

**S 19.** *Some Fluorinated Derivatives of Toluene.*

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Attempts to produce highly fluorinated toluenes have resulted in an improved process for the preparation of benzotrifluoride from benzotrichloride.

2-Nitro-4-aminotoluene has been converted into 2 : 4-difluorotoluene (I;  $R = R' = F$ ), but attempts to prepare 2 : 4-difluorobenzotrifluoride from the latter compound failed. *p*-Fluorotoluene has been converted into *p*-fluorobenzotrifluoride, using the anhydrous hydrogen fluoride method detailed in this paper.

Other fluorinated derivatives of toluene are reported.

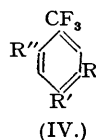
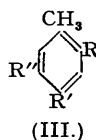
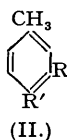
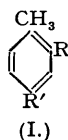
THE work described in this paper was carried out as part of a programme of research designed to investigate the preparation of highly-fluorinated toluenes, without the use of elementary fluorine. Since the completion of this research many of the compounds prepared have been described elsewhere (chiefly Finger and Reed, *J. Amer. Chem. Soc.*, 1944, **66**, 1972).

Two possible routes to the desired products were explored, (a) the nuclear fluorination of toluene followed by side-chain chlorination and subsequent replacement of the chlorine by fluorine, and (b) the introduction of fluorine into the nucleus of benzotrifluoride.

Following the first line of research 2 : 4-difluorotoluene (I; R = R' = F) was prepared from 4-nitro-2-aminotoluene (I; R = NH<sub>2</sub>, R' = NO<sub>2</sub>), by way of the intermediate 2-fluoro-4-nitrotoluene (I; R = F, R' = NO<sub>2</sub>) using the Schiemann-Balz reaction for the replacement of an aromatic amino-group by fluorine *via* the diazonium borofluoride (*Ber.*, 1927, **60**, 1186). The resultant 2 : 4-difluorotoluene could be chlorinated only as far as the benzylidene chloride and that with great difficulty. *p*-Fluorotoluene (I; R = H, R' = F); prepared from *p*-nitrotoluene (Balz and Schiemann, *Ber.*, 1927, **60**, 1188), chlorinated readily to *p*-fluorobenzotrifluoride, which fluorinated smoothly with anhydrous hydrogen fluoride to *p*-fluorobenzotrifluoride (cf. Booth, Eley, and Birchfield, *J. Amer. Chem. Soc.*, 1935, **57**, 2066, who used antimony trifluoride for the fluorination). Nitration of 2 : 4-difluorotoluene produced a *mononitro*-compound of unknown orientation, in low yield.

2-Fluoro-4-hydroxytoluene (I; R = F, R' = OH) was obtained in small amounts during the preparation of 2 : 4-difluorotoluene and characterised as the *benzoate*.

Attempts to prepare 3 : 4-difluorotoluene (II; R = R' = F) from 3-nitro-4-aminotoluene (II; R = NO<sub>2</sub>, R' = NH<sub>2</sub>) failed. Diazotisation could not be effected in aqueous sodium borofluoride, or in glacial acetic acid with the addition of sodium nitrite dissolved in concentrated sulphuric acid and subsequent addition of sodium borofluoride (Misslin, *Helv. Chim. Acta*, 1920, **3**, 626). The decomposition of the 3-nitrotoluene-4-diazonium borofluoride (II; R = NO<sub>2</sub>, R' = N<sub>2</sub>BF<sub>4</sub>) prepared by diazotising in hydrofluoroboric acid produced no 4-fluoro-3-nitrotoluene.



