372. *Aromatic Polyfluoro-compounds. Part XXI.*[1] *Reactions of the Pentafluorobenzenediazonium Ion*

By G. M. Brooke, E. J. Forbes, R. D. Richardson, M. Stacey, and J. C. Tatlow

Diazotisation of pentafluoroaniline in 80% hydrofluoric acid gives the diazonium salt in high yield. Replacement of the diazonium group by hydrogen, chlorine, bromine, and iodine (but not by hydroxyl) has been accomplished with the usual reagents. Treatment of the diazonium solution with copper bronze gives decafluorodiphenyl.

Treatment of the neutralised diazo-solution with dimethylaniline leads to 4′-dimethylamino-2,3,5,6-tetrafluoro-4-hydroxyazobenzene. This can be reduced to give 2,3,5,6-tetrafluoro-4-aminophenol, which in turn has been converted into 2,3,5,6-tetrafluorobenzoquinone and 2,3,5,6-tetrafluorophenol.

In an earlier Note [2] we reported the first synthesis of pentafluoroaniline by treatment of hexafluorobenzene with sodamide, and subsequently described [3] a more convenient alternative using aqueous ammonia. The amine has only weakly basic properties; it formed a hydrochloride under anhydrous conditions, but the free base was liberated when water

---

[1] Part XX, Allen, Burdon, and Tatlow, *J.*, 1965, 1045.

[2] Forbes, Richardson, and Tatlow, *Chem. and Ind.*, 1958, **630**.

[3] Brooke, Burdon, Stacey, and Tatlow, *J.*, 1960, 1768.

was added to the salt. The amino-group was acylated normally but relatively sluggishly, and an anil was formed with *m*-nitrobenzaldehyde. Pentafluoroaniline could be diazotised with nitrite, but under the normal conditions, in, say, hydrochloric acid, diazotisation was slow and there was almost complete conversion into decafluorodiazoaminobenzene. Diazotisation without immediate self-coupling could however be accomplished in 65% sulphuric acid and in 48% hydrobromic acid. It was also achieved in 33% hydrochloric acid when the amine was added to the nitrite. However, when such diazo-solutions were treated with alkaline β-naphthol, though an azo-product was formed, it contained hydroxyl and chlorine groups at the expense of fluorine. Coupling with β-naphthol in a non-basic medium or diazotisation in acetic acid followed by coupling with alkaline β-naphthol gave a tetrafluorohydroxyphenylazo-β-naphthol. Though fluorine in the pentafluorobenzene-diazonium ion was labile, the diazonium group itself was not. Characteristic coupling products with β-naphthol were given after the diazo-solutions had been boiled or had been kept for a month at room temperature.

When 65% sulphuric acid was used[4] as the diazotisation medium and cuprous chloride subsequently added pentafluorochlorobenzene (23%) was formed; and diazotisation in 48% hydrobromic acid followed by addition of cuprous bromide afforded pentafluorobromobenzene (30%). In these and other reactions[4] the simple diazo-replacement products were always accompanied by phenolic derivatives containing the second halogen but in which one of the fluorine atoms had been replaced by an hydroxyl group. However, when 80% hydrofluoric acid was used as the diazotisation medium and potassium iodide added, pentafluoroiodobenzene (41%) was obtained as the sole product.[4] As expected the use of a medium containing no free water molecules and with iodide and fluoride as the only negative ions present gave a product in which the effect of exchange of nuclear substituents with the medium was not apparent. Wall *et al.*[5] have recently reported the diazotisation of pentafluoroaniline in liquid hydrofluoric acid and the subsequent preparation of pentafluorobromo- and pentafluoroiodobenzene by the usual Sandmeyer reagents.

