

Studies in Azide Chemistry. Part VII.¹ Synthesis and Reactions of Perfluoro-(2-azido-4-isopropylpyridine) and 2-Azido-3,5,6-trifluoro-4-methoxypyridine

By Ronald E. Banks * and Ajai Prakash, Chemistry Department, The University of Manchester Institute of Science and Technology, Manchester M60 1QD

Treatment of perfluoro-(4-isopropylpyridine) with sodium azide gave perfluoro-(2-azido-4-isopropylpyridine) and perfluoro-(2,6-diazido-4-isopropylpyridine). The former product reacted with sodium methoxide to give 2-azido-3,5-difluoro-4-(heptafluoroisopropyl)-6-methoxypyridine, with triphenylphosphine, diphenylacetylene, or acrylonitrile to give the corresponding iminophosphorane, 1,2,3-triazole, and aziridine, respectively, and with 1,1-diphenylethylene to give, after work-up, benzophenone and perfluoro-(2-amino-4-isopropylpyridine). Pyrolysis of perfluoro-(2-azido-4-isopropylpyridine) gave nitrogen and intractable material: attempts to intercept a nitrene intermediate failed.

2-Azido-3,5,6-trifluoro-4-methoxypyridine, prepared *via* nitrosation of 3,5,6-trifluoro-2-hydrazino-4-methoxypyridine or treatment of 2,3,5,6-tetrafluoro-4-methoxypyridine with sodium azide, reacted with hot acrylonitrile to give the corresponding aziridine and nitrogen.

As part of a preliminary survey of the chemistry of perfluorinated aryl and hetaryl azides,^{2†} we have prepared the first 2-azido-derivative of the perfluoropyridine class, *viz.* perfluoro-(2-azido-4-isopropylpyridine). Methods currently available for the synthesis of 2-substituted

† For details of work on perfluoroazidobenzene and perfluoro-4-azidotoluene, see ref. 1.

¹ Part VI, R. E. Banks and A. Prakash, *J.C.S. Perkin I*, 1974, 1365.

² R. E. Banks and G. R. Sparkes, *J.C.S. Perkin I*, 1972, 2964 (for details of work on 4-azidotetrafluoropyridine).

tetrafluoropyridines³ are unsuitable for the preparation of the simplest member of the group, 2-azidotetrafluoropyridine, which therefore remains unknown.

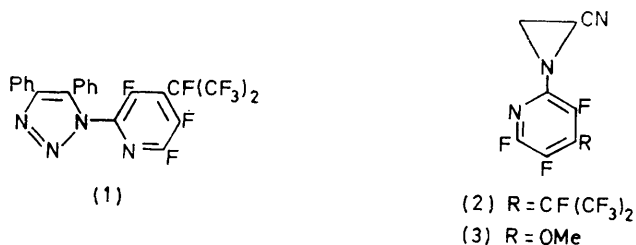
Perfluoro-(4-isopropylpyridine), readily procured *via* treatment of pentafluoropyridine with perfluoropropene-caesium fluoride,⁴ suffers nucleophilic attack by sodium

³ See R. E. Banks, R. N. Haszeldine, K. H. Legge, and F. E. Rickett, *J.C.S. Perkin I*, 1974, 2367, and references quoted therein.

⁴ R. D. Chambers, J. A. Jackson, W. K. R. Musgrave, and R. A. Storey, *J. Chem. Soc. (C)*, 1968, 2221.

