Photoreaction of Pentafluoropyridine with Cyclohexane. Evidence for Regiospecific Substitution

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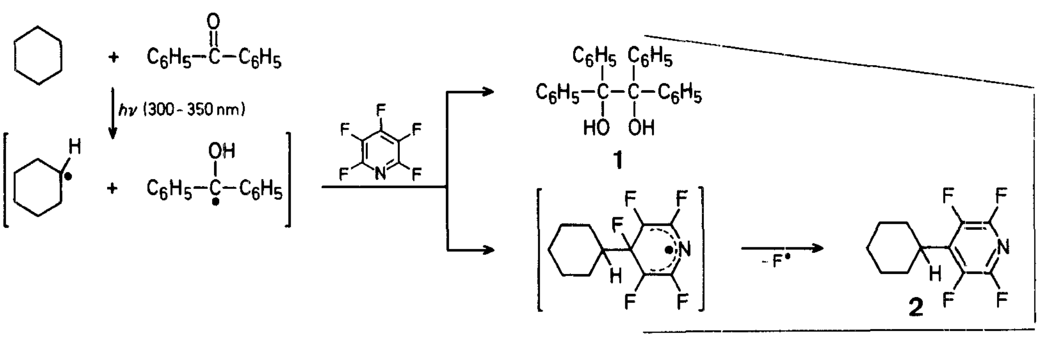
It has recently been found[1] that 2-fluoropyridine reacts readily with diethylamine to give exclusively *N*-substitution products, no evidence of *cine*-substitution [substitution via arynes or heteroarynes in which the new substituent enters at a position different from that of the leaving group], as in analogous reactions of difluorobenzenes[2], being observed. On the other hand, the reaction of 2-fluoropyridine with triethylamine[1] gives a 2:1 mixture of diethylaminopyridine and *N*,*N*-diethyl-1-(2-pyridyl)-ethanamine.

We now report that irradiation at $\lambda = 300-350$ nm of a solution of pentafluoropyridine in cyclohexane in the presence of benzophenone at 25° for 24 h leads to the formation of two products: a colorless crystalline product which precipitates from the solution and which was identified as 1,2-dihydroxytetraphenylethane (**1**), and a product which is isolated by evaporation of the filtered solution and which may be purified by preparative G.L.C. (yield: 33%). The ^{19}F-N.M.R. spectrum of this latter product shows two multiplets at $\delta = -93.75$ ppm (2F, AA'XX' type) and -145.75 ppm (2F, AA'XX' type). On the basis of these data and by their comparison with the ^{19}F-N.M.R. data of other 4-substituted 2,3,5,6-tetrafluoropyridines[3], the structure of the liquid product was established as 4-cyclohexyltetrafluoropyridine (**2**). The reaction is assumed to proceed by the free-radical mechanism formulated below.



In order to study the effect of ring size on the photosubstitution, we subjected cyclopentane and cycloheptane to the same reaction conditions. However, no reaction or formation of photoaddition products was observed. The same negative result was found when the reaction was carried out with *n*-hexane and *n*-heptane.

Photoreaction of Pentafluoropyridine with Cyclohexane:
Pentafluoropyridine (0.45 g, 3 mmol) and benzophenone (1.1 g, 6 mmol) are dissolved in cyclohexane (50 ml). The solution is irradiated with light of $\lambda = 300-350$ nm for 24 h at 25°. The precipitated 1,2-dihydroxytetraphenylethane (**1**) is isolated by filtration; yield: 0.55 g (50%); m.p. 185–186° (Ref. [4], m.p. 186–187°). The filtrate is evaporated in vacuo and the liquid residue purified by preparative G.L.C. (FFAP 30% on Chromosorb AW, 200°) to give 4-cyclohexyltetrafluoropyridine (**2**); yield: 0.23 g (33%); m.p. 27–29°.

$C_{11}H_{11}F_4N$	calc.	C 56.65	H 4.75	N 6.01
(233.2)	found	57.04	5.02	6.24

M.S.: $m/e = 233$ (M^+, 41%), 183 (16), 182 (100), 181 (14), 178 (14), 177 (38), 164 (14), 106 (19), 56 (22), 51 (46), 50 (16).

^{1}H-N.M.R. (CCl_4/TMS): $\delta = 2.9$ (m, 1H); 1.8 ppm (m, 10H).

^{19}F-N.M.R. (CCl_4/CCl_3F): $\delta = -93.75$ (2F, AA'XX'); -147.75 ppm (2F, AA'XX).

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