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STUDIES IN AZIDE CHEMISTRY. PART IX [1]. INVESTIGATIONS INVOLVING FLUORINATED AZIDOPYRIMIDINES AND 4-AZIDO-3-CHLORO-2,5,6-TRIFLUOROPYRIDINE

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SUMMARY

4-Azido-2,5,6-trifluoro- and 4,6-diazido-2,5-difluoro-pyrimidine were obtained by treating tetrafluoropyrimidine with sodium azide in acetonitrile; similar azidation of 5-chlorotrifluoropyrimidine gave 4-azido-5-chloro-2,6-difluoro- and 4,6-diazido-5-chloro-2-fluoro-pyrimidine. Each mono-azide reacted with triphenylphosphine to yield the corresponding iminophosphorane (Staudinger reaction), and the trifluoro-compound gave cycloadducts when heated with phenylacetylene [$\longrightarrow$ 4-phenyl-1-(2,5,6-trifluoro-4-pyrimidinyl)-1,2,3-triazole] and acrylonitrile [$\longrightarrow$ 2-cyano-1-(2,5,6-trifluoro-4-pyrimidinyl)aziridine]; attack on the trifluoro-azide by the sodium salt of pentafluoroaniline produced 4-azido-2,5-difluoro-6-(pentafluorophenylamino)pyrimidine and bis(4-azido-2,5-difluoro-6-pyrimidinyl)(pentafluorophenyl)amine. Attempts to intercept nitrenes during thermal decomposition of both mono-azides failed. Thermolysis of 4-azido-3-chloro-2,5,6-trifluoropyridine in the presence of dimethyl sulphoxide, cyclohexane, or pentafluoroaniline gave products [$py_FN{=}S(O)Me_2$, $py_FNHC_6H_{11}$, and $py_FN{=}NPh_F$ (py_F = 3-chlorotrifluoro-4-pyridyl), respectively] compatible with release of the corresponding nitrene.

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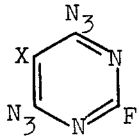
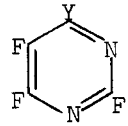
INTRODUCTION



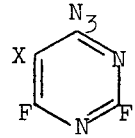
(I) X = F

(VI) X = Cl



(II) Y = F

(III) Y = SO_2Ph



(IV) X = F

(V) X = Cl

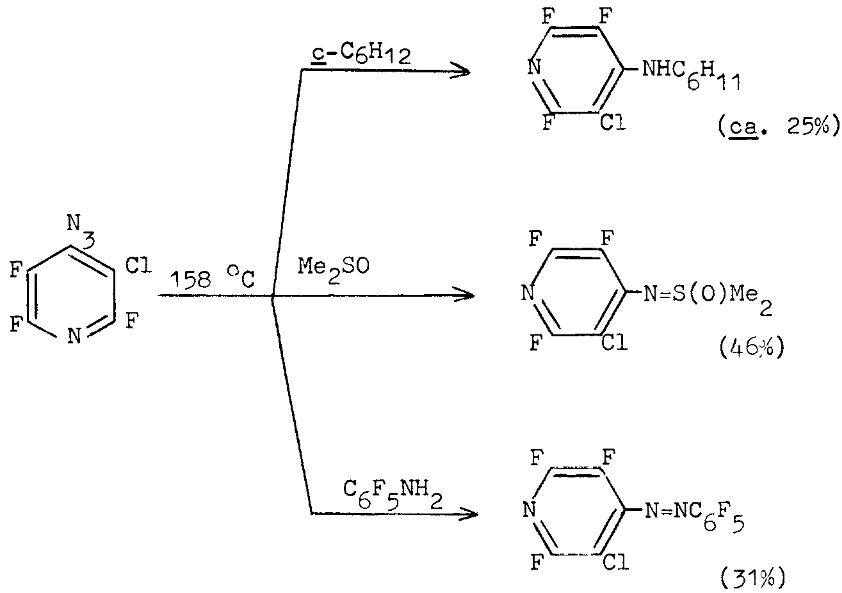
Anionic azidation of fluoropyrimidines was first undertaken in this Department by Jacques in the late 1960s [2]. He isolated only 4,6-diazido-2,5-difluoropyrimidine (I) following treatment of either tetrafluoropyrimidine {(II); ease of nucleophilic displacement: 4-(6-)>2-≫5-F [3]} or 2,5,6-trifluoro-4-pyrimidinyl phenyl sulphone (III) [4] with sodium azide in ethanol [5]; failure to obtain 4-azido-2,5,6-trifluoropyrimidine (IV) from equimolar proportions of tetrafluoropyrimidine and sodium azide in either hot (78 °C) or cold (-20 °C) ethanol [the diazide (I) was isolated in ca. 30% yield (based on $C_4F_4N_2$) in each experiment] was ascribed to the activating influence of the azido function in that system. These results provided a springboard for workers involved in (a) the synthesis of polyfluorinated azidopyridines [6,7], (b) the development of routes to 2-substituted 3,4,5,6-tetrafluoropyridines [8], and (c) the investigation now reported.

