Aromatic Polyfluoro-compounds. Part XXXIII.[1] The Synthesis of Some Derivatives of 1,2,3,4-Tetrafluoroacridine

By P. L. Coe, A. E. Jukes, and J. C. Tatlow

2,3,4,5,6-Pentafluoro-2′-nitrodiphenylmethanol has been prepared, oxidised to the corresponding ketone, and reduced to the amino- and nitroso-derivatives. Chemical, pyrolytic, and photolytic cyclisations of these compounds to derivatives of 1,2,3,4-tetrafluoroacridine are described.

A synthesis of 1,2,3,4-tetrafluoroacridine was undertaken to study the effect of fluorine substitution on the known pharmacological properties of acridine derivatives.

The methods available for synthesis of acridines have been reviewed;[2] though they mostly involve electrophilic ring closures which are unlikely to take place in the fluoro-aromatic series, two appeared feasible with the compounds available to us as starting materials. One involved ring closure by elimination of fluoride ion using an amino-group as a nucleophile,[3] and the second by the pyrolysis of a suitable diphenylmethanol.[4]

The starting material for both methods was 2,3,4,5,6-pentafluoro-2′-nitrodiphenylmethanol (I) which was prepared in surprisingly good yield by the reaction of pentafluorophenylmagnesium bromide with *o*-nitrobenzaldehyde. No products attributable to reaction of the Grignard reagent with the nitro-group could be detected. Oxidation of the nitrodiphenyl methanol (I) with chromium trioxide afforded 2,3,4,5,6-pentafluoro-2′-nitrodiphenylketone (II).

Reduction of 2,3,4,5,6-pentafluoro-2′-nitrodiphenylmethanol (I) to the corresponding amino-compound proved to be complex. Several reducing agents were investigated under a variety of reaction conditions. Reduction of the nitro-group with tin and hydrochloric acid gave different products depending on the amount of tin used. With a 40% excess of tin and aqueous ethanolic hydrochloric acid the major product was 2-amino-2′,3′,4′,5′,6′-pentafluorodiphenylmethane (III) with a small amount of 1,2,3,4-tetrafluoroacridan (VII) as the minor component; the mechanism by which the latter is formed is uncertain. Using a 25% excess of tin under slightly different conditions the sole product was 2-amino-2′,3′,4′,5′,6′-pentafluorodiphenylmethanol (IV). Thus, it appears that the formation of the diphenylmethane (III) using a 40% excess of tin occurs in a stepwise process, but that the amino-group once present accelerates the dehydroxylation, since the reaction times for each reduction were almost the same and some aminodiphenylmethanol would be expected from the reaction with a 40% excess of tin. Parallel reductions were carried out using 2,3,4,5,6-pentafluorodiphenylmethanol[5] and 2-amino-2′,3′,4′,5′,6′-pentafluorodiphenylmethanol. In the first case, two products, namely, 1,2-diphenyl-1,2-bispentafluorophenylethane and 2,3,4,5,6-pentafluorodiphenylmethane, were obtained after 10 hr. reaction, whereas the aminodiphenylmethanol gave a smooth dehydroxylation to the aminodiphenylmethane (III) in only 3 hr.

In an attempt to determine whether 1,2,3,4-tetrafluoroacridan (VII) arose from cyclisation of an intermediate in the reduction of 2,3,4,5,6-pentafluoro-2′-nitrodiphenylmethanol (I), the latter was reduced with zinc and aqueous ethanolic ammonium chloride to yield 2′-hydroxylamino- (V) and 2,3,4,5,6-pentafluoro-2′-nitrosodiphenylmethanol (VI). However, neither of these compounds could be cyclised to the acridan (VII) which was finally prepared in reasonable yield from 2-amino-2′,3′,4′,5′,6′-pentafluorodiphenylmethane (III). The free amine itself failed to cyclise under a variety of conditions, *e.g.*, with potassium carbonate in dimethyl formamide,[3] but the cyclisation was achieved by formation of a sodio-derivative of the amine by reaction with sodium hydride thus producing a more powerful nucleophile. This method has previously been used to make highly fluorinated di- and tri-phenylamines.[6]

Pyrolysis of nitrodiphenylmethanols has been used to prepare derivatives of acridone[4] and there has been considerable discussion of the mechanism of the reaction.[2] Pyrolysis of 2,3,4,5,6-pentafluoro-2′-nitrodiphenylmethanol (I) was attempted at varying temperatures, with and without solvent. At 165° in dry liquid paraffin a pale green crystalline compound was formed which was shown by analysis and ultraviolet (u.v.) spectroscopy to be 3-pentafluorophenylanthranil (VIII). The formation of anthranils is well known and the subject has recently been reviewed.[7] The mechanism of the reaction appears to be as shown in Scheme 1. Evidence to support this mechanism came from the reaction of the nitrophenylmethanol (I) with sulphuric acid, which proceeded rapidly at 100°, and also from the ready decomposition in boiling toluene of the toluene-*p*-sulphonate ester of the diphenylmethanol to give the anthranil (VIII). In each of these cases the group on the benzylcarbon, OH_2^+ and ^-OTs, respectively, is a better leaving group than ^-OH and nucleophilic displacement should thus be facilitated. This type of behaviour has recently been observed with some chlorophenylmethanols.[8] 3-Pentafluorophenylanthranil (VIII) was

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[1] Part XXXII, J. Burdon, P. L. Coe, and C. R. Marsh, *Tetrahedron*, 1966, **22**, 1183.