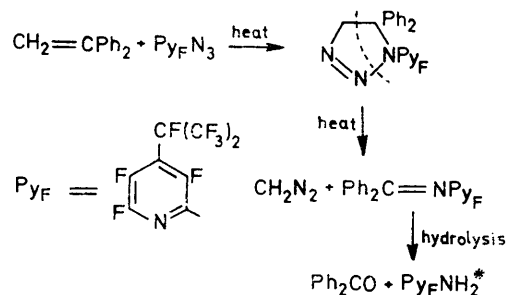
azide in acetonitrile at room temperature to give perfluoro-(2-azido-4-isopropylpyridine) and perfluoro-(2,6-diazido-4-isopropylpyridine), formation of the latter being encouraged by use of an excess of the reagent. Obviously this method is applicable to the synthesis of a variety of 4-substituted 2-azidotrifluoropyridines; for example, treatment of pentafluoropyridine with sodium methoxide⁵ followed by nucleophilic azidation of the resultant tetrafluoro-4-methoxypyridine with sodium azide in boiling acetonitrile gives 2-azido-3,5,6-trifluoro-4-methoxypyridine. This last compound has also been prepared by nitrosation of 3,5,6-trifluoro-2-hydrazino-4-methoxypyridine (from tetrafluoro-4-methoxypyridine and hydrazine hydrate), a procedure that gives material contaminated with 3,5,6-trifluoro-2-hydroxy-4-methoxypyridine. The apparently exclusive nucleophilic displacement of fluorine from the 2-position in perfluoro-(4-isopropylpyridine) or tetrafluoro-4-methoxypyridine observed in this work accords with previous experience.^{4,5} Treatment of perfluoro-(2-azido-4-isopropylpyridine) with sodium methoxide yields 2-azido-3,5-difluoro-4-(heptafluoroisopropyl)-6-methoxypyridine.

Perfluoro-(2-azido-4-isopropylpyridine) and 2-azido-3,5,6-trifluoro-4-methoxypyridine, in keeping with the effect of electron-withdrawal on the azidoazomethine \rightleftharpoons tetrazole equilibrium,⁶ appear, from i.r. and n.m.r. data, to exist preferentially or even exclusively as the azide tautomers at ambient temperature. The same applies to 2-azido-3,5-difluoro-4-(heptafluoroisopropyl)-6-methoxypyridine and perfluoro-(2,6-diazido-4-isopropylpyridine).



Perfluoro-(2-azido-4-isopropylpyridine) darkens when heated to 120 °C and visibly evolves nitrogen at 140 °C, giving a dark brown intractable solid; thermolysis of the azide at 160 °C in the absence of air but in the presence of an excess of dimethyl sulphoxide, cyclohexane, or pentafluoroaniline (*i.e.* 'traps' used to provide circumstantial evidence for the pyrolytic release of nitrenes by the related azides 4-N₃C₅F₄N₂,² C₆F₅N₃,¹ and *p*-CF₃C₆F₄N₃)¹ also gives only nitrogen and dark coloured intractable material. Smooth and virtually quantitative formation of the expected iminophosphorane occurs when perfluoro-(2-azido-4-isopropylpyridine) is subjected to a Staudinger reaction with triphenylphosphine in ether at 20–35 °C, but more forcing thermal conditions are required to effect reaction between the azide and diphenylacetylene

[\longrightarrow (1)], acrylonitrile [\longrightarrow (2)], or 1,1-diphenylethylene [\longrightarrow Ph₂CO + 2-H₂N·C₅F₃N·CF(CF₃)₂]. All the last three reactions presumably involve 1,3-dipolar cycloaddition [like the formation of the cyanoaziridine (3) from 2-azido-3,5,6-trifluoro-4-methoxypyridine and acrylonitrile at 90 °C], aziridine production, which occurs slowly at *ca.* 80 °C, involving ring-contraction⁷ of a triazoline formed initially (*cf.* ref. 1) and the more unusual type of triazoline cleavage^{7,8} exemplified in the Scheme leading to the isolation of benzophenone and perfluoro-(2-amino-4-isopropylpyridine) in the case of 1,1-diphenylethylene.



SCHEME

* An authentic sample was prepared from ammonia and perfluoro-(4-isopropylpyridine) in hot aqueous ethanol.

