

TABLE I
 REPLACEMENT OF AMINO GROUP BY HYDROGEN

Compound deaminated	Structure	Product B. p., °C.	n_D^{20}	d_4^{25}	Yield, %	
					Using C ₂ H ₅ OH	Using H ₃ PO ₄
3-H ₂ N-C ₆ H ₄ CF ₃	C ₆ H ₅ CF ₃	98-101			37	47.4
3-H ₂ N-4-Br-C ₆ H ₃ CF ₃	4-Br-C ₆ H ₄ CF ₃	154-155	1.4705	1.607	40	67
5-H ₂ N-2-Br-C ₆ H ₃ CF ₃	2-Br-C ₆ H ₄ CF ₃	165-168			60	
3-H ₂ N-2,4-Br-C ₆ H ₂ CF ₃ or 5-H ₂ N-2,4-Br-C ₆ H ₂ CF ₃	2,4-Br-C ₆ H ₃ CF ₃ ^a	97-102.5 ^b	1.5279	2.006		53
Unfractionated reaction mixture ^c				49.3	65.7

^a Calcd. for C₇H₃Br₂F₃: Br, 52.56. Found: Br, 52.51. ^b At 20.5 mm. ^c The products consisted of benzotrifluoride, *p*-bromo-, *o*-bromo- and 2,4-dibromobenzotrifluoride. They were obtained in 4.8, 21, 12 and 11.5% yield, respectively, using ethanol; in 12.5, 20, 22 and 11.2% yield using H₃PO₄.

fluxed for 8 hours in 100 ml. of *n*-propanol with 0.04 mole of alkylene dibromide. The solution was cooled, diluted with ethyl ether, the precipitate filtered off and recrystallized from hot *n*-propanol-benzene solution.

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The Formation and Deamination of Brominated *m*-Aminobenzotrifluorides¹

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m-Bromobenzotrifluoride is a useful starting material for the synthesis of a number of compounds since it readily forms a Grignard reagent.² Although *m*-bromobenzotrifluoride can be made in a straightforward reaction from benzotrifluoride, the ortho and para isomers must be made indirectly. Jones³ has prepared *p*-bromobenzotrifluoride in an over-all yield of about 40% from *p*-nitrotoluene; however, the process required the use of two bromination steps, a fluorination, a reduction and, finally, the replacement of the amino group by bromine. Jones was also able to prepare *o*-bromobenzotrifluoride, but again a lengthy procedure was used. Since the completion of this research, Benkeser and Severson⁴ have described a two-step synthesis of *o*-bromobenzotrifluoride involving the metallation and subsequent bromination of benzotrifluoride with 28% yields.

Since *m*-aminobenzotrifluoride is commercially available, it seemed probable that it might serve as a starting point for a convenient synthesis of *o*- and *p*-bromobenzotrifluoride. This paper reports a study of the bromination of *m*-aminobenzotrifluoride and the deamination of the resulting aminobromo compounds to form various bromobenzotrifluorides.

m-Aminobenzotrifluoride was brominated under a variety of conditions. The best yields of monobromobenzotrifluorides resulted when the reaction was carried out at 5-10° in an excess of the amine when no catalyst was employed. Both 3-amino-4-bromo- and 5-amino-2-bromobenzotrifluoride were obtained under these conditions but no 3-amino-2-bromobenzotrifluoride was isolated during any experiments. When larger amounts of bromine were used, a compound believed to be 5-amino-2,4-

dibromobenzotrifluoride was formed. When the brominations were conducted at 50° or when *m*-acetaminobenzotrifluoride served as the starting material, a considerable amount of unidentified high boiling material resulted.

The structure of the 3-amino-4-bromobenzotrifluoride was established by deamination to a bromobenzotrifluoride which, when hydrolyzed with sulfuric acid, was converted to *p*-bromobenzoic acid. The amine was also diazotized and treated with hydrobromic acid to give the known 3,4-dibromobenzotrifluoride. The 5-amino-2-bromobenzotrifluoride was diazotized and reduced to *o*-bromobenzotrifluoride thus establishing the position of the bromine as being adjacent to the trifluoromethyl group. Final confirmation resulted when the replacement of the amino group by chlorine gave the known 2-bromo-5-chlorobenzotrifluoride.⁵

The aminodibromobenzotrifluoride was deaminated and hydrolyzed to 2,4-dibromobenzoic acid indicating that its structure was either 3-amino-2,4-dibromo- or 5-amino-2,4-dibromobenzotrifluoride. Since no 3-amino-2-bromobenzotrifluoride was ever isolated, it seems likely that 5-amino-2,4-dibromobenzotrifluoride was formed.

Deaminations were carried out using either hypophosphorus acid or ethanol as the reducing agent. Better yields were obtained with hypophosphorus acid as indicated in Table I.

