635. *Organic Fluoro-compounds. Part I. Hydroxy-derivatives of Benzotrifluoride.*

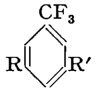
By W. B. Whalley.

The preparation of 3 : 5-dihydroxy-, 2 : 5-dihydroxy-, 3-hydroxy-4-methoxy-, and 2 : 5-dihydroxy-4-methoxy-benzotrifluoride and several derivatives thereof is recorded.

As part of an investigation into the general chemical reactions of organic fluorine-containing compounds, the preparation of representatives of the hitherto unknown polyhydroxybenzotrifluorides was undertaken.

The diazotisation of 3-nitro-5-aminobenzotrifluoride (I; $R = NO_2$, $R' = NH_2$) (Finger and Reed, *J. Amer. Chem. Soc.*, 1944, **66**, 1972) readily gave rise to 3-*nitro*-5-*hydroxybenzotrifluoride* (I; $R = NO_2$, $R' = OH$), reduced by ammonium sulphide to 3-*amino*-5-*hydroxybenzotrifluoride* (I; $R = NH_2$, $R' = OH$) and then converted by diazotisation into 3 : 5-*dihydroxybenzotrifluoride* (I; $R = R' = OH$), which very tenaciously retained a molecule of water of crystallisation (removed only by repeated vacuum-sublimation). Catalytic reduction of

3 : 5-dinitrobenzotrifluoride readily produced 3 : 5-*diaminobenzotrifluoride* (I; R = R′ = NH_2) which could not be converted into the phenol.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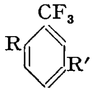
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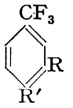
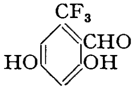

(III.)

In contrast to orcinol, the fluorine-containing analogue (I; R = R′ = OH) is very unreactive, as might be expected from the presence of the negatively-directing trifluoromethyl group. The phenol does not undergo the Hoesch condensation with methyl cyanide, and yields an *aldehyde* by the Gattermann procedure only with difficulty. The small quantity of aldehyde available was insufficient to allow a rigorous orientation, but by analogy with orcinol the reddish-brown ferric reaction probably indicates the formulation (IV).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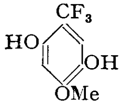
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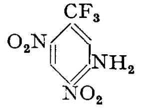
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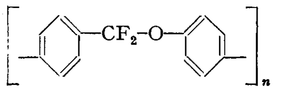
(VII.)

Oxidation of *m*-hydroxybenzotrifluoride (II; R = H, R′ = OH) by Wilson Baker's modification (*J.*, 1948, 2303) of the Elbs persulphate method (*J. pr. Chem.*, 1893, **48**, 197) readily produced 2 : 5-*dihydroxybenzotrifluoride* (II; R = R′ = OH). The orientation of this compound was proved by the preparation of the same phenol from 2-nitro-5-aminobenzotrifluoride (II; R = NO_2, R′ = NH_2) by the intermediate steps of 2-nitro-5-hydroxybenzotrifluoride (II; R = NO_2, R′ = OH) and 2-*amino*-5-*hydroxybenzotrifluoride* (II; R = NH_2, R′ = OH) and further substantiated by the production of 2 : 5-dihydroxybenzoic acid on alkaline hydrolysis of the trifluoromethyl group.

Diazotisation of 3-amino-4-methoxybenzotrifluoride (III; R = NH_2, R′ = OMe) readily gave rise to 3-*hydroxy*-4-*methoxybenzotrifluoride* (III; R = OH, R′ = OMe). Attempts to demethylate this phenol with hydriodic acid were unsuccessful, the trifluoromethyl group being rapidly hydrolysed with the production of 3-hydroxy-4-methoxybenzoic acid. The formation of this acid confirms the structure of the phenol and hence the structure allocated to the nitration product of *p*-fluorobenzotrifluoride (Brown, Suckling, and Whalley, this vol., p. S 95). Oxidation of 3-hydroxy-4-methoxybenzotrifluoride with potassium persulphate gave rise to 2 : 5-*dihydroxy*-4-*methoxybenzotrifluoride* (V), the structure of which was proved by alkaline hydrolysis of the trifluoromethyl group and conversion of the product into asaronic acid.

