Further Investigations of Trifluoromethyldiphenyl Derivatives.

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The preparations and some reactions of 2-, 3-, and 4-trifluoromethyldiphenyl are described. 2 : 2′-, 3 : 3′-, and 4 : 4′-Bistrifluoromethyldiphenyl have been made by Ullmann reactions on the corresponding iodobenzotrifluorides. The symmetrical compounds have been characterised by hydrolysis and by nitration to give known diphenyl derivatives.

IN an earlier communication (Pettit and Tatlow, *J.*, 1951, 3459), 3-trifluoromethyldiphenyl, 4 : 4′-dinitro-2 : 2′- and -3 : 3′-bistrifluoromethyldiphenyl and some of their derivatives were described. Since that publication, Ross and Kuntz (*J. Amer. Chem. Soc.*, 1952, **74**, 1297) have reported the stepwise reduction of 2 : 2′-dinitro-4 : 4′-bistrifluoromethyldiphenyl to the 2 : 2′-diamino-compound *via* cinnoline intermediates, and the deamination of the diamine to give 4 : 4′-bistrifluoromethyldiphenyl. The last-named compound has also been prepared by Markarian (*ibid.*, p. 1858) from *p*-trifluoromethylphenylmagnesium bromide by the action of silver bromide. 2 : 2′ : 4 : 4′- and 3 : 3′ : 5 : 5′-Tetrakistrifluoromethyldiphenyl were described by Ross, Markarian, and Schwarz (*ibid.*, 1953, **75**, 4967). We now report the preparation and some reactions of the hitherto unknown 2- and 4-trifluoromethyldiphenyl, and of 2 : 2′-, 3 : 3′-, and 4 : 4′-bistrifluoromethyldiphenyl.

The starting materials used in this work, which were prepared by modifications of established routes, included *o*-nitrobenzotrifluoride (cf. Maginnity and Gaulin, *ibid.*, 1951, **73**, 3579), *p*-nitrobenzotrifluoride [prepared from 3-amino-4-nitrobenzotrifluoride (Pouterman and Girardet, *Helv. Chim. Acta*, 1947, **30**, 107) by diazotisation and reaction with hypophosphorous acid], and *o*-, *m*-, and *p*-iodobenzotrifluoride (cf. Finger and Kalinowski, *Trans. Illinois Acad. Sci.*, 1944, **37**, 66; *Chem. Abs.*, 1945, **39**, 1146 : Jones, *J. Amer. Chem. Soc.*, 1947, **69**, 2346).

The three trifluoromethyldiphenyls were made by homolytic aromatic substitution reactions *via* the corresponding trifluoromethylbenzenediazo-compounds. During the diazotisation of *o*-aminobenzotrifluoride a little 2 : 2′-bistrifluoromethyldiazoaminobenzene was formed. 2-Trifluoromethyldiphenyl was prepared from the diazonium salt solution by the method of Elks, Haworth, and Hey (*J.*, 1940, 1284). Hydrolysis of this diphenyl with concentrated sulphuric acid (Le Fave, *J. Amer. Chem. Soc.*, 1949, **71**, 4148) yielded 9-oxofluorene, presumably by cyclisation of diphenyl-2-carboxylic acid, [a reaction which is known to proceed readily in the presence of concentrated sulphuric acid (Weger and Döring, *Ber.*, 1903, **36**, 878] or of its acid fluoride.

