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FLUOROCARBON DERIVATIVES OF NITROGEN. PART 16 [1]. SYNTHESIS OF SOME UNSYMMETRICAL AROMATIC AZO-COMPOUNDS via DIAZOTISATION OF FLUORINATED ARYL- AND N-HETEROARYL-AMINES IN HYDROFLUORIC OR SULPHURIC ACID [2] *

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SUMMARY

Coupling reactions of the type $Ar_FN_2^+ + ArH \longrightarrow Ar_FN{=}NAr + H^+$ have been accomplished between fluorinated arenediazonium ions selected from the benzenic, pyridinic and pyrimidinic classes [Ar_F = C_6F_5, 4-$CF_3C_6F_4$, 4-C_5F_4N, 4-C_5F_3N.Cl-3, 4-$C_5F_2N.Cl_2$-3,5, 2-$C_5F_3N.CF(CF_3)_2$-4, 4-$C_4F_3N_2$] and one or more aromatic compounds activated towards electrophilic attack (ArH = 1,3,5-$Me_3C_6H_3$, 1,3,5-$Et_3C_6H_3$, $MeOC_6H_5$, $Me_2NC_6H_5$, and naphth-2-ol). The diazonium ions were generated by addition of solid sodium nitrite to solutions of the amines Ar_FNH_2 in anhydrous hydrogen fluoride, 80% hydrofluoric acid, or 98% sulphuric acid mixed with glacial acetic acid

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* Dedicated to Emeritus Professor W.K.R.Musgrave on the occasion of his 70th birthday.

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and propionic acid. This work has established that perfluorinated arenediazonium ions rank amongst the most electrophilic species of their general class.

INTRODUCTION

This study, which, through sheer serendipity has led to a major breakthrough in the chemistry of diareno-1,2-diazepines [3], was initiated in 1975 [4] when one of us [+] joined the Fluorine Group at UMIST on the condition that he could carry out research in the field of azo-dyes. The timing was in fact excellent because Noakes had just completed his seminal work on (dichloroamino)arenes of the fluorocarbon class [5], during the last stage of which he unsuccessfully attempted to generate tetrafluoropyridine-4-diazonium chloride via treatment of tetrafluoro-4-hydrazinopyridine with t-butyl hypochlorite [6]. Fresh in our minds, therefore, were details of the previous work on this diazonium ion, carried out in Musgrave's group at Durham (U.K.) [7], and of yet earlier studies on the pentafluorobenzenediazonium ion conducted in the laboratories of Tatlow at Birmingham (U.K.) [8,9] and of Wall at the National Bureau of Standards (U.S.A.) [10].

Not surprisingly, the pioneers of aromatic fluorocarbon chemistry viewed pentafluoroaniline as a compound with strategic potential where synthetic advancement of the field was concerned. Thus, the preparation [8] and study of the classical (sodium nitrite-mineral acid) diazotisation [8-10] of this weakly-basic arylamine date back to the early years of the development of hexafluorobenzene chemistry [11]. Naturally [12], to achieve a decent rate of diazotisation and so prevent self-coupling to give decafluorodiazoaminobenzene, the 'strong acid method' had to be employed. Furthermore it was found prudent, where possible, to employ concentrated (80%) hydrofluoric acid [9] or anhydrous hydrogen

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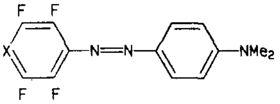
[+] H.S.V.(class of 1975 graduate of the Aristotelion University of Thessaloniki, Greece) fluoride [10] as the diazotisation medium; this maintained a high 'fluoride presence' and thereby nullified the tendency for 'media nucleophiles' to displace para-fluorine from the pentafluorobenzenediazonium ion prior to its synthetic manipulation via heterolytic dediazoniation or coupling processes [a].

Only aqueous hydrogen fluoride (80% hydrofluoric acid) was used by the Durham group during its work on the diazotisation of 4-aminotetrafluoropyridine [b], and the sole azo-coupling reaction reported involved the preparation of 4-[4-(N,N-dimethylamino)-phenylazo]tetrafluoropyridine (I) in 10% yield. N,N-Dimethylaniline was also the only coupling component used to capture the pentafluorobenzenediazonium ion (as azo-dye II; 48% yield) following application of the same diazotisation technique to pentafluoroaniline [9]. Thus the condition mentioned at the beginning of this section was easily met by proposing that the by-then-old work of Musgrave's group be extended to throw light on the electrophilicity of the tetrafluoropyridine-4-diazonium ion through examination of coupling components less nucleophilic than N,N-dimethylaniline; the programme was expected to provide new azo-compounds (and did [2(a),4]) which could be tested as dyestuffs.



(I) X = N

(II) X = CF

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[a] The remarkable nucleofugality of fluorine in fluoroarenediazonium ions seems to have been noted first about sixty years ago; the reaction involved was the formation of 2-ethoxynitrobenzene via addition of solid sodium nitrite to a hot solution of 4-fluoro-3-nitroaniline in an ethanol-concentrated sulphuric acid mixture [13]. See also the review by Suschitzky [14].

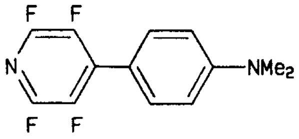
[b] Previously [15] Brooke and Musgrave had converted 4-aminononafluorobiphenyl to 4-bromononafluorobiphenyl using the same diazotisation technique, followed by a Sandmeyer stage (addition of CuBr-HBr) (cf. analogous syntheses of C_6F_5Br [9,10]).

Starting in October 1981 [16(a)], the initial study [2(a),4] was extended considerably, thanks to industrial patronage, with the objective of comparing anhydrous hydrogen fluoride (AHF) with 98% sulphuric acid as a diazotisation medium for fluoroaromatic amines. This paper is concerned with the findings of that research.

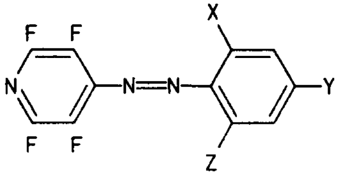
Before turning to the actual results, it must be borne in mind that the designations AHF and 80% hydrofluoric acid apply only to diazotisation media prior to the onset of experimentation. Immediately obvious is that addition of dry sodium nitrite to solutions of amines in these media generates water ($NaNO_2 + 2HF + ArNH_2 \rightarrow ArN_2^+F^- + NaF + 2H_2O$). Thus during the diazotisation of 10 mmol of an aminoarene in 10 cm^3 100% AHF (actually commercial material contains $\not>$ 0.08% H_2O and ≥ 99.8% HF) the concentration of HF falls to 96.5%; with 100 cm^3 of solvent, the value decreases to only 99.6%. In the present work, experiments were usually carried out with 10 mmol of an amine dissolved in 200 cm^3 of AHF, so the 'nitrite dilution factor' was always negligible. However, no real attempts were made to prevent ingress of atmospheric moisture to reaction vessels (open-mouthed) or, in most cases, to prevent loss of HF by evaporation; AHF in particular is very hygroscopic, of course, and noticeably volatile (b.p. AHF, 19.5 °C). In no case were steps taken to determine actual HF concentrations during coupling steps, nor to discover how product yields varied with concentration, apart from a simple experiment where anisole was involved. Since the same experimental procedure was always adopted, however, the relative yields of azo-compounds achieved with different coupling partners are considered to be meaningful.