The difference in reactivity towards alkali of these trifluoromethylphenols may be noted. 3 : 5-Dihydroxybenzotrifluoride is stable to prolonged boiling with 30% potassium hydroxide solution; 2 : 5-dihydroxy- and 2 : 5-dihydroxy-4-methoxy-benzotrifluoride are rapidly hydrolysed by cold 2N-sodium hydroxide to the corresponding acids. The observation has been made (Jones, *J. Amer. Chem. Soc.*, 1947, **69**, 2346) that *o*- and *p*-hydroxybenzotrifluoride are only partly hydrolysed under these conditions with the formation of polymeric fluorine-containing substances of type (VII).

Although it is well known that the usual methods for the production of phenols by the decomposition of the diazonium chlorides may give rise to quantities of the corresponding chloro-compounds, it may be noted that 3-aminobenzotrifluoride (I; R = H, R′ = NH_2), 3-nitro-5-aminobenzotrifluoride (I; R = NO_2, R′ = NH_2), and 2-nitro-5-aminobenzotrifluoride (II; R = NO_2, R′ = NH_2) gave rise to almost quantitative yields of the corresponding chloro-compounds under these conditions (cf. Hodgson, *Chem. Reviews*, 1947, **40**, 262).

In the course of unsuccessful attempts to secure alternative routes to 3 : 4-dihydroxybenzotrifluoride (III; R = R′ = OH) the nitration of *m*-hydroxy- and *m*-amino-benzotrifluoride was investigated. Attempts to mononitrate *m*-hydroxybenzotrifluoride failed. Under mild conditions no reaction occurred, whilst more vigorous conditions gave rise to polynitrophenols. The nitration of *m*-aminobenzotrifluoride in the presence of a large excess of sulphuric acid was unsuccessful: only amorphous material could be isolated. Nitration proceeded smoothly however in sulphuric–acetic acid solution, yielding a *dinitro*-compound, possibly (VI). Attempts to nitrate 2- and 4-nitro-5-aminobenzotrifluorides (Rouche, *Bull. Acad. roy. Belg.*, 1927, **13**, 346) in an effort to substantiate the structure (VI) were unsuccessful; only intractable materials were isolated.

A further possible route to 4-amino-3-hydroxybenzotrifluoride was investigated by the coupling of benzenediazonium chloride with *m*-hydroxybenzotrifluoride. The product was proved to be the *2-benzeneazo-5-hydroxybenzotrifluoride*, (II; R = PhN_2, R′ = OH) by fission with sodium dithionite (hydrosulphite) to 2-amino-5-hydroxybenzotrifluoride (II; R = NH_2, R′ = OH).

EXPERIMENTAL.

[With R. TOWERS and J. YATES] 3 : *5-Dihydroxybenzotrifluoride* (I; R = R′ = OH).—3-Nitro-5-aminobenzotrifluoride (Finger and Reed, *loc. cit.*) (5 g.), dissolved in a mixture of water (17 ml.) and concentrated sulphuric acid (20 ml.), was cooled to 0° and diazotised by the gradual addition of a solution of sodium nitrite (1·9 g.) in water (10 ml.). After 15 minutes the excess of nitrous acid was destroyed by the addition of urea, and the solution added to a saturated refluxing solution (250 ml.) of copper sulphate. The cooled mixture was extracted with ether (3 × 100 ml.), and the extract dried, evaporated, and distilled, giving *3-nitro-5-hydroxybenzotrifluoride* (I; R = NO_2, R′ = OH) (2·5 g.), b. p. 135°/0·5 mm., crystallising in pale yellow plates, m. p. 92°, from benzene–light petroleum (Found: N, 6·8. $C_7H_4O_3NF_3$ requires N, 6·8%). The percentage yield decreased when the diazotisation was done with larger quantities of amine.

