Heterocyclic Polyfluoro-compounds. Part 25.[1] The Photochemical Addition of Ethylene to Pentafluoropyridine: Formation of 1 : 1- and 2 : 1-Adducts

By **Michael G. Barlow, David E. Brown,** and **Robert N. Haszeldine,** * Department of Chemistry, The University of Manchester Institute of Science and Technology, Manchester M60 1QD

Ethylene adds photochemically to pentafluoropyridine to yield 1,2,4,5,6-pentafluoro-3-azabicyclo[4.2.0]octa-2,4-diene (1) and 1,2,5,6,8-pentafluoro-7-azatricyclo[4.2.2.0²·⁵]dec-7-ene (2). The adduct (2) is also slowly formed thermally from (1). Water converts the CF:N group in adduct (2) into CO·NH, and ethanol converts it into C(OEt):N. Lithium aluminium hydride effects complete reduction and replacement of fluorine atoms by hydrogen.

BENZENE has a versatile photochemistry, undergoing valence isomerization to benzvalene[2] and to bicyclo-[2.2.0]hexa-2,5-diene,[3] and addition of olefins and acetyl-

enes.[4] In contrast that of pyridine is sparce; it forms only an unstable *para*-bonded isomer.[5] This may be

¹ Part 24, R. E. Banks, R. N. Haszeldine, and E. Phillips, *J. Fluorine Chem.*, 1977, **9**, 243.

² K. E. Wilzbach, J. S. Ritscher, and L. Kaplan, *J. Amer. Chem. Soc.*, 1967, **89**, 1031; K. E. Wilzbach and L. Kaplan, *ibid.*, 1968, **90**, 3291.

³ H. R. Ward and J. S. Wishnok, *J. Amer. Chem. Soc.*, 1968, **90**, 5353.

⁴ D. Bryce-Smith, *Pure Appl. Chem.*, 1973, **34**, 193, and references cited therein; K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, 1971, **93**, 2073; D. Bryce-Smith, A. Gilbert, and J. Grzonka, *Chem. Comm.*, 1970, 498; D. Bryce-Smith and J. E. Lodge, *J. Chem. Soc.*, 1963, 695.

⁵ K. E. Wilzbach and D. J. Rausch, *J. Amer. Chem. Soc.*, 1970, **92**, 2178; perfluoroalkylation considerably enhances the stability: M. G. Barlow, R. N. Haszeldine, and J. G. Dingwall, *J.C.S. Perkin I*, 1973, 1542.

due to the fact that the highest occupied molecular orbital for pyridine is non-bonding rather than a π-orbital. In pentafluoropyridine, the fluorine substituents lower in particular the energy of the non-bonding orbital, and photoelectron spectroscopic studies have indicated that the highest occupied is a π-orbital.[6] The photochemical addition of olefins and acetylenes has thus been investigated in the expectation that the π-π^* character of the first excited state would favour the formation of cycloadducts.

Pentafluoropyridine absorbs in the u.v. region at $\lambda_{max.}$ 256 (ε 1 200) and ca. 200 nm (ε ca. 800).[7] Irradiation in silica of a solution of ethylene in pentafluoropyridine yields the 1 : 1-adduct (1) and the 2 : 1-adduct (2) in comparable amounts. Use of high pressures of

(1)   (2)   (3)   (4)
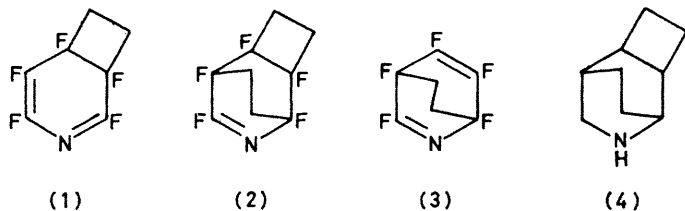
ethylene increases the yield of adduct (2), and the latter is also formed slowly when adduct (1) is heated with ethylene at 40 °C in hexane solution. The rate of conversion in this last reaction is insufficient to account for all of (2) formed in the photochemical reaction, and whilst the possibility that pentafluoropyridine photosensitizes the addition of ethylene to adduct (1) cannot be discounted completely, it appears that adduct (2) is a primary product of the reaction of ethylene with pentafluoropyridine. No evidence was found for the formation of an adduct of type (3).

