and 30.1 g. (0.16 mole) of 1,2-dibromoethane (b.p. 130°/762 mm.) was added dropwise during 0.76 hr. The reaction mixture was refluxed for an additional hour, and then a solution of 3.7 g. (0.16 g.-atom) of sodium in 100 ml. of absolute alcohol was added. After refluxing the reaction mixture for 4 hr., 185 ml. of alcohol was distilled during 1 hr. from the mixture by warming the reaction flask on the steam bath. The residue was cooled and poured into 600 ml. of ice-cold water. This mixture was extracted with one 300-ml. and four 100-ml. portions of ether. The ether extract was dried over freshly heated sodium sulfate.

After removal of the drying agent, the ether was removed through a helix-packed column. The residue was distilled through an 18 mm. o.d. × 165 mm. helix-packed column. When the oil bath used to heat the distilling flask reached 190°, the distillation was interrupted. Distillate weighing 95.0 g., b.p. 84–86°/9 mm., n_D^{25} 1.4117–1.4185, was collected, and 36.9 g. of residue remained in the flask. Pertinent refractive indexes are: diethyl malonate, n_D^{25} 1.4118; 1,1-dicarbethoxycyclopropane, n_D^{20} 1.4331; 1,1,4,4-tetracarbethoxybutane, n_D^{25} 1.4470.

The residue was stirred and refluxed with 50 ml. of concd. hydrochloric acid and 100 ml. of water for 4 hr. The mixture was filtered, and the filtrate evaporated to dryness *in vacuo* in a rotary evaporator. Water was added to the residue, and the solution again evaporated to dryness. The flask containing the solid residue was immersed in an oil bath at 180–185° until evolution of gas ceased. The residue was refluxed for 24 hr. with 170 ml. of absolute alcohol and 1 ml. of concd. sulfuric acid. This solution was poured into 700 ml. of water, and this mixture placed in a continuous benzene extractor. The benzene extract was dried over sodium sulfate, the benzene removed through a helix-packed column, and the residue distilled through a 12 mm. o.d. ×90 mm. helix-packed column to give several fractions (15.6 g., 48% yield) of diethyl adipate, b.p. 125–126°/9 mm., n_D^{25} 1.4260–1.4268. Authentic diethyl adipate had n_D^{25} 1.4254.

A second experiment was carried out with the same quantities of materials. After the first reflux and before addition of the second quantity of sodium ethoxide the reaction mixture was poured into water, the mixture extracted with ether, and the ether solution distilled. After removal of the ether there was obtained 140.8 g., b.p. 86–96°/9 mm., of distillate and 9.5 g. of high-boiling residue. This 9.5 g. of residue provided that not much tetracarbethoxy compound was formed during the first reflux with sodium ethoxide, and that the reaction proceeded primarily to give cyclic product. The 140.8 g. of distillate was refluxed with a second portion of sodium ethoxide, and the reaction mixture worked up as described above to obtain the high-boiling residue. The combined high-boiling residue was hydrolyzed, decarboxylated, and esterified to give a 49% yield of diethyl adipate, b.p. 126°/9 mm., n_D^{25} 1.4259.

1,2-Dibromoethane to adipyl chloride. The reaction was carried out as described above to obtain diethyl adipate. After the high-boiling residue was hydrolyzed and decarboxylated, the residue was refluxed with thionyl chloride. Much solid was formed and only a 25% yield (based on dibromide) of adipyl chloride was obtainable. It was clear that the preferred way to get the adipic acid from the reaction mixture was by esterification.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF NORTH CAROLINA]

The Preparation and Reaction of Some Substituted Benzotrifluorides

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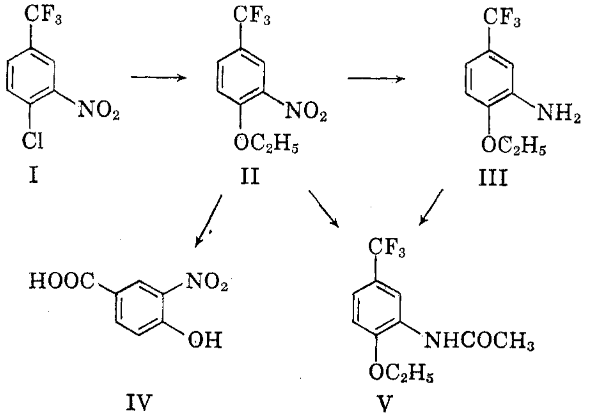
The preparation of several substituted benzotrifluorides is described, and a few reactions of these benzotrifluorides are noted.

