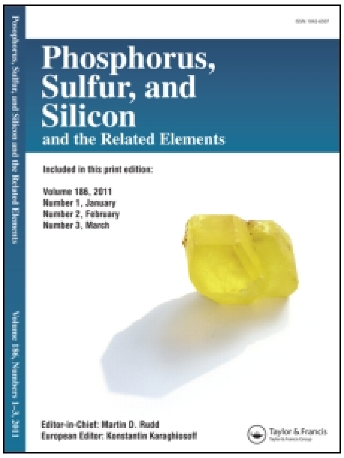

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Umpolung of α-Allenic Ketones and Esters by Phosphorus Groups

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Umpolung of α–Allenic Ketones and Esters by Phosphorus Groups

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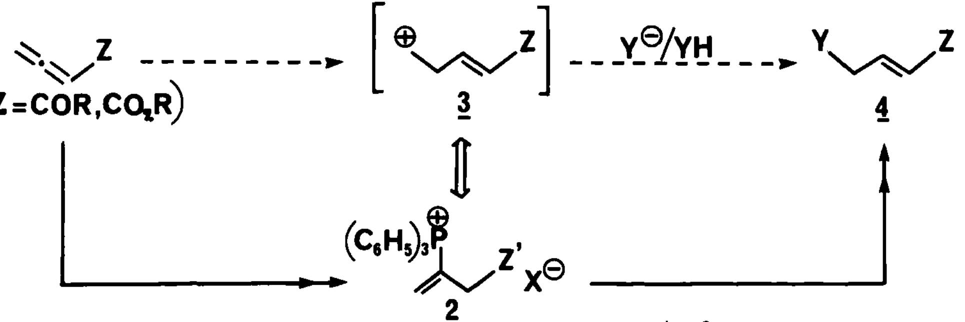
Change in the regioselectivity of the addition of nucleophilic compounds YH (ROH, RSH, RNH_2) on α -allenic ketones and esters can be achieved by using the triphenylphosphonio group as an umpolung agent[1]. In this way α , β-unsaturated ketones and esters 4 are obtained with heteroatomic substituents in the γ position. The Umpolung scheme of the activated allene 1 is charaterized by a functional vinylphosphonium salt 2 as a synthetic equivalent of the a^4-synthon 3.



The Umpolung method can also be applied, in a^4-a^3 diaddition process, to binucleophilic compounds HY⌒Y'H as a new synthesis for functionnal heterocycles such as substituted dioxan, pyrrole or piperidine. Two separate side reactions of the intermediary phosphonium salts were found to occur : a) the isomerisation of the vinylphosphonium salts with migration of the double bond, and, b) for β-substituted alkyl phosphonium salts, exchange of heteroatomic groups Y through elimination-addition. Both side reactions can however be completely controlled.

The work is till in progress by investigating a new auxiliary protection (using trimethylsiloxy group) of the carbonylfunction, and by using a^4-d^3 diaddition to have access to various heterocycles.

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1) H.J. CRISTAU, J. VIALA, H. CHRISTOL, Bull. Soc. Chim. Fr., 1985, 980.