765. *Synthesis of Certain Trifluoromethyldiphenyl Derivatives.*

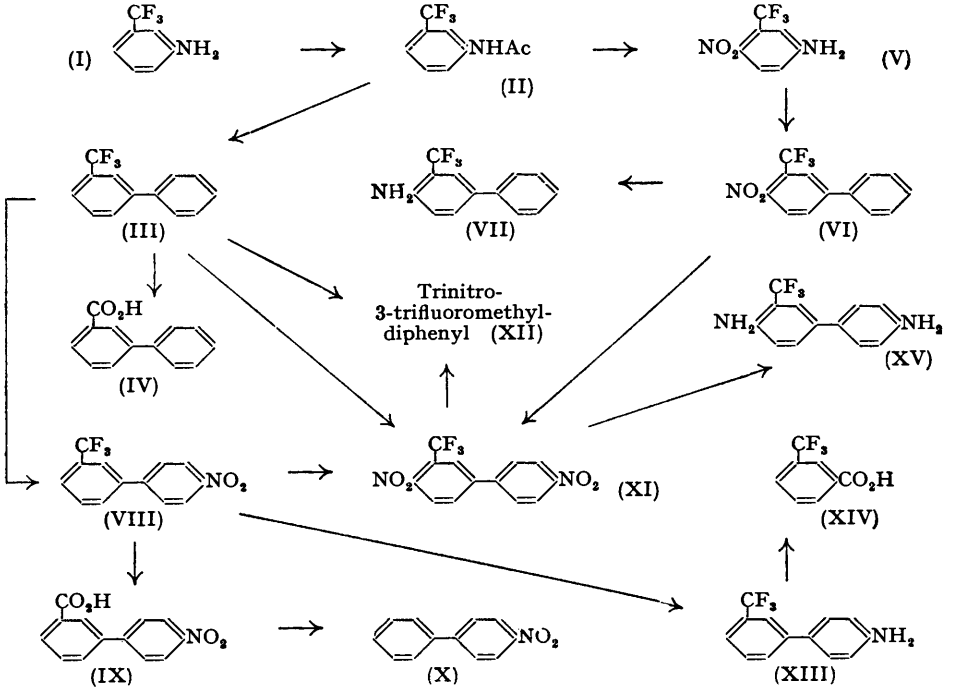
By M. R. Pettit and J. C. Tatlow.

A series of diphenyl derivatives containing trifluoromethyl groups has been prepared. It includes 3-trifluoromethyldiphenyl and certain derived nitro- and amino-compounds, together with some symmetrical dinitro- and diamino-bistrifluoromethyldiphenyls.

The chemistry of trifluoromethylbenzene derivatives has been studied fairly extensively since the parent compound, benzotrifluoride, was first prepared by Swarts (*Bull. Acad. roy. Belg.*, 1898, [iii], **35**, 375). There have been, however, few references to trifluoromethyldiphenyl compounds. Zahn and Schimmelschmidt (Fr. P. 739,053) mentioned the production of 2 : 5-dimethoxy-3′-trifluoromethyldiphenyl and of its 4-nitro- and 4-amino-derivatives, and Bradsher and Bond (*J. Amer. Chem. Soc.*, 1949, **71**, 2659) recently described the preparation of a number of diphenyls containing trifluoromethyl groups, including 3-trifluoromethyl-, 3 : 3′-bistrifluoromethyl-,

and 2 : 2′-dinitro-4 : 4′-bistrifluoromethyl-diphenyl. As part of the general study of fluoro-organic compounds in progress in this Department, a series of unsymmetrical and symmetrical trifluoromethyldiphenyls has been made, and some of this work is reported herein.

By the formation, from an acetylated aromatic amine, of the corresponding *N*-nitroso-derivative and reaction of the latter with benzene (Bamberger, *Ber.*, 1897, **30**, 366; Grieve and Hey, *J.*, 1934, 1797; Haworth and Hey, *J.*, 1940, 361), 3-trifluoromethyldiphenyl (III) was prepared from *m*-acetamidobenzotrifluoride (II). Alternative methods of synthesis of unsymmetrical diphenyls (see the summary by Bachmann and Hoffman, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, 1944, p. 224) gave poorer yields of 3-trifluoromethyldiphenyl (III) from diazotised *m*-aminobenzotrifluoride (I).



