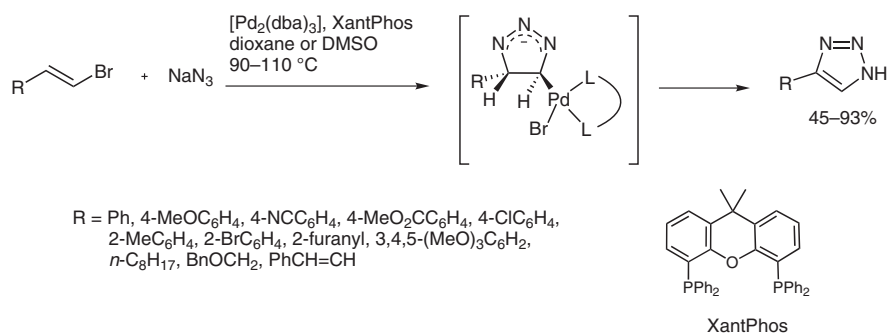


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Developments in Pd Catalysis: Synthesis of 1*H*-1,2,3-Triazoles from Sodium Azide and Alkenyl Bromides

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Palladium-Catalyzed Synthesis of 1*H*-1,2,3-Triazoles



Significance: A palladium-catalyzed synthesis of 1*H*-1,2,3-triazoles from sodium azide and alkenyl bromides with yields ranging from 45–93% is reported. Among the ligands tested, the large bite angle bidentate XantPhos shows the highest activity, which is attributed to its ability to behave as a *trans*-chelating ligand. The optimized conditions for alkyl-substituted alkenyl bromides are different from aryl-substituted ones in that increased catalyst loading, higher temperature and more polar solvents are required for the former systems. Electronic variations of the aryl ring do not significantly affect the results of the reaction and sensitive functional groups such as ester, nitrile and halogen are compatible with the reaction conditions. A mechanism involving a [3+2] cycloaddition of the azide anion with a vinylpalladium species has been proposed.

Comment: 1,2,3-Triazoles represent a significant pharmaceutical and agrochemical class of heterocycles, e.g. due to their antitumor activity (L. S. Kallander et al. *J. Med. Chem.* **2005**, *48*, 5644-5647). Methods for construction of these heterocycles include the condensation of azides with phenacylidenetriphenylphosphorane (P. Ykman et al. *Tetrahedron* **1971**, *27*, 845-849), the reaction of dichloroacetaldehyde tosylhydrazone with amines (K. Harada et al. *Tetrahedron* **1998**, *48*, 695-698) and, especially, the widely used Huisgen reaction ('click chemistry'), the copper-catalyzed reaction of terminal alkynes with azides (see review). However, these methodologies cannot directly lead to 1*H*-1,2,3-triazoles because inorganic azides are poor substrates for these reactions. This report provides a new access for 1*H*-1,2,3-triazole ring construction.

Review: V. D. Bock et al. *Eur. J. Org. Chem.* **2006**, 51-68.

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