3-Trifluoromethyldiphenyl, of which a number of syntheses has been reported previously (Bradsher and Bond, *J. Amer. Chem. Soc.*, 1949, **71**, 2659; Pettit and Tatlow, *loc. cit.*), was made also in a manner similar to that which gave the 2-trifluoromethyl isomer. It was shown in the earlier work that the principal product of the mononitration of 3-trifluoromethyldiphenyl was 4-nitro-3′-trifluoromethyldiphenyl (*idem, loc. cit.*). A further examination of this reaction has shown that a second isomer, 2-nitro-3′-trifluoromethyldiphenyl, is also formed. Evidence about the structure of this isomer was provided by reduction to a crude amine, from which *m*-trifluoromethylbenzoic acid was obtained upon oxidation. This showed that the trifluoromethyl and the amino-group were on different rings. The structure of the compound was proved completely by hydrolysis of the trifluoromethyl group to carboxyl; the product was the known 2-nitrodiphenyl-3′-carboxylic acid (Adams and Cairns, *J. Amer. Chem. Soc.*, 1939, **61**, 2179). Further nitration, with nitric acid–sulphuric acid, of 2-nitro-3′-trifluoromethyldiphenyl yielded a trinitro-derivative, identical with the product which we have previously described (*loc. cit.*). This compound must therefore be 2 : 4 : 4′-trinitro-3′-trifluoromethyldiphenyl since it can be prepared also from 4 : 4′-dinitro-3-trifluoromethyldiphenyl, which was itself derived from both 4- and 4′-nitro-3-trifluoromethyldiphenyl. Hence the position of each nitro-group of the trinitro-derivative has been established separately.

4-Trifluoromethyldiphenyl was made from *p*-acetamidobenzotrifluoride which was converted into the *N*-nitroso-derivative with nitrous fumes; this was allowed to decompose in benzene (Bamberger, *Ber.*, 1897, **30**, 366; Haworth and Hey, *J.*, 1940, 361). Nitrosation of *p*-acetamidobenzotrifluoride was also effected by trifluoroacetic anhydride–ethyl nitrite, which can nitrosate reactive aromatic compounds (Bourne, Stacey, Tatlow, and Tedder, *J.*, 1952, 1695). In addition, 4-trifluoromethyldiphenyl was prepared by diazotisation, in aqueous trifluoroacetic acid (Pettit, Stacey, and Tatlow, *J.*, 1953, 3081), of *p*-aminobenzotrifluoride, followed by the stirring together of benzene and the aqueous acidic diazonium solution so formed. The last two syntheses are examples of general reactions which diazonium derivatives of trifluoroacetic acid and other perhalogenocarboxylic acids will undergo (Pettit and Tatlow, forthcoming publication). Nitration of 4-trifluoromethyldiphenyl gave 4-nitro-4′-trifluoromethyldiphenyl, which, on hydrolysis, afforded the known 4′-nitrodiphenyl-4-carboxylic acid.

When heated with copper bronze (Ullmann and Bielecki, *Ber.*, 1901, **34**, 2174), *o*-, *m*-, and *p*-iodobenzotrifluoride were converted into 2 : 2′-, 3 : 3′-, and 4 : 4′-bistrifluoromethyldiphenyl, respectively. Finger and Kalinowski (*loc. cit.*) have reported that *m*-iodobenzotrifluoride would not undergo the Ullmann reaction to form a diphenyl with copper bronze at 250—270° (presumably in a sealed tube). The sample of 2 : 2′-bistrifluoromethyldiphenyl so prepared was identical with that obtained by deamination of 4 : 4′-diamino-2 : 2′-bistrifluoromethyldiphenyl which had been made *via* a benzidine transformation on the hydrazo-compound obtained by reduction of *m*-nitrobenzotrifluoride (Cartwright and Tatlow, *J.*, 1953, 1994). On hydrolysis with sulphuric acid, 2 : 2′-bistrifluoromethyldiphenyl gave the expected 9-oxofluorene-4-carboxylic acid and, in addition, a neutral compound (*idem, loc. cit.*). This has now been identified as 9-oxo-4-trifluoromethylfluorene, since it gave an oxime and was hydrolysed further with sulphuric acid to the oxofluorenecarboxylic acid. 3 : 3′- (Bradsher and Bond, *loc. cit.*; Markarian, *loc. cit.*) and 4 : 4′-bistrifluoromethyldiphenyl (Ross and Kuntz, *loc. cit.*; Markarian, *loc. cit.*) gave, on hydrolysis, diphenyl-3 : 3′- and -4 : 4′-dicarboxylic acid, respectively. These acids were characterised as ester derivatives. In the cases of the trifluoromethyl- and bistrifluoromethyl-diphenyls, as in other series, hydrolysis of the trifluoromethyl groups (Le Fave, *loc. cit.*) is a useful aid to structural determinations.

