Liquid-phase Photochemistry of Pyridine and 2- and 4-Picoline

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Summary Pyridine is photosubstituted by cyclohexane and gives 2- and 4-cyclohexylpyridine by a radical mechanism: 2- and 4-picoline lead to the same compounds — 4- and 6-cyclohexyl-2-picoline, indicating that the two picolines react through the same intermediate.

IT has been shown recently that pyridine and some of its derivatives react with alcohol.[1,2] We now report our results on the substitution reactions which occur on irradiation of 1%-solutions of pyridine, 2-, and 4-picoline in cyclohexane under nitrogen.†

The results are summarised in the Table.‡ 2% of the starting material is substituted.§ As in the gas phase,[5] photointerconversion of 2-picoline and 4-picoline also

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† Loader and Timmons have described substitution occurring during the cyclisation of 4-stilbazoles to benz[*h*]isoquinoline in cyclohexane.[3]

‡ Irradiation was done with a Rayonnet R.S. reactor with radiation of 2537 Å in a quartz vessel for 12 h. Products after cyclohexane distillation are isolated by g.l.c. on an Autotrep A 700 with a Carbowax 20M 10 ft column. Products were characterised by n.m.r. spectra and by elemental analysis.

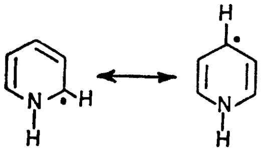
§ According to the low concentration of pyridine no dimer is formed.[4]

occurs in cyclohexane solution: 2% of the recovered picolines are isomerized.

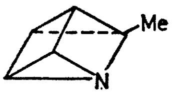
TABLE

Starting material		Products		
Pyridine	Bicyclohexyl (20)	2-cyclohexylpyridine (10)	4-cyclohexylpyridine (10)	2,5-dicyclohexylpyridine (1)
2-Methylpyridine	Bicylohexyl (20)	6-cyclohexyl-2-methylpyridine (10)	4-cyclohexyl-2-methylpyridine (10)	minor products (5)
	Methylcyclohexane[a] (1)			
4-Methylpyridine	Bicyclohexyl (20)	6-cyclohexyl-2-methylpyridine (5)	4-cyclohexyl-2-methylpyridine (5)	minor products (2·5)
	Methylcyclohexane[a] (1)			

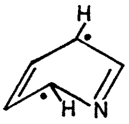
[a] Characterised by g.l.c. The figures in parentheses indicate relative amounts formed.



(I)



(II)



(III)

The products which are formed suggest:

(i) that free radicals are involved in these reactions: this is in agreement with the results published for pyridine[1,2] and with the photochemical substitution reactions of quinoline and isoquinoline.[6,7] A dihydro-compound must be formed. It has been isolated by Wynberg[1] in the case of pyridines disubstituted in position 3 and 5 by electron withdrawing groups. E.s.r. studies show that pyridine irradiated in methylcyclohexane gives radical (I).[8]

(ii) that the same intermediate is involved for 2- and 4-picoline.

If the photoreaction of the pyridines proceeds by a ring rearrangement,[5] the common intermediate must be the azaprismane (II). The fact that Wilzbach and Rausch have not been able to isolate an azaprismane[9] does not disprove this mechanism: so far only substituted prismanes[10] and diazaprismanes[11] have been isolated. If, on the other hand, the photoreaction proceeds by a methylation–demethylation process,[5] there must be a rearrangement of a radical formed from 4-picoline to one formed from 2-picoline. The isolation of a small amount of methylcyclohexane does not prove this mechanism.

2,5-Dicyclohexylpyridine (IV) is probably not formed from 2-cyclohexylpyridine, but arises directly from pyridine. The yield of monosubstituted products is *ca.* 1%. If (IV) is formed from the 2-cyclohexylpyridine, 0·001% of it would be expected, not 0·1%.

Radical (III), suggested by analogy with the Bryce-Smith and Longuet-Higgins generalisation for benzene photochemistry,[12] could be a precursor of 2,5-dicyclohexylpyridine.

It has been pointed out by Travecedo and Stenberg[2] that pyridine reacts with ethanol only in an acidic medium. According to these authors, the initial hydrogen abstraction is due to a $\pi \rightarrow \pi^*$excited state. No acid is needed when the reaction takes place in cyclohexane solution.

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