

PHOTO-ARYLATION: SYNTHESIS OF ARYL- AND HETEROARYLPYRIDINES BY PHOTOLYSIS OF IODOPYRIDINES

Koh-ichi Seki, Kazue Ohkura and Masanao Terashima

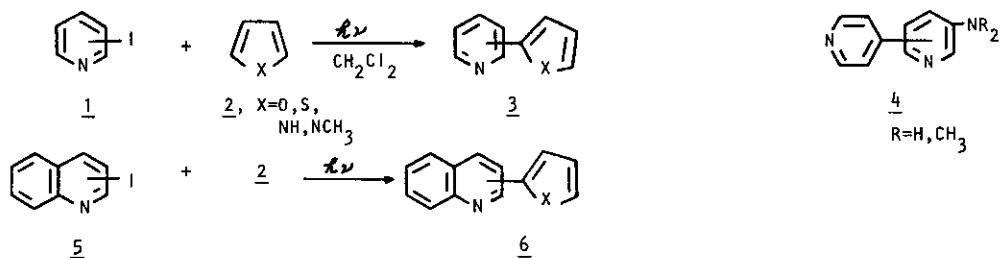
Faculty of Pharmaceutical Sciences, Higashi-Nippon-Gakuen University, Ishikari-Tobetsu, Hokkaido 061-02

Yuichi Kanaoka

Faculty of Pharmaceutical Sciences, Hokkaido University, Kita-12, Nishi-6, Kita-ku, Sapporo 060

In order to establish the synthetic utility of photo-induced aryl-heteroaryl coupling reactions using halopyridines, we investigated the photolysis of iodopyridines and iodoquinolines in the presence of heteroaromatic compounds.

Irradiation of 2- (1a) or 4-iodopyridine (1b) and a heterocyclic compound (2) in dichloromethane afforded the corresponding arylpyridines (3) in satisfactory yields with five membered heterocycles, while the reaction with six membered azaaromatics scarcely afforded the coupled products. However the coupling of the pyridine-pyridine ring was eventually achieved by introducing amino groups on the pyridine ring. Thus, aminopyridylpyridines (4) were obtained in appreciable yields from the photolysis of 1 with 3-aminopyridines in acetonitrile. Similarly, the photoreaction of iodoquinolines (5) with 2 yielded the corresponding heteroarylquinolines (6) in moderate yields.



The participation of the exciplex was suggested in the reaction mechanism by comparing the results, obtained from the competitive reaction 1a in substituted benzene-benzene systems, with those obtained from the related thermally induced 2-pyridinylation using 2-N-nitrosoaminopyridine. Further, the photoreaction of 1a with indole (possessing higher oxidation potential) conducted in varying solvents revealed that the electron transfer mechanism predominated in the reaction in polar solvents (i.e., acetonitrile, methanol).