Nitration of the symmetrical bistrifluoromethyldiphenyls gave the expected dinitro-compounds, all of which have been synthesised previously by other methods. The 2 : 2′-isomer gave 4 : 4′-dinitro-2 : 2′-bistrifluoromethyldiphenyl, and the 3 : 3′-isomer afforded 4 : 4′-dinitro-3 : 3′-bistrifluoromethyldiphenyl (Pettit and Tatlow, *loc. cit.*), whilst 2 : 2′-dinitro-4 : 4′-bistrifluoromethyldiphenyl (Bradsher and Bond, *loc. cit.*; Ross and Kuntz, *loc. cit.*) was obtained from the 4 : 4′-isomer.

EXPERIMENTAL

p-*Nitrobenzotrifluoride.*—3-Amino-4-nitrobenzotrifluoride (Pouterman and Girardet, *loc. cit.*) (25·1 g.), in glacial acetic acid (100 c.c.) and concentrated sulphuric acid (25 c.c.), was diazotised at 10° with saturated aqueous sodium nitrite. Hypophosphorous acid (30%; 80 c.c.) was added, and after 5 hr. at *ca.* 15° the mixture was heated to 100° for 15 min., cooled, and poured into ice-water. The precipitate was filtered off and distilled in steam to give *p*-nitrobenzotrifluoride (67%), m. p. 37—39°.

A similar reaction with 5-amino-2-nitrobenzotrifluoride gave the *o*-nitro-isomer (69%).

o-*Aminobenzotrifluoride.*—Reduction of a solution of *o*-nitrobenzotrifluoride (22·0 g.) in dioxan (100 c.c.) by hydrogen over Raney nickel in a stirred autoclave (20 atm.; 180°), gave, upon fractionation of the product, *o*-aminobenzotrifluoride (14·7 g.), b. p. 72—74°/21 mm. The b. p. is identical with that recorded by Jones (*loc. cit.*).

Preparation of 2-Trifluoromethyldiphenyl.—*o*-Aminobenzotrifluoride (24·4 g.) was diazotised in concentrated hydrochloric acid (45 c.c.) and water (25 c.c.) with aqueous sodium nitrite (40%). A small quantity of yellow solid separated; it was filtered off and recrystallised from light petroleum (b. p. 100—120°), giving 2 : 2′-*bistrifluoromethyldiazoaminobenzene*, m. p. 170—171·5° (Found : C, 50·8; H, 2·8. $C_{14}H_9N_3F_6$ requires C, 50·5; H, 2·7%). The filtrate, which contained 2-trifluoromethylbenzenediazonium chloride, was stirred at 0—5° with benzene (200 c.c.), and a solution of sodium acetate trihydrate (70 g.) in water (150 c.c.) was added slowly. Stirring was continued for 2 hr. at 0°, and then at 10—15° for a further 46 hr. The benzene layer was separated, washed with water, dried ($MgSO_4$), and evaporated to remove the solvent. Distillation of the residue at reduced pressure yielded a pale yellow liquid, b. p. 122—125°/23 mm., which solidified almost completely in an ice-bath. The few drops of syrupy material were removed by filtration through a cooled funnel. Redistillation of the residue afforded *2-trifluoromethyldiphenyl* (12·6 g.), b. p. 114°/19 mm., m. p. 15° (Found: C, 70·4; H, 4·2; F, 26·2. $C_{13}H_9F_3$ requires C, 70·3; H, 4·1; F, 25·6%).