The CF:N grouping in adduct (2) shows the expected [8] easy attack by nucleophiles, forming the amide grouping CO·NH with water, and C(OEt):N with ethanol. With lithium aluminium hydride in refluxing diethyl ether, unexpectedly all the fluorine atoms are slowly replaced, and the saturated compound (4) is apparently formed together with a monofluoro-derivative.

Photochemical 1,3-addition of olefins is the favoured process for benzene, a reaction which has been extensively studied [9] and may well involve an ' excimer '.[10] Photochemical 1,2-cycloadditions of olefins to benzene occur most readily with olefins having marked donor or acceptor properties,[9] and the novel formation of adducts (1) and (2) is reminiscent of the addition of maleic anhydride to benzene,[11] which involves an elusive 1 : 1-adduct.[12] Formation of (2) may involve reaction of

' hot ' ground state (1), since under the conditions used, the majority of the light is absorbed by the solvent pentafluoropyridine; the concerted nature or otherwise of the formation of the adducts or the involvement of triplet states has yet to be established.

EXPERIMENTAL

Volatile materials were manipulated in a Pyrex vacuum system. Products were identified by elemental analysis, i.r. spectroscopy (Perkin-Elmer model 257), u.v. spectroscopy (Hilger and Watts Ultrascan), n.m.r. spectroscopy (Varian HA 100 operating at 100 MHz for protons and at 94.1 MHz for ^{19}F nuclei, where positive values of chemical shifts are in p.p.m. to high field of external trifluoroacetic acid), mass spectrometry (A.E.I. model MS/902 at 70 eV), and g.l.c. (Pye 104 instrument). Pentafluoropyridine was prepared from pentachloropyridine.[13] U.v. irradiations were carried out with a Hanovia U.V.S. 500 medium-pressure mercury lamp.

Irradiation of Pentafluoropyridine with Ethylene.—Pentafluoropyridine (4.12 g, 24.4 mmol) and ethylene (0.319 g, 11.4 mmol), sealed in a silica tube (32 cm^3) and the liquid phase irradiated with u.v. light from the lamp at a distance of 25 cm for 900 h, gave recovered ethylene (0.121 g, 4.31 mmol, 38%) and pentafluoropyridine (3.01 g, 18.3 mmol, 75%), and a residue (1.15 g), which was dissolved in dry carbon tetrachloride and separated by g.l.c. (4 m SE 30 at 135 °C) to give 1,2,4,5,6-*pentafluoro-3-azabicyclo*[4.2.0]*octa-2,4-diene* (1) (0.83 g, 4.2 mmol, 37%) (Found: C, 43.2; H, 2.3; F, 48.0; N, 6.8%; M^+, 197. $C_7H_4F_5N$ requires C, 42.7; H, 2.1; F, 48.2; N, 7.1%; M, 197), as a colourless liquid, m.p. 8—10 °C, and 1,2,5,6,8-*pentafluoro-7-azatricyclo*[4.2.2.0^{2,5}]*dec-7-ene* (2) (0.27 g, 1.2 mmol, 21%) (Found: C, 48.1; H, 3.8; F, 41.8; N, 6.0%; M^+, 225.056 2. $C_9H_8FN_5$ requires C, 48.0; H, 3.6; F, 42.2; N, 6.2%; M, 225.057 6), as a white solid, m.p. 78—80 °C. A trace of intractable brown material (ca. 0.03 g) remained in the tube.

Varying the initial ratio of pentafluoropyridine : ethylene from 1.22 to 2.22 resulted in a change in the ratio of 1 : 1-adducts : 1 : 2-adducts produced from 1.43 to 4.15.

Properties of the Adducts of Ethylene and Pentafluoropyridine

The 1 : 1-*Adduct.*—The adduct showed i.r. and u.v. absorptions which indicated the presence of an azadiene chromophore: $\nu_{max.}$ 1 735 (CF:N str) and 1 695 cm^{-1} (CF:CF str) and $\lambda_{max.}$ 235 nm (ε 2 700) [cf. perfluoro-1-azacyclohexa-1,3-diene with $\nu_{max.}$ 1 750 and 1 700 cm^{-1} and $\lambda_{max.}$ 233 nm (ε 3 400) [14]]. The i.r. and ^{1}H n.m.r. (τ 7.3—8.4, complex) spectra indicated the absence of olefinic hydrogens. Its ^{19}F n.m.r. spectrum showed absorptions at -13.9 (ddd 30, 23, 6 Hz; CF:N [15]), 62.2 (ddd, 30, 30, 15, 4 Hz; CF–N), 71.0 (broad complex, showing extensive HF coupling), 73.2 (broad complex d, 30 Hz), and 81.3 p.p.m. [dt, 22, 4 Hz; cf. cis-5,6-dichlorohexafluorocyclohexa-1,3-diene,[16] where the olefinic fluorines absorb at

[6] G. H. King, J. N. Murrell, and R. J. Suffolk, *J.C.S. Dalton*, 1972, 564; C. R. Brundle, M. B. Robin, and N. A. Kuebler, *J. Amer. Chem. Soc.*, 1972, **94**, 1466.