By the employment, for most reactions, of 80% hydrofluoric acid we achieved a number of replacements of the diazonium group without replacement of fluorine. The high concentration of pentafluorobenzene diazonium ions present in these solutions was evidenced when they were coupled with dimethylaniline, 4′-dimethylamino-2,3,4,5,6-pentafluoroazobenzene (I) being obtained in almost 70% yield. The azo-compound was identified by its reduction to pentafluoroaniline and *p*-dimethylaminoaniline. Reasonable yields of pentafluorobenzene (51%), pentafluorochloro- (46%), pentafluorobromo- (63%), and pentafluoroiodobenzene (42%) have been obtained from these solutions by the use of the appropriate reagents. Decafluorodiphenyl (23%) was formed when the diazonium solution was treated with copper bronze. Somewhat surprisingly, we have not been able to make pentafluorophenol from the diazonium cation even using the most strenuous conditions such as addition to a solution of sodium sulphate and sulphuric acid at 145°.[6]

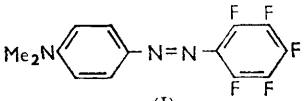
This last result, as will be explained in the sequel, reflects again the characteristic of the pentafluorobenzene diazonium cation, *viz.* the displacement of nuclear fluorine in preference to nitrogen by water or the hydroxyl ion. The orientation of this attack has been established as *para* to the diazo-group. Thus, pentafluoroaniline was diazotised in 70% sulphuric acid and the resulting solution was rendered alkaline. It was then treated with dimethylaniline. From the resulting mixture, 4′-dimethylamino-2,3,5,6-tetrafluoro-4-hydroxyazobenzene (II) was isolated in almost 50% yield. Its structure was proved as follows. Reduction with tin and hydrochloric acid gave *p*-dimethylaminoaniline and a monoaminotetrafluorophenol, which was characterised by its bis(trifluoroacetyl) derivative. When the amino-phenol was oxidised by nitric acid, tetrafluoro-*p*-benzoquinone[7] was

---

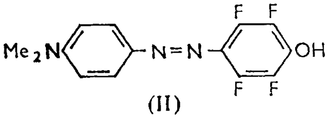
[4] Richardson, Ph.D. Thesis, Birmingham, 1958.
[5] Wall, Pummer, Fearn, and Antonucci, *J. Res. Nat. Bur. Stand.*, 1963, **67***A*, 481.
[6] Saunders, " The Aromatic Diazo-Compounds," Edward Arnold and Co., London, 1949, p. 302.
[7] Nield and Tatlow, *Tetrahedron*, 1960, **8**, 38.

obtained. Hence the phenol from the reduction must have been 4-amino-2,3,5,6-tetrafluorophenol, thus demonstrating that the fluorine substituted by hydroxyl was *para* to the diazo-group.

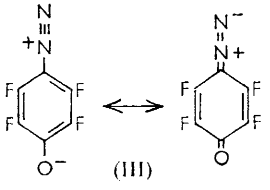
Diazotisation of 4-amino-2,3,5,6-tetrafluorophenol and reaction with hypophosphorous acid gave a good yield of authentic 2,3,5,6-tetrafluorophenol. This product was also obtained when pentafluoroaniline was diazotised and the solution rendered alkaline before reduction by hypophosphorous acid. Thus both conversions on the hydroxylated diazonium cation establish the orientating effect of the diazo-group towards the nucleophilic reagent. Some further confirmation that the *para*-fluorine is removed preferentially was afforded when pentafluoroaniline was diazotised in sulphuric acid, the solution diluted and boiled and the product reduced with zinc and hydrochloric acid. Tetrafluoroquinol[7] was obtained, though only in poor yield. Obviously some replacement of the diazonium group by hydroxyl had occurred here but alongside the replacement of fluorine.



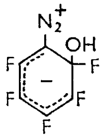
(I)



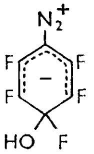
(II)



(III)



(IV)



(V)

It appears that when solutions of the diazonium salts are made alkaline the *para*-fluorine atom is so readily replaced by hydroxyl that the 4-hydroxy-2,3,5,6-tetrafluorobenzene cation is the entity formed first. It may well be stabilised by loss of the proton to give a diazo-oxide (III) in which the dipoles are nicely balanced.

Our failure to obtain pentafluorophenol, under conditions which necessitate a high concentration of water molecules, is now explicable.