EXPERIMENTAL

Spectroscopy. I.r. and n.m.r. (shifts to high field designated positive) spectra were obtained with a Perkin-Elmer spectrophotometer model 257 and a Perkin-Elmer R10 instrument (¹⁹F at 56.46, ¹H at 60 MHz), respectively.

Perfluoro-(2-azido-4-isopropylpyridine).—This was prepared from perfluoro-(4-isopropylpyridine)⁴ (10.0 g, 31.4 mmol) and sodium azide (2.02 g, 31.1 mmol) in acetonitrile (75 cm³) at 21 °C according to the procedure² used to convert pentafluoropyridine into 4-azidotetrafluoropyridine. Vacuum distillation of the crude oily product gave a mobile liquid (6.0 g, 17.6 mmol, 57%) (Found: C, 28.4; N, 16.3. C₈F₁₀N₄ requires C, 28.1; N, 16.4%), b.p. 54–56 °C at 3.5 mmHg, λ_{max} (film) 4.59 μm and 4.68 μm (doublet; N₃ asym. str.), δ_F (neat liq.; ext. CF₃·CO₂H) –1.4 [m, CF(CF₃)₂], +11.2br (m, 6-F), +51vbr (m, 3-F), +62vbr (m, 5-F), and +102.8br [m, CF(CF₃)₂] p.p.m. (rel. int. 6 : 1 : 1 : 1 : 1).

Perfluoro-(2,6-diazido-4-isopropylpyridine).—When the previous experiment was repeated but the reaction period was extended from 25 to 70 h, distillation of the product isolated by extraction with ether gave perfluoro-(2,6-diazido-4-isopropylpyridine) (6% yield) (Found: C, 26.5; N, 26.6. C₈F₈N₇ requires C, 26.3; N, 26.8%), b.p. 76 °C at 1.6 mmHg, λ_{max} (film) 4.50 μm, sh, 4.57 μm, sh, and 4.67 μm (N₃ asym. str.), δ_F (neat liq.; ext. CF₃·CO₂H) –1.5 [m, CF(CF₃)₂], +53vbr (complex, 3-, 5-F), and +103.0br [m, CF(CF₃)₂] p.p.m. (rel. int. 6 : 2 : 1), in addition to perfluoro-(2-azido-4-isopropylpyridine) (53%).

Slow addition of sodium azide (1.43 g, 22.0 mmol) to a well stirred solution of perfluoro-(4-isopropylpyridine) (3.50 g, 11.0 mmol) in acetonitrile (50 cm³) at room temperature, followed by work-up in the usual way² after the mixture had

⁷ P. Scheiner in 'Selective Organic Transformations,' ed. B. S. Thyagarajan, Wiley-Interscience, New York, 1970, vol. 1, p. 327.

⁸ T. Sheradsky in 'The Chemistry of the Azido Group,' ed. S. Patai, Wiley-Interscience, London, 1971, p. 353.

⁵ R. E. Banks, J. E. Burgess, W. M. Cheng, and R. N. Haszeldine, *J. Chem. Soc.*, 1965, 575.

⁶ M. E. C. Biffin, J. Miller, and D. B. Paul, in 'The Chemistry of the Azido Group,' ed. S. Patai, Wiley-Interscience, London, 1971, p. 90.

been stirred for 2 days, gave perfluoro-(2-azido-4-isopropylpyridine) (1.50 g, 4.39 mmol, 40%) and perfluoro-(2,6-diazido-4-isopropylpyridine) (1.0 g, 2.7 mmol, 25%).