[2] A. Albert, "The Acridines," Edward Arnold and Co., 1951.

[3] R. I. Fryer, J. Earley, and L. H. Sternbach, *J. Chem. Soc.*, 1963, 4979.

[4] A. Kliegl, *Ber.*, 1909, **42**, 591.

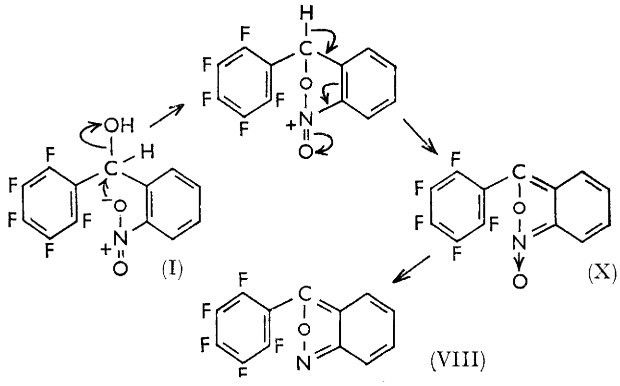
[5] A. K. Barbour, M. W. Buxton, P. L. Coe, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1961, 808.

[6] J. Burdon, J. Castaner, and J. C. Tatlow, *J. Chem. Soc.*, 1964, 5077.

[7] J. D. Loudon and G. Tennant, *Quart. Rev.*, 1964, **18**, 389.

[8] W. B. Dickinson, *J. Amer. Chem. Soc.*, 1964, **86**, 3580.

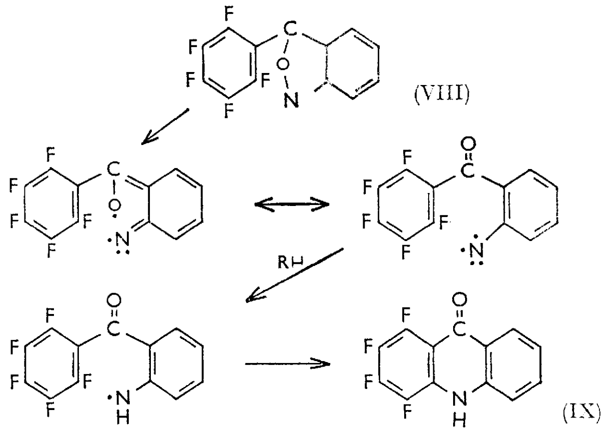
also synthesised by an alternative method from 2,3,4,5,6-pentafluoro-2′-nitrodiphenyl ketone (II) by reduction with zinc in ethanolic ammonium chloride, a method used previously to prepare anthranils.[9]



Scheme 1

Pyrolysis of the nitropentafluorodiphenylmethanol (I) at 210° afforded two products in almost equal amounts. The first was 3-pentafluorophenylanthranil (VIII) and the second was shown to be 1,2,3,4-tetrafluoroacridone (IX) (see below). Pyrolysis at 300—360° in dry liquid paraffin gave a reasonable yield (*ca.* 35%) of a pale yellow compound which did not melt below 360°. Analysis was consistent with a compound $C_{13}H_5F_4NO$, the compound showed a blue fluorescence in ethanol and its u.v. spectrum was almost identical to that of acridone.[10] The infrared (i.r.) spectrum showed a strong band at 1610 cm.$^{-1}$ attributable to a carbonyl group. Thus the compound showed the expected properties of 1,2,3,4-tetrafluoroacridone (IX).

The mechanism of the reaction by which the acridone is formed is interesting since, by similar pyrolysis of 2-nitrodiphenylmethanol, acridone itself is formed.[4] Mechanisms for the latter pyrolysis have been put forward[2] but no satisfactory explanation of the ring-closure step has been made. Clearly, in our reaction the anthranil (VIII) appeared to be an intermediate and when the pure compound was pyrolysed only, the expected, 1,2,3,4-tetrafluoroacridone (IX) was obtained. The origin of the anthranil, we suggested previously, is by intramolecular nucleophilic attack of the nitro-group on the benzylic carbon atom to yield the anthranil-*N*-oxide (X). We found that the latter (prepared from the nitrodiphenylmethanol (I) and concentrated sulphuric acid) on pyrolysis gave a mixture of the anthranil (VIII) and the acridone (IX). The ring closure step we suggest is free-radical in character, possibly *via* a nitrene. Similar ring closures from reactions of nitroso- and nitro-compounds with triethyl phosphite have been recently reported and a nitrene mechanism has been suggested.[11] Such a mechanism explains why the hydrocarbon and the fluorocarbon derivatives behave in the same way under identical conditions, which seems unlikely for an ionic process. The suggested mechanism of the reaction is outlined in Scheme 2. When this reaction was first carried out there had been no report of free-radical displacement of fluorine from polyfluoro-aromatic compounds, but subsequently the formation of diphenyls from pentafluorophenyl derivatives and aryl peroxides has been established.[12] If the N–O bond in the fluoroanthranil (VIII) will break thermally, it was felt that it should also do so photochemically. Therefore, a light petroleum solution of the anthranil was photolysed and a reasonable yield of 2-amino-2′,3′,4′,5′,6′-pentafluorodiphenyl ketone (XII) was obtained which was identical to a sample prepared by the hydrogenation of 2,3,4,5,6-pentafluoro-2′-nitrodiphenyl ketone (II). The formation of (XII), involving hydrogen abstraction, suggests the presence of free radicals in this reaction. In view of the ready photochemical decomposition of the anthranil, a photolysis of 2,3,4,5,6-pentafluoro-2′-nitrodiphenylmethanol in light petroleum was carried out to see if any further evidence for the reaction mechanism could be found. Three products were obtained; 3-pentafluorophenylanthranil (VIII) and 2,3,4,5,6-pentafluoro-2′-nitrodiphenyl ketone (II); both identical with authentic specimens, and a new red compound shown to be 2,3,4,5,6-pentafluoro-2′-nitrosodiphenyl ketone (XI). The photolysis of *o*-nitrobenzaldehyde is well known[13] and a mechanism of the reaction proposed;[14] application of a similar mechanism to our reaction is shown in Scheme 3. However, no 3-pentafluorophenylanthranil-*N*-oxide (X) or 1,2,3,4-tetrafluoroacridone could be isolated.



