ually diminished until after three hours it came to a constant rotation of $[\alpha]_D$ −83°. A similar sample of commercial inulin oxidized with sodium periodate in the same manner reached the same constant rotation within a similar period of time. The absence of formic acid was shown by the fact that no titratable acidity was produced at the end of the reaction. The amount of periodate consumed in the reaction[16] was estimated by treating 5-ml. samples with an excess of 0.1 N sodium arsenite in the presence of potassium iodide and sodium bicarbonate buffer and back titrating with 0.1 N iodine. The results showed that 1.0 and 1.03 moles of the oxidant were used for each fructose anhydride unit of the guayule fructosan and commercial inulin, respectively.

X-Ray Diffraction Data.—The sample of guayule fructosan that was used for the chemical studies was subjected to an X-ray diffraction examination by the powder method. The material was packed into a thin-walled glass tube having an internal diameter of about 0.6 mm., and exposed to molybdenum radiation filtered through a zirconium oxide screen. A pattern was obtained which contained five distinct lines on a considerably darkened background, indicating that the material was partially crystalline, but that much of it existed in random orientation capable of producing only amorphous scattering.

Apparently there are no crystal structure data for inulin available in the literature with which the above lines can be compared. Reference patterns for comparison were obtained from three authentic samples of inulin: (1) inulin from dahlia prepared by one of us (W. L. McR.), (2) commercial inulin "c. p.," Pfanstiehl and (3) inulin "pure" Pfanstiehl. All three inulin samples gave patterns identical with that obtained from the guayule fructosan, except that one of the weaker lines was lacking in the pattern from the last inulin sample.

The interplanar spacings found in the X-ray diffraction produced by guayule fructosan and by the three inulin samples are given in Table II. The close agreement between corresponding spacings in both magnitude and intensity of reflections afford independent confirmation of the conclusion, based on chemical evidence, that the fructosan from guayule has a structure indistinguishable from that of inulin.

Table II

X-Ray Diffraction Patterns of Guayule Fructosan and Inulin

Fructosan from guayule		Inulin from dahlia		Inulin "C. P." Pfanstiehl		Inulin "pure" Pfanstiehl	
d	I	d	I	d	I	d	I
7.3	Strong	7.3	Strong	7.3	Strong	7.3	Strong
5.6	Weak	5.6	Weak	5.6	Weak	...	...
5.0	Weak	5.0	Weak	5.0	Weak	5.0	Weak
4.1	Strong	4.1	Strong	4.1	Strong	4.1	Strong
3.7	Weak	3.62	Weak	3.62	Weak	3.62	Weak

d is interplanar distances expressed in ångström units. I is intensity of reflections.

The authors are indebted to Dr. H. S. Owens for the determination of viscosities of the inulins.

Summary

1. The properties and the chemical structure of the fructosan isolated from the guayule plant have been studied.

2. Methylation and hydrolysis of the polysaccharide produced chiefly 3,4,6-trimethylfructofuranose, showing that the fructose units are combined through positions 2 and 1. Data obtained from the oxidation of the fructosan with sodium periodate, show that the fructose units possess the furanose configuration.

3. The X-ray diffraction pattern of guayule fructosan is identical with that of inulin, providing additional support to the chemical evidence.

4. It is concluded that the guayule fructosan is identical with inulin.

Berkeley, California Received September 7, 1944

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[16] E. L. Jackson, "Organic Reactions," edited by R. Adams, John Wiley and Sons, Inc., New York, N. Y., 1944, Vol. II, pp. 341–375.