The nitration of 2-fluoro-4-acetamidotoluene readily produced 2-fluoro-5-nitro-4-acetamidotoluene (III; R = F, R' = Me·CO·NH, R'' = NO<sub>2</sub>), the orientation of which was determined as follows: the substance reacted with methyl- or ethyl-alcoholic potassium hydroxide, the fluorine being replaced by methoxyl or ethoxyl groups respectively. This reaction has been observed to occur only if the fluorine and nitro-groups are in the *o*- or *p*-positions to each other (Schiemann and Balz, *Ber.*, 1927, **60**, 1186). The position of the nitro-group in the supposed 5-nitro-4-amino-2-methoxytoluene (III; R = OMe, R' = NH<sub>2</sub>, R'' = NO<sub>2</sub>) was proven by deamination to a compound agreeing in properties with the 5-nitro-2-methoxytoluene of Simonsen and Nayak (*J.*, 1915, **107**, 828) and Shah, Bhatt, and Kanga (*J. Univ. Bombay*, 1934, **3**, 155; *Chem. Abs.*, 1935, **29**, 4747). Moreover, when treated with alcoholic hydrogen chloride, (III; R = F, R' = Me·CO·NH, R'' = NO<sub>2</sub>) gave the amine hydrochloride which was deaminated to 2-fluoro-5-nitrotoluene (III; R = F, R' = H, R'' = NO<sub>2</sub>), apparently identical with Schiemann's preparation (Schiemann, *Ber.*, 1929, **62**, 1794). The identity of the 5-nitro-4-amino-2-methoxytoluene was later confirmed by comparison with an authentic specimen (Curd and Robertson, *J.*, 1933, 1166).

As a necessary preliminary to the exploration of method (b) the preparation of benzotrifluoride from benzotrifluoride was investigated. The use of antimony trifluoride (Booth, Eley, and Birchfield, *J. Amer. Chem. Soc.*, 1935, **57**, 2066) as a fluorinating agent was not attractive for large-scale laboratory use and would appear to be attended by considerable practical difficulties. The use of the alternative fluorinating agent, hydrogen fluoride, was investigated. The only information available was of little value (cf. I. G. Farben. A.G., D.R.-P. 575,593). The laboratory process described by Simons and Lewis (*J. Amer. Chem. Soc.*, 1938, **60**, 492) is extremely tedious and difficult to control adequately during the extended reaction period (72 hours). This paper records a more convenient process. The presence of small quantities of benzylidene chloride (as little as 1%) in the benzotrifluoride has a very deleterious effect upon the subsequent fluorination. Slightly under-chlorinated benzotrifluoride which probably contains traces of benzylidene chloride, behaves similarly during

fluorination. This difficulty was completely eliminated by a slight over-chlorination to produce a benzotrichloride of density 1.390—1.395/16°. The density of pure benzotrichloride is 1.380/16°.

During the investigation of route (b), *m*-nitrobenzotrifluoride was converted into *m*-cyano-benzotrifluoride (IV; R = CN, R' = R'' = H) and thence by way of the Stephen reaction to the *m*-formylbenzotrifluoride (IV; R = CHO, R' = R'' = H), characterised by the 2 : 4-dinitrophenylhydrazone, agreeing in properties with those described for a specimen recently prepared by an alternative method (Gilman *et al.*, *J. Amer. Chem. Soc.*, 1946, **68**, 426). Nitration of *m*-fluorobenzotrifluoride gave 5-fluoro-2-nitrobenzotrifluoride (IV; R = F, R' = H, R'' = NO<sub>2</sub>) smoothly convertible into 2 : 5-difluorobenzotrifluoride (IV; R' = H, R = R'' = F) recently described by Finger and Reed (*J. Amer. Chem. Soc.*, 1944, **66**, 1972), and easily convertible into the 2-nitro-5-methoxy- and -5-ethoxybenzotrifluorides by the action of methyl- or ethyl-alcoholic potassium hydroxide respectively.

The nitration of *p*-fluorobenzotrifluoride readily produced a mononitro-derivative, almost certainly 4-fluoro-3-nitrobenzotrifluoride (IV; R = NO<sub>2</sub>, R' = F, R'' = H) because of the ease of replacement of the fluorine by methoxyl and ethoxyl (cf. 2-fluoro-5-nitro-4-acetamidotoluene, p. S 98), and the failure of attempts to produce a diazonium borofluoride even in hydrofluoroboric acid or with amyl nitrite in ether (v. Braun and Rudolf, *Ber.*, 1931, **64**, 2465).

