

Photochemical Addition of Ethylene to Pentafluoropyridine: Formation of 1:1- and 2:1-Adducts

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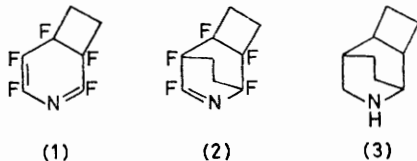
Summary Ethylene adds photochemically to pentafluoropyridine to yield 1,2,4,5,6-pentafluoro-3-azabicyclo[4.2.0]octa-2,4-diene (**1**) and 1,2,5,6,8-pentafluoro-7-azatricyclo[4.2.2.0^{2,5}]dec-7-ene (**2**).

WHEREAS benzene has a versatile photochemistry, undergoing valence-bond isomerization¹ and addition of olefins

and acetylenes,² that of pyridine is sparse. It forms an unstable *para*-bonded isomer,³ and its pentakis(pentafluoroethyl)-derivative yields rather stable valence-bond isomers.⁴ We find that, in distinct contrast to pyridine, pentafluoropyridine undergoes ready addition of simple olefins.

U.v. irradiation, in a silica vessel, of solutions of ethylene in pentafluoropyridine yields only the adducts (**1**) and (**2**),

and the latter is favoured by use of high pressures of olefin. The adduct (2) is slowly formed when (1) is heated at 40 °C with ethylene in hexane solution.



The 1:1-adduct (1) has the expected i.r. [ν_{\max} 1735 (C=N) and 1695 cm^{-1} (C=C)] and u.v. (λ_{\max} 235 nm, ϵ ca. 2700) spectral properties and shows five absorptions in its ^{19}F n.m.r. spectrum (positive values to low field of external $\text{CF}_3\text{CO}_2\text{H}$) at δ 13.9 (FC=N), -62.2, -81.3 (FC=CF), -71.0, and -73.2 p.p.m. The 2:1-adduct (2) [ν_{\max} 1702 cm^{-1} (C=N)], shows five ^{19}F n.m.r. absorptions at

δ 22.5 (FC=N), -75.1, -95.4, -107.8, and -120.3 p.p.m. It shows a prominent molecular ion in its mass spectrum and a base peak at m/e 135 corresponding to loss of a difluoro cyclobutene fragment from the molecular ion. It is slowly reduced by lithium aluminium hydride in diethyl ether to the saturated heterocycle (3) in which, remarkably, all the fluorine atoms have been lost.

This formation of 1:1- and 2:1-adducts is reminiscent of the reaction of maleic anhydride with benzene where elusive 1:1- and a 2:1-adducts are formed.⁵ Other acyclic olefins undergo similar additions to pentafluoropyridine, and a study of the reaction with *cis*- and *trans*-but-2-ene, where two 1:1- and six 2:1-adducts are formed, indicates that the reactions are not concerted. The cyclic olefins cyclopentene, cyclohexene, and *cis*-cyclo-octene each give pairs of 2:1-adducts related to (2).⁶

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