DISCUSSION

Slow addition of sodium azide to an equimolar proportion of tetrafluoropyrimidine in cold (0 °C) acetonitrile provided 4-azido-2,5,6-trifluoropyrimidine (IV) and 4,6-diazido-2,5-difluoropyrimidine (I) in 23 and 33% yield (based on $C_4F_4N_2$) respectively. The mono-azide (IV) became the major product (58% based on NaN_3) when an excess of tetrafluoropyrimidine (molar ratio $C_4F_4N_2$:NaN_3 = 2:1) was employed, the yield of 'Jacques' product' (I) falling to 7%. Treatment of 5-chloro-2,4,6-trifluoropyrimidine with sodium azide ($C_4ClF_3N_2$:NaN_3 = 1:1) in acetonitrile at 0 °C gave the 5-chloro-analogues of

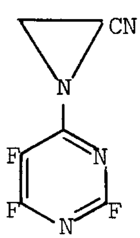
IV and I, namely 4-azido-5-chloro-2,6-difluoro- and 4,6-diazido-5-chloro-2-fluoro-pyrimidine [(V) and (VI)] in 60 and 8% (based on $C_4ClF_3N_2$) yield respectively.

4-Azido-2,5,6-trifluoropyrimidine (IV) is a colourless oil, b.p. 55 ^{o}C at ca. 18 mmHg, which darkens when heated and smoothly evolves ca. 65% of its available nitrogen ($-N_3 \longrightarrow N_2$) in the temperature range 150-170 ^{o}C, giving an intractable brown solid. Thermolysis of the azide at 185 ^{o}C (reaction temperatures were raised to this value from 20 ^{o}C in conventional fashion) under anaerobic conditions in the presence of an excess of dimethyl sulphoxide, pentafluoroaniline, cyclohexane, or benzene (i.e. 'traps' successfully employed to provide circumstantial evidence for the production of nitrenes via pyrolysis of the related azides $4\text{-}N_3C_5F_4N$ [6,9], $C_6F_5N_3$ [10], and $4\text{-}N_3C_6F_4CF_3$ [10]) also yields only nitrogen and dark-coloured intractable materials. A precedent for this failure to procure evidence for the release of trifluoro-4-pyrimidinylnitrene during thermal decomposition of 4-azido-trifluoropyrimidine can be found in studies on perfluoro-(2-azido-4-isopropylpyridine) [7], a compound in which the azido group also lies ortho to ring nitrogen. Similarly, no successful nitrene trapping reactions could be achieved with 4-azido-5-chloro-2,6-difluoropyrimidine (V), which quietly releases ca. 60% of its available nitrogen when heated alone in [redacted] in view of the behaviour of 4-azido-3-chloro-2,5,6-trifluoro-pyridine (see Scheme 1). Clearly, it could be argued that the failure to obtain tractable products in thermal reactions involving either of the azidopyrimidines [(IV) or (V)] and dimethyl sulphoxide [11] or pentafluoroaniline stems from nucleophilic attack on ring carbon by these potential nitrene traps, rather than from an ortho ring nitrogen effect; this still leaves the unsuccessful experiments involving cyclohexane and benzene to explain. Information currently being gained through study of pyrolytic transformations of neat 2- and 4-azidopyridines of the fluorocarbon class, and of related NN-dichloroamines [9,12] and their N-chlorimino counterparts [12,13], may help to resolve this mechanistic puzzle.