Conversion of 2-*Trifluoromethyldiphenyl into* 9-*Oxofluorene*.—2-Trifluoromethyldiphenyl (0·58 g.) was stirred with concentrated sulphuric acid (0·7 c.c.) at 100° for 1 hr., after which time evolution of hydrogen fluoride appeared to have ceased. The residual black liquid was poured into water (30 c.c.), and the resultant yellow suspension was extracted with ether. The extracts were washed with sodium hydroxide solution and with water, dried ($MgSO_4$), and evaporated. The yellow residue, on recrystallisation from benzene–light petroleum (b. p. 60—80°), gave 9-oxofluorene (0·12 g.), m. p. and mixed m. p. 81—83° (Found: C, 86·4; H, 4·8. Calc. for $C_{13}H_8O$: C, 86·6; H, 4·5%). Weger and Döring (*loc. cit.*) recorded m. p. 83—84° for this compound.

Preparation of 3-*Trifluoromethyldiphenyl*.—*m*-Aminobenzotrifluoride was diazotised as for the *o*-isomer (no diazoamino-compound was formed) and by the procedure described above 3-trifluoromethyldiphenyl (39%), b. p. 115—118°/13 mm., was obtained. The product solidified on nucleation with a specimen of the material previously reported (Pettit and Tatlow, *loc. cit.*). Despite our earlier experience which suggested the contrary, this method is at least as satisfactory for the production of this compound as is that by using the nitrosoacetanilide (*idem, loc. cit.*).

Nitration of 3-*Trifluoromethyldiphenyl*.—A stirred solution of 3-trifluoromethyldiphenyl (22·5 g.) in glacial acetic acid (30 c.c.) was cooled to 0°, and a mixture of fuming nitric acid (6·2 c.c.; *d*, 1·5) and concentrated sulphuric acid (5·0 c.c.) was added. The reactants were heated slowly, finally being gently refluxed for 45 min., stirring being continued. When cool, the mixture was poured into water (250 c.c.), and the semi-solid mass was extracted with ether. After being washed with dilute sodium hydroxide solution and with water, the extract was dried ($MgSO_4$), and the ether was removed by distillation. The residue was dissolved in hot ethyl alcohol, and the solution was cooled to 0°. The crystals which separated were filtered off and washed with more cooled alcohol (10 c.c.) to give 4-nitro-3′-trifluoromethyldiphenyl (10·8 g.), m. p. 83—85° not depressed by a specimen (m. p. 86°) previously described (Pettit and Tatlow, *loc. cit.*). The filtrate was concentrated and the oil remaining was distilled to give (*a*) a small amount of 3-trifluoromethyldiphenyl (1·0 g.), b. p. 70—87°/1 mm., (*b*) a pale yellow liquid (10·1 g.), b. p. 118—121°/0·2—0·3 mm., and (*c*) material of higher b. p., which on recrystallisation afforded more 4-nitro-3′-trifluoromethyldiphenyl (2·4 g.), m. p. and mixed m. p. 85°. Fraction (*b*) very slowly crystallised; the solid was recrystallised from light petroleum (b. p. 60—80°), affording very pale yellow prisms of *2-nitro-3′-trifluoromethyldiphenyl*, m. p. 60—61·5° (Found: C, 58·4; H, 2·7; F, 21·8. $C_{13}H_8O_2NF_3$ requires C, 58·4; H, 3·0; F, 21·3%). The m. p. was depressed in admixture with the 4-nitro-isomer.

Hydrolysis of 2-*Nitro*-3′-*trifluoromethyldiphenyl*.—The nitro-compound (2·25 g.) and concentrated sulphuric acid (5·0 c.c.) were stirred and heated at 130—150° for 1 hr. in an open tube. Hydrogen fluoride was evolved and the reaction mixture darkened. Water (100 c.c.) was added to the cooled mixture, and the resultant white precipitate was recrystallised from aqueous ethyl alcohol, giving 2-nitrodiphenyl-3′-carboxylic acid (1·95 g.), m. p. 208—209° unchanged by sublimation under reduced pressure (Found: C, 64·3; H, 3·8. Calc. for $C_{13}H_9O_4N$: C, 64·2; H, 3·7%). The m. p. was undepressed in admixture with the specimen described below.