[7] U.M.I.S.T. collection of u.v. spectra.

[8] R. E. Banks, W. M. Cheng, and R. N. Haszeldine, *J. Chem. Soc.*, 1962, 3407.

[9] D. Bryce-Smith, A. Gilbert, B. Orger, and H. Tyrrell, *J.C.S. Chem. Comm.*, 1974, 334.

[10] V. Y. Merritt, J. Cornelisse, and R. Srinivasan, *J. Amer. Chem. Soc.*, 1973, **95**, 8250.

[11] D. Bryce-Smith and J. E. Lodge, *J. Chem. Soc.*, 1962, 2675.

[12] W. Hartmann, H. G. Heine, and L. Schrader, *Tetrahedron Letters*, 1974, 883, 3101.

[13] R. E. Banks, R. N. Haszeldine, J. V. Latham, and I. M. Young, *J. Chem. Soc.*, 1965, 594.

[14] R. D. Chambers, D. J. Clark, T. F. Holmes, W. K. R. Musgrave, and I. Ritchie, *J.C.S. Perkin I*, 1974, 114.

[15] J. W. Emsley and L. Phillips, *Prog. in N.M.R. Spectroscopy*, 1971, **7**, 255.

[16] M. G. Barlow, R. N. Haszeldine, and D. R. Woodward, unpublished results.

72.6 (F-1, F-4) and 78.0 p.p.m. (F-2, F-3)]. Its mass spectrum showed prominent ions at m/e 197 (80.2, M), 196 (61.0, $M -$ H), 169 (100.0, C_5NF_5), 152 (36.1, $C_6H_4F_4$), 133 (21.2, $C_6H_4F_3$), 132 (24.9, $C_6H_3F_3$), 126 (C_3NF_3), and 57 (32.2%, C_2NF).

The 1 : 1 adduct reduced one molar equivalent of potassium permanganate in acetone at room temperature, indicating the presence of one C=C bond (*cf.* the 2 : 1 adduct below).

Reaction with ethylene. Aliquots (1.0 cm³) of a solution of the 1 : 1-adduct (187 mg, 0.95 mmol) in n-hexane (3.0 cm³), each contained in silica tubes (*ca.* 35 cm³) along with ethylene (270 mg, 9.6 mmol), were kept at 40 °C for 28 days, one in the dark and the other with the liquid phase exposed to u.v. light. Ethylene was then removed, and g.l.c. (2 m, SE 30 at 135 °C) and i.r. spectroscopy indicated the formation in each case of the 2 : 1-adduct (7 mg, 0.03 mmol, 10% conversion).

The 2 : 1-Adduct.—The adduct showed $\nu_{max.}$ 1 698 cm⁻¹ (vs, CF:N str). Its ¹H n.m.r. spectrum showed absorption at 7.3—8.2 (complex CH₂), and its ¹⁹F n.m.r. spectrum showed complex absorption band systems at -22.5 (CF:N), 75.1 (CF-N), and at 95.4, 107.8, and 120.3 p.p.m. which were tentatively assigned to fluorines F-5, F-2, and F-1 (the numbering corresponds to the systematic name) by comparison with the absorptions of the corresponding lactam (see below) with the expectation that F-2 and F-5 would be least affected upon conversion of the CF:N into the CONH-group. It showed prominent ions in its mass spectrum at m/e 225 (3.0, M), 197 (3.3, $C_7H_4NF_5$), 169 (14.8, C_5NF_5), 135 (100.0, $C_5H_4NF_3$), 134 ($C_5H_3NF_2$), and 90 (8.8%, $C_4H_4F_2$), whose identities were confirmed by accurate mass measurements.

The adduct showed no reaction with potassium permanganate in acetone at room temperature.