In connection with some other work in these laboratories it became of interest to study the properties and synthesis of several amino and acetamido derivatives of benzotrifluoride having an ether function. Accordingly the synthesis of the isomers 3-amino-4-ethoxybenzotrifluoride (III) and 5-amino-4-ethoxybenzotrifluoride and their corresponding acetyl derivatives was undertaken.



4-Chloro-3-nitrobenzotrifluoride (I) was treated with ethanolic potassium hydroxide to give 4-ethoxy-3-nitrobenzotrifluoride (II), which was converted to III by reduction. The corresponding acetyl derivative V was formed directly from III and by reductive acetylation from II. A similar sequence starting from 2-chloro-5-nitrobenzotrifluoride yielded 5-amino-3-ethoxybenzotrifluoride and its acetyl derivative, 5-acetamido-2-ethoxybenzotrifluoride. The structure of the intermediate nitro compounds II and 2-ethoxy-5-nitrobenzotrifluoride was demonstrated by hydrolysis to the

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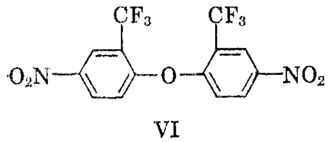
corresponding hydroxy acids IV and 2-hydroxy-5-nitrobenzoic acid using 100% sulfuric acid.[3]

In another procedure 5-acetamido-2-nitrobenzotrifluoride[4] was reduced to 5-acetamido-2-aminobenzotrifluoride, but attempted replacement of the 2-amino group with the ethoxide group by diazotization followed either by heating or treatment with ethanol and copper, resulted only in elimination of the amino group to give 3-acetamidobenzotrifluoride. The previously unknown intermediate, 5-acetamido-2-aminobenzotrifluoride, was hydrolyzed to the known 2,5-diaminobenzotrifluoride.[5]



VI

In connection with the conversion of 2-chloro-5-nitrobenzotrifluoride to 2-ethoxy-5-nitrobenzotrifluoride, the use of sodium ethoxide in ether gave a different compound the elemental analysis of which corresponded to 4,4′-dinitro-2,2′-bis(trifluoromethyl)diphenyl ether (VI). The use of potassium hydroxide in isopropyl alcohol also gave VI. Although rigorous structural proof was not carried out, the infrared absorption spectrum is consistent with this structure.

EXPERIMENTAL

Materials. 4-Chloro-3-nitrobenzotrifluoride and 2-chloro-5-nitrobenzotrifluoride were supplied by the Hooker Chemical Corp.

4-Ethoxy-5-nitrobenzotrifluoride (II). A solution of 22.5 g. (0.10 mole) of 4-chloro-3-nitrobenzotrifluoride (I) in absolute ethanol (60 cc. total volume) was added during 1 hr. to a solution of 300 cc. of absolute ethanol containing 5.6 g. of potassium hydroxide. After refluxing 72 hr. the ethanol was removed at reduced pressure, and inorganic salts were removed by slurrying the residue with ethyl ether and filtering. An oily-crystalline slurry was obtained upon evaporation of the ether. Purification was effected by dissolving the residue in petroleum ether (b.p. 60–90°) and treating with decolorizing charcoal to give 19.9 g. (84.6%) of light yellow crystals II, m.p. 31–32°. An analytical sample of II was prepared by recrystallizing from petroleum ether (b.p. 60–90°) and distilling under reduced pressure, 110–112°/4 mm. giving white crystals, m.p. 30–31°.

Anal. Calcd. for $C_9H_8F_3NO_3$: C, 45.95; H, 3.43; N, 5.96. Found: C, 45.81; H, 3.45; N, 5.94.