RESULTS AND DISCUSSION

Initially, the diazotisation of 4-aminotetrafluoropyridine and pentafluoroaniline in 80% hydrofluoric acid with sodium nitrite, followed by coupling of the resultant diazonium ions to *N*,*N*-dimethylaniline, was repeated according to the literature [7,9]. This provided azo-compounds I and II, respectively,in yields of 15 and 45%. Like Musgrave *et al*. [7], we found that the tetrafluoropyridyl compound (I) was accompanied by several other entities [4]. One of these, isolated chromatographically in 5% yield, was identified as the straightforward dediazoniation product III, but like the Durham group (apparently [7]) we did not pause to establish the structures of the coloured byproducts formed. Effort was directed instead to experiments in which the new coupling components anisole (methoxybenzene) and mesitylene (1,3,5-trimethylbenzene) were added to cold (-50 °C) diazonium solutions prepared by adding solid sodium nitrite to solutions of 4-aminotetrafluoropyridine in 80% hydrofluoric acid. Coupling occurred readily in both cases, giving the new azo-compounds IV and V in 48[c] and 30% yield, respectively (after chromatographic separations). Although addition of *meta*-xylene or toluene to yellowish solutions of the tetrafluoropyridine-4-diazonium ion in 80% hydrofluoric acid caused them to become red, only traces of coloured solids could be isolated after the reaction mixtures had been quenched with water. These solids remain unidentified.



(III)



(IV) X = Z = H, Y = OMe
(V) X = Y = Z = Me
(VI) X = Y = Z = Et

The ability of the tetrafluoropyridine-4-diazonium ion to couple with, *i.e.* effect electrophilic substitution in, an alkyl phenyl ether or an aromatic hydrocarbon is not unique [17,18]. Note, however, that the examples involving anisole and mesitylene appear to be the first to be reported [2(a)] where the arenediazonium ion

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[c] This can be increased dramatically by raising the coupling temperature (see later).

belongs to the pyridine or to the fluorinated sub-class. The best known of the relatively few previous cases where an aromatic hydrocarbon has been employed as a coupling component involves attack on mesitylene by the 2,4,6-trinitrobenzenediazonium ion [18] [d].

Diazotisation/Coupling in AHF

With mesitylene as the coupling component. Use of anhydrous hydrogen fluoride (AHF; b.p. 19.5 °C) as the diazotisation medium for 4-aminotetrafluoropyridine proved more convenient and decidedly more efficient than employing 80% hydrofluoric acid. The nitrosation stage was carried out at ambient temperature (18 °C) using dry powdered sodium nitrite; coupling of the tetrafluoropyridine-4-diazonium ion occurred readily on subsequent addition of a coupling component (again at room temperature), and crude products were isolated simply by letting reaction mixtures evaporate slowly at room temperature in a special fume cupboard. In this manner, coupling of the diazonium ion to mesitylene or its ethyl-analogue, 1,3,5,-triethylbenzene, provided the corresponding azo-compounds V and VI in 82 and 64% yield, respectively, after chromatographic purification. Attempts to capture the tetrafluoropyridine-4-diazonium cation with 1,3,5-tri-isopropylbenzene or meta-xylene failed. The latter result confirmed Vellis' observation using 80% hydrofluoric acid as diazotisation medium (see above); the somewhat unexpected failure with the trialkylbenzene presumably arose from steric effects.

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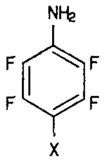
[d] 'Karrer' (Paul Karrer, Organic Chemistry, Elsevier: Amsterdam, 1950), used by one of us (R.E.B.) when taught as an undergraduate about azo-dyes by W.K.R. Musgrave, makes a special point of this (see p.483). The reaction is still highlighted, in, for example, the latest (fifth) edition of Organic Chemistry by R.T.Morrison and R.N.Boyd (Allyn and Bacon: Boston, 1987).

The structure of the new azo-compound VI, like that of its trimethyl-analogue (V) previously [4], was readily established by elemental analysis and spectroscopic measurements. Chemical proof of structure for the trimethyl-compound (V) was obtained by reductive cleavage of the azo-linkage with hydriodic acid to give 4-aminotetrafluoropyridine and 2,4,6-trimethylaniline. Furthermore, in connection with the mechanism of the conversion of V to a diareno-1,2-diazepine [3,16(a)], V was subjected to X-ray crystallographic analysis and shown to possess a perfectly planar trans-conformation in the crystalline state [16(b)]. Discussion of the photochemical conversion of the trans-isomer of V to the cis-form will be presented elsewhere. As indicated by the depths of the colours of all the other azo-compounds described in this paper, trans-conformations were preferred. Note, however, that in several cases cis-isomers were detected both by chromatographic techniques and by n.m.r. spectroscopy. N.m.r. data presented in the Experimental Section of this paper refer to the sole or major isomer present under normal laboratory conditions in the solutions examined.

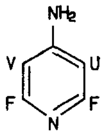
Sequential room-temperature diazotisation/coupling-to-mesitylene in anhydrous hydrogen fluoride also worked smoothly for the amino-arenes or -N-heteroarenes VII - XI to provide the novel azo-compounds XIII - XVII, respectively, in yields of 33 (XIII), 93 (XIV), 81 (XV), 59 (XVI), and 77% (XVII). As described below, another azo-compound of this series was obtained via the diazotisation of 4-amino-3-chlorotrifluoropyridine (XII) [→ XVIII (97%)] in sulphuric acid. No doubt this conversion would also proceed smoothly using AHF.

