FACILE METHOD FOR SYNTHESIS OF IODOAZINES AND ACYLAZINES FROM TRIMETHYLSTANNYLAZINES

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Pyridines, quinolines, and isoquinolines carrying trimethylstannyl(TMSn) group at each positions of their pyridine nuclei were synthesized by treatment of the respective chloro or bromo derivatives with trimethylstannyl sodium which was prepared *in situ* from chlorotrimethylstannane and sodium in DME.

These 2-, 3-, and 4-TMSn derivatives of pyridine and quinoline, and 1-, 3-, and 4-TMSn derivatives of isoquinoline were allowed to react with equimolar amounts of iodine in either chloroform or tetrahydrofuran to give the corresponding iodo derivatives of pyridine, quinoline, and isoquinoline by iododestannation in high yields, respectively.

On the other hand, 2-TMSn groups in pyridine and quinoline and 1-TMSn group in isoquinoline were readily replaced by acyl group, when treated with acyl chloride in benzene at room temperature, to yield the respective 2-acyl-pyridines and -quinolines and 1-acylisoquinolines in high yields.

Acylation of 3-TMSn derivatives of pyridine, quinoline, and isoquinoline, and 4-TMSn derivatives of 2-methyl- and 2,6-dimethyl-pyridine with acyl chloride were accomplished by catalysis of either $PdCl_2$ or $PdCl_2(PPh_3)_2$. For example, 3-TMSn-quinoline was heated with cyclohexanecarbonyl chloride in benzene under reflux for 8 hr in the presence of $PdCl_2(PPh_3)_2$ to afford cyclohexyl 3-quinolyl ketone in a 80% yield.

In comparison, the acylation of 4-TMSn-quinoline and -isoquinoline required much longer reaction time and was catalyzed only with $PdCl_2$. Namely, $PdCl_2(PPh_3)_2$ was found uneffective as a catalyst. Thus, 4-TMSn-isoquinoline and cyclohexanecarbonyl chloride in benzene was heated for 4 days under reflux in the presence of $PdCl_2$ to produce cyclohexyl 4-isoquinolyl ketone in a 62% yield. Analogously, 4-acylquinolines were synthesized.

A plausible mechanism of the palladium catalyzed acylation reaction is also described.