Experimental

The Bromination of *m*-Aminobenzotrifluoride.—The bromination of *m*-aminobenzotrifluoride and the corresponding acetamino compound were carried out under a variety of conditions. The latter compound was treated with bromine at 100° without catalyst and at 50° with a small amount of iron powder but most of the starting material was recovered. Essentially these same results have recently been reported.⁶ The bromination of *m*-aminobenzotrifluoride at 10° without catalyst produced 21% conversions each of 3-amino-4-bromo- and 5-amino-2-bromobenzotrifluoride. At 5-10° using iron a 40% conversion to 3-amino-4-bromobenzotrifluoride was obtained but no other isomeric products were isolated; at 50°, a 31% yield was obtained with no other monobromo compound isolated.

A typical procedure follows. *m*-Aminobenzotrifluoride (1 mole) was added to 300 ml. of glacial acetic acid in a one-liter flask equipped with stirrer, addition funnel and thermometer. The contents were cooled to 10° and bromine (1 mole) added dropwise; about 2.5 hours were required for the addition. After another hour of stirring, 500 ml. of concentrated ammonia solution was added slowly and the

(1) Presented at the 118th Meeting of the American Chemical Society, Chicago, 1950.

(2) J. H. Simons and E. O. Ramler, *THIS JOURNAL*, **65**, 389 (1943).

(3) R. G. Jones, *ibid.*, **59**, 2346 (1947).

(4) R. A. Benkeser and M. C. Severson, *ibid.*, **73**, 1886 (1951).

(5) E. T. McBee, R. A. Sanford and P. J. Graham, *ibid.*, **72**, 1651 (1950).

(6) E. T. McBee, G. R. Pierce, R. D. Lowry and E. Rapkin, *ibid.*, **70**, 3092 (1951).

heavy organic layer separated and steam distilled. The product was distilled through a Lecky-Ewell column 72 cm. long and of 20 mm. diameter.

The distillation curve had plateaus at three temperatures at 5 mm.: 20 g. of unreacted *m*-aminobenzotrifluoride was obtained at 60–65°; 79 g. of 3-amino-4-bromobenzotrifluoride at 80–85°; 23.5 g. of 5-amino-2-bromobenzotrifluoride at 104–108°. A considerable amount of residue was left which was undoubtedly identical with the 5-amino-2,4-dibromo- or 3-amino-2,4-dibromobenzotrifluoride found in later experiments. The formation of the dibromide could be prevented by doubling the quantity of *m*-aminobenzotrifluoride.

In some cases the crude brominated mixture was deaminated. The relative amounts of the various products under these conditions are given in Table I.

3-Amino-4-bromobenzotrifluoride.—A center fraction of the 80–85° fraction had the following properties: b.p. 81–82° at 5 mm., n_D^{25} 1.5197, d_4^{25} 1.694.

Anal. Calcd. for $C_7H_5BrF_3N$: Br, 33.29; N, 5.83. Found: Br, 33.28; N, 5.61.

The structure of the compound was established by deamination followed by hydrolysis of the $-CF_3$ group according to the method employed by Le Fave.⁷ The melting point of 254–256° for the resulting *p*-bromobenzoic acid agrees with the reported value.⁸

5-Amino-2-bromobenzotrifluoride.⁶—Although this compound was formed in the experiment described above, larger amounts were obtained when two moles of *m*-aminobenzotrifluoride was treated with one mole of bromine. The properties of this substance are as follows: b.p. 104–108° at 5 mm., 81–84° at 0.5 mm., m.p. 55–56°.

Anal. Calcd. for $C_7H_5BrF_3N$: Br, 33.29; N, 5.83. Found: Br, 33.06; N, 5.78.

Deamination of this material gave *o*-bromobenzotrifluoride. Final identification was made by converting the amine by the Sandmeyer reaction to a bromochlorobenzotrifluoride which had the following physical properties: b.p. 198°, n_D^{25} 1.5056, m.p. 14.9–16.2°. The values compare with those reported for 2-bromo-5-chlorobenzotrifluoride.⁶

5-Amino-2,4-dibromo- or 3-Amino-2,4-dibromobenzotrifluoride.—Bromination of *m*-aminobenzotrifluoride at 50° in the presence of iron filings gave a relatively large amount (13% conversion) of aminodibromobenzotrifluoride, b.p. 113–115° at 3 mm., m.p. 45–47°.

Anal. Calcd. for $C_7H_4Br_2F_3N$: Br, 50.11; N, 4.39. Found: Br, 50.08; N, 4.35.