Methylation of 2,3,5,6-tetrafluorophenol with diazomethane gave a methyl ether identical with the tetrafluoroanisole obtained[8] by the action of methoxide ion on pentafluorobenzene. Demethylation of this tetrafluoroanisole prepared earlier[8] has now given a tetrafluorophenol identical with our authentic sample of 2,3,5,6-tetrafluorophenol. Moreover, this same phenol has also been obtained by use of the potassium hydroxide t-butyl alcohol reagent[9] on pentafluorobenzene.

Thus, the reactions of sodium methoxide and of potassium hydroxide with pentafluorobenzene confirm the earlier results[3,10] that the fluorine *para* to the hydrogen is the one replaced preferentially by nucleophilic reagents.

That nucleophilic substitution in compounds C_6F_5X should go principally in the *para*-position when X is the diazonium cation and also[11] such dis-similar groups as hydrogen, methyl, trifluoromethyl, and methylthio calls for some comment. It is well known that when halogen atoms are present *ortho* or *para* to the diazonium group in the hydrocarbon series they are readily displaced.[12] Usually, however, it is the *ortho*- rather than the *para*-substituent which is lost more readily.[13] This can be explained on the basis that the closer proximity of the *ortho*-substituents to the dominating influence of the inductive effect of the diazo-group renders them more susceptible to nucleophilic displacement. This effect is clearly not the deciding factor in the fluorocarbon series.

[8] Stephens and Tatlow, *Chem. and Ind.*, 1957, 821.
[9] Birchall and Haszeldine, *J.*, 1959, 13.
[10] Brooke, Burdon, and Tatlow, *J.*, 1962, 3253.
[11] Tatlow, *Endeavour*, 1963, **22**, 89.
[12] Bunnett and Zahler, *Chem. Rev.*, 1951, **49**, 273.
[13] Saunders, " The Aromatic Diazo-Compounds," Edward Arnold and Co., London, 1949, p. 117.

The present results may perhaps best be rationalised in terms of the energy of the transition state. These nucleophilic substitutions follow a course similar to the S_N2 reactions of the hydrocarbon series.[14] On this basis a reactive intermediate of the type (IV) or (V) would be formed. In this case particularly, with the fluorine atoms combining to nullify the dipolar effect of the diazo-group, the higher symmetry of the intermediate (V) should result in a lower energy of activation thus favouring *para*-substitution. The symmetry of intermediates analogous to (V) could be a factor in other cases where *para*-substitution is favoured in compounds of the type C_6F_5X. The apparently anomalous result of the action of ammonia on pentafluoronitrobenzene[15] where *ortho*- predominates over *para*-substitution received an explanation in our previous publication.[1]

EXPERIMENTAL

Derivatives of Pentafluoroaniline.—Pentafluoroaniline[2,3] when refluxed for 2 min. with acetic anhydride and a trace of sulphuric acid gave 2,3,4,5,6-*pentafluoroacetanilide* (85% from aqueous ethanol), m. p. 131—132° (Found: C, 42·6; H, 1·8; F, 42·3. $C_8H_4F_5NO$ requires C, 42·7; H, 1·8; F, 42·2%). Refluxing for 10 min. with trifluoroacetic anhydride afforded the N-*trifluoroacetyl* derivative (95%, from aqueous ethanol, or by sublimation at 60°/0·1 mm.), m. p. 90° (Found: C, 34·6; H, 0·6; F, 53·7. C_8HF_8NO requires C, 34·4; H, 0·4; F, 54·45%). Treatment with *m*-nitrobenzaldehyde at 125° for 30 min. gave 2,3,4,5,6-*pentafluoro*-N-(3'-*nitrobenzylidene*)-*aniline* (76% from aqueous ethanol), m. p. 140° (Found: C, 49·1; H, 1·6; F, 30·1. $C_{13}H_5F_5N_2O_2$ requires C, 49·4; H, 1·6; F, 30·0%).

When dry hydrogen chloride was bubbled through diethyl ether containing pentafluoroaniline, the *hydrochloride* was precipitated, m. p. 129—131° (sealed tube) (Found: Cl, 16·6%; Equiv. 225. $C_6H_3ClF_5N$ requires Cl, 16·2%; Equiv. 219·5). Addition of the hydrochloride to water precipitated pentafluoroaniline, m. p. 33°, with a correct infrared spectrum.