Reaction with aqueous sodium hydroxide. The 2 : 1 adduct (0.250 g, 1.11 mmol) and 2м-sodium hydroxide (5 cm³), shaken for 6 h at room temperature and then neutralized (H₂SO₄) gave, after recrystallization from chloroform, 1,2,5,6-*tetrafluoro-7-azatricyclo*[4.2.2.0²,⁵]*decan-8-one* (0.190 g, 0.85 mmol, 77%) (Found: F, 33.1%; M^+, 223.061 0. $C_9H_9F_4NO$ requires F, 34.0%; M, 223.062 0), with τ 2.0 (NH) and 7.3—8.2 (CH₂), and δ_F 87.5 (F-6), 97.0 (F-5), 106.8 (F-2), and 116.7 p.p.m. (F-1). Its mass spectrum showed prominent ions at m/e 223 (60.0, M), 133 (41.2, $C_2H_5F_2ON$), 105 (100.0, $C_4H_5F_2N$), and 90 (71.9%, $C_4H_4F_2$), whose identities were confirmed by accurate mass measurement.

A similar reaction with water at room temperature for 3 h gave the same lactam (87%).

Reaction with ethanol. The 2 : 1-adduct (63 mg, 0.28 mmol) and ethanol (1 cm³) gave, after 17 h at room temperature and removal of excess of ethanol 7-*ethoxy*-1,2,5,6-

tetrafluoro 8-*azatricyclo*[4.2.2.0²,⁵]*dec-7-ene* (67 mg, 0.27 mmol, 96%) (Found: M^+, 251.091 6. $C_{11}H_{13}F_4NO$ requires M, 251.093 2).

Reaction with lithium aluminium hydride. The 2 : 1-adduct (163 mg, 0.72 mmol) in diethyl ether (2 cm³) was added dropwise to lithium aluminium hydride (0.410 g, 10.8 mmol) and ether (10 cm³) under nitrogen. The mixture was left at room temperature overnight and then heated under reflux for 6 h. The excess of hydride was destroyed with water (0.4 cm³), made alkaline with sodium hydroxide solution, and the ether layer dried (MgSO₄) and evaporated to yield a pale yellow liquid (61 mg) which g.l.c. (2 m SE 30 at 140 °C) and mass spectrometry indicated to be mainly (76%) 7-azatricyclo[4.2.2.0²,⁵]decane (Found: M^+, 137.119 6. $C_9H_{15}N$ requires M, 137.120 4) with $\nu_{max.}$ 3 300m (NH str) and 1 600 cm⁻¹ (NH bend), together with a monofluoro-derivative (Found: M^+, 155.110 0. $C_9H_{14}FN$ requires M, 155.110 9). The 7-azadecane showed prominent ions in its mass spectrum with m/e values 137 (M, 25.5), 122 (13.1, $C_8H_{12}N$), 109 (16.4, $C_7H_{11}N$), 108 (42.6, $C_7H_{10}N$), 94 (18.2, C_6H_8N), 83 (24.0, C_5H_9N), 82 (100.0, C_5H_8N), and 80 (36.6%, C_5H_6N), which were identified by accurate mass measurement.

Structure of the Adducts of Ethylene and Pentafluoropyridine.—The 1 : 1-adduct, since it contains an azadiene grouping can only possess structures (1) or (5). Since the 2 : 1-adduct possesses a CF:N group and is formed thermally from the 1 : 1-adduct, it can only possess structures (2), by 1,4-addition to (1), or (6), by 1,2-addition, assuming that the skeleton of the 1 : 1-adduct is retained.

(5)   (6)
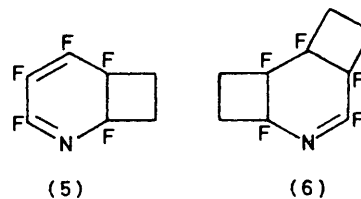
The prominent ion in its mass spectrum corresponding to loss of a $C_4H_4F_2$ fragment by retro-Diels–Alder cleavage strongly suggests structure (2). A corresponding loss was prominent in the lactam. The n.m.r. evidence is somewhat equivocal, but the ¹⁹F n.m.r. spectra of adducts formed by other cyclic and acyclic olefins strongly support structure (2), since the chemical shifts of the two fluorines of the cyclobutane portion are very variable, depending upon the presence or absence of an adjacent *cis*-alkyl group, whereas the two bridgehead fluorines are much less so. This behaviour would not be expected if structure (6) corresponded to the carbon skeleton of the various adducts.