#### EXPERIMENTAL.

*Benzotrichloride*.—Crude commercial benzylidene chloride,  $d_4^{16^\circ}$  1.156—1.180, was chlorinated in a 20 l. three-necked "Quickfit" glass flask, fitted with chlorine inlet, thermometer pocket, and vent for exit gases through a reflux condenser. The joints throughout the apparatus were of ground glass. The flask was heated by a gas-ring but was supported on a tripod slightly above the flame. The benzylidene chloride was chlorinated to  $d_4^{16^\circ}$  1.390—1.395 in 10 l. batches at a temperature of 150—160°, during 13—21 hours. The undistilled product was used directly for the fluorination stage. The use of distilled benzotrichloride did not increase the yield of benzotrifluoride.

*Benzotrifluoride*.—The apparatus has been described previously (Whalley, *J. Soc. Chem. Ind.*, 1947, **66**, 427). The autoclave was charged with 1173 g. (6 moles) of benzotrichloride, cooled to 0°, and the hydrogen fluoride added. The oil-bath temperature was raised to 135—140° during 25 minutes and thereafter maintained at that value. The autoclave pressure gradually rose during about 80 minutes to 225 lb. per sq. in., the temperature of the mixture being 80—100°. The relief valve was then opened as required to maintain the pressure at 225 lb. per sq. in. As the reaction proceeded the internal temperature decreased by 10—15°; after 1½—3 hours evolution of gas had ceased and the internal temperature had risen to 100—105°. When the pressure had remained constant for 10—15 minutes at this temperature reaction was considered complete, the oil-bath was removed, and the autoclave temperature allowed to fall to 80° when pressure was gradually released. The product, a black, mobile, lachrymatory liquid (800—825 g.; unless carbonaceous material had been formed owing to unfavourable conditions) was blown out of the autoclave. The product was distilled directly at atmospheric pressure, the fraction of b. p. 102—105° being collected as pure benzotrifluoride. The distillate was usually slightly acid and was shaken with about 1% of its weight of sodium carbonate and 1% of anhydrous sodium sulphate to dry it, and filtered to give a clear, colourless liquid (approximately 780 g.). The use of benzotrichloride to which had been added 1 or 5% of benzylidene chloride reduced the yield of pure benzotrifluoride to 315 g. or 175 g., respectively, and much carbonaceous material was produced. Similar results were obtained when benzotrichloride of density less than 1.390/16°, which possibly contained benzylidene chloride, was fluorinated.

*2-Fluoro-4-aminotoluene*.—The thermal decomposition of the diazonium borofluoride of 2-amino-4-nitrotoluene proceeded with considerable violence and could not readily be performed in the usual manner (*Org. Synth.*, 1933, **13**, 46). An improvement upon the method described (Schmelkes and Rubin, *J. Amer. Chem. Soc.*, 1944, **66**, 1631) was the use of monochlorobenzene or dichlorobenzene as a diluent, followed by direct reduction of the nitro-compound without its isolation, as follows :

The dried 4-nitrotoluene-2-diazonium borofluoride (380 g.) was stirred with dry monochlorobenzene (2000 c.c.) and run from a dropping funnel in portions of about 300 c.c. into a flask fitted with stirrer and reflux condenser and heated in an oil-bath maintained at 116°. The flask originally contained monochlorobenzene (500 c.c.) and each portion of the slurry was added after evolution of boron trifluoride from the last had subsided. The addition of the slurry took 2 hours. The dropping funnel was washed with monochlorobenzene (50 c.c.), the washings running into the flask. Heating was continued until the evolution of gas ceased (½ hour). The resultant solution of 2-fluoro-4-nitrotoluene was reduced without isolation of the product, as follows : Glacial acetic acid (100 c.c.), water (400 c.c.), and powdered iron (100 g.) were added, the contents of the flask being stirred and refluxed gently. More iron (100 g.) was added at hourly intervals for 5 hours, and refluxing continued for a further 2 hours. The mixture was made alkaline and steam-distilled. The non-aqueous distillate was extracted with 5*N*-hydrochloric acid (2 × 250 c.c.). The acid extract was basified with sodium hydroxide solution, when 2-fluoro-4-aminotoluene separated. Distillation gave the pure compound (118 g.), b. p. 202—204°/760 mm., crystallising in colourless tablets of m. p. 32°; Schmelkes and Rubin (*loc. cit.*) give b. p. 200—205°/760 mm.