Preparation of Ethyl m-*Iodobenzoate* (*By Le Fave and Scheurer's process*; J. Amer. Chem. Soc., 1950, **72**, 2464).—*m*-Iodobenzotrifluoride (11·4 g.) and concentrated sulphuric acid (8·0 c.c.) were mechanically stirred, and heated on an oil-bath. At about 120° hydrogen fluoride was evolved, and this temperature was maintained for 45 min. The mixture was then heated under reflux with ethyl alcohol (50 c.c.) for 30 min., the solution was poured into water, neutralised with sodium hydrogen carbonate, and extracted with chloroform, and the extracts were dried ($MgSO_4$), evaporated, and distilled under reduced pressure to give ethyl *m*-iodobenzoate (6·9 g.), b. p. 164—165°/23 mm. Cohen and Raper (*J.*, 1904, 1271) recorded b. p. 165—166°/24 mm. for this compound.

Preparation of 2-*Nitrodiphenyl*-3′-*carboxylic Acid*.—The above ester (6·8 g.), when heated with *o*-bromonitrobenzene (6·4 g.) and activated copper bronze (12 g.), under the conditions described by Adams and Cairns (*loc. cit.*), yielded 2-nitrodiphenyl-3′-carboxylic acid (1·49 g.), m. p. 206—208° not depressed by the material prepared as described above.

Degradation of 2-Nitro-3′-trifluoromethyldiphenyl to m-*Trifluoromethylbenzoic Acid.*—2-Nitro-3′-trifluoromethyldiphenyl (0·690 g.) was reduced with granulated tin (4 g.), concentrated hydrochloric acid (15 c.c.), water (5 c.c.), and ethyl alcohol (5 c.c.). After being worked up in the usual way, an almost colourless syrup (0·540 g.) was obtained. This crude 2-amino-3′-trifluoromethyldiphenyl (0·430 g.) was oxidised in solution in concentrated sulphuric acid (2·0 c.c.) and water (5 c.c.) with potassium permanganate (3·44 g.). Isolation as already described (Pettit and Tatlow, *loc. cit.*) for a similar reaction afforded *m*-trifluoromethylbenzoic acid (0·100 g.), m. p. and mixed m. p. 103—104°.

Preparation of 2 : 4 : 4′-Trinitro-3′-trifluoromethyldiphenyl.—2-Nitro-3′-trifluoromethyldiphenyl (0·233 g.) was heated under reflux with concentrated sulphuric acid (1·0 c.c.) and concentrated nitric acid (1·0 c.c.) for 40 min. The cooled mixture was treated with water (20 c.c.) and extracted with ether. The extract was washed with aqueous sodium hydroxide and with water, and was then dried ($MgSO_4$). Evaporation of the solvent, followed by recrystallisation from ethyl alcohol, yielded 2 : 4 : 4′-trinitro-3′-trifluoromethyldiphenyl (0·231 g.), m. p. 152—154° not depressed in admixture with the trinitro-3-trifluoromethyldiphenyl previously reported (Pettit and Tatlow, *loc. cit.*).

Preparation of 4-Trifluoromethyldiphenyl.—(*a*) *p*-Acetamidobenzotrifluoride (Jones, *loc. cit.*) (5·0 g.) was dissolved in glacial acetic acid (25 c.c.) and treated with nitrous fumes at 10°. When the deep clear green colour had developed (*ca.* 4 hr.), the solution was poured into water, and the precipitate filtered off, dried on a porous plate, and stirred with benzene (50 c.c.) for 24 hr. at *ca.* 15°. The crystalline material remaining after this treatment was unchanged *p*-acetamidobenzotrifluoride (1·94 g.), m. p. 146—150°. After removal of the benzene, the residue was distilled at reduced pressure, and any *p*-acetamidobenzotrifluoride remaining removed by hydrolysis with aqueous-alcoholic hydrochloric acid. Recrystallisation of the crude product yielded *4-trifluoromethyldiphenyl* (1·5 g.), m. p. 70° (Found : C, 70·3; H, 4·2; F, 25·9. $C_{13}H_9F_3$ requires C, 70·3; H, 4·1; F, 25·6%).

