

PALLADIUM CATALYZED ALKYLATION OF HETEROCYCLIC COMPOUNDS

Yoshinao Tamary, Yoshimi Yamada, and Zen-ichi YoshidaDepartment of Synthetic Chemistry, Kyoto UniversitySakyo, Kyoto, 606, Japan

3-Bromothiophene has been reacted with eight kinds of allylic alcohols in HMPA in the presence of a catalytic amount of palladium acetate to give 3-(3'-thienyl)-aldehydes and ketones selectively in high or fairly good yields depending on the structure of allylic alcohols. Similarly 3-(2'-thienyl)aldehydes and ketones were obtained by the reaction of 2-bromothiophene and allylic alcohols. The solvent effects and the effects of co-catalysts (sodium iodide, triphenylphosphine, and DIPHOS) and alkyl substituents of allylic alcohols on the reactivity and regioselectivity are mentioned. This palladium catalyzed reaction has been shown to be applicable to the reaction of 5-substituted 2-bromothiophene and allylic alcohols. 2-(4'-Oxo-pentyl)-5-carbomethoxythiophene and 2-(3'-oxo-butyl)-5-methylcarbomethoxythiophene, thus obtained, have been derived to the common precursor of queen substance, 9-oxo-trans-2-decenoic acid, by the ketalization, followed by desulfurization with Raney nickel (W-7). The successful alkylation of furan has also been mentioned.