Journal of Fluorine Chemistry, 9 (1977) 327–332
© Elsevier Sequoia S.A., Lausanne – Printed in the Netherlands
Received: December 9, 1976

SHORT COMMUNICATION

Studies in Azide Chemistry. Part VIII [1]. Some Reactions of 4-Azido-3,5-dichloro-2,6-difluoropyridine

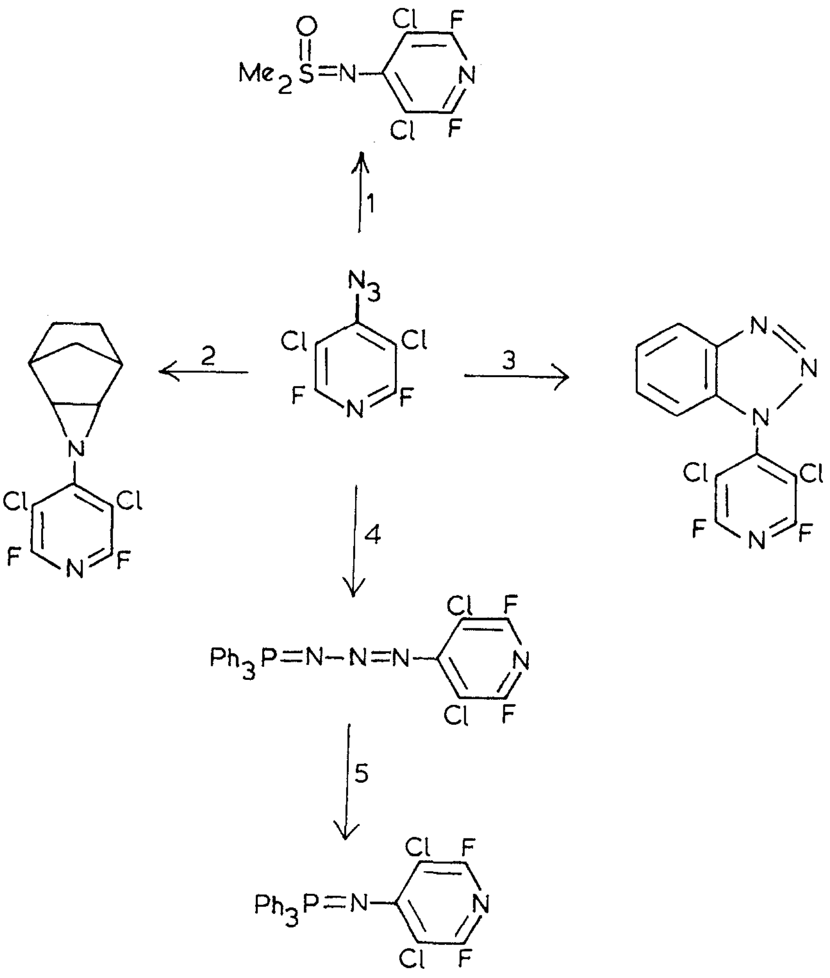
RONALD E. BANKS, ROBIN I. HIGGINS [2], AJAI PRAKASH,
MARGARET RAWSTRON [2], and GEORGE R. SPARKES

Chemistry Department, The University of Manchester
Institute of Science and Technology, Manchester M60 1QD
(Great Britain)

The recent comment [3] about the synthesis of N-arylsulphoximines from dimethyl sulphoxide and perfluoroaryl azides [4,5] prompts us to report that 4-azido-3,5-dichloro-2,6-difluoropyridine partakes in this reaction. Also (see the Scheme), it undergoes the expected [cf. ref. 4] 1,3-dipolar cycloadditions with benzyne and norbornene, and can be converted into an iminophosphorane via a Staudinger reaction with triphenylphosphine. Interestingly, the intermediate adduct (presumably [6] a phosphoranylidinetriazene) involved in the last reaction is easily isolated.

EXPERIMENTAL

I.r., n.m.r. [shifts to high field of the reference (ext. CF_3CO_2H for ^{19}F, ext. C_6H_6 for ^{1}H) designated negative], and mass spectroscopic analyses, respectively, were carried out with a Perkin-Elmer Spectrophotometer



Reagents : 1, Me_2SO, 160 °C; 2, norbornene, 20 °C;
3, o-$H_2NC_6H_4CO_2H$, i-AmONO, CH_2Cl_2, 40 °C;
4, Ph_3P, Et_2O, 20 °C; 5, boiling Me_2CO.

model 257, a Perkin-Elmer R10 instrument (^{19}F at 56.46 MHz, ^{1}H at 60 MHz), and a G.E.C.-A.E.I. MS902 spectrometer (electron beam energy 70 eV).

Reactions of 4-azido-3,5-dichloro-2,6-difluoropyridine

(a) With dimethyl sulphoxide

4-Azido-3,5-dichloro-2,6-difluoropyridine [4] (2.84 g, 12.6 mmol) was heated with dimethyl sulphoxide (35 cm^3) at 120 °C for 4 h in a flask attached to a nitrometer. No gas was evolved, so the temperature was raised to 160 °C and kept at that value until (8 h) the theoretical amount of nitrogen had been released. The brown liquid product was poured into water (300 cm^3), and the aqueous mixture was extracted with ether (4 X 100 cm^3). The extract was washed with water (3 X 50 cm^3), dried ($MgSO_4$), and evaporated *in vacuo*; the brown residue (2.2 g) was crystallised from ethanol to give pale yellow *SS*-dimethyl-*N*-(3,5-dichloro-2,6-difluoro-4-pyridyl)sulphoximine (nc) (1.59 g, 5.78 mmol, 46%) (Found: C, 30.5; H, 2.2; N, 9.9. $C_7H_6Cl_2F_2N_2OS$ requires C, 30.5; H, 2.2; N, 10.2%), m.p. 114 °C, λ_{max}(mull) 8.14, 8.19 (d; S=O str.), 8.62 (S=N str.) μm, δ_F(saturated soln. in HMPA) +3.9 (s) p.p.m., δ_H(same soln.) -3.1 (s) p.p.m., *m/e* 274 [$C_7H_6{}^{35}Cl_2F_2N_2OS^{+\cdot}$ (*M*$^{+\cdot}$), 100%][correct relative intensities for the isotope peaks (*M*+2) and (*M*+4) were observed], 78 ($C_2H_6OS^+$, 83%).