Coupling of tetrafluoropyridine-4-diazonium ion to anisole. By contrast with the experiment involving mesitylene, diazotisation of 4-aminotetrafluoropyridine in AHF at ambient temperature followed directly by addition of anisole to the solution provided a much lower yield (6%) of azo-compound IV than when 80% hydrofluoric acid was employed and the coupling component was added to the diazonium bath at -50 °C [2(a)]; also, numerous other (unidentified) products and black tarry material were produced. When, however, the original experiment [2(a),4] with 80% hydrofluoric acid was repeated but in more dilute solution (10 mmol of the amine in 200 cm^3 of HF aq



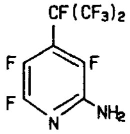
(VII) X = F

(VIII) X = CF_3

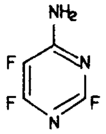


(IX) V = U = Cl

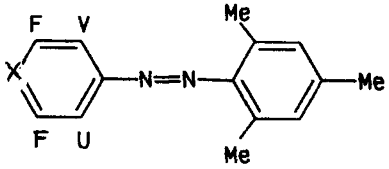
(XII) V = F, U = Cl



(X)



(XI)

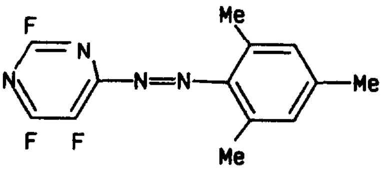


(XIII) X = CF, U = V = F

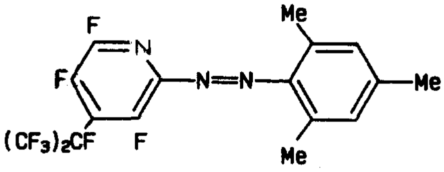
(XIV) X = CCF_3, U = V = F

(XV) X = N, V = U = Cl

(XVIII) X = N, V = F, U = Cl



(XVII)

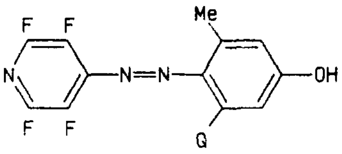


(XVI)

compared with 6 mmol in 40 cm^3 of the acid) and at room temperature (not -50 °C → 20 °C), the yield of IV increased dramatically from 48 to 91%. Presumably the near failure of the coupling reaction in AHF arises from more efficient protonation of the coupler's oxygen atom than found in 80% hydrofluoric acid.

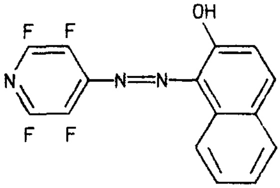
Diazotisation/Coupling of 4-Aminotetrafluoropyridine in 98% Sulphuric Acid.

Wall and Musgrave respectively reported that concentrated sulphuric acid is an impractical medium for the diazotisation of pentafluoroaniline (reaction was "extremely slow, even at 25 °C" [10]) and 4-aminotetrafluoropyridine ("only starting material was recovered"[7]); the former's group did, however, observe that the addition of glacial acetic acid "tends to hasten the reaction slightly" [10]. Having found that diazotisation of 4-aminotetrafluoropyridine in 98% sulphuric acid at 0 °C followed by the addition of mesitylene gave only a low yield (22 wt-%) of a multi-component mixture (TLC analysis) containing azo-compound V, we turned our attention to reactions in a 1:1 (v/v) medium of 98% sulphuric acid and glacial acetic acid-propionic acid (86:14 v/v). Coupling occurred much more smoothly, and azo-compound V was isolated chromatographically in 77% yield. This is only a few percent lower than achieved using AHF (82%) and clearly is the method of choice for those wishing to avoid the special precautions associated with the manipulation of hydrogen fluoride [19]. Promotion of the diazotisation of weakly basic arylamines in sulphuric acid-alkanecarboxylic acid mixtures is a well established technique [12], and we have also used it to couple the 3-chlorotrifluoropyridine-4-diazonium ion with mesitylene [→ XVIII (97%)] and the tetrafluoropyridine-4-diazonium ion with <u>meta</u>-cresol [→XIX (66%)], 3,5-dimethylphenol [→ XX (89%)], and naphth-2-ol [→ XXI (69%)]. Only black material containing none of the azo-compound XXI was obtained from diazotisation/coupling of 4-aminotetrafluoropyridine with naphth-2-ol in AHF or 80% hydrofluoric acid. The ^{19}F n.m.r. spectra of azo-compounds XIX-XXI showed only two sets of absorption systems in each case; this, plus the similarity of the chemical shifts to those found with their analogue derived from mesitylene, indicate that they exist almost predominantly or even entirely as azo and not hydrazone tautomers (e.g. XIX or XX not XXII).

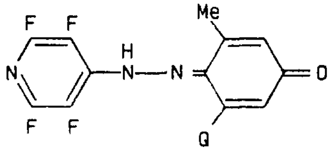


(XIX) Q = H

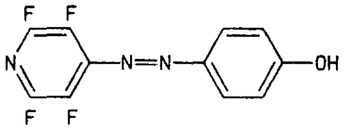
(XX) Q = Me



(XXI)



(XXII) Q = H or Me



(XXIII)

Addition of anisole to tetrafluoropyridine-4-diazonium ion generated in 98% H_2SO_4-$MeCO_2H$-$EtCO_2H$ at 0 °C gave the expected azo-compound (IV) in only 18% yield, the major product (64%) being the azo-phenol XXIII. No attempt was made to determine whether de-methylation occurred before or after coupling [cf. 20]. Since this work was completed, Japanese workers [21] have shown that no dealkylation occurs when either anisole or its naphthyl analogue (1-isomer) is coupled to the pentafluorobenzenediazonium ion generated from pentafluoroaniline and sodium nitrite in a two-phase aqueous sulphuric acid-dichloromethane system in the presence of sodium tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (phase-transfer catalyst). Use of mesitylene as a coupling component in this PTC-promoted method gave a better yield (44%) of azo-compound XIII than we achieved using AHF (33%).

CONCLUDING REMARKS

The ability of the diazonium ions derived from 4-aminotetrafluoropyridine and the related fluoroaromatic amines VII - XII to couple with mesitylene merits their classification with the most electrophilic arenediazonium entities known. Only aromatic diazonium ions derived from 5-amino-1,2,4- and 2-amino-1,3,4-thiadiazoles appear to have been found more powerful so far, as revealed by their ability to couple with meta-xylene [22].

EXPERIMENTAL

Spectroscopic Analysis

N.m.r. spectra were recorded on Perkin-Elmer R12 or R34 (^{1}H at 60 and 220 MHz respectively) or R32 (^{1}H at 90 MHz; ^{19}F at 84.6 MHz) instruments and (with dilute solutions) a Bruker WP80 spectrometer (^{1}H at 80 MHz; ^{19}F at 75.3 MHz); tetramethylsilane (^{1}H) and trifluoroacetic acid (^{19}F) were used as internal (unless stated otherwise) and external references respectively, and chemical shifts (δ_H and δ_F) were determined in p.p.m., positive values referring to downfield absorptions. Mass spectra were obtained with a Kratos M545 double-focusing instrument (50-70 eV ionisation energy). U.v. spectra were measured using a Cary 118C spectrometer (range 200 - 600 nm).