*2 : 4-Difluorotoluene*.—A fluoroboric acid solution was prepared by the cautious addition of boric acid (393 g.) to a stirred mixture of 52% hydrofluoric acid (528 c.c.) and crushed ice (650 g.) in a lead beaker cooled by a freezing mixture. Much heat was evolved and the temperature rose to 50°. The resultant solution was cooled to 0° before use. 2-Fluoro-4-aminotoluene (142 g.) was dissolved in this fluoroboric acid (1570 g.) and cooled to 0°. Sodium nitrite (80 g.), dissolved in the minimum quantity of water, was added with stirring and maintenance of the temperature below 5°.

2-Fluorotoluene-4-diazonium borofluoride (240 g.) was precipitated as an almost colourless solid. It was filtered off and washed with a minimum quantity of ice-cold water, methanol, and ether and then dried at room temperature. The dried diazonium borofluoride (975 g.) was placed in a 3-l. flask connected to a condenser and suitable receivers, cooled to  $-30^{\circ}$ . The flask was gently warmed with a free flame and decomposition occurred smoothly to give crude 2 : 4-difluorotoluene which collected in the traps while the boron trifluoride was vented to the atmosphere. When evolution of boron trifluoride was complete and all the 2 : 4-difluorotoluene had been distilled from the reaction vessel, the distillate was washed with 2N-sodium hydroxide solution ( $3 \times 100$  c.c.) and water, dried over anhydrous sodium sulphate, and distilled to give 2 : 4-difluorotoluene as a colourless liquid (440 g.), b. p.  $113-117^{\circ}/760$  mm. (Found : C, 65.8; H, 4.7; F, 29.7; *M*, 121.  $C_7H_5F_2$  requires C, 65.6; H, 4.7; F, 29.7%; *M*, 128).

Steam distillation of the filtrate from the preparation of 2-fluorotoluene-4-diazonium borofluoride, and extraction with ether gave 2-fluoro-4-hydroxytoluene (15 g.) as a colourless oil, b. p.  $194-196^{\circ}/760$  mm., exhibiting a violet colour with ferric chloride in aqueous solutions. The benzoate, prepared by the Schotten-Baumann method, crystallised in colourless plates, m. p.  $77^{\circ}$ , from ethanol (Found : C, 72.5; H, 5.0.  $C_{14}H_{11}O_2F$  requires C, 73.0; H, 4.8%).

*Nitration of 2 : 4-Difluorotoluene.*—To 2 : 4-difluorotoluene (50 g.) was added a mixture of concentrated sulphuric acid (15 c.c.) and concentrated nitric acid (35 c.c.) in portions of 10 c.c. The mixture was stirred and warmed at  $65^{\circ}$  for 2 hours. There was considerable evolution of oxides of nitrogen and some hydrogen fluoride. The product was poured on crushed ice (200 g.), separated from the spent acid, washed with 2N-sodium hydroxide and water, dried with anhydrous sodium sulphate, and distilled, giving unchanged 2 : 4-difluorotoluene (28 g.) and a mononitro-2 : 4-difluorotoluene (8 g.), b. p.  $200-210^{\circ}/760$  mm., crystallising in long, pale yellow tablets, m. p.  $37^{\circ}$  (Found : C, 48.5; H, 2.7; N, 8.1; F, 22.0.  $C_7H_4O_2NF_2$  requires C, 48.6; H, 2.9; N, 8.1; F, 22.0%).