Decafluorodiazoaminobenzene.—Pentafluoroaniline (1 g.) was dissolved in warm concentrated hydrochloric acid (10 ml.), the solution was cooled to 0°, crushed ice (6 g.) added, followed by sodium nitrite (0·41 g.) in water (3 ml.). After 15 min. the precipitate was collected, washed, dried, and crystallised from n-heptane to give *decafluorodiazoaminobenzene* (0·65 g.), m. p. 135—136° (decomp.) (Found: C, 38·2; H, 0·2; F, 50·3. $C_{12}HF_{10}N_3$ requires C, 38·2; H, 0·3; F, 50·4%).

The same compound was formed if the diazotisation was carried out analogously using hydrobromic aid.

Coupling of Diazotised Pentafluoroaniline with β-*Naphthol.*—A solution of pentafluoroaniline (0·5 g.) in concentrated hydrochloric acid (20 ml.) was added during 30 min. to a stirred solution of sodium nitrite (0·44 g.) in water (10 ml.) at 0°. Crushed ice (40 g.) was added simultaneously. The yellow solution was then added at 0° to a solution of β-naphthol (0·41 g.) and sodium hydroxide (15 g.) in water (60 ml.). After filtration the solution was acidified (HCl), and the precipitate coagulated by boiling and collected. Crystallisation from ethanol afforded a *chlorotrifluorohydroxyphenylazo*-β-*naphthol* (0·43 g.), m. p. 247—248° (Found: Cl, 9·9; F, 15·8. $C_{16}H_8ClF_3N_2O_2$ requires Cl, 10·1; F, 16·2%).

4'-*Dimethylamino*-2,3,4,5,6-*pentafluoroazobenzene.*—Pentafluoroaniline (2·00 g.) was stirred with hydrofluoric acid (75 ml.; 80% w/w) in a Polythene beaker. The mixture was cooled in an ice–salt bath and finely ground sodium nitrite (1·17 g.) was added (with stirring) over 5 min. After the mixture had been stirred for 20 hr., sulphamic acid (2·02 g.) was added, followed by dimethylaniline (10 ml.). After a further 1·5 hr., the mixture was diluted with water (450 ml.) and the bright orange precipitate (2·29 g., 66%) filtered off. Crystallisation from benzene–light petroleum (b. p. 60—80°) gave 4'-*dimethylamino*-2,3,4,5,6-*pentafluoroazobenzene* (1·65 g.) as orange crystals, m. p. 147·5—149° (Found: C, 53·7; H, 3·0; F, 30·2. $C_{14}H_{10}F_5N_3$ requires C, 53·35; H, 3·2; F, 30·1%).

In other experiments, the diazo-compound was coupled with dimethylaniline after being stirred with sodium nitrite in hydrofluoric acid (80% w/w) for 1·5 hr.; similar yields of the product were obtained.

---

[14] Burdon, Hollyhead, and Patrick, *J.*, 1964, 4663.
[15] Brooke, Burdon, and Tatlow, *J.*, 1961, 802.

Diazotisation of pentafluoroaniline (2·51 g.) in sulphuric acid (50 ml., 70% w/w) as above, over 1·5 hr., and coupling with dimethylaniline gave the same azo-product (2·16 g.).

Reductive Cleavage of 4'-*Dimethylamino*-2,3,4,5,6-*pentafluoroazobenzene*.—The azo-compound (2·503 g.), granulated tin (6·2 g.), and hydrochloric acid (25 ml., 10N) were heated on a steam-bath for 15 min. The product was distilled from the reaction mixture in steam and extracted from the distillate with ether. Evaporation of the dried ($MgSO_4$) extracts gave pentafluoroaniline [2,3] (1·437 g.), identified by its infrared spectrum.

The residue from the steam distillation was made alkaline with potassium hydroxide solution and the product was distilled in steam into hydrochloric acid (25 ml.; 11N). Evaporation of the acidic distillate *in vacuo* afforded *p*-dimethylaminoaniline dihydrochloride (1·561 g), identified by its infrared spectrum.