(*b*) Trifluoroacetic anhydride (1·8 c.c.) was added to ethyl nitrite (0·95 c.c.) at the temperature of an ice–salt bath. After 5 min., dry *p*-acetamidobenzotrifluoride (1·48 g.) was added portionwise, with shaking between the additions. The solution so obtained was then stirred with benzene (25 c.c.) for 24 hr. at 10—15°. Volatile constituents were removed by distillation at 100° under slightly reduced pressure, and the residue was steam-distilled. The distillate was extracted with ether, and after being dried ($MgSO_4$) the extracts were evaporated. Recrystallisation of the crude material from aqueous ethyl alcohol gave 4-trifluoromethyldiphenyl (0·37 g.), m. p. and mixed m. p. 70°.

(*c*) *p*-Aminobenzotrifluoride (1·80 g.) was diazotised in trifluoroacetic acid (2·5 c.c.) and water (1·0 c.c.) with 40% aqueous sodium nitrite, and the diazonium solution was stirred with benzene (25 c.c.) for 24 hr. at 25°. The organic layer was then separated, washed with dilute sodium hydroxide solution (3 times) and with water, and then distilled, steam-distilled, and treated as above. On recrystallisation from aqueous ethyl alcohol, 4-trifluoromethyldiphenyl (0·41 g.), m. p. and mixed m. p. 70°, was obtained.

Nitration of 4-Trifluoromethyldiphenyl.—4-Trifluoromethyldiphenyl (0·92 g.), glacial acetic acid (5·0 c.c.), fuming nitric acid (0·30 c.c., *d*, 1·5), and concentrated sulphuric acid (0·50 c.c.) were heated under reflux for 30 min. Isolation as usual and recrystallisation from aqueous ethyl alcohol afforded *4-nitro-4′-trifluoromethyldiphenyl* (0·45 g.), m. p. 121—122° (Found : C, 58·7; H, 2·9. $C_{13}H_8O_2NF_3$ requires C, 58·4; H, 3·0%).

Hydrolysis of 4-Nitro-4′-trifluoromethyldiphenyl.—The nitro-compound (0·120 g.) was stirred for 45 min. with concentrated sulphuric acid (0·40 c.c.) at 120—130°. The product was poured into water and extracted with ether. Recrystallisation, from aqueous ethyl alcohol, of the residue obtained by evaporation of the extracts yielded 4-nitrodiphenyl-4′-carboxylic acid (0·035 g.), m. p. 338—340° (Found : C, 64·5; H, 4·1. Calc. for $C_{13}H_9O_4N$: C, 64·2; H, 3·7%). Grieve and Hey (*J.*, 1932, 1888) reported m. p. 340° for this acid.

Preparation of 2 : 2′-Bistrifluoromethyldiphenyl.—*o*-Iodobenzotrifluoride (Jones, *loc. cit.*) (11·9 g.) was refluxed with copper bronze (4·2 g.) for 12 hr. with occasional stirring. When cool, the inorganic material was filtered off, and washed several times with ether. The combined filtrates were evaporated and the residue was distilled at atmospheric pressure to give an almost colourless liquid (4·80 g.), b. p. 233—237°, which crystallised. Recrystallisation from aqueous ethyl alcohol afforded 2 : 2′-bistrifluoromethyldiphenyl, m. p. 32—33°, b. p. 236—

237° (Found: C, 58·2; H, 2·8; F, 39·3. Calc. for $C_{14}H_8F_6$: C, 57·9; H, 2·8; F, 39·3%). Nucleation by a crystal of this compound caused solidification of material previously obtained by deamination of 4 : 4′-diamino-2 : 2′-bistrifluoromethyldiphenyl (Cartwright and Tatlow, *loc. cit.*).