Scheme 2

Some reactions of the acridone were studied, particularly attempts to prepare 1,2,3,4-tetrafluoroacridine.

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[10] "Heterocyclic Compounds," 5- and 6-Membered Ring Compounds, with Nitrogen and Oxygen," Interscience Publishers Inc., New York, 1962.

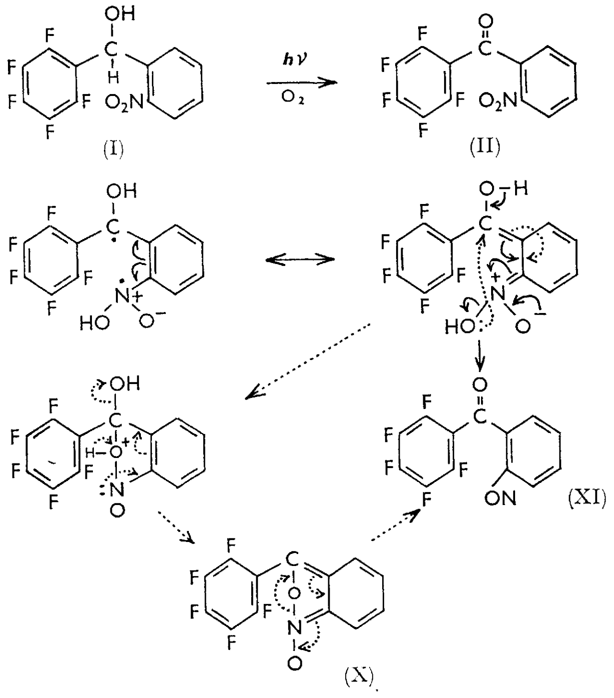
[11] J. I. G. Cadogan, M. Cameron-Wood, R. K. Mackie, and R. J. G. Searle, *J. Chem. Soc.*, 1965, 4831.

[12] P. A. Claret, J. Coulson, and G. H. Williams, *Chem. and Ind.*, 1965, 228; J. Burdon, J. G. Campbell, and J. C. Tatlow, to be published.

[13] G. Ciamician and P. Selber, *Ber.*, 1901, **34**, 2040.

[14] P. B. De Mayo and S. T. Reid, *Quart. Rev.*, 1961, **15**, 415.

Phosphorus oxychloride gave a good yield of 9-chloro-1,2,3,4-tetrafluoroacridine (XIII). Hydrogenation of the latter and also reduction of the acridone with aluminium amalgam followed by re-oxidation with ferric chloride, a known method of acridine synthesis,[2] gave a pale yellow compound, which had a u.v. spectrum very similar to that of acridine but which on analysis gave consistently slightly high values for carbon (*ca.* 1·5% high). The indications are that the compound is in fact 1,2,3,4-tetrafluoroacridine contaminated with a compound with very similar properties, *e.g.*, same R_f values on thin-layer chromatography.



Scheme 3. Path A ——, Path B · · · ·

The reactions reported above constitute a useful method of ring closure in the fluoro-aromatic series and further studies on related syntheses will be reported later.

EXPERIMENTAL

2,3,4,5,6-*Pentafluoro*-2′-*nitrodiphenylmethanol* (I).—Pentafluorophenylmagnesium bromide (from C_6F_5Br 10·1 g.) prepared as previously described[15] in ether (100 c.c.) was added slowly at 0° to *o*-nitrobenzaldehyde (5·7 g.) in dry ether (50 c.c.). After being stirred for 16 hr. at 15° the mixture was hydrolysed with 4N-hydrochloric acid (100 c.c.), the ethereal layer and the combined ethereal extracts (2 × 25 c.c.) of the aqueous layer were dried ($MgSO_4$) and the ether distilled off. The dark brown residue was distilled *in vacuo* to yield a syrupy liquid (10·2 g.), b. p. 144—148°/0·01 mm. Trituration with light petroleum (b. p. 40—60°) and crystallisation of the resulting crystals from the same solvent gave 2,3,4,5,6-*pentafluoro*-2′-*nitrodiphenylmethanol* (7·4 g.), m. p. 60—62° (Found: C, 48·9; H, 2·2. $C_{13}H_6F_5NO_3$ requires C, 48·9; H, 1·9%). The diphenylmethanol (1·0 g.) and toluene-*p*-sulphonyl chloride (0·653 g.) in pyridine (4 c.c.) were kept at −40° for 1·25 hr., after warming slowly to 15° the mixture was maintained at this temperature for 15 hr. The solid formed on pouring into ice–water was filtered off and crystallised from light petroleum to give 2,3,4,5,6-*pentafluoro*-2′-*nitrodiphenylmethyl toluene*-p-*sulphonate* (1·0 g.), m. p. 98—99° (Found: C, 50·7; H, 2·8. $C_{20}H_{12}F_5NO_5S$ requires C, 50·7; H, 2·5%).