*p-Fluorotoluene.*—This compound was readily obtained in good yield, from *p*-aminotoluene. It had b. p.  $115.5-116.5^{\circ}/760$  mm. The residues from the distillation contained a small quantity (1–2%) of a colourless liquid, b. p.  $272-276^{\circ}/760$  mm., which analysed for a monofluoroditolyl (Found : C, 83.1; H, 7.0; F, 10.1.  $C_{14}H_{13}F$  requires C, 83.5; H, 6.5; F, 9.5%).

*p-Fluorobenzotrifluoride.*—*p*-Fluorotoluene was chlorinated with phosphorus pentachloride as a catalyst, and then fractionated, giving *p*-fluorobenzotrifluoride as a colourless liquid, b. p.  $121-125^{\circ}/45$  mm. (cf. Booth, Eley, and Birchfield, *J. Amer. Chem. Soc.*, 1935, **57**, 2066). The conversion of the trichloride into the trifluoride was carried out by the method described for benzotrifluoride. *p*-Fluorobenzotrifluoride (1280 g.) and anhydrous hydrogen fluoride (480 g.) were heated in a pressure vessel. Reaction commenced at about  $85^{\circ}$ , and the hydrogen chloride evolved was released, as formed, via a condenser. Reaction was complete in  $1\frac{1}{2}$  hours. The product, a black, mobile lachrymatory liquid (930 g.) was shaken with a little solid sodium carbonate and fractionated. *p*-Fluorobenzotrifluoride, b. p.  $102-105^{\circ}/760$  mm., was collected as a clear, colourless liquid (825 g.) (Booth, Eley, and Birchfield, *loc. cit.*, give b. p.  $102.8^{\circ}/760$  mm., for material prepared by the action of antimony trifluoride on *p*-fluorobenzotrifluoride).

*2-Fluoro-5-nitro-4-acetamidotoluene.*—To a mixture of concentrated nitric acid (200 c.c.) and concentrated sulphuric acid (30 c.c.) was added dry 2-fluoro-4-acetamidotoluene (Schmelkes and Rubin, *J. Amer. Chem. Soc.*, 1944, **66**, 1631) (53 g.) in small portions, with stirring, at such a rate that the reaction temperature was maintained at  $35-40^{\circ}$ . After completion of the addition, the mixture was left for 15 minutes and then poured on crushed ice (300 g.). The yellow solid precipitate was filtered off, washed with water, and crystallised from aqueous alcohol in pale yellow needles (56 g.) of 2-fluoro-5-nitro-4-acetamidotoluene, m. p.  $94^{\circ}$  (Found : C, 50.9; H, 4.2; N, 12.5; F, 9.5.  $C_9H_7O_3N_2F$  requires C, 50.9; H, 4.3; N, 13.2; F, 9.0%). When this compound was refluxed with aqueous-alcoholic hydrochloric acid the hydrochloride was obtained in quantitative yield, crystallising in red tablets, m. p.  $158^{\circ}$ , from ethanol. Diazotisation of the hydrochloride (3 g.) with concentrated sulphuric acid (3 c.c.), ethanol (20 c.c.) and sodium nitrite (1.1 g.), followed by steam distillation gave 2-fluoro-5-nitrotoluene (0.75 g.), crystallising from alcohol in yellow needles, m. p.  $41^{\circ}$  (Schiemann, *Ber.*, 1929, **62**, 1804, gives m. p.  $41.5^{\circ}$ ). 1.5 G. of unchanged hydrochloride were recovered. 2-Fluoro-5-nitro-4-acetamidotoluene (20 g.), potassium hydroxide (13.2 g.), and methanol (150 c.c.) were refluxed for 1 hour after the initial reaction had subsided. The product was removed by filtration from the cooled solution, washed well with water, and crystallised from methanol, ethanol, or benzene in long orange tablets, m. p.  $155.5^{\circ}$ , of 5-nitro-4-amino-2-methoxytoluene (17 g.). A mixed m. p. with an authentic specimen (Curd and Robertson, *J.*, 1933, 1166) gave no depression. 5-Nitro-4-amino-2-ethoxytoluene was prepared in a similar manner, using ethyl alcoholic potassium hydroxide. The product crystallised from ethanol in fine golden, yellow needles, m. p.  $146.5^{\circ}$  (Found : C, 54.9; H, 6.3; N, 14.5.  $C_9H_{12}O_3N_2$  requires C, 55.1; H, 6.1; N, 14.3%).