Chromatography

Dry-column 'flash' chromatography (DCFC) was carried out using a sintered glass funnel packed with TLC-grade silica gel 60 (GF 254, Art.7730). Water-pump suction was employed to effect elution of products, the column being sucked dry after each addition of eluent.

Starting Materials

Pentafluoroaniline was used as received from FluoroChem (Glossop, Derbyshire, U.K.). 4-Aminoheptafluorotoluene (VIII) 4-aminotetrafluoropyridine, 4-amino-3-chlorotrifluoropyridine (XII), 4-amino-3,5-dichlorodifluoropyridine (IX), 2-amino-

3,5,6-trifluoro-4-(heptafluoroprop-2-yl)pyridine [X], and 4-aminotrifluoropyrimidine [XI] were synthesised via displacement of fluorine as fluoride from the corresponding fluoroaromatic compounds with ammonia, according to published procedures [23] or adaptations thereof.

Anhydrous hydrogen fluoride (AHF; at least 99.8% HF) was dispensed from a commercial (ICI Plc) mild steel cylinder fitted with a dip pipe (22 kg AHF). All the experiments involving this extremely hazardous material (see, for example, ICI Mond Divison Technical Service Note No. TS/C/2353) were performed with great care in a specially designed laboratory dedicated to the use of AHF under the supervision of Mr Edward A. Laing, UMIST's fluorine technician.

Diazotisation of 4-Aminotetrafluoropyridine and Coupling of the Resultant Diazonium Ion

(a) Mesitylene as coupling component

(i) Diazotisation in aqueous (80%) hydrofluoric acid. Finely powdered sodium nitrite (0.60 g, 8.5 mmol) was added during 15 minutes to a cold (-20 °C), stirred solution of 4-aminotetrafluoropyridine (1.00 g, 6.00 mmol) in hydrofluoric acid (40 cm^3; 80% HF, 20% H_2O w/w) contained in an open-mouthed polyethylene bottle. The solution was then cooled to -50 °C before mesitylene (0.72 g, 6.00 mmol) was added. After the mixture had been stirred for 30 minutes, it was poured cautiously into water (500 cm^3) and the insoluble brownish-red precipitate which appeared was recovered by filtration,washed with water until the washings were neutral to litmus, dried *in vacuo* (over P_2O_5), and finally purified by simple column chromatography [0.7 m x 5.5 cm, silica gel (80-200 mesh)] to provide 2,3,5,6-tetrafluoro-4-(2,4,6-trimethylphenylazo)-pyridine (V) (nc) (0.54 g, 1.82 mmol, 30%) [Found: C, 56.9, H, 4.0,; F, 25.1; N, 14.1%; *M* (mass spec), 297, $C_{14}H_{11}F_4N_3$ requires C, 56.6; H, 3.7; F, 25.6; N, 14.1%; *M*, 297], m.p. 140-143 °C, with the same spectroscopic properties [i.r., u.v., n.m.r. (^1H, ^{19}F), and mass] as material prepared using anhydrous hydrogen fluoride (see immediately below).

(ii) In anhydrous hydrogen fluoride. Powdered sodium nitrite (5.25 g, 75.0 mmol) (previously dried at 140 °C in a hot air oven) was added during a 20-minute period to a magnetically stirred (PTFE-coated follower) solution of 4-aminotetrafluoropyridine (12.45 g, 75.0 mmol) in AHF (500 cm^3) contained in a poly(ethylene) beaker at room temperature (18 °C). Dropwise addition of mesitylene (9.0 g, 75 mmol) caused the mixture to become deep red in colour. The reaction mixture was stirred until all of the AHF had evaporated, then the reddish-brown solid residue was dissolved in chloroform and the resulting solution [after being filtered and dried ($MgSO_4$)] was chromatographed [DCFC; silica, 70 x 55 mm; light petroleum (b.p. 40 - 60 °C)-dichloromethane] to give red needles of 2,3,5,6-tetrafluoro-4-(2,4,6-trimethylphenylazo)pyridine (V) (18.3 g, 61.6 mmol, 82%) (Found: C, 56.6; H, 3.7; F, 25.6; N, 14.3. Calc. for $C_{14}H_{11}F_4N_3$: C, 56.6; H, 3.7; F, 25.6; N, 14.1%), m.p. 146-146.5 °C, *m/z* 297 ($M^{+\cdot}$, 42%), 147 ($C_7H_{11}N_2^+$, 7%), 119 ($C_7H_{11}^+$, 100%), δ_H (90 MHz; 10% soln. in $CDCl_3$) 2.35 (s; 4-Me), 2.46 (s; 2-,6-Me), 6.95 (s; 3-,5-H) p.p.m. (rel.int.3:6:2), δ_F (84.6 MHz; same soln.) -11.4 (mult; 2-,6-F), -75.4 (mult.; 3-,5-F) p.p.m. (AA'XX' pattern), δ_C (20.1 MHz; saturated soln, in $CDCl_3$; $^{13}CDCl_3$ ref., set at 77.00 p.p.m.; ORD multiplicities in parentheses), 20.20 [s (t); 2-,6-Me], 21.35 [s, (t); 4-Me], 130.67 [s (d); 3-,5-C], 135.28 [s (s); 2-,6-C], 143.53 [s (s); 4- or 1-C], 148.22 [s (s); 1- or 4-C] p.p.m., λ_{max} [ethanol (hexane)] 238 (239) [log ε 3.87 (3.90)], 336 (333) [log ε 4.30 (4.29)], 464 (465) [log ε 2.81 (2.76)] nm, and a red solid which was recrystallized from methanol to yield red crystalline material (0.27 g) [Found: C, 65.0; H, 5.5; N, 13.0%; *M* (mass spec.), 430] which contained a tetrafluoro-4-pyridyl moiety [δ_F (soln. in $CDCl_3$) -11.1 and 75.3 p.p.m. (rel.int 1:1; AA'XX' pattern)] but otherwise remained unidentified.

(iii) In 98% sulphuric acid. An 86:14 mixture (20 cm^3) of anhydrous acetic and propionic acids was added dropwise to a stirred solution of dry sodium nitrite (0.7 g, 10 mmol) in 98% sulphuric acid (20 cm^3) kept at ≤ 30 °C by means of an ice bath; the nitrosating medium thus produced was cooled to ≤ 0 °C, treated with 4-aminotetrafluoropyridine (1.65 g, 10 mmol), then stirred (cooling was maintained) for 3 hours before mesitylene (1.2 g, 10 mmol) was added dropwise. A red precipitate formed immediately. After 3 hours more (stirring was continued), the reaction mixture was poured into water (300 cm^3) and the red solid was recovered by filtration, dried (air oven at 70 °C), and purified by DCFC to provide tetrafluoro-4-(2,4,6-trimethylphenylazo)pyridine (V) (2.3 g, 7.7 mmol, 77%), m.p. 143 °C, with correct spectroscopic [i.r., n.m.r., (^{1}H, ^{19}F) and mass] properties.