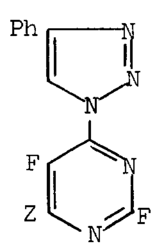


SCHEME 1

4-Azidotrifluoropyrimidine, 4-azido-5-chlorodifluoropyrimidine, and 4-azido-3-chlorotrifluoropyridine smoothly partake in a Staudinger reaction with triphenylphosphine, giving nitrogen and the corresponding iminophosphoranes. 4-Azidotrifluoropyrimidine combines with acrylonitrile at 80 °C to yield 2-cyano-1-(2,5,6-trifluoro-4-pyrimidinyl)-aziridine (VII), presumably *via* initial formation of a 1,3-cycloadduct [triazoline; *cf*. ref. 7]; 1,3-cycloaddition of phenylacetylene to the azide in boiling carbon tetrachloride appears to occur regiospecifically, the only product isolated



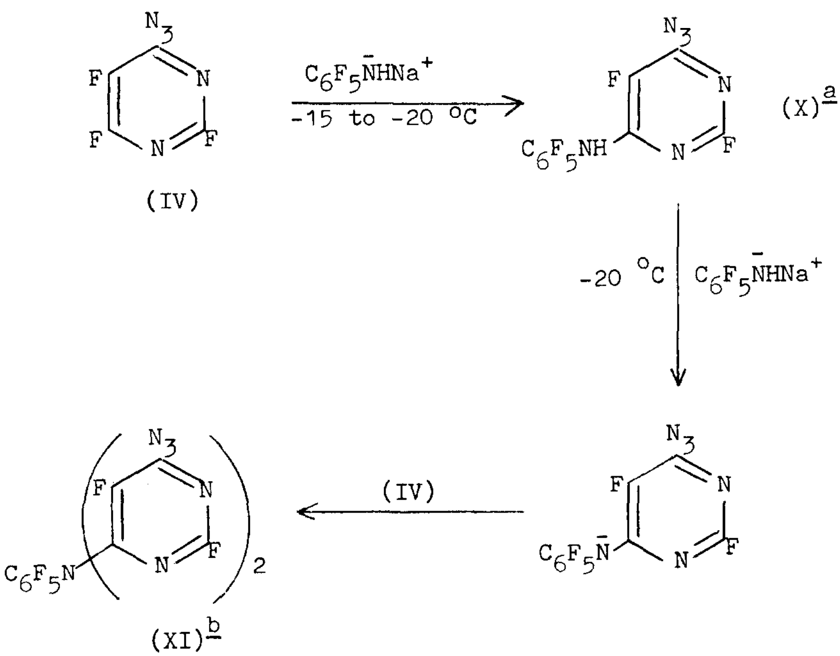
(VII)



(VIII) Z = F

(IX) Z = OEt

being 4-phenyl-1-(2,5,6-trifluoro-4-pyrimidinyl)-1,2,3-triazole (VIII), a compound which reacts with hot ethanol to yield the ethoxy derivative IX. Nucleophilic attack on 4-azidotrifluoropyrimidine itself by the sodium salt of pentafluoroaniline occurs readily at sub-zero temperatures in tetrahydrofuran or acrylonitrile to yield, depending on the conditions (see the Experimental Section and Scheme 2), the secondary amine X or a mixture of X and the related tertiary amine XI.



SCHEME 2

[a] Isolated (as a mixture with $C_6F_5NH_2$) from the product obtained by adding C_6F_5NHNa to the azide (IV), and identified by i.r. and ^{19}F n.m.r. spectroscopy.

[b] Isolated (as a mixture with X) from the product obtained by adding the azide (IV) to an excess of C_6F_5NHNa, and identified by ^{19}F n.m.r. spectroscopy.

EXPERIMENTAL

N.m.r. Spectroscopy

N.m.r. spectra were obtained with a Perkin-Elmer R32 instrument operating at 84.6 MHz (^{19}F) and 90 MHz (^{1}H). Chemical shifts to high field of reference signals are designated negative.

Starting Materials

Tetrafluoro- and 5-chlorotrifluoro-pyrimidine were prepared by heating tetrachloropyrimidine with anhydrous potassium fluoride [3]. Treatment of 3-chlorotetrafluoropyridine (from C_5Cl_5N + KF [14]) with sodium azide in acetonitrile provided 4-azido-3-chlorotrifluoropyridine [6].

Safety Precautions

All reactions, distillations, etc. involving the azidoheterocycles were conducted behind stout blast screens. Once isolated, the azides were stored in small stoppered Pyrex tubes housed in a compartmentalised steel box with perforated sides; each compartment was fitted with its own sliding lid so that the operator, wearing a polycarbonate face shield and heavy-duty gloves, need expose only one tube at a time. No explosions were experienced during the course of the work.