Pentafluorobenzene.—Pentafluoroaniline (5·00 g.) in hydrofluoric acid (75 ml., 80% w/w) was treated with sodium nitrite (3·00 g.) as before. After the mixture had been stirred for 16 hr., sulphamic acid (3·02 g.) was added, and the diazo-solution was heated with hypophosphorous acid (150 ml., d, 1·226) in a nickel flask on a steam-bath for 1·25 hr. The product was distilled from the reaction mixture in steam through a water-cooled copper condenser into excess of sodium hydroxide solution and redistilled in steam. It was separated from the lighter aqueous layer, dried over phosphorus pentoxide, and distilled to give pentafluorobenzene [8] (2·36 g.), b. p. 84—84·5°, identified by its infrared spectrum.

Chloropentafluorobenzene.—Pentafluoroaniline (5·02 g.) in hydrofluoric acid (25 ml., 80% w/w) was treated with sodium nitrite (3·01 g.) as before. After the mixture had been stirred for 16 hr., sulphamic acid (1·40 g.) was added, and the diazo-solution was added with stirring to cuprous chloride (30 g.) in hydrochloric acid (100 ml., 10N) from a wax-lined funnel over 5 min. The mixture was heated on a steam-bath for 2·25 hr. and worked up in the usual manner. Chloropentafluorobenzene (2·54 g.) was obtained as a colourless liquid, b. p. 116—117° (Found: C, 35·5; F, 46·0. Calc. for C_6ClF_5: C, 35·6; F, 46·9%).

Bromopentafluorobenzene.—Pentafluoroaniline (3·01 g.) in hydrofluoric acid (25 ml., 80% w/w) was treated with sodium nitrite (1·79 g.). After the mixture had been stirred for 2·5 hr., the diazo-solution was added to cuprous bromide in hydrobromic acid at 100°. [This solution was prepared by the addition of hydrated sodium sulphite (7·5 g.) to a solution of hydrated copper sulphate (12 g.) and sodium bromide (13 g.) in boiling water (30 ml.). Hydrobromic acid (40 ml., 48% w/w) was added to dissolve the precipitated cuprous bromide.] The mixture was heated on a steam-bath for 1·5 hr., and the product, bromopentafluorobenzene (2·56 g.), b. p. 134·5—135·5°,[16] identified by its infrared spectrum, was isolated as before.

Pentafluoroiodobenzene.—Pentafluoroaniline (5·01 g.) in hydrofluoric acid (75 ml., 80% w/w) was treated with sodium nitrite (3·01 g.). After the mixture had been stirred for 18·5 hr., sulphamic acid (3·04 g.) was added, followed by finely ground potassium iodide. The mixture was warmed to 40° for 0·5 hr. and the product was distilled from the reaction mixture in steam and redistilled in steam. Extraction of the distillate with ether and evaporation of the dried ($MgSO_4$) extracts left an oil (4·30 g.), which on distillation gave pentafluoroiodobenzene (3·36 g.), b. p. 162·5—163·5°, identified by its infrared spectrum.[16]

Decafluorodiphenyl.—Pentafluoroaniline (7·53 g.) in hydrofluoric acid (50 ml., 80% w/w) was treated with sodium nitrite (4·50 g.). After the mixture had been stirred for 5 hr., sulphamic acid (1·02 g.) was added and the diazo-solution was refluxed in a nickel flask with copper bronze (75 g.) for 1 hr. The product was distilled from the reaction mixture in steam and redistilled in steam. Extraction of the distillate with ether and evaporation of the dried ($MgSO_4$) extracts gave decafluorodiphenyl (1·54 g.), m. p. 67°, identified by its infrared spectrum.[16]

4'-*Dimethylamino*-2,3,5,6-*tetrafluoro*-4-*hydroxyazobenzene*.—Pentafluoroaniline (3·03 g.) in sulphuric acid (20 ml., 70% w/w) was treated with sodium nitrite (1·81 g.). After being stirred for 2 hr., the solution was rendered alkaline by the addition (over 4 hr.) of a solution of anhydrous sodium carbonate (26·5 g.) in water (130 ml.) with vigorous stirring, the temperature being kept at 0°. After a further 30 min., the mixture was acidified with sulphuric acid (10 ml.; 70% w/w) and treated with dimethylaniline (20 ml.). One hour later the orange-red precipitate which had formed was filtered off, washed with water, and dried. The filtrate was extracted with ether, and the combined extracts dried and evaporated. The residue was combined with the initial precipitate and the whole chromatographed on alumina (30 × 4 cm.), methanol being used as eluant. After an initial quantity of tar (0·48 g.) there was obtained a red sodium