(b) 1,3,5-Triethylbenzene as coupling component

Coupling of 2,3,5,6-tetrafluoropyridyl-4-diazonium ion [from 4-NH$_2$.C$_5$F$_4$N (0.83 g, 5.0 mmol) and NaNO$_2$ (0.35 g, 5.0 mmol) in AHF (50 cm^3), as in Experiment (ii) above] with 1,3,5-triethylbenzene [0.81 g, 5.0 mmol; reaction mixture stirred for 15 hours with the beaker sealed with poly(ethylene) foil before the AHF was allowed to evaporate] gave (isolation by DCFC) red 2,3,5,6-tetrafluoro-4-(2,4,6-triethylphenylazo)pyridine (VI) (nc) (1.08 g 3.2 mmol; 64%) (Found: C, 60.5; H,5.2; N, 12.4. $C_{17}H_{17}F_4N_3$ requires C, 60.2; H, 5.0; N, 12.4%), m.p. 76-78 °C, *m/z* 339 ($\underline{M}^{+\cdot}$, 64%), 324 ($C_{16}H_{14}F_4N_3^+$ 100%), 189 ($C_{12}H_7N_2^+$, 15%), δ_H (90 MHz; 10% soln. in CDCl$_3$) 1.12 - 1.38 (two overlapping t; 2-,4-,6-C$\underline{H}_3$CH$_2$), 2.57-3.01 (two overlapping q; 2-,4-,6-CH$_3$C$\underline{H}_2$), 7.08 (s; 3-,5-H) p.p.m. (rel.int. 9:6:2), δ_F (84.6 MHz; same soln.) -11.5 (mult.; 2-,6-F), -76.3 (mult.; 3-,5-F) p.p.m. (AA'XX' pattern), λ_{max} (ethanol) 239 (log ε 3.94), 338 (log ε 4.27), 464 (log ε 2.87) nm.

(c) Anisole as coupling component

(i) *In 80% hydrofluoric acid*. Sodium nitrite (0.7 g, 10 mmol) was added during 5 minutes to a magnetically stirred solution of 4-aminotetrafluoropyridine (1.7 g, 10 mmol) in 80% hydrofluoric acid (200 cm^3) contained in a poly(ethylene) beaker at 18 °C. Dropwise addition of anisole (1.1 g, 10 mmol) caused the mixture to turn red; subsequent removal of the hydrofluoric acid (by natural evaporation) left orange needles that were washed with copious amounts of water then recrystallized from aqueous ethanol to provide 2,3,5,6-tetrafluoro-4-(4-methoxyphenylazo)pyridine (IV) (nc) (2.6 g, 9.1 mmol, 91%) (Found: C, 50.8; H, 2.3, F, 26.9; N, 14.8;

$C_{12}H_7F_4N_3O$ requires C, 50.5; H, 2.5; F, 26.7; N, 14.7%), m.p. 114-115 °C, m/z 285 ($M^{+\cdot}$, 100%), 135 ($C_7H_7N_2O^+$, 21%), 107 ($C_7H_7O^+$, 43%), δ_H (60 MHz; 15% soln.in $CDCl_3$) 3.95 (s; CH_3O), and 7.09 (8.4 Hz d; 3'-,5'-H), 8.04 (8.4 Hz d; 2'-,6'-H) p.p.m., δ_F (84.6 MHz; same soln.) -11.5 (mult.; 2-,6-F), -75.0 (mult.; 3-,5-F) p.p.m. (AA'XX' pattern), λ_{max} (ethanol) 245 (log ε 4.10), 358 (log ε 4.39) nm.

(ii) In anhydrous hydrogen fluoride. The experiment above (i) was repeated using AHF (100 cm^3) instead of hydrofluoric acid. Subjection of the black solid remaining after evaporation of the AHF to DCFC [silica (45 x 50 mm) dichloromethane-light petroleum (b.p. 40 - 60 °C)] gave 2,3,5,6-tetrafluoro-4-(4-methoxyphenylazo)pyridine (IV) (0.17 g, 0.6 mmol, 6%), identified by i.r. spectroscopy, and a mixture, eluted as several pale yellow and orange "bands", that was sublimed (80 °C, ca. 1 mmHg) to give spectroscopically-pure (i.r.) 4-aminotetrafluoropyridine (0.2 g, 12%). Black material remained on the column.

(iii) Diazotisation in 98% sulphuric acid. Using the technique applied in the experiment with mesitylene as the coupling component [Experiment (a) (iii) above], except that the reaction mixture was stirred over a weekend (60 hours), the diazonium salt derived from 4-aminotetrafluoropyridine (0.83 g, 5.0 mmol) was treated with anisole (0.54 g, 5.0 mmol) to provide 2,3,5,6-tetrafluoro-4-(4-methoxyphenylazo)pyridine (IV) (0.25 g, 0.88 mmol, 18%), m.p. 114 - 115 °C [identified spectroscopically (^1H and ^{19}F n.m.r. and mass spectrometry)], and orange-brown 2,3,5,6-tetrafluoro-4-(4-hydroxyphenylazo)pyridine (XXIII) (nc) (0.87 g, 3.2 mmol, 64%) (Found: C, 48.4; H,1.5; N,15.4. $C_{11}H_5F_4N_3O$ requires C, 48.7; H, 1.8; N, 15.5%), m.p. 116-117 °C, m/z 271 ($M^{+\cdot}$, 59.5%), 121 ($C_6H_5N_2O^+$, 48.5%), 93 ($C_6H_5O^+$, 100%), δ_H (60 MHz; 20% soln. in $CDCl_3$) 6.3 (br. s; OH), 7.03 (9 Hz d; 3'-, 5'-H), 8.00 (9 Hz d; 2'-,6'-H) p.p.m; δ_F -11.2 (mult.; 2-,6-F), -74.6 (mult; 3-,5-F) p.p.m. (AA'XX' pattern), λ_{max} (ethanol) 248 (log ε 4.03), 364 (log ε 4.35) nm.