3-Amino-4-ethoxybenzotrifluoride (III). *Method A.* To a solution of 7.05 g. (0.03 mole) 4-ethoxy-3-nitrobenzotrifluoride (II) dissolved in a solution of 10 cc. of ethanol and 30 cc. of concd. hydrochloric acid was added 15.0 g. of mossy tin at a rate to give a brisk reaction. The reaction mixture was refluxed for 1 hr., then made basic to litmus with sodium hydroxide. Steam distillation of the mixture gave 5.5 g. (89%) III, m.p. 50.0–52.5°.

Method B. To a mixture of 20.0 g. of iron powder, 3.0 g. of ammonium chloride and 300 cc. of water was added during 30 min. a solution of 20 g. (0.085 mole) of 4-ethoxy-3-nitrobenzotrifluoride (II) dissolved in 150 cc. of methanol. After refluxing the mixture for 4 hr. a white crystalline product was collected by steam distillation. After cooling the distillate, filtering and drying, 11.7 g. (67%) III was obtained.

An analytical sample was obtained by recrystallizing crude III from petroleum ether (b.p. 60–90°) giving white crystals, m.p. 51.4–52.5°.

Anal. Calcd. for $C_9H_{10}F_3NO$: C, 52.68; H, 4.91; N, 6.83. Found: C, 52.52; H, 4.76; N, 6.87.

4-Hydroxy-3-nitrobenzoic Acid (IV). A mixture of 2.35 g. (0.01 mole) of 4-ethoxy-3-nitrobenzotrifluoride (II) and 1.0 g. of 100% sulfuric acid was heated in an oil bath until evolution of gas ceased. The reaction mixture was poured on ice and the product collected by filtration. Recrystallization of the product from water and treating with decolorizing charcoal gave 1.2 g. of IV, m.p. 183–185° (lit.,[6] m.p. 184°).

The ethyl ester was prepared by reacting IV with ethanol in the presence of concentrated sulfuric acid. Upon recrystallization from ethanol-water a yellow solid was obtained, m.p. 69–70° (lit.,[7] m.p. 69°).

3-Acetamido-4-ethoxybenzotrifluoride (V). *Method A.* To a solution of 7.05 g. (0.03 mole) of 4-ethoxy-3-nitrobenzotrifluoride (II) in 30 cc. of acetic anhydride was added *ca.* 25 mg. of platinum oxide and reduction effected in a Parr low pressure hydrogenation apparatus at 59 p.s.i.g. The catalyst was removed by filtration and the filtrate heated for 30 min. on a steam cone. Four volumes of ice water were added and 3 g. (40%) of V as white crystals was obtained upon filtration and drying, m.p. 110–113°.

Method B. To a suspension of 4.98 g. (0.025 mole) of 3-amino-4-ethoxybenzotrifluoride (III) and 2.1 cc. of concd. hydrochloric acid in 100 cc. of water, heated at 50°, was added 2.91 g. (0.03 mole) of acetic anhydride. Immediately thereafter a solution of 3 g. sodium acetate in 20 cc. of water was added. On cooling to 0° the product separated and was collected by filtration. Recrystallization from ethanol-water gave 4.0 g. (54%) of V; further recrystallization from ethanol water gave white crystals, m.p. 113.5–114.7°.

Anal. Calcd. for $C_{11}H_{12}F_3NO_2$: C, 53.44; H, 4.89; N, 5.65. Found: C, 53.23; H, 4.59; N, 5.73.

2-Ethoxy-5-nitrobenzotrifluoride. A solution of 45.10 g. (0.20 mole) of 2-chloro-5-nitrobenzotrifluoride in 225 cc. of absolute ethanol was added during 1 hr. to a solution of 11.2 g. of potassium hydroxide in 250 cc. of absolute ethanol. After stirring at room temperature 24 hr. the mixture was heated at 50° for 12 hr. followed by 24 hr. of refluxing. Inorganic salts were removed by filtration and the filtrate concentrated under reduced pressure to *ca.* 60 cc. Upon cooling the solution the crude product separated and was collected by filtration. Recrystallization from ethanol-water gave 19.5 g. (41.5%) of 2-ethoxy-5-nitrobenzotrifluoride, m.p. 47.5–49.5°, b.p. 106–108°/3 mm.

Anal. Calcd. for $C_9H_8F_3NO_3$: C, 45.95; H, 3.43; N, 5.96. Found: C, 45.65; H, 3.59; N, 5.86.