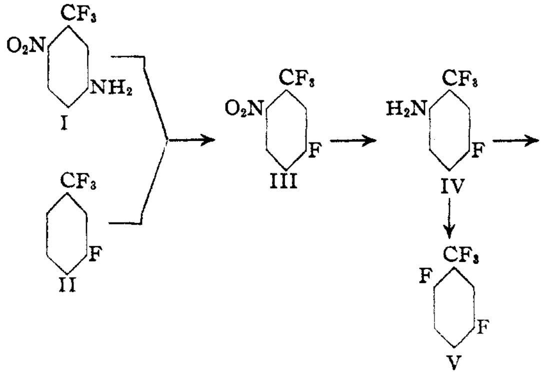
[Contribution from the Geochemical Section of the Illinois State Geological Survey]

Aromatic Fluorine Compounds. I. The Synthesis of 2,5- and 3,5-Difluorobenzotrifluorides[1]

By G. C. Finger[2] and F. H. Reed[3]

As part of a study in this Laboratory, of the synthesis and properties of aromatic fluorine compounds, 2,5- and 3,5-difluorobenzotrifluoride have been synthesized.

A Schiemann reaction[4] on 2-nitro-5-aminobenzotrifluoride (I) gave 2-nitro-5-fluorobenzotrifluoride (III), but this compound was found to be more conveniently prepared by the nitration of 3-fluorobenzotrifluoride (II); the structure of the nitro compound in this synthesis was established by the identity of the acetyl derivatives at (IV). An iron reduction[5] of III gave a quantita-



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[1] Presented before the Organic Division at the 107th Meeting of the American Chemical Society, Cleveland, Ohio, April 5, 1944. Published with the permission of the Chief of the Illinois State Geological Survey.

[2] Chemist.

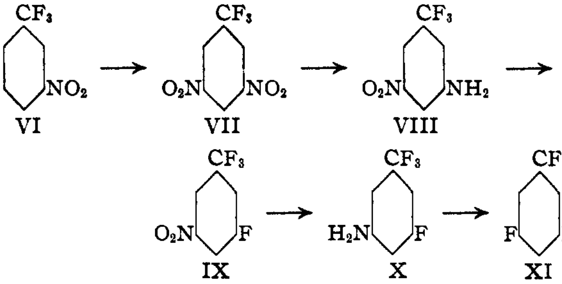
[3] Chief Chemist.

[4] Schiemann and Winkelmüller, *Ber.*, **60**, 1186 (1927).

[5] Lukasevich and Vorshilova, *Compt. rend. acad. sci. U. R. S. S.*, **2**, 344 (1935).

tive yield of 2-amino-5-fluorobenzotrifluoride (IV). This amine was converted to 2,5-difluorobenzotrifluoride (V) by the Schiemann reaction.[6]

A fuming nitric–sulfuric acid mixture with 3-nitrobenzotrifluoride (VI) gave a 50% yield of 3,5-dinitrobenzotrifluoride (VII). By means of the Murray and Waters[7] ammonium sulfide method, the dinitro compound was reduced to 3-amino-5-nitrobenzotrifluoride (VIII). The subsequent compounds were prepared by the same general reactions as applied to I, III, and IV, respectively.



The boiling points of 2,5- and 3,5-difluorobenzotrifluoride, 107–108 and 94–95°, respectively, are not appreciably different from the less fluorinated compounds, toluene, b. p. 110.8; benzotrifluoride, b. p. 102.3; and *m*-fluorobenzotrifluoride, b. p. 100.9, in spite of the great difference in their molecular weights.

Experimental[8,9]

2-Nitro-5-fluorobenzotrifluoride (III).—This compound was prepared by two methods; (1) the Schiemann reaction on 2-nitro-5-aminobenzotrifluoride (I), and (2) the nitration of 3-fluorobenzotrifluoride (II).

Approximately 15 g. of 2-nitro-5-aminobenzotrifluoride[10] in 75 cc. of concd. hydrochloric acid was diazotized with a solution of 6.9 g. of sodium nitrite in 15 cc. of water at 0°, and finally diluted with 25 cc. of water. The diazonium fluoborate was obtained by adding a solution of 40 g. of sodium fluoborate in 75 cc. of water to the filtered diazonium chloride. After recovery by filtration, the insoluble diazonium fluoborate was dried and 21 g. or 94% of the theoretical yield was obtained. After a thermal decomposition of the diazonium fluoborate in the usual manner, the crude product was isolated. A yield of 6 g., 41% based on the diazonium fluoborate, or 39% based on the amine, was obtained. Pure 2-nitro-5-fluorobenzotrifluoride is a heavy almost colorless liquid with a mild nitrobenzene odor; b. p. 198–199°.