3-Nitro-5-hydroxybenzotrifluoride (10 g.) dissolved in ethyl alcohol (50 ml.) was gently refluxed during the gradual addition of a solution of sodium sulphide (50 g.) in alcohol (200 ml.). After 1½ hours' refluxing 10% ethyl alcoholic sodium hydroxide solution (25 ml.) was added, refluxing continued for 1 hour, and the alcohol removed by distillation under reduced pressure. The mixture was acidified (Congo-red) with hydrochloric acid and then neutralised by the addition of sodium hydrogen carbonate solution, and after isolation with ether (4 × 100 ml.) *3-amino-5-hydroxybenzotrifluoride* (I; R = NH_2, R′ = OH) (8 g.) separated from benzene–light petroleum in pale buff-coloured needles, m. p. 81° (Found: C, 47·4; H, 3·5; N, 8·2. $C_7H_6ONF_3$ requires C, 47·5; H, 3·4; N, 7·9%). Acetylation with pyridine–acetic anhydride gave *3-acetamido-5-acetoxybenzotrifluoride*, separating from aqueous methanol in colourless needles, m. p. 138° (Found: C, 50·7; H, 4·1; N, 5·0. $C_{11}H_{10}O_3NF_3$ requires C, 50·6; H, 3·8; N, 5·4%).

3-Amino-5-hydroxybenzotrifluoride (5 g.), dissolved in a mixture of water (19 ml.) and concentrated sulphuric acid (20 ml.), was diazotised and converted into the phenol as described for 3-nitro-5-aminobenzotrifluoride. On isolation with ether (4 × 100 ml.), 3 : *5-dihydroxybenzotrifluoride* (2·5 g.), b. p. 120°/0·001 mm., separated from benzene in massive colourless prisms, m. p. 54° (Found: C, 43·3; H, 3·7; F, 28·1. $C_7H_5O_2F_3,H_2O$ requires C, 43·0; H, 3·6; F, 29·1%). Repeated sublimation in a high vacuum gave the anhydrous *compound* as massive, colourless prisms, m. p. 65°, readily soluble in water and alcohol, moderately soluble in benzene, sparingly soluble in light petroleum, and exhibiting a deep-violet ferric reaction in water (Found: C, 47·6; H, 3·0. $C_7H_5O_2F_3$ requires C, 47·2; H, 2·8%). The *di*-p-*nitrobenzoate* separated from acetic acid or much alcohol in rosettes of colourless needles, m. p. 166° (Found: N, 6·3. $C_{21}H_{11}O_2N_2F_3$ requires N, 5·9%). The *bisbenzeneazo*-derivative separated from ethyl acetate in bright crimson needles, m. p. 233—234° (decomp.) (Found: N, 14·4. $C_{19}H_{13}O_2N_4F_3$ requires N, 14·6%).

When a solution of 3 : 5-dinitrobenzotrifluoride (Finger and Reed, *loc. cit.*) (5 g.) in alcohol (100 ml.) was shaken in an atmosphere of hydrogen with a palladium–charcoal catalyst [from charcoal (1 g.) and palladium chloride (0·2 g.)], absorption of hydrogen was rapid and was complete in 20 minutes. The filtered solution was evaporated under reduced pressure, giving 3 : *5-diaminobenzotrifluoride* (II; R = R′ = NH_2) (3·5 g.) which separated from benzene–light petroleum in long, slender, colourless needles, m. p. 88°, oxidising slowly in solution and in the solid state (Found: N, 16·0. $C_7H_7N_2F_3$ requires N, 15·9%). The *diacetyl* derivative crystallised from much methyl alcohol in colourless hexagonal tablets, m. p. 298° (Found: N, 10·9. $C_{11}H_{11}O_2N_2F_3$ requires N, 10·8%).

3 : *5-Dihydroxy-2-formylbenzotrifluoride* (IV).—A mixture of 3 : 5-dihydroxybenzotrifluoride (1 g.), zinc cyanide (1 g.), hydrogen cyanide (2 ml.), and benzene (25 ml.) was cooled to 0° and powdered anhydrous aluminium chloride (1 g.) added alowly. A rapid stream of hydrogen chloride was passed through the cooled mixture for 4 hours. After being kept overnight the benzene solution was removed by decantation. The remaining solid and the benzene solution were decomposed by the addition of dilute hydrochloric acid and ice. The solid residue yielded only a trace of aldehyde. The benzene solution was steam-distilled and the benzene evaporated off; upon cooling, the *aldehyde* separated in colourless plates (0·1 g.), recrystallising in colourless prisms, m. p. 147°, from light petroleum–benzene, and exhibiting a reddish-brown ferric reaction in alcohol (Found: C, 46·5; H, 2·7. $C_8H_5O_3F_3$ requires C, 46·6; H, 2·4%). The 2 : *4-dinitrophenylhydrazone* crystallised from alcohol in bright scarlet small needles, m. p. 276° (decomp.) (Found: N, 14·7. $C_{14}H_9O_6N_4F_3$ requires, N, 14·5%).