Preparation of 4-Azidotrifluoro- and 4,6-Diazidodifluoropyrimidine

Sodium azide (3.8 g, 58.5 mmole) was added slowly (1.5 h) to a vigorously stirred solution of tetrafluoropyrimidine (17.7 g, 116 mmole) in cold (0 °C) acetonitrile (25 cm^3). The mixture was stirred at 0 °C for 6 h, then allowed to warm up to room temperature and stirred for a further 30 min before being poured into water (1.5 l). Extraction of the aqueous product with diethyl ether (4 x 200 cm^3) followed by distillation of the dry ($MgSO_4$) extract provided 4-azido-2,5,6-trifluoropyrimidine (nc) (5.9 g, 34 mmole, 58% based on NaN_3) (Found: C, 27.3; F, 32.3; N, 39.8. $C_4F_3N_5$ requires C, 27.4; F, 32.6; N, 40.0%), b.p. 55 °C at 18 mmHg, $\lambda_{max.}$ (film) 4.40w(sh.), 4.46m, 4.54s, and 4.67vs (t; N_3 asym. str.) µm, δ_F (neat liq.; ext. CF_3CO_2H ref.) +29.6 (2-F; broadened d), 0.0 (6-F; dd; $|\underline{J}_{5,6}|$ 17, $|\underline{J}_{2,6}|$ 2.5 Hz), and -90.4 (5-F; dd; $|\underline{J}_{2,5}|$ 25 Hz) p.p.m. (rel. int. 1:1:1). The stillpot residue proved to be 4,6-diazido-2,5-difluoropyrimidine (0.4 g, 2.0 mmole, 7%), identified by i.r. spectroscopy after recrystallization from ethanol.

Similar work-up of the product obtained by more rapid addition (0.5 h) of sodium azide (4.8 g, 74 mmole) to tetrafluoropyrimidine (11.2 g, 73.6 mmole) in acetonitrile (25 cm^3) at 0 °C, followed by a 5 h reaction period at 20 °C, gave 4-azido-2,5,6-trifluoropyrimidine (2.9 g, 17 mmole, 23%) and 4,6-diazido-2,5-difluoropyrimidine (nc) (4.8 g, 24 mmole, 65% based on NaN_3) (Found: C, 24.0; F, 19.2; N, 56.9. $C_4F_2N_8$ requires C, 24.2; F, 19.2; N, 56.6%), m.p. 106 °C, $\lambda_{max.}$ (mull) 4.46w, 4.54m, 4.65vs, 4.69s, 4.76s (q; N_3 asym. str.) µm, δ_F (60% w/v soln. in $CHCl_3$; ext. CF_3CO_2H ref.) +30.4 (2-F; broadened d, $|\underline{J}_{2,5}|$ 27 Hz) and -84.8 (5-F; d) p.p.m.

Preparation of 4-Azido-5-chlorodifluoro- and 4,6-Diazido-5-chlorofluoro-pyrimidine

A reaction between sodium azide (2.3 g, 35 mmole) and 5-chlorotrifluoropyrimidine (6.0 g, 36 mmole) at 0 °C in acetonitrile (25 cm^3) was carried out exactly as described for the first $C_4F_4N_2$-NaN_3 reaction above; the product was worked up using the same techniques too, giving impure 4-azido-5-chloro-2,6-difluoropyrimidine (nc) (4.0 g, 21 mmole, 60%) (Found: C, 26.0; F, 20.3; N, 37.1. $C_4ClF_2N_5$ requires C, 25.0; F, 19.8; N, 36.6%), m.p. 34-36 °C, b.p. 82 °C at _ca_. 18 mmHg, $\lambda_{max.}$ (film) 4.50s, 4.66s, 4.71m-w (t; N_3 asym.

str.) μm, δ_F (soln. in $CDCl_3$; ext. CF_3CO_2H ref.) +33.4 (2-F) and +19.3 (6-F) p.p.m. (rel. int. 1:1) (minor impurity bands were present in the region +19.5 to +24.5 p.p.m.), and pale green 4,6-diazido-5-chloro-2-fluoropyrimidine (nc) (0.6 g, 2.8 mmole, 16% based on NaN_3) (Found: C, 24.5; Cl, 16.6; F, 8.8; N, 51.2. C_4ClFN_8 requires C, 22.4; Cl, 16.55; F, 8.9; N, 52.2%), m.p. 121-122 °C, $\lambda_{max.}$ (mull) 4.62, 4.70 (d; N_3 asym. str.), δ_F (soln. in $CDCl_3$; ext. CF_3CO_2H ref.) +34.6 (br. s; 2-F) p.p.m.