In conformity with Le Fave's observations (*J. Amer. Chem. Soc.*, 1949, **71**, 4148) that compounds with trifluoromethyl groups attached to a benzene ring are converted into carboxylic acids by being heated with concentrated sulphuric acid, it was found that 3-trifluoromethyldiphenyl (III), treated in this way, gave diphenyl-3-carboxylic acid (IV), though in addition a proportion of a sulphur-containing product, probably a sulphonic acid, was isolated.

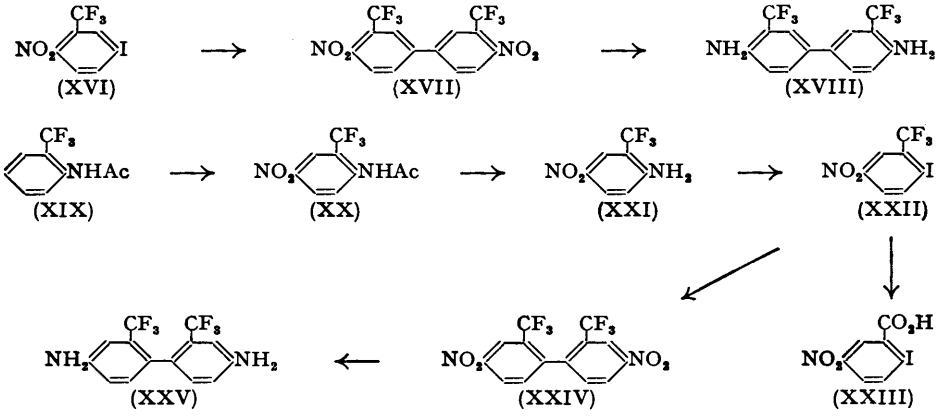
4-Nitro-3-trifluoromethyldiphenyl (VI) was best prepared by diazotisation of 5-amino-2-nitrobenzotrifluoride (V) (Rouche, *Bull. Acad. roy. Belg., Classe Sci.*, 1927, **13**, 346) and subsequent reaction with benzene in the presence of sodium acetate, according to the method of Elks, Haworth, and Hey (*J.*, 1940, 1284). Reduction of this nitro-compound (VI) gave 4-amino-3-trifluoromethyldiphenyl (VII).

By treatment of 3-trifluoromethyldiphenyl (III) with nitric–sulphuric acid mixtures a dinitro-3-trifluoromethyldiphenyl (XI) and a trinitro-3-trifluoromethyldiphenyl (XII) were formed. Mononitration was effected with a mixture of nitric, sulphuric, and acetic acids under carefully controlled conditions, though with nitric–acetic acid mixtures, under conditions which effect mononitration of diphenyl itself, there was no reaction. The mononitro-compound (VIII) could be prepared also by treatment of 3-trifluoromethyldiphenyl (III) with a mixture of nitric acid and trifluoroacetic anhydride, which is an active nitrating mixture (Bourne, Stacey, Tatlow, and Tedder, unpublished results). The derivative (VIII) was shown to be 4-nitro-3′-trifluoromethyldiphenyl by the following reactions. With concentrated sulphuric acid (Le Fave, *loc. cit.*) a nitrodiphenylcarboxylic acid (IX) was obtained, and this on decarboxylation yielded 4-nitrodiphenyl (X). Reduction of the nitro-3-trifluoromethyldiphenyl (VIII) with tin and hydro-

chloric acid gave the corresponding amino-3-trifluoromethyldiphenyl (XIII) which, on oxidation with potassium permanganate by a method similar to that which gives trifluoroacetic acid from 3-aminobenzotrifluoride (Haworth and Stacey, B.P. 625,098), gave benzotrifluoride-3-carboxylic acid (XIV). Thus, since the oxidation showed that the amino- and trifluoromethyl groups were substituted in different rings, the compounds must have been 4-nitro-3′-trifluoromethyldiphenyl (VIII) and 4-amino-3′-trifluoromethyldiphenyl (XIII).