Reactions of Perfluoro-(2-azido-4-isopropylpyridine).—(i) *With sodium methoxide.* Sodium methoxide (0.33 g, 6.11 mmol) in dry methanol (20 cm³) was added dropwise to a stirred solution of perfluoro-(2-azido-4-isopropylpyridine) (2.0 g, 5.85 mmol) in dry methanol (15 cm³) at room temperature. The mixture was stirred for 90 min then heated under reflux for 4 h. The product was poured into water (300 cm³) and the aqueous mixture was extracted with ether (3 × 100 cm³); the extract was dried (MgSO₄) and distilled, to give 2-azido-3,5-difluoro-4-(heptafluoroisopropyl)-6-methoxy-pyridine (1.30 g, 3.66 mmol, 63%) (Found: C, 30.8; H, 1.0; N, 15.6. C₉H₃F₉N₄O requires C, 30.5; H, 0.8; N, 15.8%), b.p. 70–71 °C at 2.5 mmHg, λ_{max} (film) 4.59 μm and 4.68 μm (doublet; N₃ asym. str.), δ_F (neat liq.; ext. CF₃·CO₂H) –1.5 [m, CF(CF₃)₂], +60 to +64 (complex, 3- and 5-F), and +103br [m, CF(CF₃)₂] p.p.m. (rel. int. 6 : 2 : 1), δ_H (neat liq.; ext. C₆H₆) +2.72 p.p.m.

(ii) *With triphenylphosphine.* This reaction was carried out with perfluoro-(2-azido-4-isopropylpyridine) (2.0 g, 5.8 mmol) and the phosphine (1.5 g, 5.8 mmol) as described for the corresponding reaction involving 4-azidotetrafluoropyridine,² to give [perfluoro-(4-isopropyl-2-pyridylimino)]-triphenylphosphorane (3.0 g, 5.2 mmol, 90%) (Found: C, 54.5; H, 2.8; N, 5.0. C₂₆H₁₅F₁₀N₂P requires C, 54.2; H, 2.6; N, 4.8%) as needles, m.p. 159–160 °C (from diethyl ether).

(iii) *With diphenylacetylene.* Perfluoro-(2-azido-4-isopropylpyridine) (1.5 g, 4.4 mmol), diphenylacetylene (0.95 g, 5.3 mmol), and carbon tetrachloride (25 cm³) were heated together at 170 °C for 15 h in a stainless steel rocking autoclave (100 cm³). Carbon tetrachloride was distilled from the product and the dark brown viscous residue was heated under reflux with light petroleum (b.p. 80–100 °C); the solution obtained was filtered to remove an intractable brown solid (0.34 g) and then evaporated by distillation. The residue was dissolved in carbon tetrachloride and subjected to column chromatography (silica gel) to give diphenylacetylene (0.70 g, 74% recovery) and, by elution with chloroform, 1-[perfluoro-(4-isopropyl-2-pyridyl)]-4,5-diphenyl-1,2,3-triazole (0.10 g, 0.19 mmol, 4%) (Found: C, 51.1; H, 1.9; F, 37.0; N, 10.7. C₂₂H₁₀F₁₀N₄ requires C, 50.8; H, 1.9; F, 36.5; N, 10.8%), m.p. 150–151 °C, δ_F (ca. 10% soln. in Me₂CO; ext. CF₃·CO₂H) –2.0 [m, CF(CF₃)₂], +7.5br (m, 6-F), +45.0br (m, 3-F), +50.0br (m, 5-F), and +103br [m, CF(CF₃)₂] p.p.m.

A similar reaction between the azide (2.00 g) and diphenylacetylene (1.03 g) in boiling carbon tetrachloride (50 cm³) for 210 h gave, after removal of the solvent by distillation, a brown oil which partly solidified when cooled. The solid material was separated by fractional crystallisation (from petroleum, b.p. 60–80 °C) into 1-[perfluoro-(4-isopropyl-2-pyridyl)]-4,5-diphenyl-1,2,3-triazole (0.07 g, 2%), m.p. 150–151 °C, and diphenylacetylene (0.70 g); perfluoro-(2-azido-4-isopropylpyridine) (1.5 g, 75%) was recovered from the mother liquor by vacuum distillation.