2,3,4,5,6-*Pentafluoro*-2′-*nitrodiphenyl ketone* (II).—Chromium trioxide (0·6 g.) and 2,3,4,5,6-pentafluoro-2′-nitrodiphenylmethanol (2·0 g.) in glacial acetic acid (15 c.c.) were kept at 15° for 4 days. The mixture was poured into water and the aqueous layer extracted with ether (4 × 40 c.c.). The combined extracts were dried ($MgSO_4$) and the ether distilled to give 2,3,4,5,6-*pentafluoro*-2′-*nitrodiphenylketone* (1 g.), m. p. 65—66° (from ethanol) (Found: C, 49·1; H, 1·4. $C_{13}H_4F_5NO_3$ requires C, 49·2; H, 1·3%).

Reduction of 2,3,4,5,6-*Pentafluoro*-2′-*nitrodiphenylmethanol with Tin and Hydrochloric Acid*.—(*a*) 40% *excess of tin*. The diphenylmethanol (4 g.) in aqueous ethanol (50 c.c.), granulated tin (3 g.), and concentrated hydrochloric acid (7 c.c.) were heated under reflux for 2 hr. After 1 hr., more hydrochloric acid (5 c.c.) was added. The mixture was steam-distilled under both acid conditions to remove any unreacted starting material (none obtained), and again on making alkaline (KOH). The distillate from the alkaline solution was extracted with ether (10 × 40 c.c.), the combined extracts dried ($MgSO_4$), and the ether distilled to yield a yellow oil, which on distillation *in vacuo* gave 2-*amino*-2′,3′,4′,5′,6′-*pentafluorodiphenylmethane* (III) (0·9 g.), b. p. 126—128°/0·05 mm. which crystallised on standing to fine needles m. p. 86—87° from light petroleum (Found: C, 57·2; H, 2·8. $C_{13}H_8F_5N$ requires C, 57·1; H, 2·9%). The amine gave an N-*benzoate* derivative, m. p. 158—159° (Found: C, 63·5; H, 2·8. $C_{20}H_{12}F_5NO$ requires C, 63·7; H, 3·2%).

The residue from the steam distillation was extracted with ether (3 × 50 c.c.) and the combined ethereal extracts washed with water and dried ($MgSO_4$). Distillation of the ether afforded a pale yellow solid (0·3 g.) which on crystallisation from light petroleum gave 1,2,3,4-tetrafluoroacridan identical to an authentic sample (see below).

(*b*) 25% *excess of tin*. The diphenylmethanol (4 g.) in ethanol (30 c.c.), granulated tin (2·8 g. 25% excess), and concentrated hydrochloric acid (9 c.c.) were heated under reflux. More hydrochloric acid (10 c.c.) was added over 2·5 hr. to maintain a gentle reaction. The solution was made alkaline and extracted with benzene (6 × 50 c.c.). The combined extracts were dried ($MgSO_4$) and the solvent evaporated. The residue was distilled *in vacuo* to yield a green liquid, b. p. 118—122°/0·01 mm., which solidified on standing. Crystallisation from light petroleum gave 2-*amino*-2′,3′,4′,5′,6′-*pentafluorodiphenylmethanol* (IV) (1·0 g.), m. p. 107—108° (Found: C, 53·8; H, 2·8. $C_{13}H_8F_5NO$ requires C, 54·0; H, 2·8%). The i.r. spectrum showed peaks at 3450, 3400, 1620 cm.$^{-1}$ ($-NH_2$), 3180 cm.$^{-1}$ (–OH).

The aminodiphenylmethanol was characterised as its N-*benzoylbenzoate* derivative, m. p. 150—151° (Found: C, 65·2; H, 3·0. $C_{27}H_{16}F_5NO_3$ requires C, 65·2; H, 3·2%).

Reductive Dehydroxylation of 2,3,4,5,6-*Pentafluorodiphenylmethanol*.—(*a*) *With tin and hydrochloric acid*. The pentafluorodiphenylmethanol[5] (2·1 g.), granulated tin