5-Amino-3-ethoxybenzotrifluoride. Method A. Same as Method A used for III. The crude product weighed 5.3 g. (86%). Recrystallization from 95% ethanol gave 5-amino-3-ethoxybenzotrifluoride as a white crystalline solid, m.p. 55–56°.

Method B. Same as Method B used for III. Quantities of reagents used were, 9.0 g. (0.039 mole) of 2-ethoxy-5-nitrobenzotrifluoride, 100 cc. of methanol, 20 g. of iron powder, 3 g. of ammonium chloride, and 100 cc. of water. The crude product 5-amino-3-ethoxybenzotrifluoride weighed 5.1 g. (67.8%). Recrystallization from 95% ethanol (decolorizing charcoal) gave white crystals, m.p. 55.5–56.4°.

Anal. Calcd. for $C_9H_{10}F_3NO$: C, 52.68; H, 4.91; N, 6.83. Found: C, 52.49; H, 4.84; N, 6.84.

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(3) LeFave, G. M., *J. Am. Chem. Soc.*, **71**, 4148 (1949).

(4) Jones, R., *J. Am. Chem. Soc.*, **69**, 2346 (1947).

(5) Rouche, H., *Bull. aci. acad. roy. Belg.*, **13**, 346 (1927); *Chem. Abstr.*, **22**, 2149 (1928).

(6) Cavill, G. W. K., *J. Soc. Chem. Ind.*, **64**, 212 (1945).

(7) Thieme, P., *J. fur. Prakt. Chem.* (2), **43**, 453 (1891).

2-Hydroxy-5-nitrobenzoic acid. Same as procedure used for IV. There was obtained 1.8 g. of the crude acid. The acid was purified by recrystallizing from water (decolorizing charcoal) m.p. 225–229° (lit.,[8] m.p. 227°, 229–230°). The ethyl ester prepared as before, was recrystallized from ethanol-water, m.p. 96–97° (lit.,[9] m.p. 102°).

5-Acetamido-2-ethoxybenzotrifluoride. Method A. Same as Method A, used for V. Recrystallization of the product from ethanol-water gave 4.2 g. (57%) of 5-acetamido-2-ethoxybenzotrifluoride as white crystals, m.p. 137.5–139.0°.

Method B. Same as Method B, used for V. Recrystallization of the product from ethanol-water (decolorizing charcoal) gave 4.8 g. (65%) of 5-acetamido-2-ethoxybenzotrifluoride as white crystals, m.p. 138.0–139.0°.

Anal. Calcd. for $C_{11}H_{12}F_3NO_2$: C, 53.44; H, 4.89; N, 5.65. Found: C, 53.48; H, 4.93; N, 5.67.

5-Acetamido-2-aminobenzotrifluoride. Method A. A solution of 30.0 g. (0.12 mole) of 5-acetamido-2-nitrobenzotrifluoride in 200 cc. of ethanol was added dropwise during 1 hr. to a boiling mixture of 25.0 g. of iron powder, 3.0 g. of ammonium chloride, and 250 cc. of water. After refluxing the reaction mixture for 4 hr. the hot mixture was filtered. The product was removed from the cooled filtrate by several ether extractions. After drying the ether extract over anhydrous magnesium sulfate the ether was removed by evaporation giving 15.0 g. (57%) of crude product. Several recrystallizations from benzene gave 5-acetamido-2-aminobenzotrifluoride as white crystals, m.p. 118–119°.

Method B. To a solution of 6.2 g. (0.025 mole) of 5-acetamido-2-nitrobenzotrifluoride in 50 cc. of methanol *ca.* 25 mg. of platinum oxide was added. Reduction was effected in a Parr low pressure catalytic hydrogenation apparatus at 60 p.s.i.g. After removal of the catalyst by filtration, the filtrate was evaporated to near dryness. The product was purified by recrystallization from benzene giving 4.0 g. (76%) of 5-acetamido2-aminobenzotrifluoride as tan crystals m.p. 116–118°.

Anal. Calcd. for $C_9H_9F_3N_2O$: C, 49.54; H, 4.16; N, 12.85. Found: C, 49.29; H, 4.00; N, 13.04.