The dinitro-3-trifluoromethyldiphenyl (XI) formed by direct nitration of 3-trifluoromethyldiphenyl was also the product of mononitration of both 4-nitro-3′-trifluoromethyldiphenyl (VIII) and 4-nitro-3-trifluoromethyldiphenyl (VI) and hence was 4 : 4′-dinitro-3-trifluoromethyldiphenyl. Reduction with tin and hydrochloric acid gave 4 : 4′-diamino-3-trifluoromethyldiphenyl (XV).

The trinitro-compound (XII) prepared from 3-trifluoromethyldiphenyl was formed also by further nitration of 4 : 4′-dinitro-3-trifluoromethyldiphenyl and so the positions of two of the nitro-groups are established, but the location of the third is not known at present.



Symmetrical diphenyls were made by the Ullmann reaction (Ullmann and Bielecki, *Ber.*, 1901, **34**, 2174). 5-Iodo-2-nitrobenzotrifluoride (XVI), prepared by Jones's method (*J. Amer. Chem. Soc.*, 1947, **69**, 2346), gave, on treatment with copper bronze, 4 : 4′-dinitro-3 : 3′-bistrifluoromethyldiphenyl (XVII), which was reduced to the corresponding benzidine derivative (XVIII).

Nitration of *o*-acetamidobenzotrifluoride (XIX) (Rouche, *loc. cit.*; Jones, *loc. cit.*) gave the expected 5-nitro-derivative (XX), from which there was obtained, after hydrolysis, 2-amino-5-nitrobenzotrifluoride (XXI), and thence by a diazo-reaction 2-iodo-5-nitrobenzotrifluoride (XXII). The structure of this, and hence those of the intermediate compounds, were proved by conversion with sulphuric acid into the known 2-iodo-5-nitrobenzoic acid (XXIII). With copper bronze 2-iodo-5-nitrobenzotrifluoride (XXII) gave 4 : 4′-dinitro-2 : 2′-bistrifluoromethyldiphenyl (XXIV) which on reduction afforded the 4 : 4′-diamine (XXV), identical with that obtained from 3-nitrobenzotrifluoride by conversion into the corresponding hydrazo-derivative and rearrangement of this with mineral acid (Cartwright and Tatlow, unpublished work).

Further aspects of the chemistry of trifluoromethyldiphenyls are being studied, in order to investigate the influence of trifluoromethyl groups on the reactions of aromatic compounds.

Experimental.

Preparation of 3-Trifluoromethyldiphenyl.—*m*-Acetamidobenzotrifluoride (20·0 g.) was dissolved in glacial acetic acid (100 c.c.) and nitrous fumes were passed into the stirred solution at 10° for *ca.* 4 hours until a deep clear green solution was obtained. The liquid was then poured into ice-cold water (500 c.c.) with vigorous stirring, and the yellowish precipitate of the *N*-nitroso-derivative was removed by filtration, and, after being washed with water, was dried on a porous plate. The solid was dissolved in benzene (150 c.c.), and the solution, together with the benzene extracts (2 × 50 c.c.) of the aqueous phase, was stirred at room temperature for 20 hours. There was gradual evolution of nitrogen and the solution became deep red. After removal of the excess of benzene by distillation, the residue was distilled and, in order to hydrolyse any unchanged *m*-acetamidobenzotrifluoride, the distillate was refluxed for 2 hours with concentrated hydrochloric acid (10·0 c.c.), water (10·0 c.c.), and ethyl alcohol (10·0 c.c.). The mixture was distilled to remove alcohol and then extracted exhaustively with ether. The ethereal extracts were dried ($MgSO_4$) and filtered, the ether removed by distillation, and the residue distilled under reduced pressure. The fraction, b. p. 117—120°/13 mm., was recrystallised from ethyl alcohol

