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THE META MONOHALOGENATED BENZOTRIFLUORIDES

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CHEMISTRY

THE META MONOHALOGENATED
BENZOTRIFLUORIDES*G. C. FINGER and M. L. KALINOWSKI
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Information was needed in the Survey laboratories on the properties of a complete series of monohalogenated benzotrifluorides. This information was obtained by synthesizing the *m*-fluoro-, *m*-chloro-, *m*-bromo-, and *m*-iodobenzotrifluorides. The object of this paper is to describe the synthesis of the bromo and iodo derivatives, and to compare also some of the properties of all of these compounds.

All of the compounds were synthesized from *m*-aminobenzotrifluoride by well known diazotization reactions. The *m*-fluoro¹ and *m*-chloro² derivatives were prepared as described in the literature. The bromo and iodo compounds were prepared by the Sandmeyer reaction. Simons³ prepared the bromo compound by the direct bromination of benzotrifluoride; he reported only the boiling point and gave no analysis.

Table I gives the physical properties of these compounds and some closely related analogs. In all cases, the meta halogen derivatives of benzotrifluoride have lower boiling points than the corresponding toluene analogs. By comparison to the simple monohalogen benzene compounds, the first member, *m*-fluorobenzotrifluoride boils higher than fluoroben-

zene; however, this order gradually reverses with increasing molecular weight as iodobenzene boils higher than *m*-iodobenzotrifluoride. The densities are higher and the index of refraction values are lower when compared to toluene analogs or the simple halobenzenes.

In general, these compounds are quite stable, are fairly volatile, and have a mild odor. The iodo derivative will slowly darken on standing, but will not undergo the Ullmann reaction to form a biphenyl with copper bronze at 250-270° C.

The authors are indebted to Mr. H. S. Clark, microanalyst, for the analyses given in this investigation.

EXPERIMENTAL

m-Bromobenzotrifluoride. — The general procedure given in Organic Syntheses⁴ for *p*-bromotoluene was used for the synthesis of *m*-bromobenzotrifluoride.

A mixture of 20 grams of crystallized copper sulfate, 10 grams of copper turnings, 77 grams of sodium bromide, 8.2 cc. of concentrated sulfuric acid, and 500 cc. of water was refluxed for 3-4 hours. A small amount of sodium bisulfite was added to complete the reduction and obtain a pale yellow solution.

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

TABLE 1.—PHYSICAL PROPERTIES OF META MONOHALOGEN
SUBSTITUTED BENZOTRIFLUORIDES

Compound	M. P. °C	B. P. °C	Density 20° C	n _D ²⁰
C ₆ H ₄ (CF ₃)(F)1,3 ²	-81.5°	100.9	1.289/25°	1.398/25°
C ₆ H ₄ (CH ₃)(F)1,3	-110.8	116	0.9972/13°	1.4691
C ₆ H ₅ F	-41.9	84.8	1.024	1.4646/22.8°
C ₆ H ₄ (CF ₃)(Cl)1,3 ²	-55.4	138.4	1.336/25°	1.4466/25°
C ₆ H ₄ (CH ₃)(Cl)1,3	-47.8	162	1.0722	1.5214/19°
C ₆ H ₅ Cl	-55	132	1.1066	1.5247
C ₆ H ₄ (CF ₃)(Br)1,3	151-53*	1.632*	1.4738*
C ₆ H ₄ (CH ₃)(Br)1,3	-39.8	183.7	1.4099	1.551
C ₆ H ₅ Br	-30.6	155-56	1.4991/15	1.5597
C ₆ H ₄ (CF ₃)(I)1,3	173*	1.887*	1.5198*
C ₆ H ₄ (CH ₃)(I)1,3	204	1.698
C ₆ H ₅ I	-31.4	188.6	1.832	1.6214/18.5°

* Data determined by authors.

With stirring, 80.5 grams of *m*-aminobenzotrifluoride¹ was added to a solution of 54 cc. of concentrated sulfuric acid in 500 cc. of water, and digested with heating. After the amine hydrosulfate was cooled to 10°, it was diazotized with a solution of 40 grams of sodium nitrite in 60 cc. of water and the temperature not allowed to exceed 20°. The diazonium sulfate solution was filtered.

The hydrobromic acid-cuprous bromide solution in a flask arranged for steam distillation was heated to boiling. By means of a separatory funnel, the diazonium solution was slowly added to the copper solution while a vigorous current of steam was passed through the mixture. The aqueous distillate was made alkaline with dilute sodium hydroxide solution and the *m*-bromobenzotrifluoride was separated from the water layer. The crude product was consecutively washed with cold concentrated sulfuric acid, water, dilute alkali, water, and dried over anhydrous magnesium sulfate. The crude product weighed 71 grams. This product was

distilled and 50 grams (44.5 percent of the theoretical amount) boiling at 151-153° was obtained.

Analysis calculated for C₇H₄F₃Br: C, 37.36; H, 1.79; Br, 35.51. Found: C, 37.49; H, 1.79; Br, 35.14.

m-Iodobenzotrifluoride. — To a solution of 200 cc. concentrated hydrochloric acid in 200 cc. of water, 80.5 grams of *m*-aminobenzotrifluoride was added and then digested by heating. After cooling the amine hydrochloride mixture to 5° C, it was diazotized with a solution of 40 grams of sodium nitrite in 60 cc. of water. The diazonium solution was filtered. To the clear filtrate, a solution of 89 grams of potassium iodide in 90 cc. of water was added in small amounts with stirring. Nitrogen was vigorously evolved and the rate was controlled by the addition of the potassium iodide solution. After the mixture had been allowed to stand overnight, it was heated on a steam cone for one-half hour to complete the decomposition. The heavy oily layer was separated, made slightly alkaline with dilute sodium hydrox-

ide solution, and steam distilled. The crude iodo compound was decolorized with dilute sodium thiosulfate solution, and dried over anhydrous magnesium sulfate. The crude product weighed 118 grams. It was distilled under reduced pressure giving a main fraction of 110 grams (81 percent of the theoretical amount) boiling at 73-75°/23 mm (173° at atmospheric). Redistillation gave a product boiling at 82-82.5°/25 mm.

Analysis calculated for $C_7H_4F_3I$: C, 30.91; H, 1.48; I, 46.66. Found: C, 30.74; H, 1.47; I, 46.69.

SUMMARY

m-Bromo and *m*-iodobenzotrifluoride were prepared from *m*-aminobenzotrifluoride by the Sandmeyer reaction in 44 and 81 percent yields, respectively.

The physical properties of the *m*-fluoro-, *m*-chloro-, *m*-bromo-, and *m*-iodobenzotrifluorides were tabulated and compared.

m-iodobenzotrifluoride will not undergo the Ullman biphenyl synthesis with copper at 250-270° C.

BIBLIOGRAPHY

1. Aelony, J. Am. Chem. Soc. 56, 2063 (1934).
2. Booth, Elsey and Burchfield, *ibid.*, 57, 2066 (1935).
3. Simons, *ibid.*, 65, 391 (1943).
4. Gilman, "Organic Syntheses," Coll. Vol. I, p. 131 (1932).