(iv) *With acrylonitrile.* Perfluoro-(2-azido-4-isopropylpyridine) (1.0 g, 2.9 mmol) and acrylonitrile (5.0 g, 94 mmol) in tetrachloroethylene (10 cm³) were heated under reflux for 5 days. Volatile material was removed by vacuum distillation, leaving a viscous oil that solidified as it cooled. Recrystallisation of the solid residue from petroleum (b.p. 60–80 °C) provided 1-[perfluoro-(4-isopropyl-2-pyridyl)]aziridine-

2-carbonitrile (0.7 g, 1.9 mmol, 66%) (Found: C, 36.2; H, 1.0; F, 52.2; N, 11.4. C₁₁H₃F₁₀N₃ requires C, 36.0; H, 0.8; F, 51.8; N, 11.4%), m.p. 74–76 °C, λ_{max} (mull) 4.43 μm (C≡N str.), δ_F (ca. 10% soln. in CDCl₃; ext. CF₃·CO₂H) –3.0 [m, CF(CF₃)₂], +10.0 (m, 6-F), +50.0br (m, 3-F), +61.0br (m, 5-F), and +103.0 [m, CF(CF₃)₂] p.p.m. (rel. int. 6 : 1 : 1 : 1 : 1), δ_H (same soln.; ext. C₆H₆) +3.23 (d of d, *J*_{trans} 3.5, *J*_{cis} 5.8 Hz, CHCN), +3.48 (d, *trans*-CH·CH·CN), and +3.63 (d, *J*_{gem} ca. 0 Hz, *cis*-CH·CH·CN) p.p.m. (rel. int. 1 : 1 : 1).

Treatment of perfluoro-(2-azido-4-isopropylpyridine) (1.7 g, 5.0 mmol) with acrylonitrile (0.3 g, 5.7 mmol) in boiling acetonitrile (20 cm³) for 12 h gave 1-[perfluoro-(4-isopropyl-2-pyridyl)]aziridine-2-carbonitrile (0.1 g, 0.3 mmol, 20% based on azide consumed) and 1.2 g (71%) of the azide was recovered.

(v) *With 1,1-diphenylethylene.* Perfluoro-(2-azido-4-isopropylpyridine) (1.7 g) was recovered in 86% yield by distillation of the product obtained by heating it (2.0 g, 5.8 mmol) with 1,1-diphenylethylene (1.48 g, 8.2 mmol) in boiling light petroleum (50 cm³; b.p. 60–80 °C) for 15 days.

Reaction of the azide (1.5 g, 4.4 mmol) with 1,1-diphenylethylene (3.0 g, 16.7 mmol) in carbon tetrachloride (35 cm³) at 150 °C for 20 h in a stainless steel rocking autoclave (100 cm³) in the absence of air gave, after removal of solvent by distillation, a viscous black oil that was subjected to column chromatography (alumina type H). Elution with chloroform-light petroleum (b.p. 60–80 °C) gave a mixture (0.1 g) of benzophenone and perfluoro-(2-amino-4-isopropylpyridine) (identified by i.r. and n.m.r. spectroscopy), and pure benzophenone (0.02 g); elution with chloroform gave a black unidentified gum (1.0 g).

