[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY, WESTERN RESERVE UNIVERSITY]

Benzotrifluoride and its Halogenated Derivatives[1]

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The purpose of this paper is to describe an improved method for the preparation of benzotrifluoride, the preparation and study of the isomeric monofluoro- and monochlorobenzotrifluorides, 3,4-dichlorobenzotrifluoride, and two mixtures of more fully chlorinated derivatives.

Wertyporoch[4] prepared the more or less impure monochlorobenzotrifluorides and small amounts of the dichloro derivative by the direct action of chlorine on benzotrifluoride in the presence of antimony pentachloride.

Since the investigation described in this paper was completed, Aelony[5] published a description of the preparation and properties of *m*-fluorobenzotrifluoride. The properties as described agree closely with our findings with the exception of the index of refraction.

Determination of Physical Properties.—Vapor pressures (Table I) were determined as described by Booth, Elsey and Burchfield.[6] The boiling points were read from the temperature–vapor pressure curves plotted on a large scale. The latent heats of vaporization were calculated from the Rankine and Clausius–Clapeyron equations. Melting points were determined as described by Booth and Stillwell.[7]

TABLE I

VAPOR PRESSURES OF BENZOTRIFLUORIDE AND ITS HALOGENATED DERIVATIVES

T, °C.	Press., mm. $C_6H_5CF_3$	*T*, °C.	Press., mm. m-$C_6H_4FCF_3$
0.0	8.5	0.0	9.0
27.7	43.5	15.0	22.5
34.4	60.0	20.7	30.5
41.3	82.5	35.6	65.5
50.2	122.5	41.2	84.5
57.5	165.5	50.5	127.0
64.9	220.5	55.4	155.0
70.0	268.5	65.4	230.5
75.8	326.0	71.0	284.5
80.7	385.0	80.8	400.0
91.3	542.0	91.3	567.5
96.3	632.5	96.8	670.0
100.5	720.0	100.2	745.5
103.5	789.6	103.5	822.5
107.2	877.0	105.4	868.5
	o-$C_6H_4ClCF_3$		m-$C_6H_4ClCF_3$
19.6	3.5	20.7	6.5
28.4	6.0	26.9	9.5
35.6	9.5	33.2	14.0
42.8	13.5	41.8	20.5
51.3	20.5	57.3	43.5
65.2	39.0	71.1	79.5
78.6	67.5	83.8	131.0
86.6	93.0	90.7	169.5
93.5	120.5	103.4	264.5
124.0	333.5	110.2	329.0
131.7	422.5	121.9	473.5
139.1	522.5	128.5	574.5
145.8	631.0	133.5	662.5
153.4	774.0	137.3	738.0
157.7	868.5	141.6	831.5
	p-$C_6H_4FCF_3$		p-$C_6H_4ClCF_3$
13.4	22.0	19.3	5.0
16.4	26.5	27.1	9.0
21.1	33.5	33.5	12.0
25.7	41.0	45.6	22.5
30.3	50.5	51.2	31.0
35.7	65.0	63.5	55.0
40.6	81.5	77.9	100.5
55.6	150.5	97.0	206.5
61.4	188.0	103.4	257.5
71.0	270.0	116.1	387.5
81.2	384.5	121.9	462.5
91.9	542.5	128.5	562.5
96.6	631.0	133.5	646.5
102.3	749.0	139.8	770.5
107.1	865.5	143.5	851.5
	3,4-$C_6H_3Cl_2CF_3$		3,4-$C_6H_3Cl_2CF_3$
24.6	2.0	113.9	124.5
35.1	4.0	130.1	216.0
44.2	6.0	146.1	358.0
52.1	9.0	154.8	462.0
59.8	12.5	169.9	694.0
71.8	22.0	174.3	774.5
81.5	35.0	179.8	888.5
99.7	73.0		

Analyses.—The compounds described in this paper were analyzed for hydrogen and carbon by the combustion method. The volatilized sample was led with an excess of oxygen over cerium nitrate and copper oxide followed by molecular silver on asbestos and lead chromate, the two latter reagents serving to remove completely free

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(4) Wertyporoch, *Ann.*, **493**, 153–165 (1932).

(5) Aelony, THIS JOURNAL, **56**, 2063 (1934).