containing a few drops of water, to give colourless plates of 3-trifluoromethyldiphenyl (7·0 g., 35%), m. p. 26—27°, b. p. 117—120°/13 mm., n_D^{30} 1·5304 (Found: C, 70·4; H, 4·0; F, 25·2. Calc. for $C_{13}H_9F_3$: C, 70·3; H, 4·1; F, 25·6%). Bradsher and Bond (*loc. cit.*) gave b. p. 118—119°/13 mm. and n_D^{25} 1·5302 for this compound. *m*-Aminobenzotrifluoride (1·6 g.) was isolated from the aqueous residues of the hydrolysis.

Conversion of 3-*Trifluoromethyldiphenyl into Diphenyl-*3-*carboxylic Acid.*—3-Trifluoromethyldiphenyl (1·00 g.) and concentrated sulphuric acid (0·35 c.c.) were heated to 130° for 2 hours with stirring. After being cooled, the mixture was poured into aqueous sodium hydroxide and the aqueous phase was filtered, extracted with ether, and then acidified with concentrated hydrochloric acid. The precipitated acid was filtered off and twice recrystallised from aqueous ethyl alcohol, to give diphenyl-3-carboxylic acid (0·209 g., 23%), m. p. 164° (Found: C, 78·8; H, 5·2. Calc. for $C_{13}H_{10}O_2$: C, 78·8; H, 5·1%). Repetition of this experiment gave, in addition to the desired product, varying proportions of a water-soluble compound containing sulphur, probably a sulphonic acid. Jacobson and Lischke (*Ber.*, 1895, **28**, 2541) gave m. p. 166° for diphenyl-3-carboxylic acid.

Mononitration of 3-*Trifluoromethyldiphenyl.*—3-Trifluoromethyldiphenyl (2·43 g.) was refluxed for 30 minutes with glacial acetic acid (3·00 c.c.), fuming nitric acid (0·90 c.c.; *d* 1·5), and concentrated sulphuric acid (0·60 c.c.). The mixture was then poured into water (20.0 c.c.), and the aqueous phase was extracted with ether. The ethereal extract was washed with sodium hydroxide solution, then with water, and dried ($MgSO_4$), and the ether was removed by distillation. Recrystallisation of the residue from aqueous ethyl alcohol gave 4-*nitro*-3′-*trifluoromethyldiphenyl* (1·74 g., 60%), m. p. 86° (Found: C, 58·6; H, 3·3; F, 20·9. $C_{13}H_8O_2NF_3$ requires C, 58·4; H, 3·0; F, 21·3%).

Conversion of 4-*Nitro*-3′-*trifluoromethyldiphenyl into* 4-*Nitrodiphenyl*-3′-*carboxylic Acid.*—The above nitro-compound (0·64 g.) was stirred at 110° with 100% sulphuric acid (0·50 c.c.) and the temperature was gradually increased to 150° during 45 minutes, the nitro-compound slowly passing into solution. When cool, the mixture was poured into excess of sodium hydroxide solution, and the aqueous phase was filtered, extracted with ether, and acidified with concentrated hydrochloric acid. The precipitate was filtered off and boiled with ethyl alcohol, the alcoholic solution being then filtered and evaporated, to give 4-*nitrodiphenyl*-3′-*carboxylic acid* (0·39 g., 67%), m. p. 229—231° unchanged by recrystallisation and by sublimation under reduced pressure (Found: C, 64·2; H, 3·8%; Equiv., 247. $C_{13}H_9O_4N$ requires C, 64·2; H, 3·7%; Equiv., 243).