3-Chloro-5-acetamidobenzotrifluoride (I; R = Cl, R′ = NHAc).—(*a*) A solution of 3-nitro-5-aminobenzotrifluoride (5 g.) in concentrated hydrochloric acid (15 ml.) and water (15 ml.) was diazotised at 0° by the addition of sodium nitrite (1·9 g.) in water (10 ml.). The resultant solution was gradually added to a refluxing saturated solution (250 ml.) of copper sulphate, and the product steam-distilled and extracted with ether, and the extract dried, evaporated, and distilled, yielding 3-chloro-5-nitrobenzotrifluoride (3 g.), b. p. 206—208°/760 mm., as a pale yellow oil, characterised by reduction to the amine with tin and hydrochloric acid and subsequent acetylation to give *3-chloro-5-acetamidobenzotrifluoride*, crystallising in colourless needles, m. p. 134°, from aqueous ethyl alcohol and identical with a synthetic specimen (Found: N, 5·5; Cl, 15·0. $C_9H_7ONClF_3$ requires N, 5·9; Cl, 15·0%).

(*b*) A solution of the diazonium chloride from 3-nitro-5-aminobenzotrifluoride (5 g.) was added to a refluxing solution of cuprous chloride (5 g.) in hydrochloric acid (25 ml.) and water (25 ml.). The steam-distilled product (4 g.) was reduced with tin (5 g.) and concentrated hydrochloric acid (15 ml.), and the amine steam-distilled and acetylated, giving 3-chloro-5-acetamidobenzotrifluoride (3 g.), crystallising from aqueous alcohol in colourless needles, m. p. 134° (Found: N, 6·5%).

[With F. W. D. KING] 2 : *5-Dihydroxybenzotrifluoride* (II; R = R′ = OH).—2-Nitro-5-aminobenzotrifluoride (5 g.) (Rouche, *loc. cit.*) was diazotised in concentrated sulphuric acid (20 ml.) and water (15 ml.), and after conversion into the phenol as described for the preparation of 3-nitro-5-hydroxybenzotrifluoride gave 2-nitro-5-hydroxybenzotrifluoride (II; $R = NO_2$, $R' = OH$) (3·3 g.), b. p. 135—138°/0·01 mm., which crystallised from benzene–light petroleum in almost colourless prisms, m. p. 72° (Found: C, 40·6; H, 1·8; N, 6·9. Calc. for $C_7H_4O_3NF_3$: C, 40·6; H, 1·9; N, 6·8%). De Brouwer (*Bull. Soc. chim. Belg.*, 1930, **39**, 298) gives m. p. 76°.

2-Nitro-5-hydroxybenzotrifluoride was converted into the amine by two methods:

(*a*) 2-Nitro-5-hydroxybenzotrifluoride (3·6 g.) was reduced by alcoholic sodium sulphide as for the preparation of 3-amino-5-hydroxybenzotrifluoride, giving the amine (1·4 g.), which crystallised in almost colourless needles, m. p. 158°, from benzene–acetone.

(*b*) Concentrated hydrochloric acid (25 ml.) was added gradually to a mixture of the nitrophenol (8·5 g.) and tin (10 g.), with cooling as required to moderate the vigorous reaction. After refluxing for 15 minutes the mixture was diluted with water (100 ml.) and partly neutralised by the addition of 2N-sodium hydroxide, and neutralisation was completed by the addition of aqueous sodium hydrogen carbonate. 2-*Amino*-5-*hydroxybenzotrifluoride* (6 g.), isolated with ether, was soluble in dilute sodium hydroxide and dilute acid, oxidised slowly in the solid state and more rapidly in solution, and crystallised from benzene–acetone in almost colourless prisms, m. p. 158°, identical with the product produced by method (*a*) (Found: N, 7·9. $C_7H_6ONF_3$ requires N, 7·9%). Acetylation with pyridine–acetic anhydride gave 2-*acetamido*-5-*acetoxybenzotrifluoride* in long colourless needles, m. p. 142° (from aqueous methanol) (Found: N, 5·3. $C_{11}H_{10}O_3NF_3$ requires N, 5·4%).

