

Regioselective Palladium(II)-Catalyzed Synthesis of Five- or Seven-Membered Ring Lactones and Five-, Six- or Seven-Membered Ring Lactams by Cyclocarbonylation Methodology.

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Abstract

The reaction of 2-allylphenols with carbon monoxide and hydrogen in the presence of catalytic quantities of a cationic palladium(II) complex $[(PCy_3)_2Pd(H)(H_2O)]^+BF_4^-$ or palladium acetate and 1,4-bis(diphenylphosphino)butane, gave five- or seven-membered ring lactones (bicyclic, tricyclic, and pentacyclic) as the principal products, often in excellent yields. Use of 2-aminostyrenes as reactants and catalytic quantities of palladium acetate and tricyclohexylphosphine, gave five-membered ring lactams in high yield and selectivity. Bicyclic and tricyclic heterocycles contg. six-membered ring lactams were synthesized from the reaction of 2-allylanilines with CO/H₂ using the catalytic system Pd(OAc)₂/PPh₃, while use of 1,4-bis(diphenylphosphino)butane instead of PPh₃ in the latter process results in the formation of the seven-membered lactams benzazepinones in good yield. The regiochem. control depends on the nature of the palladium catalyst, the relative pressures of the gases, and the solvent. For example, the cyclocarbonylation of 2-allylphenol gave 4,5-dihydro-1-benzoxepin-2(3H)-one (59% yield) and 3-ethyl-2(3H)-benzofuranone (13% yield) and 3,4-dihydro-2H-1-benzopyran-2-one (28% yield).