---

[16] Nield, Stephens, and Tatlow, *J.*, 1959, 166.

salt (2·02 g.), m. p. 210—215° (decomp.). The column was then extracted with glacial acetic acid to give a red solid (1·03 g.), m. p. 154° (decomp.) which crystallised from methanol to give 4'-*dimethylamino*-2,3,5,6-*tetrafluoro*-4-*hydroxyazobenzene*, m. p. 157° (decomp.) (Found: C, 53·6; H, 3·5; F, 24·6. $C_{14}H_{11}F_4N_3O$ requires C, 53·7; H, 3·5; F, 24·3%).

Treatment of the sodium salt with glacial acetic acid gave more (1·47 g.) of the azo-compound. Treatment of the azo-compound with sodium hydroxide solution gave a deep red sodium salt, m. p. 220° (decomp.), having an infrared spectrum identical with that of the sodium salt obtained from the column.

Reductive Cleavage of 4'-*Dimethylamino*-2,3,5,6-*tetrafluoro*-4-*hydroxyazobenzene*.—The azo-compound (0·558 g.), granulated tin (1·31 g.), and hydrochloric acid (5 ml., 10N) were heated on a steam-bath for 20 min. The solution was made alkaline with sodium hydroxide solution, and the product distilled in steam into hydrochloric acid (25 ml., 10N). Evaporation of the acidic distillate *in vacuo* gave *p*-dimethylaminoaniline dihydrochloride (0·347 g.), identified by its infrared spectrum. The residual solution from the steam distillation was acidified with hydrochloric acid, extracted with ether, and the extracts dried ($MgSO_4$) and evaporated to give a white solid (0·421 g.). This was recrystallised from water and sublimed *in vacuo* (130°/0·25 mm.) to give pure 4-*amino*-2,3,5,6-*tetrafluorophenol* (0·313 g.), m. p. 177·5—178° (decomp.) (Found: C, 40·0; H, 1·6; F, 42·4. $C_6H_3F_4NO$ requires C, 39·8; H, 1·7; F, 42·0%).

The aminophenol (0·52 g.) was refluxed with trifluoroacetic anhydride (5·0 ml.) and five drops of concentrated hydrochloric acid for 8 hr. Evaporation of the solution to dryness gave a white solid (1·07 g.), m. p. 141·5—143·5°. Crystallisation of a sample (0·49 g.) from benzene gave the pure *bis(trifluoroacetyl) derivative* (0·44 g.), m. p. 142·5—143·5° (Found: C, 32·1; H, 0·1. $C_{10}HF_{10}NO_3$ requires C, 32·2; H, 0·3%).

Oxidation of 4-*Amino*-2,3,5,6-*tetrafluorophenol*.—The aminophenol (0·88 g.) was warmed with nitric acid (5 ml.; 50 g./100 ml.). After a vigorous exothermic reaction, tetrafluoro-*p*-benzoquinone (0·47 g.), m. p. 178—179·5°, was filtered off, washed with water, and dried. Its infrared spectrum was identical with that of an authentic specimen.[7]

Tetrafluoroquinol from Pentafluoroaniline.—Finely-ground sodium nitrite (2·5 g.) was added to a solution of pentafluoroaniline (2·5 g.) in sulphuric acid (20 ml. conc. acid, 10 ml. water) at 0—3°. The solution was then stirred at 0° for 2 hr. and run into boiling water (300 ml.). After 30 min. at 90—95° the mixture was cooled and extracted with ether. The extracts were evaporated and the residual red oil suspended in 5N-hydrochloric acid (20 ml.) whilst zinc dust was added until it became colourless. Extraction with ether followed by drying, evaporation, and sublimation of the residue at 70°/0·05 mm. gave tetrafluoroquinol (0·17 g.), m. p. 159—160° (Found: C, 39·6. Calc. for $C_6H_2F_4O_2$: C, 39·6%). The cited value [7] was 168—169° (rapidly falling in moist air) and the infrared spectra of the two samples were identical.