*m-Acetamidobenzotrifluoride.*—*m*-Aminobenzotrifluoride (Booth, Eley, and Birchfield, *J. Amer. Chem. Soc.*, 1935, **57**, 2066) was acetylated with acetic anhydride to give *m*-acetamidobenzotrifluoride, m. p.  $105^{\circ}$ , in long colourless needles, from aqueous alcohol. Rouché (*Bull. Acad. roy. Belg.*, 1927, **13**, 346) erroneously gives m. p.  $203^{\circ}$  (Found : N, 6.9. Calc. for  $C_7H_8NOF_3$  : N, 6.9%).

*2-Nitro-5-methoxy- and -5-ethoxy-benzotrifluoride.*—Nitration of *m*-fluorobenzotrifluoride produced 5-fluoro-2-nitrobenzotrifluoride (Finger and Reed, *J. Amer. Chem. Soc.*, 1944, **66**, 1972), b. p.  $200^{\circ}/764$  mm., which crystallised in almost colourless prisms, m. p.  $23.5^{\circ}$ . 2-Nitro-5-methoxybenzotrifluoride, crystallising from light petroleum in large, pale yellow prisms, m. p.  $39^{\circ}$  (Found : C, 43.2; H, 2.7; N, 6.3.  $C_8H_6O_3NF_3$  requires C, 43.4; H, 2.7; N, 6.3%), and 2-nitro-5-ethoxybenzotrifluoride, a pale yellow liquid, b. p.  $268^{\circ}/755$  mm. (Found : C, 45.6; H, 3.2; N, 5.7.  $C_9H_8O_3NF_3$  requires C, 46.0; H, 3.4; N, 6.0%), were obtained by refluxing 5-fluoro-2-nitrobenzotrifluoride with methyl- and ethyl-alcoholic potassium hydroxide respectively.

*4-Fluoro-3(?)-nitrobenzotrifluoride.*—A mixture of concentrated nitric acid (350 c.c.) and concentrated sulphuric acid (400 c.c.) was added at  $50^{\circ}$ , with stirring, to *p*-fluorobenzotrifluoride during 2½ hours. The temperature of the reaction mixture was then raised to  $60^{\circ}$ , and maintained for  $1\frac{1}{2}$  hours. The mixture was cooled, and the organic layer separated, taken up in ether, washed free from acid, dried ( $Na_2SO_4$ )

and distilled. 4-Fluoro-3(?)-nitrobenzotrifluoride (334 g.), b. p. 204—208°/762 mm., was obtained as a pale yellow liquid.

**4-Fluoro-3(?)-acetamidobenzotrifluoride.**—Concentrated hydrochloric acid (400 c.c.) was added in portions to 4-fluoro-3(?)-nitrobenzotrifluoride (250 g.) and granulated tin (270 g.), with cooling as required. Water (500 c.c.) was then added, the mixture refluxed for 90 minutes, made alkaline, and steam distilled. The non-aqueous layer was taken up in ether, separated, dried, and distilled, giving 4-fluoro-3(?)-aminobenzotrifluoride (365 g.), as a colourless liquid of b. p. 188—190°/770 mm. Acetylation with acetic anhydride and crystallisation from aqueous alcohol gave 4-fluoro-3(?)-acetamidobenzotrifluoride in colourless needles, m. p. 121° (Found: C, 49.1; H, 3.3; N, 6.3.  $C_8H_7ONF_4$  requires C, 48.9; H, 3.2; N, 6.3%). The m. p. of 5-fluoro-2-acetamidobenzotrifluoride is also 121° (present authors and Finger and Reed, *J. Amer. Chem. Soc.*, 1944, **66**, 1972). The mixed m. p. is 80—85°. Treatment of 4-fluoro-3(?)-nitrobenzotrifluoride with methyl-alcoholic potassium hydroxide gave 3(?)-nitro-4-methoxybenzotrifluoride, crystallising from alcohol in lemon-yellow needles, m. p. 48° (Found: C, 43.0; H, 3.1; N, 6.1.  $C_8H_8O_2NF_3$  requires C, 43.4; H, 2.7; N, 6.3%).