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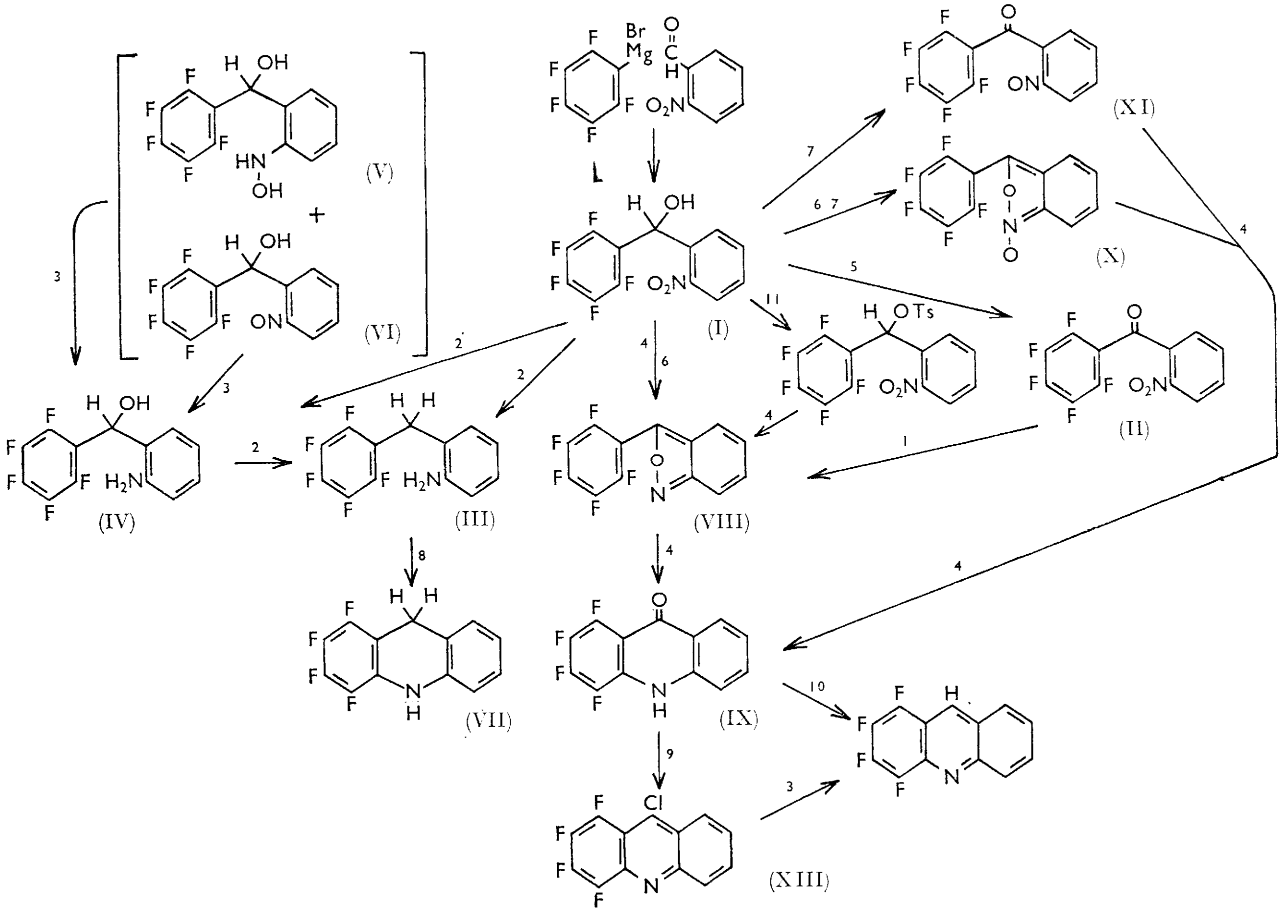
[15] E. Nield, R. Stephens, and J. C. Tatlow, *J. Chem. Soc.*, 1959, 166.

(6 g.), and concentrated hydrochloric acid (4 c.c.) in ethanol (50 c.c.) were heated under reflux for 10 hr. Most of the ethanol was distilled off and the residual solution filtered. A white solid (0·9 g.) was obtained which gave 1,2-*diphenyl-1,2-bispentafluorophenylethane* (0·9 g.), m. p. 175—176° from light petroleum [Found: C, 60·9; H, 2·5. $C_{26}H_{12}F_{10}$ requires C, 60·7; H, 2·3%. *M* (Rast) 484 required 514.] The proton magnetic resonance spectrum showed two groups of peaks centred at 5·6 and 7·2 p.p.m. downfield from tetramethylsilane (external) in integral ratio 1 : 5, consistent with the proposed structure. The distillate and filtrate from the reaction mixture were neutralised with potassium hydroxide and extracted with ether (4 × 100 c.c.). The combined ethereal layers were dried ($MgSO_4$) and distilled to give an oil (0·3 g.) from which was obtained a small quantity of 2,3,4,5,6-pentafluorodiphenylmethane (see below).

(*b*) *By catalytic hydrogenation.* Pentafluorodiphenylmethanol (0·7 g.) in ethanol (30 c.c.) was shaken in an atmosphere of hydrogen, with palladium (10%) on carbon as catalyst for three days. After filtration the ethanol was distilled off to give an oil. Distillation of the oil gave a clear viscous liquid which solidified on cooling to give 2,3,4,5,6-*pentafluorodiphenylmethane* (0·25 g.), m. p. 50—51° (Found: C, 60·5; H, 3·1. $C_{13}H_7F_5$ requires C, 60·5; H, 2·7%).

Reductive Dehydroxylation of 2-Amino-2′,3′,4′,5′,6′-pentafluorodiphenylmethanol.— 2-Amino-2′,3′,4′,5′,6′-pentafluorodiphenylmethanol (0·4 g.) and granulated tin (3 g.) were heated in ethanol (15 c.c.) under reflux for 3 hr., concentrated hydrochloric acid (10 c.c.) was slowly added during the reaction. The mixture was made alkaline (NaOH), cooled, and extracted with ether (4 × 100 c.c.). The ethereal solution was dried ($MgSO_4$) and evaporated to leave a brown oil. Crystallisation from light petroleum afforded 2-amino-2′,3′,4′,5′,6′-pentafluorodiphenylmethane (0·2 g.), m. p. 85—87° identical with an authentic specimen.

