

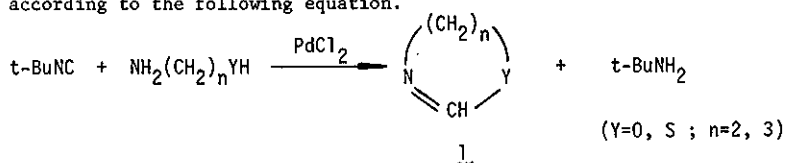
HETEROCYCLE SYNTHESIS BY DIAMINOCARBENE Pd(II) COMPLEX INTERMEDIATE

Yoshihiko Ito, Toshikazu Hirao, and Takeo Saegusa

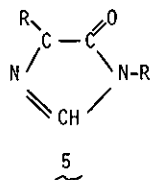
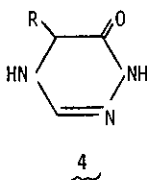
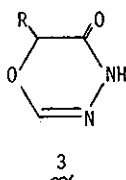
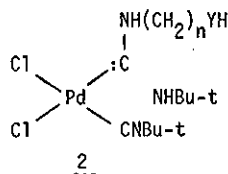
Department of Synthetic Chemistry, Kyoto University

Yoshida, Kyoto, 606

Synthesis of heterocycles containing -N=CH-Y- unit by diaminocarbene Pd(II) complex intermediates is reported. Pd(II)Cl₂ catalyzed reaction of tert-butyl isocyanide with aminoalcohol and with aminothiols afforded the heterocycles (1) such as oxazoline, dihydro-oxazine and thiazoline in moderate yields according to the following equation.



Carbene-coordinated Pd(II)Cl₂ complexes (2), which are key intermediates in the heterocycle synthesis were isolated from the reactions of Pd(II)-Cl₂(tert-BuNC)₂ with aminoalcohol. Similarly, reactions of alkyl isocyanide with α-hydroxycarbohydrazide, with α-aminocarbohydrazide and with α-aminocarboester produced dihydro-oxadiazinone (3), tetrahydro-triazinone (4) and imidazolone (5), respectively.



Furthermore, diaminocarbene Pd(II)Cl₂ complexes (6) were treated with Ag₂O to produce imino-oxazolines (7) in good yields. This cyclization reaction involves β-hydroxycarbohydrazide intermediate which is formed by oxidation of diaminocarbene ligand with Ag₂O.