Decarboxylation of 4-*Nitrodiphenyl*-3′-*carboxylic Acid.*—This acid (0·099 g.) was refluxed for 6 hours with freshly distilled quinoline (1·00 c.c.) and copper bronze (0·05 g.). The mixture, when cool, was diluted with ether (25 c.c.) and filtered, and the ethereal solution was washed with 50% hydrochloric acid (4 × 25 c.c.), then with sodium hydroxide solution, and water, and was dried ($MgSO_4$). Removal of the ether left a residue, which, after recrystallisation from ethyl alcohol, afforded 4-nitrodiphenyl (0·050 g., 62%), m. p. 114° alone and in admixture with an authentic specimen (Found: C, 72·1; H, 4·8. Calc. for $C_{12}H_9O_2N$: C, 72·35; H, 4·55%).

Preparation of 4-*Amino*-3′-*trifluoromethyldiphenyl.*—4-Nitro-3′-trifluoromethyldiphenyl (2·48 g.) was heated under reflux for 3 hours with concentrated hydrochloric acid (15·0 c.c.), ethyl alcohol (5·0 c.c.), and granulated tin (10·0 g.). The liquid was filtered and evaporated to remove the alcohol. It was then made alkaline with sodium hydroxide solution and extracted with ether. The ethereal extracts were washed with water and then dried ($MgSO_4$), and the ether was removed by distillation. Recrystallisation of the crude product from aqueous ethyl alcohol afforded 4-*amino*-3′-*trifluoromethyldiphenyl* (1·89 g., 86%), m. p. 65° (Found: C, 65·7; H, 4·0; F, 24·0. $C_{13}H_{10}NF_3$ requires C, 65·8; H, 4·2; F, 24·0%).

Treatment of the amine with benzoyl chloride and aqueous sodium hydroxide gave the *benzoyl* derivative, m. p. 195—196°, which crystallised from ethyl alcohol (Found: C, 70·2; H, 4·3. $C_{20}H_{14}ONF_3$ requires C, 70·4; H, 4·1%).

Oxidation of 4-*Amino*-3′-*trifluoromethyldiphenyl.*—The amine (0·351 g.) was added gradually and with rapid stirring to a mixture of potassium permanganate (3·05 g.), water (5·0 c.c.), and concentrated sulphuric acid (2·0 c.c.) at 50°. When the addition was complete, the mixture was stirred at 100° for 1 hour. Water (30 c.c.) was added and a stream of sulphur dioxide was passed through the mixture until all the manganese dioxide had dissolved. The whole was then extracted exhaustively with ether. The ethereal extracts were shaken with sodium hydroxide solution and the aqueous phase was separated from the ether, acidified with concentrated hydrochloric acid, and extracted with ether. These ethereal extracts were washed with water, dried ($MgSO_4$), and evaporated. The residue, after two recrystallisations from carbon tetrachloride, afforded benzotrifluoride-3-carboxylic acid (0·107 g., 38%), m. p. 104° alone and in admixture with an authentic specimen (Found: C, 50·6; H, 2·7. Calc. for $C_8H_5O_2F_3$: C, 50·5; H, 2·6%). Swarts (*loc. cit.*) cited m. p. 103° for this compound.

Preparation of 4 : 4′-*Dinitro*-3-*trifluoromethyldiphenyl.*—(*a*) 4-Nitro-3′-trifluoromethyldiphenyl (0·275 g.), glacial acetic acid (0·30 c.c.), fuming nitric acid (0·10 c.c.), and concentrated sulphuric acid (0·07 c.c.) were gently refluxed for ½ hour. When cool, the mixture was poured into water, and the precipitate was filtered off, washed, and recrystallised from aqueous ethyl alcohol to give 4 : 4′-*dinitro*-3-*trifluoromethyldiphenyl* (0·190 g., 59%), m. p. 180—181°, alone or in admixture with the material obtained as in (*b*) (Found: C, 50·1; H, 2·3; F, 18·2. $C_{13}H_7O_4N_2F_3$ requires C, 50·0; H, 2·3; F, 18·3%).

(*b*) 4-Nitro-3-trifluoromethyldiphenyl (1·120 g.), treated as above with glacial acetic acid (1·50 c.c.), fuming nitric acid (0·35 c.c.), and concentrated sulphuric acid (0·40 c.c.), gave the same dinitro-derivative (1·128 g., 86%), m. p. 181°.