Reduction of 2,3,4,5,6-Pentafluoro-2′-nitrodiphenylmethanol with Zinc Dust and Ammonium chloride.—Zinc dust (1·3 g.) was added in small portions over 30 min. to 2,3,4,5,6-pentafluoro-2′-nitrodiphenylmethanol (2 g.) and ammonium chloride (0·4 g.) in 75% aqueous ethanol (50 c.c.) at 0°. After stirring at 0° for 1·5 hr. the zinc oxide was filtered off and the filtrate poured into water (250 c.c.) containing sodium chloride (80 g.). The solution was extracted with ether (6 × 50 c.c.), and the ethereal extracts were dried



Scheme 4. Summary of reactions

(1) Zn, aq.NH_4Cl. (2) Sn, HCl. (3) H_2, Pd. (4) Heat. (5) CrO_3, HOAc. (6) H_2SO_4. (7) *h*ν. (8) NaH, dioxan. (9) $POCl_3$. (10) Al–Hg, ag.EtOH. (11) $MeC_6H_4SO_2Cl$, C_6H_5N.

($MgSO_4$) and distilled. Crystallisation from light petroleum afforded 2,3,4,5,6-*pentafluoro-2′-hydroxylaminodiphenylmethanol* (V) (1·4 g.), m. p. 121—122° (Found: C, 50·5; H, 2·5. $C_{13}H_8F_5NO_2$ requires C, 51·2; H, 2·6%).

Concentration of the mother-liquors gave a second crystalline compound, which on repeated recrystallisation from light petroleum gave 2,3,4,5,6-*pentafluoro-2′-nitrosodiphenylmethanol* (VI) (0·19 g.), m. p. 180—181° (Found: C, 51·8; H, 2·2. $C_{13}H_6F_5NO_2$ requires C, 51·5; H, 2·0%).

The nitroso-compound (0·16 g.), was heated in acetic anhydride (15 c.c.) for 5 hr. Most of the acetic anhydride was distilled off and sodium hydrogen carbonate solution (100 c.c.) was added and the aqueous layer extracted with ether. The ether was dried ($MgSO_4$) and distilled, recrystallisation of the residue from light petroleum gave 2,3,4,5,6-*pentafluoro-2′-nitrosodiphenylmethyl acetate* (0·1 g.), m. p. 140—141° (Found: C, 53·1; H, 2·4. $C_{15}H_8F_5NO_3$ requires C, 52·2; H, 2·3%).

Reduction of 2,3,4,5,6-*Pentafluoro-2′-nitrosodiphenylmethanol*.—The nitroso-compound (0·14 g.) in light petroleum (10 c.c.) was shaken with 10% palladised charcoal in an atmosphere of hydrogen until the theoretical quantity of hydrogen was taken up. Filtration and evaporation of the filtrate gave 2-amino-2′,3′,4′,5′,6′-pentafluorodiphenylmethanol (0·02 g.), identical with an authentic sample.

1,2,3,4-*Tetrafluoroacridan*.—2-Amino-2′,3′,4′,5′,6′-pentafluorodiphenylmethane (1·04 g.) and sodium hydride (0·8 g.) were heated together in dry dioxan (25 c.c.) for 5 hr. and left at 15° for 10 hr. The excess sodium hydride was destroyed by careful addition of water and then the whole was poured into water (250 c.c.). The mixture was extracted continuously with ether for 10 hr., the ethereal layer dried ($MgSO_4$), and evaporated to leave an oily residue. Separation by alumina chromatography gave a brown gum, which on recrystallisation from benzene–light petroleum gave 1,2,3,4-*tetrafluoroacridan* (VII) (0·33 g.), m. p. 171—172° (Found: C, 61·8; H, 2·7. $C_{13}H_7F_4N$ requires C, 61·7; H, 2·8%).

Pyrolysis of 2,3,4,5,6-*Pentafluoro-2′-nitrodiphenylmethanol*.—(*a*) *At* 165°. The diphenylmethanol (I) (4·6 g.) in dry liquid paraffin (30 c.c.) was heated at 165° for 45 min. On cooling the mixture was passed down a column of silica gel (28 × $1\frac{3}{4}$ in.) using light petroleum as eluent: liquid paraffin only was eluted. Elution with benzene afforded an oil (3·0 g.). Crystallisation from light petroleum gave unreacted starting material (1·8 g.). The mother-liquors were re-chromatographed on an alumina column (15 × $1\frac{1}{4}$ in.) using benzene as eluent. An orange oil (0·3 g.) which crystallised on standing was shown to be 3-pentafluorophenylanthranil (VIII) (see below), elution of a slower moving band gave further unreacted starting material (0·4 g.).

(*b*) *At* 210°. The nitrodiphenylmethanol (I) (1·3 g.) was heated alone at 210° for 15 min. Chromatography as in (*a*) afforded 3-pentafluorophenylanthranil (VIII) (0·2 g.), (see below), unchanged starting material (I) (0·4 g.), and a new compound (0·22 g.) shown to be 1,2,3,4-tetrafluoroacridone (IX) (see later).

(c) *At* 360°. The nitrodiphenylmethanol (I) (2 g.) in liquid paraffin (30 c.c.) was slowly heated to 220° to obtain a clear solution. Heating was continued to raise the temperature to 360° over 30 min., at 310° yellow fumes were observed, the reaction mixture was slowly cooled to 300° over 35 min. and then rapidly cooled to room temperature. The mixture was poured into light petroleum (100 c.c.), filtered, and the residue washed with light petroleum to give a dark brown powder (1·5 g.). Sublimation *in vacuo* at 250°/8 mm. gave 1,2,3,4-*tetrafluoroacridone* (IX) (0·6 g.), m. p. >360° with decomposition (Found: C, 58·4; H, 1·9; N, 5·4. $C_{13}H_5F_4NO$ requires C, 58·4; H, 1·9; N, 5·2%).