5-Acetamido-2-aminobenzotrifluoride was hydrolyzed in the presence of hydrochloric acid. Neutralization of the acid solution gave 2,5-diaminobenzotrifluoride, m.p. 55–57°, (lit.,[10] m.p. 58°).

Diazotization of 5-acetamido-2-aminobenzotrifluoride, sulfuric acid and sodium nitrite, followed by reduction with copper in the presence of ethanol or by heating, gave 3-acetamidobenzotrifluoride, m.p. 103–104° (lit., [11] m.p. 105°).

4,4'-Dinitro-2,2'-bis(trifluoromethyl)diphenyl ether (VI) *Method A.* A solution of 22.55 g. (0.1 mole) of 2-chloro-5-nitrobenzotrifluoride in 50 cc. of absolute ethyl ether was added to an etheral suspension of 8.15 g. of sodium ethylate. After refluxing the heterogeneous reaction mixture 34 hr. 8 g. of starting material was recovered by steam distillation. The residual mixture from the steam distillation was filtered and the solid product recrystallized several times from absolute ethanol (decolorizing charcoal) gave 5.5 g. (14%) of VI light cream-colored needles, m.p. 140–141°.

Method B. A solution of 22.55 g. (0.1 mole) of 2-chloro-5-nitrobenzotrifluoride in 150 cc. of absolute isopropyl alcohol was added to a solution of 14.0 g. of potassium hydroxide dissolved in 200 cc. of absolute isopropyl alcohol. After agitating the solution 4 hr. at room temperature, the mixture was refluxed 1 hr. Isopropyl alcohol was removed by distillation leaving *ca.* 100 cc. of the reaction mixture. After removing the inorganic salts by filtration an equal volume of ice and water was added to the filtrate. The solid product was collected by filtration. Product was purified by recrystallization from 95% ethanol giving 4.5 g. (11%) VI. The product had the same melting point as that prepared by Method A and there was no depression when the two were mixed.

Anal. Calcd. for $C_{14}H_6F_6N_2O_5$: C, 42.44; H, 1.53; N, 7.07. Found: C, 42.35; H, 1.56; N, 7.09.

HOPEWELL, VA.

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(8) Causse, M. H., *Bull. Soc., Chem. Fr.*, **11**, 1188 (1894).

(9) Thieme, P., *op. cit.*, p. 469.

(10) Rouche, *op. cit.*

(11) Brown, J. H., Suckling, C. W., and Whalley, W. B., *J. Chem. Soc.*, 1949 (Suppl. Issue No. 1), S95–99 (1949).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MISSOURI]

Substituted Styrenes. VI. Syntheses of the Isomeric Formylstyrenes and *o*- and *m*-Vinylbenzoic Acid

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Laboratory methods have been devised for the preparation of *o*-, *m*-, and *p*-formylstyrene and for *o*- and *m*-vinylbenzoic acid.

In a continuation of studies[1] concerning the preparation, absorption spectra and reactions of substituted styrenes, syntheses were devised for the isomeric formylstyrenes and for *o*- and *m*-vinylbenzoic acid.

Wiley and Hobson[2] have reported the preparation of *p*-formylstyrene by the decarboxylation of *p*-formylcinnamic acid. Impure *m*-formylstyrene was obtained by the same method but attempts to prepare the *ortho* isomer by the decarboxylation of *o*-formylcinnamic acid afforded only 1-indanone. Morris and co-workers[3] have observed that a

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[1] W. J. Dale and C. W. Strobel, *J. Am. Chem. Soc.*, **76**, 6172 (1954); W. J. Dale and G. Buell, *J. Org. Chem.*, **21**, 45 (1956); W. J. Dale and H. E. Hennis, *J. Am. Chem. Soc.*, **80**, 3645 (1958); W. J. Dale and H. E. Hennis, *J. Am. Chem. Soc.*, **81**, 2143 (1959); W. J. Dale and P. E. Swartzentruber, *J. Org. Chem.*, **24**, 955 (1959).

[2] R. H. Wiley and P. H. Hobson, *J. Am. Chem. Soc.*, **71**, 2429 (1949).

[3] L. R. Morris, R. A. Mock, C. A. Marshall, and J. H. Howe, *J. Am. Chem. Soc.*, **81**, 377 (1959).