Anal. Calcd. for $C_7H_3O_2NF_4$: C, 40.21; H, 1.45; N, 6.70. Found: C, 40.22; H, 1.49; N, 6.95.

The second method is a "mixed acid" nitration of 3-fluorobenzotrifluoride. To a stirred mixture of 105 g. of concd. nitric acid and 336 g. of concd. sulfuric acid, 164 g. of 3-fluorobenzotrifluoride (II)[11,12] was added at such a rate that the temperature was maintained at 30–35°. At the end, the temperature was raised to 60° for fifteen minutes. After the removal of the lower "spent acid" layer, the crude product was washed successively with water, 2% sodium carbonate solution, and water, and dried with anhydrous magnesium sulfate. A yield of 188 g., or 90%, of crude 2-nitro-5-fluorobenzotrifluoride was obtained. This material was sufficiently pure for the subsequent reduction.

In order to establish the composition of the crude nitration product, it was reduced with iron to the crude amine, and the resulting amine was acetylated with a mixture of acetic anhydride in acetic acid. Recrystallization of the crude acetyl derivative from carbon tetrachloride, along with the concentration of the mother liquor, gave only one compound, namely, the acetyl derivative of 2-amino-5-fluorobenzotrifluoride. As no other acetyl derivative or readily isolable compound was obtained it was concluded that the nitration of 3-fluorobenzotrifluoride with "mixed acid" gives almost exclusively 2-nitro-5-fluorobenzotrifluoride.

2-Amino-5-fluorobenzotrifluoride (IV).—To a stirred, refluxing mixture of 272 g. of iron filings in 375 cc. of ammonium chloride (0.78 *N*), 313.5 g. of 2-nitro-5-fluorobenzotrifluoride was added slowly. The reduction is exothermic and the rate of refluxing is readily controlled by the addition of the nitro compound. Refluxing and stirring were continued for three hours after the nitro compound had been added. Steam distillation removed the amine as a colorless, heavy liquid, giving a yield of 256 g. or 96%. The pure amine has a mild aniline odor, b. p. 70–72° (17.5 mm.) or 170.5°.

The acetyl derivative was prepared in the usual way, and recrystallization from 50% aqueous ethanol gave white needles, m. p. 121–121.5°. This derivative served as a reference compound in proving the structure of the nitro compound derived in the nitration of 3-fluorobenzotrifluoride.

Anal. Calcd. for $C_9H_7ONF_4$: C, 48.87; H, 3.19; N, 6.33. Found: C, 48.82; H, 3.32; N, 6.45.

2,5-Difluorobenzotrifluoride (V).—A mixture of 89.5 g. of 2-amino-5-fluorobenzotrifluoride in 300 cc. of concd. hydrochloric acid was diazotized at 0° with a solution of 37 g. of sodium nitrite dissolved in 50 cc. of water. To the filtered diazonium solution at 0°, 109.8 g. of sodium fluoborate dissolved in 132 cc. of water was added, and the diazonium fluoborate precipitated as a white product. After removal of the diazonium fluoborate by filtration and drying, a yield of 118 g. or 85% was obtained. It was necessary to use an efficient condensing system for the thermal decomposition of the fluoborate due to the high volatility of 2,5-difluorobenzotrifluoride. The condensing system consisted of two vertical Graham condensers (60 cm. long) cooled with brine at 0–10°, and connected so that the gases and vapors from the decomposition flask passed through one condenser and a receiver to the second condenser and receiver. The receivers were cooled also and the major portion of the product collected in the first receiver. The diazonium fluoborate is quite stable and it is necessary to apply heat continually for a progressive decomposition. After the crude product was taken up in ether, the ether extract was made faintly alkaline with dilute sodium hydroxide, and steam distilled. As the difluoro compound is also volatile with steam, it collected as an ether extract in the distillate. After the ether extract was dried, the ether and the difluoro compound were separated by distillation through a 24-inch vacuum-jacketed column. A yield of 52 g. or 52% of 2,5-difluorobenzotrifluoride, b. p. 107–108°, based on the amine or 67% based on the diazonium fluoborate was obtained.

