.25	95.5	92.5	82.9	86.7
1.42–1.425	10	1.55	1.1	95.5	93.1	86.8	90.8
1.42–1.425	10	2.25	0.85	95.5	90.3	84.3	88.3
1.42–1.425*	10	2.25	0.85	95.5	92.8	85.5	89.5
1.42–1.425	10	5.36	0.5	95.5	92.4	81.4	85.2
1.42–1.425	100	4.17	.92	95.5	90.3	85.3	89.2
1.49–1.5	568	3.14	.57	95.5	90.4	73.9	77.2
1.49–1.5*†	568	6.28	.57	191	176	166.8	87.3
1.59–1.6*†	602	6.4	.38	191	180	164.5	86.2

* Nitration at 30-35° throughout; all others finished off at 60°.
† One mol of $C_6H_5CF_3$ used; all others based on 0.5 mol quantities.
‡ Total water at the end of the nitration.

The yield of nitro compound is almost entirely independent of amount or specific gravity of the nitric acid above certain limits. The amount of sulfuric acid is the most important factor and the optimum condition is approached when the mol ratio of water to sulfuric acid is one. This includes the water present in the original reagents plus the water theoretically formed in the reaction. High concentrations of sulfuric acid cause a decrease in the yield, probably due to sulfonation. Preliminary experiments indicated that a nitration temperature of 0°C. was of no yield advantage and involved a great loss of time and an increased cooling cost. On the other hand, a temperature around 30-35° was very convenient to control and the reaction was finished off at 60°C. Raising the temperature after all of the benzotrifluoride had been added cut the total reaction time down from about 2½ hours to one hour.

In summary, the optimum conditions involve (1) a 10 per cent excess of concentrated nitric acid, (2) sufficient amount of concentrated sulfuric acid to form a monohydrate with the final total water content, (3) and a temperature of 30-35° for nitration with a finishing off at 60°C. Ninety per cent yields of a pure product are obtained under these conditions.

b. Sodium nitrate-sulfuric acid mixture

Commercially, many nitrations are made by adding solid sodium nitrate to a mixture of sulfuric acid and the compound to be nitrated. Sodium nitrate is not only much lower in cost than nitric acid but the equipment overhead is also much less. This method with benzotrifluoride can be illustrated as follows:

$$C_6H_5CF_3 + NaNO_3 + H_2SO_4 \rightarrow CF_3 \cdot C_6H_4 \cdot NO_2\ (1,3) + NaHSO_4 + H_2O$$

Finely ground sodium nitrate was added in small amounts from a porcelain spatula to the benzotrifluoride-sulfuric acid mixture. The reaction mixture was cooled by tap water and the sodium nitrate was added at such a rate that the temperature did not exceed 30°C. The reaction was finished off at 60°C. The experimental results are indicated in Table II.

TABLE II—YIELDS OF $CF_3.C_6H_4.NO_2$ 1,3

(Sodium Nitrate-Sulfuric Acid Method)

Per cent excess $NaNO_3$	Moles of H_2SO_4	Yield of $CF_3.C_6H_4.NO_2$ (1,3) in grams			
		Theor.	Crude	Pure	% (Pure)
0.0	2.74	95.5	88.1	78.0	81.6
10	2.5	95.5	91.8	82.4	86.2
10	2.74	95.5	89.5	83.7	87.6
10	3.0	95.5	98.2	82.9	86.8
10	4.0	95.5	87.5	81.4	85.2
10	5.0	95.5	89.7	79.9	83.6
10	5.0	95.5	88	81.9	85.8
20	2.92	95.5	89.8	85	89
20	2.92	95.5	88.9	85	89
20*	2.92	95.5	83.8	64.8	67.9
30	3.5	95.5	86.8	82	86
30	3.5	95.5	87.5	82.4	86.2

All nitrations were run at 25-30° and finished at 60° C.
* Not finished off at 60° C.

The yield of nitro compound is almost independent of the amount of sodium nitrate, 20 per cent excess being the optimum condition with only a slightly lower yield at 10 per cent. A H_2O to H_2SO_4 mol ratio is of no particular significance because of the large excess of acid needed to prevent the mixture from becoming too viscous as the sodium bisulfate progressively precipitates. Investigation of the mol ratio of H_2SO_4 to $C_6H_5CF_3$ with a 10 per cent excess of sodium nitrate showed an optimum yield of approximately 87.5 per cent at 5.5. The decrease in yield beyond this point is also probably due to sulfonation. A temperature of 25-30°C. was selected for convenience of control and it was necessary to finish the nitration at 60°, as indicated in Table II, in order to convert all of the sodium nitrate to nitric acid. The formation of the nitric acid at the end was indicated by the rapid rise in temperature.

In conclusion, the optimum conditions involve, (1) a 10-20 per cent excess of sodium nitrate, (2) a mol ratio of sulfuric acid to benzotrifluoride of 5.5, and (3) a temperature of 25-30°C. with a finishing off at 60°C. The maximum yield of pure product was 89 per cent.

Summary

It has been found possible to obtain meta nitrobenzotrifluoride in 90 and 89 per cent yields with concentrated nitric acid-sulfuric acid mixtures and sodium nitrate-sulfuric acid mixtures, respectively. A 10 per cent excess of nitric acid or sodium nitrate at room temperature was used.

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