(d) m-Cresol and 3,5-dimethylphenol as coupling components

4-Aminotetrafluoropyridine (1.66 g, 10 mmol) was diazotised with dry powdered sodium nitrite (0.7 g, 10 mmol) in 98% sulphuric acid (20 cm^3) and glacial acetic-propionic acids (86:4 v/v, 20 cm^3) as described in Experiment (a)(iii) above. The resulting solution was divided into two equal parts, the first being treated with m-cresol (0.54 g, 5.0 mmol) and the second with 3,5-dimethylphenol (0.61 g, 5.0 mmol); coupling occurred immediately in each case, and the following products were isolated (after reaction mixtures had been stirred for 2 hours) as described in Experiment (a) (iii) using DCFC (silica, 45 x 50 mm):

2,3,5,6-tetrafluoro-4-(4-hydroxy-2-methylphenyl-azo)pyridine (XIX) (nc) (0.94 g, 3.3 mmol, 66%) (Found: C, 50.2; H, 2.4; N, 14.5. $C_{12}H_7N_3F_4O$ requires C, 50.5; H, 2.5; N, 14.7%), eluted with dichloromethane-trichloromethane-light petroleum (b.p. 40-60 °C), a red solid with m.p. 172-173 °C, m/z 285 ($M^{+\cdot}$, 31%), 135 ($C_7H_7N_2O^+$, 18%), 107 ($C_7H_7O^+$, 100%), δ_H (80 MHz; soln. in $CDCl_3$; ext. TMS ref.) 2.69 (s; CH_3), 5.5 (v. br s; OH), 6.76 (complex; 3-,5-H), 7.76 (d; 6-H) p.p.m. δ_F (75.3 MHz; same soln.) -11.4 (mult.; 2-,6-F), -74.8 (mult; 3-,5-F) p.p.m. (AA'XX' pattern), λ_{max} (KBr disc) 3340 cm^{-1} (br. O-H str.), λ_{max} (ethanol) 252 (log ε 4.01), 285 (log ε 3.71), 443 (log ε 4.37) nm

and

2,3,5,6-tetrafluoro-4-(4-hydroxy-2,6-dimethylphenylazo)pyridine (XX) (nc) (1.34 g, 4.5 mmol, 89%) (Found: C, 51.9; H,2.9; F,25.6; N,14.0. $C_{13}H_9F_4N_3O$ requires C, 52.2; H, 3.0; F, 25.4; N, 14.0%), eluted with dichloromethane-light petroleum (b.p. 40-60 °C), a red solid with m.p. 156-158 °C, m/z 299 ($M^{+\cdot}$, 49%), 149 ($C_8H_9N_2O^+$, 8%), 121 ($C_8H_9O^+$, 100%), δ_H (80 MHz; soln. in $CDCl_3$) 2.54 (s; 2-,6-CH_3), 5.40 (br.s; OH), 6.61 (s; 3-,5-H) p.p.m., δ_F (75.3 MHz; same soln.) -11.5 (mult.; 2-,6-F), -75.4 (mult.; 3-,5-H) p.p.m. (AA'XX' pattern), λ_{max} (5% soln. in CCl_4) 3600 cm^{-1} (O-H str.), λ_{max} (ethanol) 252 (log ε 4.00), 380 (log ε 4.39) nm.

(e) Naphth-2-ol as coupling component

(i) In 98% sulphuric acid. Addition of a solution of naphth-2-ol (1.44 g, 10 mmol) in an 84:16 (v/v) mixture (20 cm^3) of anhydrous acetic and propionic acids to a diazonium solution prepared {see Experiment (a) (iii) above] from 4-aminotetrafluoropyridine (1.66 g, 10 mmol) caused the production of a deep red colouration. After 20 hours (stirring was maintained), the reaction mixture was poured into water (1000 cm^3) and the brown solid which precipitated was recovered (filtration), dried (over P_2O_5 *in vacuo*), and purified by DCFC [silica (45 x 50 mm); dichloromethane-light petroleum (b.p. 40 - 60 °C)] to give orange 2,3,5,6-tetrafluoro-4-(2-hydroxynaphth-1-ylazo)pyridine (XXI) (nc) (2.20 g, 6.85 mmol, 69%) (Found: C,55.9; H,1.9; N,12.9. $C_{15}H_7F_4N_3O$ requires C, 56.1; H, 2.2; N, 13.1%), m.p. (dec.) 188-189 °C, *m*/*z* 321 ($\underline{M}^{+\cdot}$, 100%), 171 ($C_{10}H_7N_2O^+$, 18.5%), 143 ($C_{10}H_7O^+$, 97%), δ_H (80 MHz; soln. in $CDCl_3$) 6.55 (10.4 Hz d; 3-H), 6.80 (complex), 7.55 (10.4 Hz d; 4-H), 8.20 (complex), 15.50 (s; OH) p.p.m. (rel.int. 1:3:1:1:1) δ_F (same soln.) -11.7 (mult; 2-, 6-F), -76.5 (mult,; 3-,5-F) p.p.m. (AA'XX' pattern), λ_{max} (ethanol) 215 (log ε 4.29), 297 (log ε 4.46), 411 (log ε 4.56) nm.

(ii) *In anhydrous hydrogen fluoride*. Addition of a solution of naphth-2-ol (1.44 g, 10 mmol) in AHF (50 cm^3) to a solution of tetrafluoropyridine-4-diazonium fluoride [from 1.66 g (10 mmol) of $4\text{-}H_2NC_5F_4N$ and 0.7 g (10 mmol) of $NaNO_2$ in AHF (200 cm^3)] immediately produced a purplish-black mixture, evaporation of which left a black solid which was shown by t.l.c. to contain none of the expected azo-compound (XXI).

(f) *N,N-Dimethylaniline as coupling component*

Experiment (a)(i) above was repeated exactly, except that *N*,*N*-dimethylaniline (0.8 g, 6.6 mmol) was used as the coupling component instead of mesitylene, and the diazonium solution was cooled to only -40 °C. When quenched with water (after 1 hour), the reaction mixture yielded up a dark red precipitate. This was dried (over P_2O_5 *in vacuo*), dissolved in a mixture (2:3 v/v) of toluene and petroleum ether (b.p. 60-80 °C), and subjected to classical column chromatography [silica gel (80-200 mesh; 0.70 m x 5.5 cm) eluted with the same solvent]. This provided four fractions, the first and third respectively being identified as 4-[4-(dimethylamino)phenyl]-2,3,5, 6-tetrafluoropyridine (III) (nc) (0.08 g, 0.30 mmole, 5%) (Found: C,57.5; H, 3.8; F, 28.2; N, 10.5. $C_{13}H_{10}F_4N_2$ requires C, 57.8; H, 3.7; F, 28.1; N, 10.4%), as white needles, m.p. 195 - 196 °C, *m*/*z* ($M^{+\cdot}$, 82%), 269 ($M^{+\cdot}$-H·, 100%), δ_H (90 MHz; soln. in CCl_4 at 70 °C; ext. 1,4-$Cl_2C_6H_4$ ref.) -3.86 (s; NMe_2), -0.18 (9 Hz d; 3'-,5'-H), 0.50 (9 Hz d; 2'-,6'-H) p.p.m. (rel.int. 3:1:1). δ_F (84.6 MHz; soln. in toluene at 95 °C) -14.3 (2-,6-F), -68.3 (3-,5-F), p.p.m., and 4-[4-(dimethylamino)phenylazo]-2,3,5,6-tetrafluoropyridine (I) (0.27 g, 0.9 mmol, 15%) (Found: C, 52.6; H, 3.6; F, 26.0; N, 18.5. Calc. for $C_{13}H_{10}F_4N_4$: C, 52.3; H, 3.3; F, 25.5; N, 18.8%),*m*/*z* 298 ($M^{+\cdot}$, 86%), 149 ($C_8H_{11}N_3^+$, 100%), 148 ($C_8H_{10}N_3^+$, 27%), 120 ($C_8H_{10}N^+$,98%), δ_H (90 MHz; soln. in $CDCl_3$ at 60 °C; ext.C_6H_6 ref.) -5.00 (s; NMe_2), -1.41 (9 Hz d;3'-,5'-H), -0.26 (9 Hz d, 2'-,6'-H) p.p.m. λ_{max} (hexane) 267 (log ε 3.64), 428 (log ε 4.07)nm, λ_{max} (ethanol) 27.5 (log ε 3.39), 467 (log ε 3.92) nm, as red crystals subliming at 198 °C (lit. [7], m.p. 209- 210 °C). Insufficient of the other two fractions (both coloured, one orange and the other red) were obtained for identification purposes.