**3(?)-Acetamido-4-methoxybenzotrifluoride.**—Reduction of 3(?)-nitro-4-methoxybenzotrifluoride (10 g.), with tin (10 g.) and hydrochloric acid (100 c.c.), followed by steam distillation, gave 3(?)-amino-4-methoxybenzotrifluoride as a colourless oil which rapidly solidified. Crystallisation from light petroleum gave the amine in colourless plates, m. p. 59° (Found: C, 49.7; H, 4.4; N, 7.5.  $C_8H_8ONF_3$  requires C, 50.3; H, 4.2; N, 7.3%). Acetylation with acetic anhydride and crystallisation from alcohol gave 3(?)-acetamido-4-methoxybenzotrifluoride in colourless needles, m. p. 84° (Found: N, 6.2.  $C_{10}H_{10}O_2NF_3$  requires N, 6.0%).

**2-Acetamido-5-methoxybenzotrifluoride.**—2-Nitro-5-methoxybenzotrifluoride (10 g.) was reduced by tin (10 g.) and hydrochloric acid (100 c.c.). After steam distillation the *product* was obtained as a colourless oil which was acetylated directly by acetic anhydride and crystallised from aqueous alcohol in colourless needles, m. p. 134° (Found: C, 51.2; H, 4.2; N, 6.2.  $C_{10}H_{10}O_2NF_3$  requires C, 51.5; H, 4.3; N, 6.0%).

***m*-Trifluoromethylbenzaldehyde.**—*m*-Aminobenzotrifluoride (80 g.) was stirred with concentrated hydrochloric acid (95 c.c.) and water (400 c.c.) and diazotised at 0° by the addition of sodium nitrite (34.5 g.) in water (82 c.c.). The diazonium solution was made just alkaline to litmus by the addition of 10% sodium carbonate solution and run into a solution of cuprous cyanide, prepared from sodium cyanide (50 g.) (Barber, *J.*, 1943, 79), and covered with benzene (200 c.c.). The mixture was warmed to 50° and filtered and the benzene layer separated, dried, and fractionated, to give *m*-trifluoromethylbenzonitrile (45 g.), b. p. 99°/40 mm., as a colourless liquid, which quickly darkened on standing. Thus it was not analysed but converted immediately into the aldehyde as follows: *m*-trifluoromethylbenzonitrile (107 g.) was added with shaking to anhydrous stannous chloride (215 g.) in ether (500 c.c.) saturated with hydrogen chloride and the mixture left overnight. The aldimine stannichloride was removed by filtration, decomposed by the addition of water (500 c.c.), and steam-distilled. The crude aldehyde was purified *via* the hydrogen sulphite compound and then fractionated in an atmosphere of nitrogen. It had b. p. 83—86°/30 mm. The aldehyde rapidly oxidised in air to *m*-trifluoromethylbenzoic acid, m. p. 104° (Roberts and Curtin, *J. Amer. Chem. Soc.*, 1946, **68**, 1660, give m. p. as 103—104.5°). The aldehyde readily formed a 2:4-dinitrophenylhydrazone, crystallising from ethanol-chloroform in yellow needles, m. p. 259° (Gilman *et al.*, *ibid.*, p. 426, give m. p. 259—260°).

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