Photoalkylation of Pyridine with Methanol

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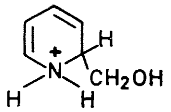
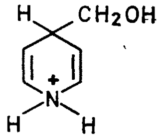
Summary Pyridine is photoalkylated in acid methanol solutions to yield 2- and 4-methylpyridines (I and II), 1-(2-pyridyl)-2-(4-pyridyl)ethane (III), and 1,2-di-(4-pyridyl)ethane (IV).

THERE has been considerable current interest in pyridine photochemical reactions.[1-4] Previous attempts to photoalkylate pyridine have been unsuccessful.[3] Linschitz and Connolly[4] reported changes in the absorption spectrum of alcohol solutions of pyridine upon irradiation. Irradiation of 0·1M-solutions of pyridine in HCl–methanol solutions with the 253·7 nm line of Hg through quartz (Srinivasan–Griffin–Rayonet reactor) under nitrogen produces the methylpyridines, (I) and (II), and the pyridylethanes, (III) and (IV). The results are given in the Table. The products were compared (i.r., n.m.r., g.l.c., retention time, and t.l.c.) with authentic materials except for (III). The structure of (III) was inferred by i.r. and n.m.r. spectrum correlation with 1,2-di-(2-pyridyl)ethane and (IV).



(V)



(VI)

The photoalkylation mechanism can be explained by analogy with the pathway suggested by Stermitz, Wei, and Huang[5] in the quinoline system using the intermediates (V) and (VI). In support of this hypothesis, Kellogg and his co-workers[1] isolated an intermediate like these in the photolysis of 3,5-dialkoxycarbonyl-substituted pyridines.

Products and yields of the pyridine irradiation[a]

Solvent[b]	Alcohol[d] (%)	Yield[d] I (%)	Yield[d] II (%)	Yield[d] III (%)	Yield[d] IV (%)	Recovered starting material (%)
Anhydrous CH_3OH–saturated HCl	—	2·5	6·0	1·0	1·3	10
2N[c]-aqueous HCl–CH_3OH	80	2·0	10·0	1·0	3·0	20
6N[c]-aqueous HCl–CH_3OH	50	0·5	1·7	0·0	0·0	20
CH_3OH	100	0·0	0·0	0·0	0·0	36

[a] G.l.c. analysis was done on a 15 ft × ¼ in 18% OV-I (Applied Science Labs) Chromosorb Q 60/80 column.

[b] The solvent was evaporated to dryness under reduced pressure, made basic with $NH_{3(g)}$ and extracted with ether. Aqueous HCl was added to the anhydrous methanol reaction solutions after irradiation and before work-up.

[c] Based on total volume of solution.

[d] Based on total amount of starting material.

The dehydration and rearrangement is favoured in relatively strong acid solution (see Table). The low yield in 6N-HCl solution is most probably due to the decrease of the hydrogen-donor concentration, methanol. Since no photoalkylation was found in the absence of hydrochloric acid, it can be assumed that the $\pi \rightarrow \pi^*$ excited state is causing the initial hydrogen abstraction. The pyridylethane derivatives, (III) and (IV), are formed from the corresponding hydroxymethylpyridine compounds and not the methylpyridines.[6] We are engaged in the study of the mechanism as well in the nature of the excited states involved in the reaction.

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[4] H. Linschitz and J. S. Connolly, *J. Amer. Chem. Soc.*, 1968, **90**, 2979.

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[6] V. I. Stenberg and E. F. Travecedo, submitted for publication in *Tetrahedron*.