(*c*) The same product was produced by nitration of 3-trifluoromethyldiphenyl under similar conditions.

Preparation of 4 : 4′-*Diamino*-3-*trifluoromethyldiphenyl*.—4 : 4′-Dinitro-3-trifluoromethyldiphenyl (0·806 g.) was heated under reflux with concentrated hydrochloric acid (10·0 c.c.), ethyl alcohol (3·0 c.c.), and granulated tin (10·0 g.). After working up as in the case of the 4-amino-3′-trifluoromethyl derivative there was obtained 4 : 4′-*diamino*-3-*trifluoromethyldiphenyl* (0·578 g., 89%), m. p. 86° (Found : C, 61·7; H, 4·5; F, 22·2. $C_{13}H_{11}N_2F_3$ requires C, 61·9; H, 4·4; F, 22·6%).

This amine, on treatment with a mixture of acetic acid and acetic anhydride, yielded the *diacetyl* derivative, m. p. 285—286° after recrystallisation from ethyl alcohol (Found : C, 61·0; H, 4·5. $C_{17}H_{15}O_2N_2F_3$ requires C, 60·7; H, 4·5%).

With benzoyl chloride and sodium hydroxide solution the amine gave the *dibenzoyl* derivative, m. p. 286—287° after recrystallisation from ethyl alcohol (Found : C, 70·4; H, 4·1. $C_{27}H_{19}O_2N_2F_3$ requires C, 70·4; H, 4·2%).

Preparation of Trinitro-3-*trifluoromethyldiphenyl*.—(*a*) 3-Trifluoromethyldiphenyl (5·79 g.) was refluxed for 40 minutes with a mixture of concentrated nitric acid (15·0 c.c.) and concentrated sulphuric acid (20·0 c.c.). The reaction mixture, treated as in the case of 4-nitro-3′-trifluoromethyldiphenyl, afforded *trinitro*-3-*trifluoromethyldiphenyl* (5·60 g., 60%), m. p. 153·5—154·5° (Found : C, 43·8; H, 1·6; F, 15·8. $C_{13}H_6O_6N_3F_3$ requires C, 43·7; H, 1·7; F, 16·0%).

(*b*) 4 : 4′-Dinitro-3-trifluoromethyldiphenyl (0·235 g.), refluxed for 2 hours with concentrated nitric acid (1·0 c.c.) and concentrated sulphuric acid (1·0 c.c.), gave the same product (0·238 g., 89%), m. p. 153—154° alone or in admixture with the specimen mentioned above.

Preparation of 4-*Nitro*-3-*trifluoromethyldiphenyl*.—5-Amino-2-nitrobenzotrifluoride (Jones, *loc. cit.*) (13·1 g.) was treated at 5° with concentrated sulphuric acid (7·0 c.c.), water (13·0 c.c.), and a solution of sodium nitrite (4·7 g.) in water (8·0 c.c.). The filtered diazonium solution was stirred for 1 hour at 0—5° with benzene (100 c.c.) whilst a solution of sodium acetate trihydrate (50·0 g.) in water (150 c.c.) was added dropwise, and then the mixture was stirred for a further 2 hours at 0—5° and for 15 hours at room temperature. The benzene layer was separated, washed, dried ($MgSO_4$), and distilled to remove the benzene, the residue being distilled under diminished pressure. The fraction having b. p. 123—128°/0·3 mm. (3·8 g., 22%) crystallised on storage and was 4-*nitro*-3-*trifluoromethyldiphenyl*, m. p. 30·5—31·5° (unchanged by recrystallisation from aqueous ethyl alcohol) (Found : C, 58·3; H, 3·3; F, 20·9. $C_{13}H_8O_2NF_3$ requires C, 58·4; H, 3·0; F, 21·3%).

