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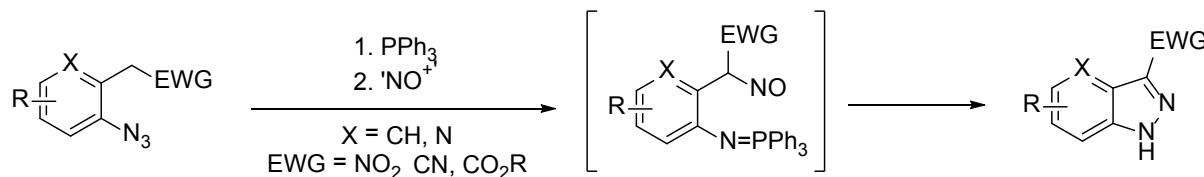


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A Staudinger-diaza-Wittig tandem reaction and its application to the synthesis of 1H-indazoles, 1H-benzoindazoles and 1H-azaindazoles from (het)aryl azides

The aza-Wittig reaction is a widely known and used reaction, which consists of the coupling between an iminophosphorane (obtained from the reaction of a trialkylphosphine on an azide) and an unsaturated carbonyl-type compound. In its intramolecular version, the aza-Wittig reaction gives access to many aza-heterocycles from 5- to 7-membered rings. In such processes, the use of N-electrophiles has never been reported. We investigated nitroso compounds as electrophiles to promote the formation of a N=N double bond. In particular, we found that aromatic iminophosphoranes (coming from the reaction between an aromatic azide and a trialkylphosphine) could cyclize onto an ortho benzylic nitroso moiety, leading to a 3H-indazole that isomerized into its more stable 1H analogue. This process can be operated one-pot, without isolation of the intermediate iminophosphorane. This means that, in a single operation starting from an aromatic azide, the targeted 1H-indazole is generated. Various aryl- and hetaryl azides were used to demonstrate the generality of the method, leading to 1H-indazoles, 1H-benzoindazoles and 1H-azaindazoles (scheme 1).



Scheme 1 – Synthesis of (aza)indazoles from (het)aryl azides

The reaction pathway will also be discussed. It involves a mechanism analogous to that reported for the aza-Wittig reaction. Therefore the key transformation of the process was given the name ‘diaza-Wittig’.

Biography

Eric Pasquinet has completed his PhD from the University of Rouen. He has been working for more than 15 years at CEA on synthesis projects, mainly involving nitrogen heterocycles. He has published more than 25 papers and 12 patents.

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