Action of Sulphuric Acid on 2 : 2′-*Bistrifluoromethyldiphenyl.*—2 : 2′-Bistrifluoromethyldiphenyl (0·88 g.) and concentrated sulphuric acid (0·9 c.c.) were heated at 100° for 1 hr. with vigorous stirring. The mixture was then treated with water (70 c.c.) and extracted with ether. The extract was washed with portions of dilute sodium hydroxide solution until the aqueous phase was colourless. After being washed with water, the ether was dried ($MgSO_4$) and evaporated. By recrystallisation of the residue from ethyl alcohol, 9-*oxo*-4-*trifluoromethylfluorene* (0·42 g.), m. p. 125—126°, was obtained (Found: C, 67·9; H, 2·7; F, 22·8. $C_{14}H_7OF_3$ requires C, 67·7; H, 2·8; F, 23·0%). This compound, on treatment with hydroxylamine, afforded the *oxime*, m. p. 165—166° (from aqueous ethyl alcohol) (Found: C, 63·6; H, 3·4. $C_{14}H_8ONF_3$ requires C, 63·9; H, 3·1%).

The alkaline washings of the ethereal phase were acidified with concentrated hydrochloric acid. A yellow precipitate formed, and was filtered off and recrystallised to give 9-oxofluorene-4-carboxylic acid (0·14 g.), m. p. and mixed m. p. 226—227° (Found: C, 75·2; H, 3·7. Calc. for $C_{14}H_8O_3$: C, 75·0; H, 3·6%). Graebe and Aubin (*Ber.*, 1887, **20**, 845) gave m. p. 227° for this compound.

Hydrolysis of 9-*Oxo*-4-*trifluoromethylfluorene.*—Hydrolysis of 9-oxo-4-trifluoromethylfluorene (0·060 g.) by 85% sulphuric acid (1·0 c.c.) during 1 hr. at 120—130°, afforded, after isolation as above, unchanged ketone (0·028 g.) and 9-oxofluorene-4-carboxylic acid (0·011 g.), m. p. and mixed m. p. 225—227°.

Nitration of 2 : 2′-*Bistrifluoromethyldiphenyl.*—2 : 2′-Bistrifluoromethyldiphenyl (0·91 g.) was stirred at room temperature with concentrated sulphuric acid (6·0 c.c.), and fuming nitric acid (*d* 1·5; 0·40 c.c.) was added slowly. After being stirred for 16 hr., the mixture was treated with water (40 c.c.) and extracted with ether. The extract was washed with dilute sodium hydroxide, and then with water, and was dried ($MgSO_4$). The solvent was evaporated and the residue recrystallised from aqueous ethyl alcohol, giving light yellow crystals of 4 : 4′-dinitro-2 : 2′-bistrifluoromethyldiphenyl (0·63 g.), m. p. 137·5—138·5° (Found: C, 44·3; H, 1·8. Calc. for $C_{14}H_6O_4N_2F_6$: C, 44·2; H, 1·6%). Pettit and Tatlow (*loc. cit.*) recorded m. p. 137·5° for this compound.

Preparation of 3 : 3′-*Bistrifluoromethyldiphenyl.*—*m*-Iodobenzotrifluoride (b. p. 176—178°; Finger and Kalinowski, *loc. cit.*, recorded b. p. 173°) (23·5 g.) was heated under gentle reflux with copper bronze (8·15 g.) for 19 hr. with occasional stirring. The product was treated as for the 2 : 2′-isomer above, to give an almost colourless liquid (8·79 g.), b. p. 231—242°, which crystallised. Recrystallisation of a sample from aqueous ethyl alcohol gave needles of 3 : 3′-bistrifluoromethyldiphenyl, m. p. 24·5—26°, b. p. 237—240° (Found: C, 58·2; H, 3·0; F, 39·2. Calc. for $C_{14}H_8F_6$: C, 57·9; H, 2·8; F, 39·3%). Bradsher and Bond (*loc. cit.*) cited b. p. 93—94°/3 mm.

Hydrolysis of 3 : 3′-*Bistrifluoromethyldiphenyl.*—Hydrolysis of 3 : 3′-bistrifluoromethyldiphenyl (1·13 g.) by concentrated sulphuric acid (0·7 c.c.) at 130—150° for 1 hr. yielded, by the usual method of isolation, diphenyl-3 : 3′-dicarboxylic acid (0·38 g.), m. p. 346—348°. Williamson and Rodebush (*J. Amer. Chem. Soc.*, 1941, **63**, 3018) recorded m. p. 350—352° for this compound. Unchanged 3 : 3′-bistrifluoromethyldiphenyl (0·48 g.) was recovered.