The i.r. spectrum showed strong bands at 1610 cm.$^{-1}$ (C=O) and 1590, 1510 cm.$^{-1}$ (C_6F_4); the u.v. spectrum showed maxima at $\lambda_{max.}$ (EtOH), 2480, 2960, 3750, and 3890 Å (ε 51,200, 3160, 3890, 7700, and 7400.)

3-*Pentafluorophenylanthranil*.—(*a*) Zinc dust (1·5 g.) was added in small portions over $\frac{1}{2}$ hr. to a stirred solution of 2,3,4,5,6-pentafluoro-2′-nitrodiphenyl ketone (II) (0·9 g.) and ammonium chloride (0·6 g.) in aqueous ethanol (60 c.c. 1 : 4 v/v) at 0°. After being stirred for $1\frac{1}{2}$ hr. at 0° the mixture was filtered and the residue washed with ether. The filtrate and ether were washed with water (200 c.c.) and the aqueous phase further extracted with ether (4 × 60 c.c.). The combined extracts were dried ($MgSO_4$) and the ether distilled to give a yellow oil. The oil was dissolved in 1 : 1 benzene–carbon tetrachloride to leave a solid (0·055 g.) shown to be 1,2,3,4-tetrafluoroacridone (IX). The solution was chromatographed on a column of silica gel (15 × $1\frac{1}{4}$ in.) and two bands developed.

The first band gave a small quantity of an unidentified green oil, the second band eluted with benzene gave an orange gum (0·4 g.), which crystallised on standing. Recrystallisation from a light petroleum–ether mixture gave 3-*pentafluorophenylanthranil* (VIII) (0·3 g.), m. p. 114° (Found: C, 54·7; H, 1·5. $C_{13}H_4F_5NO$ requires C, 54·7; H, 1·4%).

(*b*) 70% Sulphuric acid (60 c.c.) was added to 2,3,4,5,6-pentafluoro-2′-nitrodiphenylmethanol (I) (1·6 g.), the mixture was warmed to 100° to obtain a clear solution *ca.* 1 min. The solution was shaken at 15° for 1·5 hr. and was then poured into water (500 c.c.). The aqueous layer was extracted with ether (5 × 100 c.c.), the combined ethereal extracts dried ($MgSO_4$), and the ether evaporated to give a dark brown tarry residue which was chromatographed on a silica gel column (22 × $1\frac{1}{4}$ in.) using benzene as eluent, to give 3-pentafluorophenylanthranil (VIII) (0·2 g.) identical with an authentic sample, and a tarry residue (0·6 g.) which was not investigated. In a similar experiment but using 50% sulphuric acid (0·5 g.) of the diphenylmethanol gave the anthranil (0·3 g.).

(*c*) 2,3,4,5,6-Pentafluoro-2′-nitrodiphenylmethyl toluene-*p*-sulphonate (0·65 g.) was heated in toluene (50 c.c.) under reflux for 2 hr. Ether (50 c.c.) was added and the organic layer washed with dilute sodium carbonate and then distilled under reduced pressure. The residual oil was chromatographed on a column of silica gel (7 × $\frac{3}{4}$ in.) in carbon tetrachloride–benzene (1 : 1). Evaporation of the first eluate and crystallisation of the residue afforded 3-pentafluorophenylanthranil (VIII) (0·2 g.), identified by i.r. spectroscopy.

Pyrolysis of 3-*Pentafluorophenylanthranil* (VIII).—The anthranil (VIII) (27 mg.) was heated in a small tube on an oil-bath at 250° for 15 min. The residue was dissolved in light petroleum (15 c.c.), the solution filtered and the residue sublimed to yield 1,2,3,4-tetrafluoroacridone (IX) (6·5 mg.).

3-*Pentafluorophenylanthranil*-N-*oxide*.—2,3,4,5,6-Pentafluoro-2′-nitrodiphenylmethanol (I) (0·5 g.) was melted and concentrated sulphuric acid (30 ml.) was added. The mixture was cooled in ice–water and shaken for 10 min. The deep red solution was poured into water (250 ml.)

and a yellow precipitate formed, which was dissolved in ether, and the aqueous layer extracted (5 × 100 c.c.) with ether. The combined ethereal layers were dried ($MgSO_4$), the ether removed, and the residual oil chromatographed on alumina (15 × $1\frac{1}{4}$ in. column) with benzene as solvent. A yellow band was rapidly eluted and removal of the solvent followed by crystallisation from acetone gave yellow-green crystals of 3-*pentafluorophenylanthranil*-N-*oxide* (X) (0·4 g.), m. p. 132—133° (with decomposition) (Found: C, 51·6; H, 1·5. $C_{13}H_4F_5NO_2$ requires C, 51·8; H, 1·3%); the u.v. spectrum showed maxima at $\lambda_{max.}$ (EtOH) 237 mμ (ε 16,600), $\lambda_{max.}$ 285 mμ (ε 7590), $\lambda_{max.}$ 313 mμ (ε 5890).

Pyrolysis of 3-*Pentafluorophenylanthranil*-N-*oxide*.—The *N*-oxide (X) (0·09 g.) was heated in a glass tube, fitted with an air condenser, at 250° for 20 min. The resulting dark mass was chromatographed on an alumina column (7 × $\frac{3}{4}$ in.) in ethanol as solvent. The second eluate possessing strong violet fluorescence was concentrated to yield 1,2,3,4-tetrafluoroacridone (IX) (0·02 g.), identified by u.v. and i.r. spectroscopy.