(6) Booth, Elsey and Burchfield, *ibid.*, **57**, 2064 (1935).

(7) Booth and Stillwell, *ibid.*, **56**, 1532 (1934).

or combined fluorine. The resulting water and carbon dioxide were absorbed in a Fischer absorption bottle filled with calcium chloride and a Gomberg type absorber filled with 50% potassium hydroxide solution. The results of the analyses are given in Table II.

Experimental Part

(a) **Benzotrifluoride.**—Benzotrifluoride was prepared by the action on benzotrichloride of an excess of sublimed antimony trifluoride instead of the ratios recommended by Swarts[8] and by Aelony.[5] The reaction was initiated and carried to completion as quickly as possible and the product was distilled from the reaction vessel as fast as it was formed since antimony salts, etc., greatly decrease the yield of benzotrifluoride by the production of resinous products.

The distillate was washed successively with 6 *N* hydrochloric acid, sodium bicarbonate and 20% sodium hydroxide solutions, dried by shaking with barium oxide and twice distilled at a high reflux ratio through an insulated, electrically-heated column 2.5 cm. in diameter and 110 cm. high packed with jack-chain and surmounted by a Vigreux condenser.

(b) ***o*-Fluorobenzotrifluoride.**—An attempt was made to prepare *o*-fluorobenzotrifluoride by chlorinating *o*-fluorotoluene to *o*-fluorobenzotrichloride and fluorinating the side chain with sublimed antimony trifluoride.

Accordingly, one mole (110 g.) of *o*-fluorotoluene from the Eastman Kodak Co. was chlorinated until the system gained 95 g. The compound chlorinated very slowly, and phosphorus pentachloride as a catalyst does not increase the speed or the extent of chlorination. Fractionation yielded a liquid boiling at 215–223°, which supposedly was *o*-fluorobenzotrichloride.

Fluorination of the above liquid produced volumes of hydrogen fluoride, a large quantity of resin, but only a few grams of a compound boiling between 114 and 116°. The products of several fluorinations were combined, purified and fractionated. Approximately 10 cc. of a liquid was obtained which boiled at 113.8–114.3° at 740.6 mm., and which resembled benzotrifluoride in odor and physical properties. It was thought that the compound was *o*-fluorobenzotrifluoride.

Anal. Calcd. for $C_6H_4FCF_3$: C, 51.21; H, 3.45. Found: C, 47.1; H, 2.42.

These analyses revealed that the compound was not *o*-fluorobenzotrifluoride. Since the yields were so small this was probably some secondary decomposition product.

(c) ***m*-Fluorobenzotrifluoride.**—*m*-Fluorobenzotrifluoride ($C_6H_4FCF_3$) was prepared by the following reactions: benzotrifluoride was nitrated, the nitro group was reduced to an amino group[9] and the amino group was replaced by a fluorine atom by the method of Balz and Schiemann.[10]

m-Nitrobenzotrifluoride was prepared in 96% yield using a nitrating mixture composed of one part fuming nitric (sp. gr. 1.5) and 1.5 parts of concentrated sulfuric acids.

One mole (191 g.) of *m*-nitrobenzotrifluoride was reduced with tin and concd. hydrochloric acid with a yield of 154 g. of *m*-aminobenzotrifluoride corresponding to 95%.

A solution of the diazonium salt was prepared by the addition of a saturated solution containing 15 g. of sodium nitrite to 32 g. of *m*-aminobenzotrifluoride and 40 cc. of concentrated hydrochloric acid. The addition of an excess of fluoboric acid precipitated the diazonium fluoborate. There was obtained 46 g. of the salt corresponding to 87% yield. The decomposition taking place below 140° was effected by gentle heat. There remained in the flask a small amount of a slightly brown residue which was probably sodium fluoborate. From 166 g. of diazonium fluoborate 86 g. of fluorobenzotrifluoride was recovered—a yield of 82% calculated from the weight of the salt decomposed. The compound was chemically and physically purified in the usual manner.

(d) ***p*-Fluorobenzotrifluoride.**—One hundred and thirty grams of *p*-fluorotoluene[11] was chlorinated in the usual manner with phosphorus pentachloride as a catalyst. After eighteen hours of chlorination, the reaction stopped and the products were fractionated. There was obtained 220 g. of *p*-fluorobenzotrichloride ($C_6H_4FCCl_3$) which boiled at 212–213° (uncorr.) at 741.6 mm.; a yield of 76%.