Coupling of Diazonium Ions derived from 4-amino-3-chlorotrifluoropyridine (XII), 4-Amino-3,5-dichlorodifluoropyridine (IX), 2-Amino-3,5,6-trifluoro-4-(heptafluoroprop-2-yl)pyridine (X), 4-Aminotrifluoropyrimidine (XI), Pentafluoroaniline (VII) and 4-Aminoheptafluorotoluene (VIII) with Mesitylene

(a) Procedures

4-Amino-3-chlorotrifluoropyridine (XII) was diazotised in a sulphuric acid-acetic acid-propionic acid medium as described for the diazotisation/coupling experiment [(a)(iii) above] involving 4-aminotetrafluoropyridine and mesitylene. The other five amines (VII → XI) were converted to the corresponding 2,4,6-trimethylphenylazo-compounds using anhydrous hydrogen fluoride, as described for 4-aminotetrafluoropyridine [Experiment (a)(ii) above]. In every case, the molar ratio of amino-compound to mesitylene employed was 1.0:1.0; and, unless stated otherwise, the azo-compounds were isolated by DCFC [silica eluted with light petroleum (b.p. 40 - 60 °C)-dichloromethane].

(b) Results

(i)[*] 3-Chloro-2,5,6-trifluoro-4-(2,4,6-trimethylphenylazo)pyridine (XVIII) (nc) (10.3 g, 32.9 mmol, 97%) (Found: C, 53.9; H, 3.4; F, 18.7; N, 13.3. $C_{14}H_{11}ClF_3N_3$ requires C, 53.6; H, 3.5; F, 18.2; N, 13.4%), an orange-red solid, m.p. 145 - 146 °C, m/z 315 [M $(^{37}Cl)^{+}$, 11%], 313 [M $(^{35}Cl)^{+\cdot}$, 33%], 147 ($C_9H_{11}N^+$, 8%), 119 ($C_9H_{11}^+$, 100%), δ_H (220 MHz; soln. in $CDCl_3$) 2.37 (s; 4-Me), 2.53 (s; 2-,6-Me), 7.03 (s; 3-,5-H) p.p.m., δ_F (84.6 MHz; same soln.) 4.6 (dd; 2-F), -8.8 (dd; 6-F), -78.3, (dd; 5-F), p.p.m. ($J_{2,6}$ 13.5, $J_{5,6}$ 21 Hz), was prepared from 6.1 g (34 mmol) of 4-amino-3-chlorotrifluoropyridine (XII) and isolated by recrystallization (from ethanol) of the crude product obtained by pouring the acidic (H_2SO_4-$MeCO_2H$-$EtCO_2H$) reaction mixture into water.

(ii) 3,5-Dichloro-2,6-difluoro-4-(2,4,6-trimethylphenylazo)pyridine (XV) (nc) (2.70 g, 8.2 mmol, 81%) (Found: C,50.4; H,3.1; Cl, 21.3; N, 12.3. $C_{14}H_{11}Cl_2F_2N_3$ requires C, 50.9; H, 3.3; Cl, 21.5; N, 12.7%), as red needles, m.p. 101 - 103 °C, m/z 333 [$M^{+\cdot}$ $(^{37}Cl_2)$,1%], 331 [$M^{+\cdot}$ $(^{37}Cl,\ ^{35}Cl)$ 6%], 329 [$M^{+\cdot}$ $(^{35}Cl_2)$, 9.5%], 119 ($C_9H_{11}^+$, 100%), δ_H (90 MHz; soln. in $CDCl_3$) 2.37 (s; 4-Me), 2.56 (s; 2-,6-Me), 7.03 (s; 3-,5-H) p.p.m. δ_F (84.6 MHz; same soln.) 7.3 (s; 2-,6-F) p.p.m. λ_{max} (ethanol) 321 (log ε 4.27), 452 (log ε 2.78) nm, was prepared from 2.02 g (10 mmol) of 4-amino-3,5-dichlorodifluoropyridine (IX).

(iii) 2,3,5-Trifluoro-4-(heptafluoroprop-2-yl)-6-(2,4,6-trimethylphenylazo)pyridine (XVI) (1.31 g, 2.9 mmol) (Found: C,45.6; H,2.4; N, 9.3. $C_{17}H_{11}F_{10}N_3$ requires C, 45.6; H, 2.5; N, 9.4%),red needles with m.p. 147 - 148 °C, m/z 447 ($M^{+\cdot}$, 9%), 147 ($C_9H_{11}N_2^+$, 9%), 119 ($C_9H_{11}^+$, 100%), δ_H (80 MHz; soln. in $CDCl_3$) 2.31 (s; 4-Me), 2.48 (s; 2-,6-Me), 6.90 (s; 3-,5-H) p.p.m., δ_F (75.3 MHz; same soln.) 3.93 [complex; $(CF_3)_2C$], -6.10 (br.t; 2-F), -47.88 and -50.47 (each br.s; 3- or 5-F), -101.11 [br. complex; $C\underline{F}(CF_3)_2$] p.p.m.

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[*] This preparation was carried out by Sean Hindley, a UMIST final-year undergraduate student.

(rel.int 6:1:1:1:1), λ_{max} (ethanol) 357 (log ε 4.27), 482 (log ε 3.00) nm, was prepared from 1.58 g (5.0 mmol) of 2-amino-3,5,6-trifluoro-4-(heptafluoroprop-2-yl)pyridine (X).