Reduction of 4-*Nitro*-3-*trifluoromethyldiphenyl*.—This nitro-compound (2·00 g.), reduced as described for the 4-nitro-3′-trifluoromethyl isomer, yielded, after recrystallisation of the crude product from aqueous ethyl alcohol, 4-*amino*-3-*trifluoromethyldiphenyl* (1·49 g., 84%), m. p. 61·5°, depressed by the 4-amino-3′-trifluoromethyl isomer (Found : C, 65·6; H, 4·2; F, 23·7. $C_{13}H_{10}NF_3$ requires C, 65·8; H, 4·2; F, 24·0%).

Treatment of the amine in ethereal solution with dry hydrogen chloride gave the *amine hydrochloride*, m. p. 134—135° [Found : C, 57·2; H, 4·0%; Equiv. (by titration with sodium hydroxide), 273·0. $C_{13}H_{11}NClF_3$ requires C, 57·05; H, 4·05%; Equiv., 273·7].

The amine gave, with acetic acid–acetic anhydride an *acetyl* derivative, m. p. 160—161° (Found : C, 64·3; H, 4·1; F, 20·4. $C_{15}H_{12}ONF_3$ requires C, 64·5; H, 4·3; F, 20·4%), and with benzoyl chloride–sodium hydroxide a *benzoyl* derivative, m. p. 168·5—169·5° (Found : C, 70·2; H, 4·2; F, 16·2. $C_{20}H_{14}ONF_3$ requires C, 70·4; H, 4·1; F, 16·7%).

Preparation of 4 : 4′-*Dinitro*-3 : 3′-*bistrifluoromethyldiphenyl*.—5-Iodo-2-nitrobenzotrifluoride (Jones, *loc. cit.*) (3·12 g.) was heated with copper bronze (0·60 g.) for 30 minutes, the temperature being increased gradually from 265° to 300°. When cool, the mixture was extracted with boiling benzene and after filtration and distillation to remove the benzene, the residue was recrystallised from aqueous ethyl alcohol and then twice from aqueous acetone, to give 4 : 4′-*dinitro*-3 : 3′-*bistrifluoromethyldiphenyl* (0·65 g., 35%), m. p. 181—182° (Found : C, 44·3; H, 1·5; F, 29·5. $C_{14}H_6O_4N_2F_6$ requires C, 44·2; H, 1·6; F, 30·0%).

Preparation of 4 : 4′-*Diamino*-3 : 3′-*bistrifluoromethyldiphenyl*.—4 : 4′-Dinitro-3 : 3′-bistrifluoromethyldiphenyl (0·815 g.), reduced as before with tin and aqueous alcoholic hydrochloric acid yielded, after three recrystallisations of the product from aqueous ethyl alcohol, 4 : 4′-*diamino*-3 : 3′-*bistrifluoromethyldiphenyl* (0·602 g., 88%), m. p. 115—116·5° (Found : C, 52·5; H, 3·2; F, 35·2. $C_{14}H_{10}N_2F_6$ requires C, 52·5; H, 3·1; F, 35·6%).

Treatment of an ethereal solution of this amine with trifluoroacetic anhydride gave the *bistrifluoroacetyl* derivative, m. p. 202° (Found : C, 42·1; H, 1·8. $C_{18}H_8O_2N_2F_{12}$ requires C, 42·2; H, 1·6%).

Preparation of 2-*Amino*-5-*nitrobenzotrifluoride*.—*o*-Acetamidobenzotrifluoride (Jones, *loc. cit.*) (2·98 g.) was added slowly and with stirring to concentrated sulphuric acid (16·5 c.c.) cooled to 0°, and then a mixture of fuming nitric acid (0·80 c.c.; *d* 1·5) and concentrated sulphuric acid (1·5 c.c.) was added. After being kept for 15 minutes at 0° and for 30 minutes at 15°, the mixture was heated to 40° for 15 minutes, becoming golden-yellow, and was then poured slowly on crushed ice. The precipitate was collected by filtration, dried, and recrystallised from ethyl alcohol, to give 2-*acetamido*-5-*nitrobenzotrifluoride* (2·81 g., 77%), m. p. 148° (Found : C, 43·9; H, 2·9; F, 23·0. $C_9H_7O_3N_2F_3$ requires C, 43·6; H, 2·8; F, 23·0%).