Two hundred and twenty grams of *p*-fluorobenzotrichloride ($C_6H_4FCCl_3$) was converted into 130 g. of *p*-fluorobenzotrifluoride ($C_6H_4FCF_3$) in the usual manner by means of antimony trifluoride. This yield corresponded to 73%. After purification the compound had a boiling point range of 0.3°.

(e) ***o*-Chlorobenzotrifluoride.**—*o*-Chlorobenzotrifluoride was prepared from *o*-toluidine by replacing the amino group by chlorine, chlorinating and subsequently fluorinating the side chain.

One hundred and seventy-five grams of *o*-chlorotoluene[12] and 5 g. of phosphorus pentachloride were introduced into a suitable flask. A slow stream of chlorine was led into the flask, the contents of which were maintained at the boiling point throughout the chlorination. This treatment resulted in the formation of much tarry matter, but with small yield of the desired product. It was thought that possibly phosphorus pentachloride at the elevated temperatures may have caused the formation of the decomposition products.

Accordingly, 170 g. of *o*-chlorotoluene was chlorinated at 160–190° without a catalyst, with the formation of only traces of tarry products. Chlorination took place much less readily in the case of *o*-chlorotoluene compared with that of the para isomer.

Two hundred grams of *o*-chlorobenzotrichloride was obtained, corresponding to a yield of 64%.

Two hundred grams of *o*-chlorobenzotrichloride was mixed with 190 g. (excess) of sublimed antimony trifluoride. The mixture was heated rapidly until reaction set in. The product weighed 124 g. after washing several times with 6 *N* hydrochloric acid, corresponding to a yield of 85%, on the basis of *o*-chlorobenzotrichloride. After purifying and drying in the usual manner, the *o*-chlorobenzotrifluoride boiled at 148.2–148.7° (uncorr.) at 741 mm.

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(8) Swarts, *Bull. acad. roy. sci. Belg.*, **113**, 241 (1913); **35**, 375 (1898); *Rec. trav. chim.*, **35**, 155 (1915); **33**, 263, 299 (1914).

(9) Beilstein and Kurbatow, *Ann.*, **176**, 29 (1875).

(10) Balz and Schiemann, *Ber.*, **60**, 1186 (1927).

(11) G. Schiemann, *ibid.*, **62**, 1794 (1929).

(12) Gattermann, *ibid.*, **23**, 1218 (1890).

(f) **m-Chlorobenzotrifluoride.**—The starting compound for the preparation of *m*-chlorobenzotrifluoride was *m*-aminobenzotrifluoride, the preparation of which was previously described.

The amino group was replaced by a chlorine atom by the method of Sandmeyer.[13] One hundred and thirty-eight grams of *m*-aminobenzotrifluoride was mixed with 200 cc. of concentrated hydrochloric acid in 180 cc. of water. The amine was diazotized by the addition of a concentrated solution of sodium nitrite which contained 60 g. of the salt. The diazotized solution was slowly poured into 400 cc. of boiling, 10% cuprous chloride solution. The resulting mixture was distilled with steam and the water-oil distillate was extracted with ether. The *m*-chlorobenzotrifluoride–ether solution was dried with anhydrous calcium chloride and was fractionated. There was obtained 110 g. of product which boiled between 136–140°, corresponding to a yield of 70%. The product was agitated with a saturated solution of sodium carbonate, dried by refluxing with barium oxide for five hours and was distilled through a column filled with glass beads.

(g) **p-Chlorobenzotrifluoride.**—In order to prepare *p*-chlorobenzotrifluoride it was necessary to prepare *p*-chlorotoluene, chlorinate the side chain to *p*-chlorobenzotrichloride, and replace the chlorine atoms in the side chain by fluorine atoms by means of antimony trifluoride.

p-Chlorotoluene was prepared by the Gattermann[12] method. One mole of *p*-chlorotoluene was introduced into a 500-cc. flask provided with conical ground glass joints for a chlorine inlet and a reflux condenser. Five grams of phosphorus pentachloride was added to serve as a catalyst for the chlorination of the side chain. The contents of the flask were heated to boiling and were maintained at the boiling point during the chlorination. A slow stream of dry chlorine was led into the liquid until the weight of the system gained 105 g. The chlorination process required ten hours. The product was fractionally distilled, and a yield of 215 g. of *p*-chlorobenzotrichloride (93%) boiling between 248–250° was obtained.