A treatment with cold concd. sulfuric acid improved the odor of the product. It has a very mild and sweet odor as compared to benzotrifluoride.

Additional physical constants are: f. p. *ca.* −14°, $n^{20}D$ 1.3942; sp. gr. 1.4244 (15°).

Anal. Calcd. for $C_7H_3F_5$: C, 46.17; H, 1.66. Found: C, 46.20; H, 1.69.

3,5-Dinitrobenzotrifluoride (VII).—To a stirred mixture of 450 g. of fuming nitric acid (d. 1.49–1.5) and 900 g. of fuming sulfuric acid (20% SO_3) at 95–100°, 57 g. of 3-

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(6) In all cases where the Schiemann reaction was used, a solution of sodium fluoborate was used in place of fluoboric acid.

(7) Murray and Waters, This Journal, **60**, 2818 (1938).

(8) All melting points are uncorrected.

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

(10) Rouche, *Bull. classe sci., Acad. roy. Belg.*, 346 (1927).

(11) Booth, Elsey and Burchfield, This Journal, **57**, 2066 (1935).

(12) Aelony, *ibid.*, **56**, 2063 (1934).

nitrobenzotrifluoride[13] was added slowly and the temperature was controlled carefully so as not to exceed 100° for the first ninety minutes. Then the temperature was raised slowly and maintained at 115° for the next four to five hours. The entire reaction mixture was poured over crushed ice with rapid stirring, and the crude product separated as a white solid. It was removed on a large Buchner filter, washed with ice water, and dried. A yield of 43 g. or 52% was obtained. Recrystallization from methanol gave pure 3,5-dinitrobenzotrifluoride as white crystals, m. p. 49–50°.

Anal. Calcd. for $C_7H_3O_4N_2F_3$: C, 35.6; H, 1.28; N, 11.86. Found: C, 35.61; H, 1.25; N, 11.83.

3-Amino-5-nitrobenzotrifluoride (VIII).—To a refluxing solution of 47.2 g. of 3,5-dinitrobenzotrifluoride dissolved in 700 cc. of ethanol, 500 cc. of an alcoholic ammonium sulfide solution was added slowly over a period of thirty minutes, and refluxing was continued for approximately five hours. The ammonium sulfide[7] was prepared by treating 96 g. of crystalline sodium sulfide with 85.6 g. of ammonium chloride in ethanol, and removing the precipitated sodium chloride by filtration. After the reduction was complete, the reaction mixture was concentrated by evaporation to about 200 cc., cooled, filtered, and the precipitate of sulfur and inorganic salts was washed with ethanol to dissolve any residual nitroamine. The filtrate was poured into a large volume of water thus precipitating the nitroamine. After the crude product had been removed by filtration, it was extracted several times with hot, dilute hydrochloric acid. The acid extract was made alkaline and the nitroamine was isolated. A yield of 33 g. or 80% was obtained. Recrystallization from carbon tetrachloride gave pure 3-amino-5-nitrobenzotrifluoride as yellow flakes, m. p. 80–81.5°.

Anal. Calcd. for $C_7H_5O_2N_2F_3$: C, 40.78; H, 2.44; N, 13.59. Found: C, 40.87; H, 2.46; N, 13.48.

The acetyl derivative was recrystallized from carbon tetrachloride as white needles, m. p. 134–135°.

Anal. Calcd. for $C_9H_7O_3N_2F_3$: C, 43.53; H, 2.84; N, 11.29. Found: C, 43.69; H, 2.83; N, 11.20.

3-Fluoro-5-nitrobenzotrifluoride (IX).—This compound was prepared from 3-amino-5-nitrobenzotrifluoride by the Schiemann reaction. An 88% yield of the diazonium fluoborate was obtained. The thermal decomposition of the diazonium fluoborate gave a 43% yield of 3-fluoro-5-nitrobenzotrifluoride based on the amine. After purification the pure compound boiled at 180.5°.