(iv) 2,5,6-Trifluoro-4-(2,4,6-trimethylphenylazo)pyrimidine (XVII) (nc) (2.16 g, 7.70 mmol, 77%) (Found: C, 55.7; H, 3.9; F,20.4; N, 20.0%. $C_{13}H_{11}F_3N_4$ requires C, 56.0; H, 3.7; F, 20.2; N, 19.9%) as deep red needles, m.p. 152 - 153 °C, *m/z* 280 ($M^{+\cdot}$, 24%), 147 ($C_9H_{11}N_2^+$, 11%), 119 ($C_9H_{11}^+$, 100%), δ_H (60 MHz; soln. in $CDCl_3$) 2.38 (s; 4'-Me), 2.56 (s; 2'-,6'-Me), 7.05 (s; 3'-,5'-H) p.p.m., δ_F (84.6 MHz; same soln.) +33.3 (d; 2-F), +5.5 (d; 6-F), -87.2 (dd; 5-F) p.p.m. ($J_{2,5}$ 26.2, $J_{5,6}$ 19.5 Hz), λ_{max} (ethanol) 353 (log ε 4.29), 487 (log ε 2.93) nm was prepared from 1.49 g (10 mmol) of 4-aminotrifluoropyrimidine (XI).

(v) 2,3,4,5,6-Pentafluoro-2',4',6'-trimethylazobenzene (XIII) (nc) (2.06 g, 6.6 mmol, 33%) (Found: C, 57.6; H, 3.3; N, 8.6. $C_{15}H_{11}F_5N_2$ requires C, 57.3; H, 3.5; N, 8.9%), as bright orange needles with m.p. 154 - 155 °C, *m/z* 314 ($M^{+\cdot}$, 43%), 147 ($C_9H_{11}N_2^+$, 7%), 119 ($C_9H_{11}^+$, 100%), δ_H (90 MHz; soln. in $CDCl_3$; ext. TMS ref.) 2.19 (s; 4'-Me), 2.29 (s; 2'-,6'-Me), 7.29 (s; 3'-,5'-H) p.p.m., δ_F (84.6 MHz; same soln.) -73.1 (mult.; 2-,6-F), -76.2 (21 Hz t; 4-F), -84.4 (mult., 3-,5-F) p.p.m. (rel.int. 2:1:2), λ_{max} (hexane) 240 (log ε 3.92), 330 (log ε 4.33), 464 (log ε 2.81) nm, was prepared from 3.66 g (20 mmol) of pentafluoroaniline (VII) and purified by DCFC and subsequent recrystallization (from aqueous ethanol).

(vi) 2,3,5,6-Tetrafluoro-2',4',6'-trimethyl-4-(trifluoromethyl)azobenzene) (XIV) (nc) (3.38 g, 9.3 mmol, 93%) (Found: C, 52.4; H, 3.1; F, 36.7; N, 7.5. $C_{16}H_{11}F_7N_2$ requires C, 52.7; H, 3.0; F, 36.5; N, 7.7%), as red needles, m.p. 134 - 135 °C, *m/z* 364 ($M^{+\cdot}$, 40.5%.), 147 ($C_9H_{11}N_2^+$, 9%), 119 ($C_9H_{11}^+$, 100%), δ_H (90 MHz; soln. in $CDCl_3$) 2.36 (s; 4'-Me), 2.48 (s; 2'-,6'-Me), 7.02 (s; 3'-,5'-H), δ_F (84.6 MHz; same soln.) 21.9 (br. mult.; CF_3), -6.27 (mult.; 2-,6-F), -71.0 (mult.; 3-,5-F) p.p.m. (rel.int. 3:2:2), λ_{max} (ethanol) 244 (log ε 3.92), 336 (log ε 4.31), 464 (log ε 2.84) nm, was prepared from 2.33 g (10 mmol) of 4-aminoheptafluorotoluene (VIII).

Synthesis of 4'-Dimethylamino-2,3,4,5,6-pentafluoroazobenzene

Diazotisation of pentafluoroaniline (2.0 g, 11 mmol) in hydrofluoric acid (80% w/w), followed by coupling of the resultant diazonium salt with *N*,*N*-dimethylaniline was repeated exactly as described in the literature [9]. Recrystallization of the product from petroleum ether (b.p. 60 - 80 °C) gave red 4'-dimethylamino-2,3,4,5,6-pentafluoroazobenzene (II) (1.6 g, 5.1 mmol, 45%) (Found: C, 53.3; H, 3.2; F, 30.6; N, 13.2. Calc. for $C_{14}H_{10}F_5N_3$: C, 53.3; H, 3.2; F, 30.2; N, 13.3%), m.p. 149 °C (lit.[9], m.p. 147-5 - 149 °C), *m*/*z* 315 ($\underline{M}^{+\cdot}$, 64%), 148 ($C_8H_{10}N_3^+$, 20%), 120 ($C_8H_{10}N^+$, 100%), δ_H (60 MHz; soln. in $CDCl_3$) 3.05 (s; NMe_2), 6.56 (9 Hz d; 3'-,5'-H), 7.67 (9 Hz d; 2'-,6'-H) p.p.m., δ_F (84.6 MHz; soln. in CCl_4 at 66 °C) -72.0 (complex 2-,6-F), -78.0 (complex; 4-F), 85.3 (complex; 3-,5-F) p.p.m., λ_{max} (hexane) 265 (log ε 4.10), 409 (log ε 4.45) nm λ_{max} (ethanol) 272 (log ε 3.61), 435 (log ε 4.09) nm.

Reductive Cleavage of 2,3,5,6-Tetrafluoro-4-(2,4,6-trimethylphenylazo)pyridine (V) [cf.24]

A mixture of the azo-compound (0.40 g, 1.35 mmol) and 55% aqueous hydriodic acid (5 cm^3) was heated under reflux for one hour. The resulting dark red solution (containing a dark-coloured sediment) was decolorized by the addition of sodium metabisulphite then poured into water (20 cm^3). The pale yellow solution (containing traces of a black sediment) was neutralized (Na_2CO_3), extracted with diethyl ether (3 x 10 cm^3), and the extract washed with 2M-hydrochloric acid (3 x 10 cm^3). Evaporation of the ether layer (after it had been dried with $MgSO_4$) provided a pale brown solid that was recrystallized from light petroleum (b.p. 60 - 80 °C) to provide white needles of 4-aminotetrafluoropyridine (0.07 g, 0.42 mmol, 31%), identified by i.r. spectroscopy. Conventional work-up (neutralization followed by extraction with diethyl ether) of the hydrochloric acid washings yielded 2,4,6-trimethylaniline (0.17 g, 1.26 mmol, 93%), identified spectroscopically (i.r., ^1H n.m.r., and mass).

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