The compound was deaminated and hydrolyzed to 2,4-dibromobenzoic acid.⁹

Deamination Reactions with Ethanol.—The procedure was adapted from that of Clarke and Taylor.¹⁰ To 300 ml. of 95% ethanol in a one-liter flask equipped with a stirrer, thermometer and addition funnel were added 0.5 mole of the amine and 55 ml. of 96% sulfuric acid. The solution was cooled to -5° and 0.58 mole of sodium nitrite dissolved in the minimum amount of water slowly added. The temperature was maintained between 0 and 5° during the reaction and for one hour afterwards. The addition funnel was replaced by a reflux condenser and the temperature of the solution slowly raised to 30° where it was maintained for an hour, finally being raised slowly until reflux began and the evolution of nitrogen ceased. The reaction mixture was then distilled through a 12-inch column packed with Berl saddles until the temperature reached 80°. The distillate was added to 1500 ml. of water and the lower layer separated. The residue from the fractionation was steam distilled and the oil obtained added to the water-insoluble layer. The combined products were dried and distilled through an 18-inch column packed with 1/8 inch glass helices.

Deamination Reactions with Hypophosphorus Acid.—The procedure was adapted from that of Kornblum.¹¹ About 125 ml. of concentrated hydrochloric acid was added to a 500-ml. flask equipped as for the ethanol deaminations.

(7) G. M. Le Fave, *THIS JOURNAL*, **71**, 4148 (1949).

(8) H. Hübner, J. Ohly and O. Philipp, *Ann.*, **143**, 247 (1867).

(9) R. H. C. Neville and O. Winther, *Ber.*, **13**, 972 (1880).

(10) H. T. Clarke and E. R. Taylor, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1941, p. 415.

(11) N. Kornblum, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 294.

One-quarter mole of the amine was added slowly, the mixture cooled to -5° and 0.36 mole of sodium nitrite dissolved in a small amount of water added while the temperature was held below 10°. The resulting solution was stirred for half an hour and a precooled 50% solution containing one mole of hypophosphorus acid slowly added. Stirring was continued for two hours after all the acid had been added and the flask stored at 10° for 18 hours. The heavy, red liquid which separated was dried and distilled.

2-Bromo-5-chlorobenzotrifluoride.—A solution of 98 g. of 5-amino-2-bromobenzotrifluoride dissolved in 100 ml. of concentrated hydrochloric acid was treated at 0–5° with a solution containing 140 g. of sodium nitrite. After the diazotization was complete, 1.5 g. of copper powder was added and the solution heated gently. When the evolution of nitrogen had ceased, the mixture was steam distilled and the resulting oil dried and distilled. 2-Bromo-5-chlorobenzotrifluoride (45 g.), b.p. 197–202°, was obtained. A center fraction had a boiling point of 198°, m.p. 14.9–16.2° and n_D^{25} 1.5056.

3,4-Dibromobenzotrifluoride.—By essentially the method described above, 0.2 mole of 3-amino-4-bromobenzotrifluoride was treated with 202 g. of 40% hydrobromic acid solution, 69 g. of sodium nitrite and, subsequently, copper powder to give a 71% yield of 3,4-dibromobenzotrifluoride, b.p. 101–102° at 25 mm., n_D^{25} 1.5189, d_4^{25} 1.973, A_{470} 1.19.

Anal. Calcd. for $C_7H_4Br_2F_3$: Br, 52.56. Found: Br, 52.54.

Hydrolysis with 100% sulfuric acid gave 3,4-dibromobenzoic acid, m.p. 235–236.5°. 3,4-Dibromobenzotrifluoride has previously been prepared by the direct bromination of benzotrifluoride.²

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Heat Capacities at Low Temperatures and Entropies at 298.16°K. of Hafnium Dioxide and Hafnium Tetrachloride

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Thermodynamic values of hafnium compounds have been lacking because of unavailability of adequately pure materials. Recently, substantially pure hafnium and some of its compounds have been produced in considerable amounts. This paper reports low-temperature heat capacity data and entropy values at 298.16°K. for hafnium dioxide and hafnium tetrachloride. No previous, similar data exist for either substance.

Materials.—The hafnium dioxide and hafnium tetrachloride were furnished by the Northwest Electrodevelopment Laboratory of the Bureau of Mines at Albany, Ore., along with the results of chemical and spectrographic analyses, which were reported in the recent paper of Orr,¹ who measured high-temperature heat contents of identical materials. The hafnium dioxide contained 1.66% zirconium dioxide and a 0.37% total of minor impurities. The hafnium tetrachloride contained 3.31% zirconium tetrachloride and 0.08% of minor impurities.

Heat Capacities.—The heat capacities were determined with previously described apparatus.² The results are expressed in defined calories (1 cal. = 4.1840 abs. joules), molecular weights accord with the 1951 International Atomic Weights,³ and all weighings were reduced to vacuum. The measurements employed 339.96 g. of the dioxide and 277.65 g. of the tetrachloride.

The experimental heat capacity values are listed

(1) R. L. Orr, *THIS JOURNAL*, **75**, 1231 (1953).

(2) K. K. Kelley, B. F. Naylor and C. H. Shomate, U. S. Bur. Mines Tech. Paper 686 (1946).

(3) E. Wibers, *THIS JOURNAL*, **74**, 2447 (1952).