

PHOTOAMINATION OF PYRIDINES

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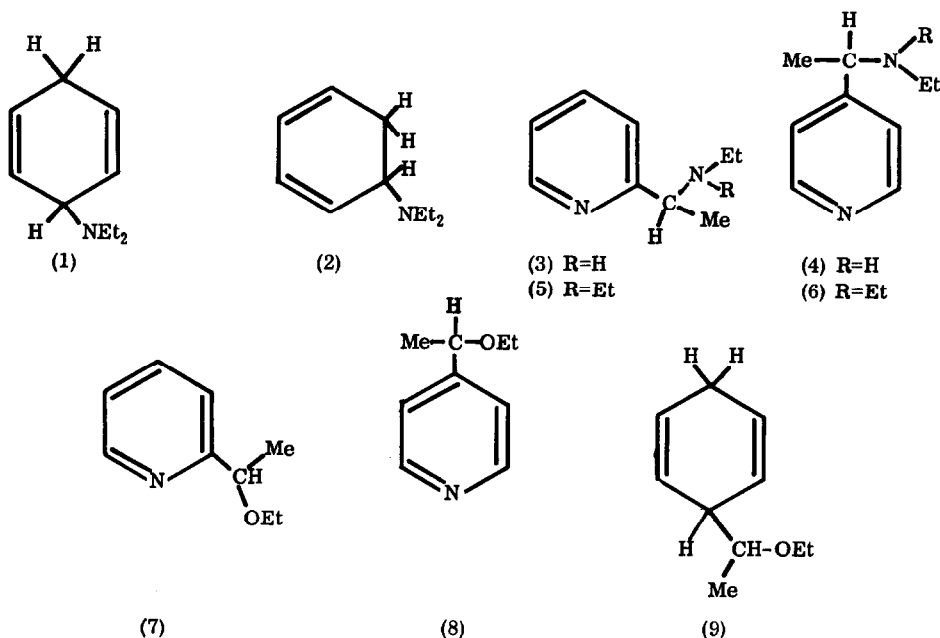
As the known photoadditions of amines to benzene (ionisation potential 9.24 eV) appear to have as a common feature a degree of electron transfer from S_0 amine to S_1 benzene,^{1,2} we have investigated the corresponding photoreactions of amines with pyridine (I. P. 9.37 eV). No photoreactions of amines with pyridines or other nitrogen heterocycles (other than photoreduction³) have hitherto been described.

Whereas benzene gives mainly photoadducts, e.g. (1) and (2) from Et_2NH , pyridine under similar conditions (1:1 v/v mixture; low-pressure Hg lamp; 20° ; N_2) gives a 1:1 mixture of substitution products which from diethylamine are assigned structures (3) and (4) on the basis of spectroscopic data.

Thus both showed N-H absorption in the infrared spectrum, and other i. r. features were consistent with α - and γ -substitution of the pyridine ring respectively. Identification of the products as (3) and (4) follows from their n. m. r. spectra (60 MHz, CCl_4); δ 8.40 [1H, doublet of quartets α -H], 7.5 [1H, triplet of doublets, γ -H], 7.1 [2H, multiplet, β -H's], 3.75 [1H, quartet $J = 7\text{Hz}$, methine], 2.40 [2H, quartet, $J = 7\text{Hz}$, methylene], 1.50 [1H, singlet, removed with D_2O , N-H], 1.30 [3H, doublet, $-\text{CH}_3$ adj. methine] and 1.00 p. p. m. [3H, triplet, CH_3 in Et group]; and δ 8.40 [2H, doublet of doublets, α -H's], 7.15 [2H, doublet of doublets, β -H's], 3.70 [1H, quartet $J = 7\text{Hz}$ methine], 2.25 [2H, quartets $J = 7\text{Hz}$, methylene], 1.25 [2H, doublet, CH_3 adj. methine], 1.1 [1H, singlet removed with D_2O , N-H], and 1.05 p. p. m. [3H, triplet, CH_3 in Et group] respectively.

The overall quantum efficiency for formation of (3) + (4) was ca. 0.01, a figure similar to that for the formation of (1) + (2) from benzene.

The formation of α -C- rather than N-substitution products from diethylamine and pyridine is unprecedented, and indeed no traces of NN-diethylaminopyridines could be detected. In line with this observation, t-butylamine gave no photoproducts on irradiation in pyridine. On the other hand, triethylamine and pyridine readily gave a 0.82:1 mixture of the 2- and 4-photosubstitution products (5) and (6) together with dehydro-dimers of the amine. The latter were also formed during the corresponding photoaddition to benzene;¹ but whereas proton donors such as methanol and water inhibited the reaction with pyridine, they promoted the benzene reaction.

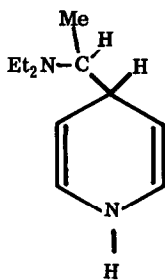


Although the photoaddition of diethylamine to benzene tends to be inhibited by increased solvent polarity,⁴ the corresponding photosubstitution in pyridine shows relatively small solvent effects, the interpretation of which is complicated by the tendency of some solvents to photoreact with pyridine. Thus cyclohexane and methanol gave the products described in ref. 5. Diethyl ether gave a 1:1 mixture of the substitution products (7) and (8), the structures of which were unambiguously confirmed by their spectroscopic properties: contrast the acid-catalysed photoaddition of diethyl ether to benzene which yields (9).⁶

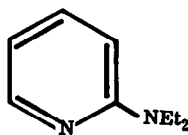
Following Lablache-Combiér,⁵ one might express the initial reaction as H-abstraction to give the radicals C_5H_5NH and Et_2NCHMe , followed by combination of the radical pair to give 2- and 4-

substituted dihydropyridines which then suffer fortuitous oxidation to the pyridines. Alternatively, the above amine-derived radicals might engage in homolytic substitution into unreacted pyridine. Unfortunately, objections can be raised to both of these mechanisms. Thus we have been unable to detect any traces of dihydro-compounds of type (10) despite the use of conditions as anaerobic as possible for irradiation and subsequent work-up. Likewise, we would have expected homolytic substitution into pyridine to give a mixture of 2-, 3-, and 4-isomers. In view of the notorious susceptibility of dihydropyridines to oxidation, we are inclined to favour the former alternative at this time.

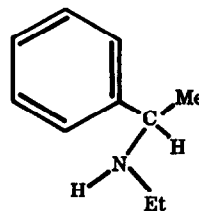
The anomalous C-substitution of diethylamine into pyridine was not found in a more conventional photonucleophilic substitution into the pyridine ring, but other unexpected features were observed. Thus 2-fluoropyridine and diethylamine gave exclusively the N-substitution product (11), and the cine-substitution found with difluorobenzenes⁷ was not detected. *t*-Butylamine reacted analogously. Although monofluorobenzene and 2-fluoropyridine undergo similar N-photosubstitutions with diethylamine, it is interesting that chlorobenzene and diethylamine give a substantial proportion of the C-substitution product (12) analogous to (3) formed from pyridine, together with NN-diethylaniline and adducts similar to those formed from fluorobenzene.⁷ This tendency towards C-substitution with chlorobenzene may well reflect the greater susceptibility to homolysis of C-Cl than C-F. Triethylamine and 2-fluoropyridine gave a 2:1 mixture of the 2-substitution products (11) and (5). The formation of amine (11) involves the unusual loss of an ethyl group, and we are investigating the possibility that it occurs by an addition-elimination mechanism related to that of the von Braun reaction.



(10)



(11)



(12)

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