Preparation of 2 : 5-*Dihydroxybenzotrifluoride*.—(*a*) A solution of *m*-hydroxybenzotrifluoride (10 g.) in 2N-sodium hydroxide (140 ml.) was stirred at 0° during the addition of a saturated aqueous solution of potassium persulphate (16·5 g.) during 4 hours. 24 Hours later the solution was acidified (Congo-red) with hydrochloric acid, extracted with ether (3 × 100 ml.), then strongly acidified with more hydrochloric acid, warmed on a steam-bath for 30 minutes, and again extracted with ether (5 × 100 ml.), The latter extract was dried, evaporated, and distilled (bath temperature 130—140° at 0·01 mm.), giving 2 : 5-*dihydroxybenzotrifluoride* (3·5 g.) which crystallised from benzene–light petroleum as slender colourless needles, m. p. 109°, readily soluble in water, acetone, or alcohol, and sparingly soluble in light petroleum, exhibiting an olive-green ferric reaction in water, and readily sublimed in a high vacuum as stout colourless prisms (Found: C, 47·0; H, 3·0; F, 32·2. $C_7H_5O_2F_3$ requires C, 47·2; H, 2·8; F, 32·0%). Unchanged phenol (3·3 g.) was recovered. The *di*-p-*nitrobenzoate* crystallised from glacial acetic acid in clusters of tiny colourless needles, m. p. 230° (Found: N, 6·2. $C_{21}H_{11}O_8N_2F_3$ requires N, 5·9%).

A solution of 2 : 5-dihydroxybenzotrifluoride (0·3 g.) in 2N-sodium hydroxide was set aside for 3 hours. The brown solution was acidified and extracted with ether, and the dried extract evaporated and then sublimed in a high vacuum, whereupon 2 : 5-dihydroxybenzoic acid (0·3 g.) was obtained as colourless needles, m. p. 200°, exhibiting a violet ferric reaction and identical with an authentic specimen.

(*b*) 2-Amino-5-hydroxybenzotrifluoride (5 g.), dissolved in concentrated sulphuric acid (20 ml.) and water (15 ml.), was diazotised and converted into the phenol as described for the preparation of 3-nitro-5-hydroxybenzotrifluoride. On isolation with ether (5 × 100 ml.) the product was sublimed in a high vacuum, to give 2 : 5-dihydroxybenzotrifluoride (1 g.), m. p. 109°, identical with a specimen prepared by method (*a*) and giving rise to the same di-*p*-nitrobenzoate, m. p. 230°.

5-*Chloro*-2-*acetamidobenzotrifluoride* (II; $R' = Cl$, $R = NHAc$).—(*a*) 2-Nitro-5-aminobenzotrifluoride (10 g.) was diazotised at 0° in a mixture of concentrated hydrochloric acid (30 ml.) and water (20 ml.), poured into boiling saturated copper sulphate (400 ml.), and steam-distilled. 5-*Chloro*-2-*nitrobenzotrifluoride* (II; $R' = Cl$, $R = NO_2$) was obtained as a pale yellow oil (6·4 g.), b. p. 222—224°/760 mm (Found: Cl, 15·8; F, 25·3. $C_7H_3O_2NClF_3$ requires Cl, 15·8; F, 25·3%). Reduction of this nitro-compound (4 g.) was effected with tin (10 g.) and concentrated hydrochloric acid (25 ml.), and completed by heating under a reflux during 15 minutes, whereafter the mixture was made alkaline with concentrated aqueous sodium hydroxide, and steam-distilled. The product was directly acetylated with acetic anhydride. The *acetamido*-compound crystallised in colourless needles (4 g.), m. p. 148°, from dilute methanol (Found: N, 5·6; Cl, 15·0. $C_9H_7ONClF_3$ requires N, 5·9; Cl, 15·0%). The preparation of 5-chloro-2-nitrobenzotrifluoride is claimed by I. G. Farbenindustrie, A.-G. (B.P. 452,436), but few details are available.