Perfluoro-(2-amino-4-isopropylpyridine).—A mixture of perfluoro-(4-isopropylpyridine) (6.0 g, 19 mmol), aqueous ammonia (d 0.880; 25 cm³), and ethanol (75 cm³) was heated under reflux for 5 h. The product was poured into water (200 cm³) and the mixture was extracted with ether (3 × 200 cm³). The extract was dried (MgSO₄) and distilled, to give a two-component (by t.l.c.) oil (4.0 g), b.p. 68–75 °C at 7.5 mmHg, which was separated by column chromatography (alumina) into 2-ethoxy-3,5,6-trifluoro-4-heptafluoroisopropylpyridine (1.4 g, 4 mmol; 21%; eluted with light petroleum, b.p. 60–80 °C) (Found: C, 34.8; H, 1.5; F, 54.1; N, 4.1. C₁₀H₅F₁₀NO requires C, 34.8; H, 1.4; F, 55.1; N, 4.1%), δ_F (neat liq.; ext. CF₃·CO₂H) –1.5 [m, CF(CF₃)₂], +15.5br (m, 6-F), +59vbr (m, 3-F), +73vbr (m, 5-F), and +103.5br [m, CF(CF₃)₂] p.p.m. (rel. int. 6 : 1 : 1 : 1 : 1), δ_H (neat liq.; ext. C₆H₆) +2.35 (q) and +5.35 (t) p.p.m. (rel. int. 2 : 3), and perfluoro-(2-amino-4-isopropylpyridine) (2.6 g, 8 mmol, 44%; eluted with chloroform) (Found: C, 30.5; H, 0.6; F, 59.6; N, 9.0. C₈H₂F₁₀N₂ requires C, 30.4; H, 0.6; F, 60.1; N, 8.9%), λ_{max} 2.84, 2.91, 2.98, and 3.10 μm (N–H str.), δ_F (neat liq.; ext. CF₃·CO₂H) –1.5 [m, CF(CF₃)₂], +16.5br (m, 6-F), +61vbr (m, 3-F), +77vbr (m, 5-F), and +103br [m, CF(CF₃)₂] p.p.m. (rel. int. 6 : 1 : 1 : 1 : 1), δ_H (neat liq.; ext. C₆H₆) +1.3 (s) p.p.m.

2-Azido-3,5,6-trifluoro-4-methoxypyridine.—(i) *Direct method.* 2,3,5,6-Tetrafluoro-4-methoxypyridine⁵ (1.7 g, 9.4 mmol) in acetonitrile (50 cm³) was heated under reflux with sodium azide (0.6 g, 9.2 mmol) for 90 h. The product was worked up by the usual procedure,² the final vacuum distillation yielding 2,3,5,6-tetrafluoro-4-methoxypyridine (1.0 g, 59% recovery) and 2-azido-3,5,6-trifluoro-4-methoxypyridine (0.3 g, 1.55 mmol, 40% based on tetrafluoro-4-methoxypyridine consumed), identified by comparison of its

i.r. spectrum with that of the sample prepared by the following method.

(ii) *Indirect method.* A mixture of 2,3,5,6-tetrafluoro-4-methoxy-pyridine (12.0 g, 66 mmol), methanol (30 cm³), and hydrazine hydrate (6.0 g, 120 mmol) was stirred at room temperature for 20 h. The solid that precipitated was washed with water and crystallised from light petroleum (b.p. 60–80 °C) to give 3,5,6-trifluoro-2-hydrazino-4-methoxy-pyridine (8.0 g, 41.5 mmol, 61%) (Found: C, 37.6; H, 3.3; F, 29.3; N, 21.6. C₆H₆F₃N₃O requires C, 37.3; H, 3.1; F, 29.5; N, 21.8%) as yellow needles, m.p. 122–124 °C, δ_{F} [ca. 10% soln. in PO(NMe₂)₃; ext. CF₃·CO₂H] +17.3 (d of d, $J_{3,6} \approx J_{5,6} \approx 26$ Hz, 6-F), +84.8 (d with further fine splitting, 3-F), and +99.5 (d with further fine splitting, 5-F) p.p.m. (rel. int. 1 : 1 : 1).

