Valence-bond Isomers of Heterocyclic Compounds: Isomers of Pentakis(pentafluoroethyl)pyridine

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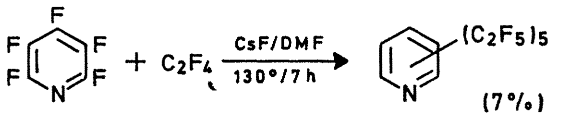
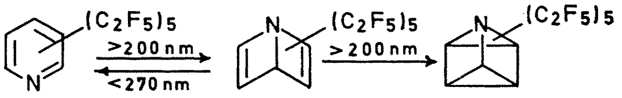
Summary U.v. irradiation of pentakis(pentafluoroethyl)-pyridine produces the corresponding 1-azabicyclo[2,2,0]-hexa-2,5-diene, and hence the 1-azatetracyclo[2,2,0,0^{2,6},0^{3,5}]hexane; these, the first valence-bond isomers of a six-membered-ring heterocycle to be isolated, are stable for several hours at 160°.

PENTAKIS(PENTAFLUOROETHYL)PYRIDINE, produced by the fluoride-catalysed reaction of pentafluoropyridine with tetrafluoroethylene:[1]



absorbs in the u.v. region at 209—210 (ε 8540, hexane) and 269 nm (1340). Its ^{19}F n.m.r. spectrum indicates that rotation of the pentafluoroethyl groups is highly hindered. Irradiation (> 270 nm) at room temperature of its solution in perfluoro-n-pentane gives a *para*-bonded valence-isomer, pentakis(pentafluoroethyl)-1-azabicyclo[2,2,0]hexa-2,5-diene. Light of > 200 nm produces the corresponding prismane, pentakis (pentafluoroethyl)-1-azatetracyclo[2,2,0,0^{2,6},0^{3,5}]hexane, and the *para*-bonded isomer is apparently an intermediate in the reaction:



Either isomer can thus be obtained in essentially quantitative yield. The photochemistry of pentakis(pentafluoroethyl)pyridine is reminiscent of that of hexakis(pentafluoroethyl)benzene[2] in that both the *para*-bonded and prismane isomers are formed. Both isomers show substantial thermal stability. For example, the prismane isomer, after 16 h at 160°, is converted (90%) into a 3 : 2 mixture of *para*-bonded isomer and pyridine.

Pentakis(pentafluoroethyl)-1-azabicyclo[2,2,0]hexa-2,5-diene is a colourless liquid, b.p. 176°. It has ν_{max} 1691 cm^{-1} (C : C str.). The ^{19}F n.m.r. spectrum (relative to ext. $CF_3 \cdot CO_2H$ in hexafluorobenzene) shows the presence of three types of pentafluoroethyl groups, with band systems at 5·1 (bridgehead CF_3), 7·3 and 7·8 (CF_3's at the double bond), 38·7 (bridgehead CF_2), 35·3 and 43·9 p.p.m. (CF_2's at the double bond).

Pentakis(pentafluoroethyl)-1-azaprismane is a colourless liquid, b.p. 184°, which shows no strong absorptions at frequencies > 1410 cm^{-1}. The n.m.r. spectrum shows band systems at 5·5 (6F), 6·1 (9F), 35·6 (AB-type multiplet; 4F), 40·1 (4F), and 45·8 p.p.m. (2F; CF_2 at the 4-carbon).

The mass spectra (at 70 ev) of the pyridine and its two isomers show many similarities. Each shows a parent ion, that of the *para*-bonded isomer being most intense, ions due to loss of F are very intense, and the base peak corresponds to loss of CF_3.

These valence-bond isomers of a six-membered nitrogen heterocycle represent the first examples isolated, although 2-azabicyclo[2,2,0]-hexa-2,5-diene has been identified as the unstable product (half-life 2·5 min. at 25°) of irradiation of pyridine at 254 nm.[3] Valence-bond isomers have been postulated, but not isolated, as intermediates in the photochemical and thermal isomerizations of perfluoroalkylpyridazines.[4]

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