Two hundred and fifteen grams of *p*-chlorobenzotrichloride was mixed with 200 g. (excess) of sublimed antimony trifluoride and the mixture was heated rapidly to initiate the reaction. The reaction proceeded smoothly and rapidly. The product was washed several times with 6 *N* hydrochloric acid, followed by several washings with water. The compound thus treated weighed 148 g., a yield of 95% calculated on the basis of the weight of *p*-chlorobenzotrichloride used.

(h) **3,4-Dichlorobenzotrifluoride.**—The preparation of 3,4-dichlorobenzotrifluoride was carried out in a manner similar to that whereby the monochloro derivatives of benzotrifluoride were obtained. The starting compound was *p*-toluidine which was successively converted into 3,4-dichlorotoluene, 3,4-dichlorobenzotrichloride and 3,4-dichlorobenzotrifluoride. The preparation of 3,4-dichlorotoluene was carried out as described by Cohen and Dakin.[14]

The side chain of the above compound chlorinated readily at 160–190° without a catalyst. The chlorinated product was not distilled, but was fluorinated without further purification. The compound was fluorinated with resublimed antimony trifluoride with a yield of 59% of the desired product calculated on the basis of the dichlorotoluene used. The crude 3,4-dichlorobenzotrifluoride was purified in the usual manner. The final product had a boiling point range of 0.5°.

(i) **Exhaustive Chlorination of Benzotrifluoride.**—Two hundred grams of benzotrifluoride and several pieces of iron gauze were introduced into a flask provided with a reflux condenser. The temperature of the contents of the flask was maintained at 60–70° by means of a water-bath.

Volumes of hydrogen chloride were liberated when dry chlorine was bubbled through the mixture. After the system had gained 60–70 g. in weight the reaction slowed considerably. The temperature was then raised to 100°, with a noticeable increase in the speed of the reaction. The chlorination was continued for twenty-five hours until the system had gained 97 g.

The first distillation of the chlorinated product revealed a boiling point of 180–230°, with only 10–15 g. of a higher boiling liquid remaining in the distilling flask. The distillate had a dark brown color, which color changed to a light yellow when water was added. The compound was agitated with concentrated hydrochloric acid to remove traces of aluminum chloride or iron chloride, carefully washed with saturated sodium carbonate solution, 20% sodium hydroxide solution, followed by several treatments with distilled water. The clear yellow liquid was dried with calcium chloride and fractionated. The small amount of residue from this fractionation was liquid at 0° but partially solidified at −15°. The first fractionation gave a clear colorless liquid, boiling between 180 and 220° and melting below −15°.

From a comparison of the boiling points of the *o*-, *m*- and *p*-monochlorobenzotrifluorides and the 3,4-dichlorobenzotrifluoride, one would surmise that this mixture consists of dichlorobenzotrifluorides and trichlorobenzotrifluorides.

To introduce more chlorine into the ring, the contents of the flask were heated over a direct flame, below the boiling point of the contents but to such a temperature that crystals of ferric chloride formed in the flask, while a stream of dry chlorine was simultaneously led in. It was surprising to note that practically no decomposition products were formed by this drastic treatment. After purification in the usual manner the mixture boiled between 230 and 260° and crystals appeared if it cooled to 15°. On the basis of previous experience it seems reasonable to assume that this mixture consists of the isomeric tri- and tetrachlorobenzotrifluorides.

Discussion of Results

The physical properties of the compounds prepared and studied in this research are listed with their analyses in Table II.

The introduction of chlorine into the benzotrifluoride ring raises the boiling point of the original compound 35–37° for each chlorine atom replacing an atom of hydrogen, except in the case of the ortho compound where the elevation of the boiling point is decidedly higher. Practically the same elevation is noted when chlorine is introduced into the benzotrichloride ring, and the same inconsistency with the ortho chloro compound. These facts are shown in Table III.

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(13) Sandmeyer, *Ber.*, **17**, 1633, 2650 (1884).

(14) Cohen and Dakin, *J. Chem. Soc.*, **81**, 1336 (1902).