Sodium nitrite (1.0 g) in water (10 cm³) was added slowly to a cold (0 °C) stirred mixture of 3,5,6-trifluoro-2-hydrazino-4-methoxy-pyridine (2.6 g, 13 mmol), 5M-hydrochloric acid (40 cm³), and ether (10 cm³). The mixture was stored at 0 °C for 1 h then poured into water (200 cm³); the aqueous product was extracted with ether (3 × 150 cm³), the extract was dried (MgSO₄) and evaporated, and the residual oil was distilled to yield, as a mobile oil, 2-azido-3,5,6-trifluoro-4-methoxy-pyridine (1.0 g, 4.9 mmol, 36%) (Found: C, 35.6; H, 1.7; F, 27.4; N, 27.2. C₆H₃F₃N₄O requires C, 35.3; H, 1.5; F, 27.9; N, 27.4%), b.p. 47–48 °C at 0.7 mmHg, λ_{max} (film) 4.58m, 4.65s, and 4.72s μm (triplet; N₃ asym. str.), δ_{F} (neat liq.; ext. CF₃·CO₂H) +13.0 (d of d, $J_{3,6} \approx J_{5,6} \approx 23$ Hz, 6-F), +74.5 (d with further fine splitting, 3-F), and +85.0 (d with further fine splitting, 5-F) p.p.m. (rel. int. 1 : 1 : 1), δ_{H} (neat liq.; ext. C₆H₆) +2.4 (t, $J_{3,5\text{-F},\text{OH}}$, 2.6 Hz) p.p.m.

In a similar experiment involving treatment of 3,5,6-trifluoro-2-hydrazino-4-methoxy-pyridine (5.0 g) in cold (0 °C)

5M-hydrochloric acid (70 cm³) and ether (20 cm³) with sodium nitrite (2.5 g) in water (30 cm³), the oily product isolated by extraction with ether was left at room temperature over the weekend before work-up. The oil partly solidified, and re-crystallisation of the solid from light petroleum (b.p. 60–80 °C) yielded pale green needles of 3,5,6-trifluoro-2-hydroxy-4-methoxy-pyridine (0.15 g, 3%) (Found: C, 40.3; H, 2.3; F, 31.6; N, 7.7. C₆H₄F₃NO₂ requires C, 40.2; H, 2.2; F, 31.8; N, 7.8%), m.p. 122–124 °C, λ_{max} (mull) 3.3vbr (O–H str.) μm , δ_{F} (ca. 30% soln. in Me₂CO; ext. CF₃·CO₂H) +18.4 (24 Hz 'triplet,' 6-F), +84.5 (d with further fine splitting, 3-F), and +92.8 (d with further fine splitting, 5-F) p.p.m. (rel. int. 1 : 1 : 1), δ_{H} (same soln.; ext. C₆H₆) –2.8br (OH) and +2.75 (t, CH₃) p.p.m. (rel. int. 1 : 3). Distillation of the remaining oil provided 2-azido-3,5,6-trifluoro-4-methoxy-pyridine (2.7 g, 51%), b.p. 35–37 °C at 0.3 mmHg.

1-(3,5,6-Trifluoro-4-methoxy-2-pyridyl)aziridine-2-carbonitrile.—No reaction appeared to occur between 2-azido-3,5,6-trifluoro-4-methoxy-pyridine (0.8 g, 4.0 mmol) and an excess of acrylonitrile (5 cm³) at 21 °C during 15 days, as revealed by i.r. analysis and the failure to collect any gas in a nitrometer attached to the apparatus. At 90 °C, however, ca. 4 mmol of nitrogen was evolved during 5 h. The liquid product was distilled to remove acrylonitrile and the solid residue was crystallised from light petroleum (b.p. 60–80 °C), to give the aziridine (0.5 g, 2.2 mmol, 55%) (Found: C, 47.5; H, 2.9; F, 25.0; N, 18.2. C₉H₆F₃N₃O requires C, 47.2; H, 2.6; F, 24.9; N, 18.3%), m.p. 114 °C, λ_{max} (mull) 4.44 μm (C≡N str.), δ_{F} (8% soln. in CDCl₃; ext. CF₃·CO₂H) +12.8 (m, 6-F), +74.4 (m, 3-F), and +84.6 (m, 5-F) p.p.m. (rel. int. 1 : 1 : 1), δ_{H} (same soln.) +2.23 (t, OCH₃), +3.36 (m, CH·CN), and +3.6 to +3.8 (complex, CH₂·CH·CN) p.p.m. (rel. int. 3 : 1 : 2).

[4/1206 Received, 20th July, 1974]