

Photochemical Reaction of Ethylene with 3-Chlorotetrafluoropyridine: a Novel Insertion into a C-Cl Bond

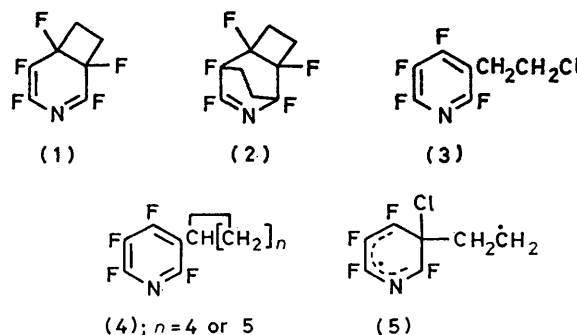
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Summary The photochemical reaction of ethylene with 3-chlorotetrafluoropyridine yields 3-(2-chloroethyl)tetrafluoropyridine, whereas cyclo-pentene and -hexene yield 3-cycloalkyltetrafluoropyridines.

WHEN compared with benzene, pyridine has rather a sparse photochemistry. It forms an unstable *para*-bonded isomer,¹ but no adducts with olefins and acetylenes.² Pentafluoropyridine is somewhat more versatile, and it forms 1:1- and 1:2-adducts, (1) and (2), with ethylene.³ In contrast, no cycloadducts are formed from 3-chlorotetrafluoropyridine.

Irradiation with u.v. light ($\lambda > 200$ nm) of a solution of ethylene in 3-chlorotetrafluoropyridine yields 3-(2-chloro-



ethyl)tetrafluoropyridine (**3**, 77%) in a reaction which involves a novel insertion into the C-Cl bond. Similar irradiation of mixtures of 3-chlorotetrafluoropyridine and cyclo-pentene or -hexene gives good yields of 3-cyclo-alkyltetrafluoropyridines (**4**) (80–90%), and 3,3'-bicyclo-alkenyls. Tetrafluoropyridyl radicals do not appear to be involved, since there is no telomerisation of the ethylene, or hydrogen abstraction to give tetrafluoropyridine with the cycloalkenes, and it is tempting to invoke the biradical (**5**), formed by attack of the excited chlorotetrafluoropyridine

on the ethylene, which gives (**3**) by chlorine migration. Loss of a chlorine atom from a similar biradical, rather than migration, followed by hydrogen abstraction from a further molecule of olefin, appears favoured for the cycloalkenes, possibly for steric reasons.

These reactions provide a route to the not readily accessible 3-substituted tetrafluoropyridines,⁴ apart from their photochemical interest.

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¹ K. E. Wilzbach and D. J. Rausch, *J. Amer. Chem. Soc.*, 1970, **92**, 2178; perfluoroalkylation leads to a considerable enhancement of stability: M. G. Barlow, R. N. Haszeldine, and J. G. Dingwall, *J.C.S. Perkin I*, 1973, 1542.

² Benzene readily forms adducts with olefins and acetylenes: D. Bryce-Smith, *Pure Appl. Chem.*, 1968, **16**, 47; K. E. Wilzbach and L. Kaplan, *J. Amer. Chem. Soc.*, 1971, **93**, 2073.

³ M. G. Barlow, D. E. Brown, and R. N. Haszeldine, *J.C.S. Chem. Comm.*, 1977, 669.

⁴ Potentially available from tetrafluoro-3-pyridyl-lithium: R. D. Chambers, C. A. Heaton, W. K. R. Musgrave, and L. Chadwick, *J. Chem. Soc. (C)*, 1969, 1700.