Anal. Calcd. for $C_7H_3O_2NF_4$: C, 40.21; H, 1.45; N, 6.70. Found: C, 40.40; H, 1.44; N, 6.53.

3-Amino-5-fluorobenzotrifluoride (X).—This amine was prepared from 3-nitro-5-fluorobenzotrifluoride (IX) by the same general synthesis as indicated for IV. A 90% yield of crude 3-amino-5-fluorobenzotrifluoride was obtained. Recrystallization of the acetyl derivative from carbon tetrachloride gave white needles, m. p. 99.5–100.5°.

Anal. Calcd. for $C_9H_7ONF_4$: C, 48.88; H, 3.19; N, 6.33. Found: C, 49.11; H, 3.10; N, 6.57.

3,5-Difluorobenzotrifluoride (XI).—This compound was prepared from 3-amino-5-fluorobenzotrifluoride by the same general procedure as outlined under V. The yield of the diazonium fluoborate was 94%. Thermal decomposition of this compound gave 3,5-difluorobenzotrifluoride. The pure compound gave the following constants: f. p. *ca.* −40°, b. p. 94–95°, n^{20}_D 1.3873.

Anal. Calcd. for $C_7H_3F_5$: C, 46.17; H, 1.66. Found: C, 46.10; H, 1.53.

Summary

The preparation of 2,5- and 3,5-difluorobenzotrifluoride and some of their intermediates is described.

3,5-Dinitrobenzotrifluoride was prepared from 3-nitrobenzotrifluoride with a fuming nitric–sulfuric acid mixture.

URBANA, ILLINOIS RECEIVED JULY 17, 1944

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[13] Finger, Nachtrieb and Reed, *Trans. Illinois State Acad. Sci.*, **31**, 132 (1939).

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

The Structures of Biphenyl, *o*-Terphenyl and Tetraphenylene[1]

BY ISABELLA LUGOSKI KARLE[2] AND L. O. BROCKWAY

The nature of the binding between benzene rings which has been of considerable interest to the chemist has led us to investigate by electron diffraction the molecular structures of biphenyl, *o*-terphenyl and tetraphenylene (1,2,3,4,5,6,7,8-tetrabenz-$\Delta^{1,3,5,7}$-cyclooctatetraene). Although the original purpose of this investigation was to study the type of binding between aromatic groups, the problems of the orientation of the benzene rings in biphenyl and *o*-terphenyl and the structure of a substituted cyclooctatetraene ring presented themselves. The structures of biphenyl[3] and *o*-terphenyl[4] were studied previously by X-ray diffraction.

We wish to thank Dr. L. F. Fieser of Harvard University who forwarded to us a sample of tetraphenylene synthesized by Drs. W. S. Rapson and R. G. Shuttleworth of the University of Cape Town. This sample contained 10% benzene which was removed by placing the sample in the nozzle and heating it to 200° in a vacuum before electron diffraction photographs were taken. The *o*-terphenyl was supplied to us by Dr. W. E. Bachmann of the University of Michigan. It was recrystallized from petroleum ether according to the method of Allen and Pingert[5] and its m. p. was 58°. The biphenyl was obtained from the Eastman Kodak Co. and recrystallized from ethyl alcohol; m. p. 70°.

The electron diffraction photographs were obtained using a high temperature nozzle consisting of a monel metal cylinder closed by a screw cap in which a very tiny hole was bored. The cylinder

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[1] Taken from a dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in the University of Michigan. Original manuscript received December 13, 1943.

[2] Horace H. Rackham Fellow, 1943.

[3] Jagattaran Dhar, *Indian J. Physics*, **7**, 43–60 (1932).

[4] C. J. Birkett Clews and Kathleen Lonsdale, *Proc. Roy. Soc.* (London), **A161**, 493–504 (1937).

[5] Allen and Pingert, THIS JOURNAL, **64**, 1369 (1942).