(b) With triphenylphosphine

A solution of triphenylphosphine (2.74 g, 10.5 mmol) in diethyl ether (20 cm^3) was added dropwise to a solution of 4-azido-3,5-dichloro-2,6-difluoropyridine (2.00 g, 8.89 mmol) in the same solvent (10 cm^3). Nitrogen (presumably) evolution occurred immediately and the mixture turned pale yellow; this was followed by the appearance of deep lemonyellow crystals. The mixture was heated under reflux for 2.25 h then filtered whilst warm to remove the yellow crystals of a compound presumed to be 1-(3,5-dichloro-2,6-difluoro-4-pyridyl)-3-triphenylphosphoranylidenetriazene (nc) (2.94 g, 6.04 mmol, 68%) (Found: C,56.4; H, 3.5; N, 11.2. $C_{23}H_{15}F_2Cl_2N_4P$ requires C, 56.7; H, 3.1; N, 11.5%), m.p. 124-126 °C (dec.); the filtrate was cooled to 0 °C and the white crystals which formed were recrystallised twice from diethyl ether to provide triphenyl-(3,5-dichloro-2,6-difluoro-4-pyridylimino)phosphorane (nc) (0.43 g, 0.94 mmol, 11%), m.p. 149.5 °C, with an unsatisfactory elemental analysis (Found: C, 60.9; H, 3.6; N, 6.0. $C_{23}H_{15}F_2Cl_2N_2P$ requires C, 60.1; H, 3.3; N, 6.1%). The ^{19}F n.m.r. spectrum of the iminophosphorane (5% w/w soln. in Me_2CO) showed only a singlet at +1.2 p.p.m.; the base peak in the mass spectrum possessed an m/e value corresponding to that of the molecular ion $[C_{23}H_{15}F_2{}^{35}Cl_2N_2P]^{+\cdot}$ (458).

When a solution of 1-(3,5-dichloro-2,6-difluoro-4-pyridyl)-3-triphenylphosphoranylidenetriazene (0.42 g) in acetone (50 cm^3) was heated under reflux, nitrogen (presumably) was evolved; evaporation of the solution followed by recrystallisation of the residue from diethyl ether provided triphenyl-(3,5-dichloro-2,6-difluoro-4-pyridylimino)phosphorane (Found: C, 60.3; H, 3.2; F, 8.0; N, 5.9. $C_{23}H_{15}F_2Cl_2N_2P$ requires C, 60.1; H, 3.3; F, 8.3; N, 6.1%).

(c) With benzyne

Anthranilic acid (2.16 g, 15.8 mmol) in acetone (20 cm^3) was added slowly to boiling methylene chloride (60 cm^3) containing isoamyl nitrite (1.93 g, 16.5 mmol) and 4-azido-3,5-dichloro-2,6-difluoropyridine (3.42 g, 15.2 mmol). Evaporation of the product, in vacuo, followed by recrystallisation (twice) of the residue from methylated spirit provided 1-(3,5-dichloro-2,6-difluoro-4-pyridyl)benzotriazole (nc) (0.91 g, 3.02 mmol, 20%) (Found: C, 43.7; H, 1.4; N, 18.2. $C_{11}H_4Cl_2F_2N_4$ requires: C, 43.85; H, 1.3; N, 18.6%), m.p. 119.5 °C, δ_F(25% w/w soln. in HMPA) +7.2 (s) p.p.m., δ_H(same soln.) +1.1 (5-, 6-H), +1.6 (4-, 7-H) p.p.m. (rel. int. 1:1).

(d) With norbornene

The azide(2.0 g, 8.9 mmol) was added slowly to a stirred solution of norbornene (1.0 g, 11 mmol) in light petroleum (b.p. 60-80 °C; 30 cm^3). After 72 h, the product was evaporated at water pump pressure and the colourless oily residue was cooled in ice. The white crystals which formed were recrystallised from light petroleum (b.p. 60-80 °C) to provide 3-(3,5-dichloro-2,6-difluoro-4-pyridyl)-3-azatricyclo$[3,2,1,0^{2,4}]$octane (nc) (2.6 g, 8.9 mmol, 100%) (Found: C, 49.9; H, 3.6; F, 13.0; N, 9.4. $C_{12}H_{10}F_2Cl_2N_2$ requires C, 49.5; H, 3.4; F, 13.0; N, 9.6%), m.p. 54 °C, δ_H(10% w/w soln. in $CDCl_3$) τ2.87 (s; CHNCH), τ2.68 (br. s; bridgehead $>\!\!\!-$CH), τ1.8-1.2 (complex).

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

2 Final-year undergraduate students.

3 R.W. Heintzelman, R.B. Bailey, and D. Swern, J.Org.Chem., 41, (1976) 2207.

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

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

6 H. Goldwhite, P. Gysegem, S. Schow, and C. Swyke, J.C.S. Dalton Trans., (1975) 16.