PHOTO-ARYLATION; SYNTHESIS OF ARYL- AND HETEROARYLPYRIDINES BY PHOTOLYSIS OF 2-HALOPYRIDINES.

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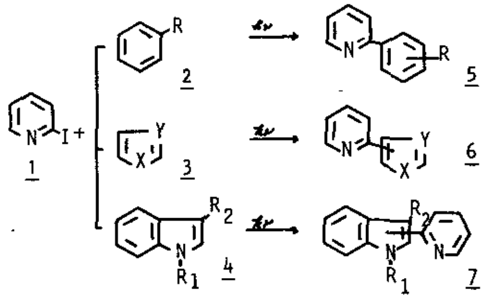
Photolysis of 2, 3, and 4-halopyridines (halogen: Cl, Br, I) in benzene afforded corresponding phenylpyridines in fair yields.

The reactivities of halopyridines in the reaction were examined and were found to be depending on halogens, positions of halo-substituent, substrates and solvents.

Although remarkable changes of the reactivities were observed in chloropyridines rather than in iodo-derivatives, chlorides were found to be less reactive in general.

Reactivities of 2-iodopyridine (1)found to be electrophilic in character to some extent, while those of 3-isomer was quite similar to iodobenzene in homolytic aromatic substitutions, suggesting that 1 might react favorably with electron-rich substrates.

To investigate the utility of the present reaction, 2-aryl(5) and 2-heteroarylpyridines (6, 7) were prepared by the reaction of 1 with substituted benzenes (2), five membered heterocycles (3) and indoles (4).



R= $(OCH_3)_2$, OCH_3, OH, CH_3, Cl, CO_2CH_3

X= O, S, NH, NCH_3, Y= CH
X= NCH_3, Y= N

R_1, R_2= H or CH_3

In the case of 2-pyridinylation of indoles, the participation of the electron transfer mechanism was suggested on the bases of isomer distributions, solvent effects and fluorescence quenching experiments.