Hydrolysis of this compound (5·94 g.) with sodium hydroxide (3·0 g.) in water (15·0 c.c.) and ethyl alcohol (8·0 c.c.) gave, after recrystallisation of the crude product from benzene–light petroleum (b. p. 60—80°), 2-amino-5-nitrobenzotrifluoride (4·13 g., 84%), m. p. 94° (Found : C, 40·9; H, 2·5; F, 27·6; Calc. for $C_7H_5O_2N_2F_3$: C, 40·8; H, 2·4; F, 27·7%). Daudt and Woodward (U.S.P. 2,194,926) gave m. p. " about 88°."

Conversion of 2-*Amino*-5-*nitrobenzotrifluoride into* 2-*Iodo*-5-*nitrobenzotrifluoride*.—The amine (5·70 g.), dissolved in a mixture of glacial acetic acid (25·0 c.c.) and concentrated sulphuric acid (5·0 c.c.), was

diazotised at 0° with sodium nitrite (2·5 g.) in water (5·0 c.c.). The solution was poured into potassium iodide (15·0 g.) dissolved in water (50·0 c.c.) and, after 3 hours, the precipitate was filtered off, distilled in steam and recrystallised from aqueous ethyl alcohol. The product, *2-iodo-5-nitrobenzotrifluoride* (7·21 g., 82%), had m. p. 82° (Found: C, 26·4; H, 1·0; F, 17·6. $C_7H_3O_2INF_3$ requires C, 26·5; H, 1·0; F, 18·0%).

Conversion of 2-Iodo-5-nitrobenzotrifluoride into 2-Iodo-5-nitrobenzoic Acid.—The iodo-derivative (0·36 g.) was stirred at 120—130° for 1½ hours with 100% sulphuric acid (0·80 c.c.). When cool, the solution was poured into water, and the aqueous phase was extracted with ether. The ethereal extracts, after being washed with water, were shaken with aqueous sodium hydroxide which was separated, acidified, and ether-extracted. The second ethereal extracts were washed with water and dried ($MgSO_4$). The ether was removed by distillation and the residue on recrystallisation from water afforded 2-iodo-5-nitrobenzoic acid (0·109 g., 33%), m. p. 193—195° (alone or in admixture with an authentic specimen prepared by the method of Goldstein and Grampoloff, *Helv. Chim. Acta*, 1930, **13**, 310) (Found: C, 28·6; H, 1·1. Calc. for $C_7H_4O_4IN$: C, 28·7; H, 1·4%).

Ullmann Reaction on 2-Iodo-5-nitrobenzotrifluoride.—The iodo-compound (3·57 g.) was heated with copper bronze (1·90 g.) for 30 minutes at 250—300°. After isolation as before, the product, *4 : 4′-dinitro-2 : 2′-bistrifluoromethyldiphenyl* (0·362 g., 17%), had m. p. 137·5° (Found: C, 44·2; H, 1·5; F, 29·7. $C_{14}H_6O_4N_2F_6$ requires C, 44·2; H, 1·6; F, 30·0%).

Preparation of 4 : 4′-Diamino-2 : 2′-bistrifluoromethyldiphenyl.—The corresponding dinitro-derivative (0·173 g.), treated as in the case of 4-nitro-3′-trifluoromethyldiphenyl, gave, after recrystallisation of the crude product from aqueous ethyl alcohol, *4 : 4′-diamino-2 : 2′-bistrifluoromethyldiphenyl* (0·125 g., 86%), m. p. 182° (Found: C, 52·6; H, 3·3; F, 35·7. $C_{14}H_{10}N_2F_6$ requires C, 52·5; H, 3·1; F, 35·6%). The m. p. of this compound was not depressed in admixture with the product obtained by acid treatment of the hydrazo-derivative prepared from 3-nitrobenzotrifluoride (Cartwright and Tatlow, unpublished results).

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