TABLE II

SUMMARY OF PROPERTIES OF NEW AROMATIC FLUORIDES

Compound	B. p., °C.	M. p., °C.	Refractive index n_D	Refractive index °C.	Sp. gr., 25°C.	ΔH cal./mole at b. p.
$C_6H_5CF_3$	102.3	−29.05[a]				8,110
m-$C_6H_4FCF_3$	100.9	−81.5	1.3980	25	1.289	8,250
p-$C_6H_4FCF_3$	102.8	−41.7	1.3996	22	1.293	8,450
o-$C_6H_4ClCF_3$	152.8	− 7.4 to −7.6	1.4544	22	1.364	9,445
m-$C_6H_4ClCF_3$	138.4	−55.4	1.4466	21.2	1.336	9,165
p-$C_6H_4ClCF_3$	139.3	−34.0	1.4469	21.0	1.334	8,985
3,4-$C_6H_3Cl_2CF_3$	173.5	−12.3 to −12.5	1.4736	22.0	1.478	10,310

[a] Value obtained by F. Swarts.

Compound	Constants of Rankine equation *A*	*B*	*C*	Average deviation of calcd. values from obsd. values, mm.	Analyses, % Calcd. C	H	Found C	H
$C_6H_5CF_3$	−2777.4	−6.166	26.153	±1.0	...	..	...	..
m-$C_6H_4FCF_3$	−2718.8	−5.589	24.575	±0.5	51.20	2.45	51.29	2.39
p-$C_6H_4FCF_3$	−1741.9	0.650	5.841	±0.8	51.20	2.45	51.40	2.45
o-$C_6H_4ClCF_3$	−2410.0	−1.752	13.149	±1.0	46.54	2.23	46.60	2.25
m-$C_6H_4ClCF_3$	−2698.0	−3.887	19.600	±0.7	46.54	2.23	46.32	2.30
p-$C_6H_4ClCF_3$	−3431.0	−8.193	32.627	±1.2	46.54	2.23	46.34	2.28
3,4-$C_6H_3Cl_2CF_3$	−2587.3	−1.719	13.229	±1.2	39.08	1.41	39.55	1.52

TABLE III

BOILING POINTS OF BENZOTRIFLUORIDE, BENZOTRICHLORIDE AND HALOGENATED DERIVATIVES

Parent compound	B. p., °C.	Chlorine derivative	B. p., °C.	Increase in b. p., °C.
$C_6H_5CF_3$	102.3	*o*-$C_6H_4ClCF_3$	152.8	50.3
		m-$C_6H_4ClCF_3$	138.4	36.1
		p-$C_6H_4ClCF_3$	139.3	37.0
		3,4-$C_6H_2Cl_2CF_3$	173.5	2(35.6)
$C_6H_5CCl_3$	212–213	*o*-$C_6H_4ClCCl_3$	260	47–48
		m-$C_6H_4ClCCl_3$	247–250	35–38
		p-$C_6H_4ClCCl_3$	248–250	36–38

The melting points of the compounds prepared in this investigation are in line with the generalization that the introduction of fluorine in place of hydrogen in the benzene ring lowers the melting point of the original compound. It should be noted that the chlorinated benzotrifluorides, with the exception of the ortho compound, have lower melting points than even the analogous chlorine derivatives of toluene, *o*-, *m*- and *p*-chlorotoluene, which melt at −34, −47.8 and 6.5 to 7.5°, respectively.

The latent heats of vaporization are in accordance with the values usually found in non-associated liquids of similar boiling points.

Summary

1. It was found that the best yields of benzotrifluoride were obtained when an excess of antimony trifluoride was distilled with benzotrichloride.
2. The preparation and properties of *p*-fluorobenzotrifluoride, *o*-, *m*- and *p*-chlorobenzotrifluoride and 3,4-dichlorobenzotrifluoride have been described.
3. The vapor pressures of benzotrifluoride, *m*- and *p*-fluorobenzotrifluoride, *o*-, *m*- and *p*-chlorobenzotrifluoride and 3,4-dichlorobenzotrifluoride were measured over temperature ranges.
4. The preparation and boiling point of *p*-fluorobenzotrichloride (unanalyzed) was described.
5. Two exhaustively chlorinated mixtures of benzotrifluoride were prepared.

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