Esterification by Bülow and Reden's technique (*Ber.*, 1898, **31**, 2574) afforded the diethyl ester, m. p. 68°. Bülow and Reden reported m. p. 68° for this ester.

Nitration of 3 : 3′-*Bistrifluoromethyldiphenyl.*—3 : 3′-Bistrifluoromethyldiphenyl (1·40 g.) was stirred for 12 hr. at room temperature with concentrated sulphuric acid (10 c.c.) and fuming nitric acid (*d* 1·5; 0·50 c.c.). The mixture was worked up as in the case of the 2 : 2′-bistrifluoromethyl isomer, and on recrystallisation from ethyl alcohol, 4 : 4′-dinitro-3 : 3′-bistrifluoromethyldiphenyl (0·98 g.) was obtained, m. p. 180—181° [alone or in admixture with material prepared by an Ullmann reaction on 5-iodo-2-nitrobenzotrifluoride (Pettit and Tatlow, *loc. cit.*)] (Found: C, 44·5; H, 1·3. Calc. for $C_{14}H_6O_4N_2F_6$: C, 44·2; H, 1·6%).

Preparation of 4 : 4′-*Bistrifluoromethyldiphenyl.*—*p*-Iodobenzotrifluoride (2·30 g.) and copper bronze (0·78 g.) were gently refluxed for 24 hr. An ethereal solution of the product was filtered and evaporated; recrystallisation of the residue from aqueous ethyl alcohol afforded 4 : 4′-bistrifluoromethyldiphenyl (0·51 g.), m. p. 92—93° (Found: C, 58·1; H, 3·1; F, 38·7. Calc. for $C_{14}H_8F_6$: C, 57·9; H, 2·8; F, 39·3%). Ross and Kuntz (*loc. cit.*) recorded m. p. 93—94·5° for this compound, while Markarian (*loc. cit.*) cited 91—92°.

Hydrolysis of 4 : 4′-*Bistrifluoromethyldiphenyl.*—4 : 4′-Bistrifluoromethyldiphenyl (0·051 g.) was hydrolysed by concentrated sulphuric acid (0·4 c.c.) at 100° for 1 hr. By the usual method of extraction, diphenyl-4 : 4′-dicarboxylic acid (0·037 g.), which did not melt below 360° (cf. Doebner, *Annalen*, 1874, **172**, 109), was obtained. The crude acid was converted into the acid chloride by Work's method (*J.*, 1940, 1315). Methyl alcohol (1·0 c.c.) was added to the unpurified product, and the mixture was heated under reflux for 15 min. By recrystallisation from benzene, dimethyl diphenyl-4 : 4′-dicarboxylate (0·011 g.), m. p. 214°, was obtained (Found: C, 71·4; H, 4·9. Calc. for $C_{16}H_{14}O_4$: C, 71·1; H, 5·2%). Ullmann and Meyer (*Annalen*, 1901, **332**, 73) cited m. p. 214° for this ester.

Nitration of 4 : 4′-*Bistrifluoromethyldiphenyl.*—The diphenyl derivative (0·086 g.) was stirred for 1 hr. with concentrated sulphuric acid (2·0 c.c.) and fuming nitric acid (*d* 1·5; 0·30 c.c.). Treatment as in the case of the 2 : 2′-bistrifluoromethyl isomer afforded 2 : 2′-dinitro-4 : 4′-bistrifluoromethyldiphenyl (0·082 g.), m. p. 121·5—123° (after recrystallisation from ethyl alcohol) (Found: C, 44·5; H, 1·7. Calc. for $C_{14}H_6O_4N_2F_6$: C, 44·2; H, 1·6%). Bradsher and Bond (*loc. cit.*) recorded m. p. 121—122°, and Ross and Kuntz (*loc. cit.*), m. p. 124—125°, for this compound.

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