Reactions of 4-Azidotrifluoropyrimidine

(a) With triphenylphosphine

A solution of triphenylphosphine (1.5 g, 5.7 mmole) in diethyl ether (15 cm^3) was added dropwise to a solution of the azide (1.0 g, 5.7 mmole) in the same solvent (20 cm^3). The mixture turned yellow and evolution of a gas (presumed to be nitrogen) commenced immediately. The mixture was heated under reflux for 4 h, then cooled, and the white crystals which deposited were recrystallised from carbon tetrachloride to give triphenyl-(2,5,6-trifluoro-4-pyrimidinyl-imino)phosphorane (nc) (1.9 g, 4.6 mmole, 81%) (Found: C, 64.8; H, 3.7; F, 14.0; N, 10.4; P, 7.3. $C_{22}H_{15}F_3N_3P$ requires C, 64.6; H, 3.7; F, 13.9; N, 10.3; P, 7.6%), m.p. 216-217 °C, δ_F (soln. in $CDCl_3$; ext. CF_3CO_2H ref.) +27.2 (2-F), -13.2 (6-F), and -96.2 (5-F) p.p.m. (rel. int.1:1:1).

(b) With phenylacetylene

A solution of the azide (1.5 g, 8.6 mmole) and an excess of phenylacetylene (3.5 g) in carbon tetrachloride (25 cm^3) was heated under reflux for 4 days. The product was then allowed to cool to room temperature, whereupon white needles, m.p. 184-185 °C, of 4-phenyl-1-(2,5,6-trifluoro-4-pyrimidinyl)-1,2,3-triazole (nc) (0.8 g, 2.9 mmole, 34%) (Found: C, 52.0; H, 1.9; F, 20.5; N, 25.4. $C_{12}H_6F_3N_5$ requires C, 52.0; H, 2.2; F, 20.6; N, 25.3%), δ_F (soln. in Me_2CO; ext. CF_3CO_2H ref.) +29.5 (2-F), +4.3 (6-F), and -92.5 (5-F) p.p.m. (rel. int. 1:1:1), δ_H (soln. in $CDCl_3$; ext. TMS ref.) +7.45 (complex;

m-, p-H), 7.9 (complex; o-H), and +8.64 br (s; =CHN) p.p.m. (rel. int. 3:2:1), precipitated. After isolation of this product by filtration etc., the filtrate was evaporated and the residue was recrystallized from ethanol to provide 4-phenyl-1-(6-ethoxy-2,5-difluoro-4-pyrimidinyl)-1,2,3-triazole (nc) (0.1 g, 0.3 mmole, 3.5%) (Found: C, 55.3; H, 3.1; F, 13.2; N, 23.8. $C_{14}H_{11}F_2N_5O$ requires C, 55.4; H, 3.6; F, 12.5; N, 23.1%) as very pale yellow needles, m.p. 146 °C, δ_F (soln. in $CDCl_3$; ext. CF_3CO_2H) +31.8 (2-F; d, $|J_{2,5}|$ 27 Hz), -90.9 (5-F; D) p.p.m. (rel. int. 1:1), and δ_H (same soln.; ext. TMS ref.) +1.5 (CH_3;t), +4.54 (CH_2;q), +7.42 (complex; m-, p-H), +7.9 (complex; o-H), and +8.58 (s; =CHN) p.p.m. (rel. int. 3:2:3:2:1).

(c) With acrylonitrile

A mixture of the azide (1.0 g, 5.7 mmole) and acrylonitrile (15 cm^3) was heated under reflux (ca. 80 °C) for 8 h. The solid which separated when the mixture was cooled to 20 °C was sublimed (145 °C at ca. 2 mmHg) to provide 2-cyano-1-(2,5,6-trifluoro-4-pyrimidinyl)aziridine (nc) (0.8 g, 4.0 mmole, 70%) (Found: C, 42.3; H, 1.3; F, 28.9; N, 27.9.

(nc) (0.85 g, 2.0 mmole, 87%) (Found: C, 62.1; H, 3.5; F, 8.8; N, 9.9. $C_{22}H_{15}ClF_2N_3P$ requires C, 62.0; H, 3.5; F, 8.9; N, 9.9%), m.p. 233-235 °C, δ_F (soln. in CF_3CO_2H; ext. CF_3CO_2H ref.) +30.1 (2-F; s) and +17.5 (6-F; s) p.p.m. (rel. int. 1:1).