(*b*) Diazotisation of 2-nitro-5-aminobenzotrifluoride (5 g.), dissolved in concentrated hydrochloric acid (30 ml.) and water (10 ml.), was effected at 0°. The resultant solution was poured into a solution of boiling cuprous chloride (5 g.) in concentrated hydrochloric acid (50 ml.). After isolation, reduction, and acetylation as in (*a*), 5-chloro-2-acetamidobenzotrifluoride was obtained in colourless needles, m. p. 148° (from dilute methanol), identical with the product prepared by method (*a*) (Found: N, 5·9%).

3-*Hydroxy*-4-*methoxybenzotrifluoride* (III; $R = OH$, $R' = OMe$).—3-Amino-4-methoxybenzotrifluoride (6 g.) (Brown, Suckling, and Whalley, *loc. cit.*), dissolved in a mixture of concentrated sulphuric acid (40 ml.) and water (35 ml.), was diazotised and converted into the phenol in the manner described for the preparation of 3-nitro-5-hydroxybenzotrifluoride, giving 3-hydroxy-4-methoxybenzotrifluoride (2·8 g.) as a clear, colourless liquid, b. p. 104—105°/15 mm., which was characterised as the p-*nitrobenzoate*, long, colourless prisms (from aqueous alcohol), m. p. 120° (Found: C, 52·8; H, 3·0; N, 5·3. $C_{15}H_{10}O_5NF_3$ requires C, 52·8; H, 2·9; N, 4·5%).

When the foregoing methoxyphenol (4 g.) was refluxed for 5 minutes with hydriodic acid (5 ml.; *d* 1·7), hydrogen fluoride was evolved (glass attacked). After dilution with water (100 ml.), extraction with ether, and separation into phenolic and acidic components by the use of sodium hydrogen carbonate solution, unchanged phenol (1·9 g.) and 3-hydroxy-4-methoxybenzoic acid (1 g.), m. p. 252°, exhibiting a negative ferric reaction in alcohol, were obtained. Esterification of the acid with diazomethane, methylation with methyl iodide and potassium carbonate in acetone solution, and subsequent hydrolysis of the ester gave veratric acid, identical with an authentic specimen.

2 : 5-*Dihydroxy*-4-*methoxybenzotrifluoride* (V).—3-Hydroxy-4-methoxybenzotrifluoride (6 g.), dis-

solved in a solution of sodium hydroxide (6·5 g.) in water (60 ml.), was stirred at 0° with the gradual addition during 6 hours of a saturated aqueous solution of potassium persulphate (8·5 g.). 24 Hours later the solution was decanted from a sticky precipitate, acidified (Congo-red) with hydrochloric acid, extracted with ether (2 × 150 ml.), strongly acidified with more hydrochloric acid, heated on a steam-bath during 30 minutes, cooled, and again extracted with ether (5 × 100 ml.). Evaporation of the dried ethereal extracts furnished unchanged phenol (2·8 g.) and 2 : 5-*dihydroxy*-4-*methoxybenzotrifluoride*, purified by sublimation in a high vacuum. It formed colourless needles (0·5 g.), m. p. 136°, exhibiting a negative ferric reaction in alcohol, sparingly soluble in water, readily soluble in alcohol, acetone, or ether, and crystallising in small needles from benzene–light petroleum (Found : C, 46·5; H, 3·4; F, 27·5. $C_8H_7O_3F_3$ requires C, 46·2; H, 3·4; F, 27·4%).

The *di*-p-*nitrobenzoate* separated from glacial acetic acid in colourless, feathery needles, m. p. 227° (Found : N, 5·9. $C_{22}H_{13}O_9N_2F_3$ requires N, 5·5%).