Heating the product with acetic anhydride and a trace of sulphuric acid for 2 min. gave the *diacetate* (75%, from ethanol), m. p. 109° (Found: C, 45·4; H, 2·2; F, 28·2. $C_{10}H_6F_4O_4$ requires C, 45·1; H, 2·3; F, 28·6%).

2,3,5,6-*Tetrafluorophenol*.—(*a*) 4-Amino-2,3,5,6-tetrafluorophenol (2·05 g.) in sulphuric acid (20 ml., 70% w/w) was treated with sodium nitrite (1·25 g.) as before. After the mixture had been stirred for 2 hr., sulphamic acid (1·20 g.) was added, and the diazo-solution was heated with hypophosphorous acid (150 ml., d 1·226) on a steam-bath for 2 hr. The product was distilled from the reaction mixture in steam and extracted with ether. Evaporation of the dried ($MgSO_4$) extracts gave an oil which was distilled to give 2,3,5,6-tetrafluorophenol (1·06 g.), b. p. 146·5°, m. p. 30° (cited,[5] b. p. 47°/20 mm.) (Found: C, 43·3; H, 1·5. Calc. for $C_6H_2F_4OC$: 43·4; H, 1·2%).

(*b*) Pentafluoroaniline (5·08 g.) in sulphuric acid (20 ml., 70% w/w) was treated with sodium nitrite (3·00 g.). After the mixture had been stirred for 2 hr., anhydrous sodium carbonate (26·7 g.) in water (130 ml.) was added with vigorous stirring to the mixture at 0° over 2 hr. The mixture was acidified with sulphuric acid (10 ml., 70%) and heated with hypophosphorous acid (150 ml.; *d* 1·226) on a steam-bath for 45 min. The product, 2,3,5,6-tetrafluorophenol (2·71 g.), b. p. 144—147°, was isolated as before and identified by its infrared spectrum.

(*c*) 2,3,5,6-Tetrafluoroanisole [8] (1·5 g.) and finely-ground aluminium chloride (1·5 g.) were heated at 120° for 3 hr. The reaction mass was cooled and powdered. Water (10 ml.) was added and 2,3,5,6-tetrafluorophenol, b. p. 144—145°, m. p. 30°, was isolated as before and identified by its infrared spectrum.

(*d*) Pentafluorobenzene (2·49 g.) and potassium hydroxide (5 g.) in t-butyl alcohol (15 ml.) were refluxed for 6 hr. After the mixture had been diluted with water, the alcohol was distilled off and the residue extracted with ether. The aqueous layer was acidified, ether-extracted, and the dried ($MgSO_4$) extracts evaporated. Distillation of the residual oil gave 2,3,5,6-tetrafluorophenol (0·37 g.), b. p. 144°, identified by its infrared spectrum.

2,3,5,6-Tetrafluorophenol gave a *toluene*-p-*sulphonate*, m. p. 80—81° (from ethanol) (Found: C, 49·1; H, 2·5; F, 23·6. $C_{13}H_8F_4O_3S$ requires C, 48·8; H, 2·5; F, 23·7%), and a p-*nitrobenzyl ether*, m. p. 96—97° (from ethanol) (Found: C, 51·4; H, 2·5; F, 25·0. $C_{13}H_7F_4O_3N$ requires C, 51·8; H, 2·3; F, 25·2%). Methylation of 2,3,5,6-tetrafluorophenol (0·74 g.) with diazomethane in ether gave 2,3,5,6-tetrafluoroanisole (0·57 g.), b. p. 143·5—145°, identified by its infrared spectrum.

We thank the D.S.I.R. for a maintenance award (to R. D. R.).

THE UNIVERSITY OF BIRMINGHAM, EDGBASTON,
BIRMINGHAM 15.

[*Received, July 7th,* 1964.]