Reactions of 4-azido-3-chlorotrifluoropyridine

(a) With triphenylphosphine

Addition of triphenylphosphine (1.2 g, 4.6 mmole) in diethyl ether (10 cm^3) to a solution of the azide (1.0 g, 4.8 mmole) in the same solvent (20 cm^3) caused it to turn yellow but nitrogen evolution was not obvious, and even after 3 days unchanged azide (detected by i.r. spectroscopy) was still present. Therefore the mixture was heated under reflux for 5 h then allowed to cool to room temperature. The white solid which precipitated was purified by recrystallisation from diethyl ether followed by column chromatography (100 x 1.5 cm silica gel) to provide white needles, m.p. 165-166 °C, of triphenyl-(3-chloro-2,5,6-trifluoro-4-pyridylimino)-phosphorane (nc) (0.6 g, 1.4 mmole, 30%) (Found: C, 62.2; H, 3.2; Cl, 8.0; F, 12.7; N, 6.3%. $C_{23}H_{15}ClF_3N_2P$ requires C, 62.4; H, 3.4; Cl, 8.0; F, 12.9; N, 6.3%), δ_F (soln. in $CDCl_3$; ext. CF_3CO_2H ref.) +1.2 (2-F), -16.7 (6-F), and -76.4 (5-F) p.p.m. (rel. int. 1:1:1), m.p. 165-166 °C.

(b) With dimethyl sulphoxide

The azide (1.5 g, 7.2 mmole) and dimethyl sulphoxide (5 cm^3) were heated together at 158 °C for 5 h, and the resulting brown solution was poured into water (1.5 l). The aqueous mixture was extracted with diethyl ether (4 x 100 cm^3); the dried ($MgSO_4$) extract was evaporated at water-pump pressure, and the brown residue was recrystallised from ethanol then purified further by column chromatography (100 x 1.5 cm silica gel) to afford pale yellow platelets of SS-dimethyl-N-(3-chloro-2,5,6-trifluoro-4-pyridyl)sulphoximine (nc) (0.85 g, 3.3 mmole, 46%) (Found: C, 32.5; H, 2.3; Cl, 14.0; F, 21.9; N, 10.6. $C_7H_6ClF_3N_2OS$ requires C, 32.5; H, 2.3; Cl, 13.7; F, 22.05; N, 10.8%), m.p. 97-98 °C, $\lambda_{max.}$ (mull) 7.95, 8.06 (d; S=O str.), 8.62 (S=N str.) μm, δ_F (soln. in $CDCl_3$; ext. CF_3CO_2H ref.) +3.2 (2-F), -13.3 (6-F), and -73.0 (5-F) p.p.m. (rel. int. 1:1:1), and δ_H (same soln.; ext. p-$C_6H_4Cl_2$ ref.) -3.75 (s) p.p.m.

(c) With cyclohexane

The azide (1.0 g, 4.8 mmole) was heated with cyclohexane (12 cm^3) at 158 °C for 19 h in the absence of air in a Pyrex ampoule (200 cm^3). The product was filtered to remove a black solid and the filtrate was evaporated, leaving a brown oil (0.3 g) that was shown by i.r. and n.m.r. spectroscopy to contain much 4-cyclohexylamino-3-chloro-2,5,6-trifluoropyridine (estimated yield 25%).

An authentic sample of the cyclohexylamino-compound (nc) (Found: C, 50.1; H, 4.7; Cl, 13.2; F, 21.8; N, 10.5. $C_{11}H_{12}ClF_3N_2$ requires C, 49.9; H, 4.5; Cl, 13.4; F, 21.6; N, 10.6%), b.p. 118 °C at ca. 0.5 mmHg, $\lambda_{max.}$ (film) 2.94 μm (N-H str.), δ_F (neat liq.; ext. CF_3CO_2H ref.) +1.5 (2-F), -14.5 (6-F), and -88.1 (5-F) p.p.m. (rel. int. 1:1:1), was obtained in 58% yield (4.0 g, 15 mmole) by adding cyclohexylamine (5.2 g, 52.5 mmole) to a stirred solution of 3-chlorotetrafluoropyridine (4.8 g, 25.9 mmole) in acetonitrile (30 cm^3), followed by conventional work-up [pour product into water; extract with ether; distil the dried ($MgSO_4$) extract].