A solution of 2 : 5-dihydroxy-4-methoxybenzotrifluoride (0·2 g.) in cold 2N-aqueous sodium hydroxide was acidified after 2 hours, and the product isolated with ether and esterified by the addition of ethereal diazomethane. After evaporation of the solvent the ester (0·15 g.) was methylated in acetone (30 ml.) during 12 hours with anhydrous potassium carbonate (1 g.) and methyl iodide (3 ml.), the crude methylated ester hydrolysed by warming on a steam-bath with 20% methyl-alcoholic potassium hydroxide (3 ml.), and the product vacuum-sublimed, giving rise to asaronic acid (0·1 g.), m. p. 144°, identical with an authentic specimen.

m-*Chlorobenzotrifluoride* (I; R = H, R′ = Cl).—3-Aminobenzotrifluoride (21 g.), dissolved in a mixture of water (30 ml.) and concentrated hydrochloric acid (38 ml.), was diazotised and then poured into boiling saturated copper sulphate solution (300 ml.), and the mixture steam-distilled. The distillate was dissolved in ether, and the ethereal extract washed with 2N-sodium hydroxide. The ethereal solution was dried and distilled, giving 3-chlorobenzotrifluoride (15·7 g.) as a clear, colourless liquid, b. p. 136—138°/760 mm. (McBee *et al.*, *J. Amer. Chem. Soc.*, 1947, **69**, 947, give b. p. 135—136°/745 mm.) (Found : Cl, 19·7; F, 31·0. Calc. for $C_7H_4ClF_3$: Cl, 19·7; F, 31·7%). Acidification of the alkaline washings gave *m*-hydroxybenzotrifluoride (2 g.).

2-*Benzeneazo*-5-*hydroxybenzotrifluoride* (II; R = PhN_2, R′ = OH).—Aniline (6·5 g.), dissolved in concentrated hydrochloric acid (20 ml.) and water (60 ml.), was diazotised at 0° with sodium nitrite (5 g.), and the resultant solution added slowly with stirring to *m*-hydroxybenzotrifluoride (10 g.) dissolved in a solution of sodium hydroxide (9 g.) in water (150 ml.). The dark brown solution was acidified with 50% acetic acid, and the resultant sticky precipitate crystallised from acetic acid in reddish-brown needles (5 g.), m. p. 118° (decomp.) (Found : N, 10·3. $C_{13}H_9ON_2F_3$ requires N, 10·5%).

Fission of the *azo*-derivative (2 g.) dissolved in 50% aqueous alcohol (30 ml.) was achieved during 3 hours by the gradual addition of sodium dithionite (5 g.). The pale yellow solution was diluted with water (100 ml.), the aniline removed by steam-distillation, and the residue acidified (Congo-red) with hydrochloric acid, neutralised with sodium hydrogen carbonate, and extracted with ether (4 × 100 ml.). Evaporation of the ether gave 2-amino-5-hydroxybenzotrifluoride, identical with an authentic specimen. Acetylation gave 2-acetamido-5-acetoxybenzotrifluoride, identical with an authentic specimen.

Nitration of m-*Aminobenzotrifluoride*.—The base (5 g.), dissolved in a mixture of concentrated sulphuric acid (50 ml.) and acetic acid (40 ml.), was cooled to 0° and a solution of fuming nitric acid (5 ml.) in concentrated sulphuric acid (20 ml.) added with stirring. 4 Days later the deep-yellow solution was poured on an excess of crushed ice, and the pale yellow crystalline solid collected, washed with water, and sodium hydrogen carbonate solution, and dried. The *product* (7 g.) crystallised in pale lemon-yellow needles, m. p. 126° (decomp.), from ethyl acetate–light petroleum (Found : C, 33·4; H, 1·5; N, 16·9. $C_7H_4O_4N_3F_3$ requires C, 33·5; H, 1·6; N, 16·7%). The compound was oxidised rapidly in hot solution, and more slowly on exposure to the air in solution at room temperature; the solid appears to be quite stable. The *acetate*, prepared in moderate yield by pyridine–acetic anhydride, crystallised from benzene–acetone in golden-yellow, long, silky needles, m. p. 149° (decomp.) (Found : N, 13·9. $C_9H_6O_5N_3F_3$ requires 14·3%).

CAUTION. The nitro-amine reacts explosively with pyridine but may be dissolved in a mixture of pyridine–acetic anhydride with safety.

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