In a similar experiment the *N*-oxide (X) (0·2 g.) was heated in toleuene under reflux for 1·5 hr. to yield the acridone (IX) (0·03 g.), unchanged starting material (X) (0·1 g.), and 3-pentafluorophenylanthranil (VIII) (0·05 g.).

Photolysis of 2,3,4,5,6-*Pentafluorophenyl*-2′-*nitrodiphenylmethanol*.—The diphenylmethanol (I) (0·5 g.) in light petroleum (100 c.c.) was irradiated with u.v. light for 4 days at 15°. The solution underwent colour changes during the course of the irradiation from green, through yellow, to a brown.

The solution, after irradiation, was chromatographed on a silica gel column (17 × $1\frac{1}{4}$ in.) with light petroleum as solvent to give three clear bands. The first band was eluted with carbon tetrachloride, the second with carbon tetrachloride–benzene (1 : 1), and the third with benzene. Examination of the separate bands gave (*a*) band (I) a yellow oil (0·1 g.) which had a similar i.r. spectrum to that of 3-pentafluorophenylanthranil (VIII), but contaminated with a second compound which could not be separated. (*b*) Band (II). Re-chromatography of this band on a similar column to the one used above gave 2,3,4,5,6-pentafluoro-2′-nitrodiphenyl ketone (II) (0·1 g.), m. p. 60—62° identical with a sample previously prepared, and a trace of a red compound shown to be 2,3,4,5,6-pentafluoro-2′-nitrosodiphenyl ketone (XI) (see below). (*c*) Band (III). Evaporation of the solvent gave a red oil which on crystallisation twice from light petroleum–benzene (2 : 1) gave red crystals of 2,3,4,5,6-*pentafluoro*-2′-*nitrosodiphenyl ketone* (XI) (0·1 g.), m. p. 150—152° (Found: C, 51·9; H, 1·3. $C_{13}H_4F_5NO_2$ requires C, 51·8; H, 1·3%). Mass spectrum top mass peak 602. Calc. for $(C_{13}H_4F_5NO_2)_2$ 602.

Photolysis of 3-*Pentafluorophenylanthranil*.—The anthranil (VIII) (0·4 g.) in light petroleum–ether (100 c.c.) (10 : 1) was irradiated with u.v. light for 50 hr. at 15°. Chromatography on an alumina column of the resulting wine-red solution afforded a red oil (0·25 g.), which was crystallised twice from light petroleum to give a small quantity of crystals which had a similar i.r. spectrum to that of 2-amino-2′,3′,4′,5′,6′-pentafluorodiphenyl ketone (XII) (see below), and an orange oil (0·1 g.) which could not be identified.

9-*Chloro*-1,2,3,4-*tetrafluoroacridine*.—1,2,3,4-Tetrafluoroacridone (X) (1·0 g.) and phosphorus oxychloride (50 ml.) were heated together at 135° for 3 hr. and then at 165° for 1 hr. The unreacted phosphorus oxychloride was distilled off and the residue was dissolved in chloroform. The chloroform layer was washed with dilute ammonia and dried ($CaCl_2$). Evaporation of the solvent and crystallisation of the yellow residue from light petroleum–benzene (1 : 1) gave 9-*chloro*-1,2,3,4-*tetrafluoroacridine* (XIII) (0·93 g.), m. p. 182—183° (Found: C, 54·8; H, 1·7. $C_{13}H_9ClF_4N$ requires C, 54·6; H, 1·4%).

Reduction of 1,2,3,4-*Tetrafluoroacridone*.—Small pieces of amalgamated Al foil (0·55 g. total) were added over 2 hr. to a solution of the acridone (0·5 g.) in 90% ethanol (100 c.c.) heated under reflux. After the mixture had been heated under reflux for a further 1 hr., the solution was filtered and the residue washed with hot ethanol. The filtrate and washings were distilled to leave a red oil, which was heated with ferric chloride and concentrated hydrochloric acid at 100° for 1 hr., and then the mixture was extracted with ether. The ethereal layer was dried ($MgSO_4$) and distilled to leave a buff solid. Sublimation of the solid followed by crystallisation from light petroleum–ether (1 : 1) gave pale yellow crystals (0·2 g.), m. p. 141—143° (Found: C, 63·8; H, 2·0. $C_{13}H_5F_4N$ requires C, 62·2; H, 2·0%). The u.v. spectrum was very similar to that of acridine.

In another experiment catalytic hydrogenation of 9-chloro-1,2,3,4-tetrafluoroacridine (0·3 g.) gave pale yellow crystals (0·15 g.) identical to those obtained above, but again no satisfactory analysis could be obtained for tetrafluoroacridine.

2-*Amino*-2′,3′,4′,5′,6′-*pentafluorodiphenylketone*.—2,3,4,5,6-Pentafluoro-2′-nitrodiphenyl ketone (VI) (1·6 g.) in ethanol (70 c.c.) was shaken in an atmosphere of hydrogen, using 10% palladium on charcoal as catalyst, for 24 hr. The theoretical amount (360 c.c.) of hydrogen was taken up. The catalyst was filtered off and washed with a little ether. The washings and the filtrate were combined, dried ($MgSO_4$) and the solvents evaporated to give a yellow solid (1·0 g.). Crystallisation from light petroleum afforded 2-*amino*-2′,3′,4′,5′,6′-*pentafluorodiphenylketone* (XII) (0·8 g.), m. p. 91—92° (Found: C, 54·7; H, 1·9. $C_{13}H_6F_5NO$ requires C, 54·4; H, 2·1%).

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