(d) With pentafluoroaniline

The azide (1.5 g, 7.2 mmole) was added slowly (1 h) to hot (158 °C) stirred pentafluoroaniline (6.0 g, 32.8 mmole) kept under nitrogen. The mixture was then stirred at the same temperature for 5 h then cooled to room temperature. Fractional sublimation of the solid product at ca. 3 mmHg provided an orange solid, shown by t.l.c. to contain two components. Subjection of the sublimate to column chromatography (100 x 1.5 cm silica gel) provided 3-chloro-2,5,6-trifluoro-4-(pentafluorophenylazo)pyridine (nc) (0.8 g, 2.2 mmole, 31%; eluent: light petroleum, b.p. 60-80 °C) (Found: C, 36.6; Cl, 9.8; F, 42.1; N, 11.7. $C_{11}ClF_8N_3$ requires C, 36.5; Cl, 9.8; F, 42.0; N, 11.6%), as orange crystals, m.p. 75 °C, δ_F (soln. in Me_2CO; 56.5 MHz spectrum; ext. CF_3CO_2H ref.) +2.5 (2-F; dd; $|J_{2,6}|$ 13.5, $|J_{2,5}|$ 28 Hz), -11.5 (6-F; dd; $|J_{5,6}|$ 19 Hz), -70.5 (2′-,4′-,6′-F; complex), -78.5 (5-F; dd), and -84.5 (3′-,5′-F) p.p.m. (rel. int. 1:1:3:1:2).

REFERENCES

1 Part VIII, R.E. Banks, R.I. Higgons, A. Prakash, M. Rawstron, and G.R. Sparkes, J. Fluorine Chem., 9 (1977) 327.

2 R.S. Jacques, M.Sc. Thesis, University of Manchester, 1968; R.E. Banks, R.N. Haszeldine, and R.S. Jacques, unpublished work.

3 R.E. Banks, D.S. Field, and R.N. Haszeldine, J.Chem.Soc. (C), (1967) 1822.

4 This sulphone was prepared in two ways: (i) by heating tetrafluoropyrimidine with sodium benzenesulphinate in DMF at 120 °C [cf. ref. 8(b)]; and (ii) via the route $C_4F_4N_2$ (II) $\longrightarrow$ (with $PhSH\text{-}Na_2CO_3$) 4-$PhSC_4F_3N_2$ $\longrightarrow$ (with CF_3CO_3H in CH_2Cl_2) 4-$PhSO_2C_4F_3N_2$ (III).

5 Not a good choice of medium owing to the possibility of solvolysis, leading to the formation of ethoxypyrimidines (cf. the conversion of VIII into IX during recrystallisation from ethanol).

6 R.E. Banks and G.R. Sparkes, J.C.S. Perkin Trans. I, (1972) 2964.

7 R.E. Banks and A. Prakash, J.C.S. Perkin Trans. I, (1974) 2479.

8 (a) R.E. Banks, R.N. Haszeldine, K.H. Legge, and F.E. Rickett, J.C.S. Perkin Trans. I, (1974) 2367; (b) R.E. Banks, R.N. Haszeldine, D.R. Karsa, F.E. Rickett, and I.M. Young, J.Chem.Soc. (C), (1969) 1660.

9 R.E. Banks and T.J. Noakes, J.C.S. Perkin Trans. I, (1975) 1419.

10 R.E. Banks and A. Prakash, J.C.S. Perkin Trans. I, (1974) 1365.

11 Storage at 100 ^{o}C for 2 h of a dilute solution of 4-azido-5-chloro-2,6-difluoropyrimidine in DMSO results in the appearance of three small extra and unassigned low-field (ext. CF_3CO_2H) absorptions in the ^{19}F n.m.r. spectrum of the sample.

12 R.E. Banks, M.G. Barlow, T.J. Noakes, and M.M. Saleh, J.C.S. Perkin Trans. I, (1977) 1746.

13 R.E. Banks, M.G. Barlow, J.C. Hornby, and M. Mamaghani, J. Fluorine Chem., 14 (1979) 183; B.A. Al-Saleh, R.E. Banks, M.G. Barlow, and J.C. Hornby, ibid., 12 (1978) 341.

14 R.E. Banks, R.N. Haszeldine, J.V. Latham, and I.M. Young, J.Chem.Soc., (1965) 594.