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Umpolung of α -Allenic Ketones and Esters by Phosphorus Groups

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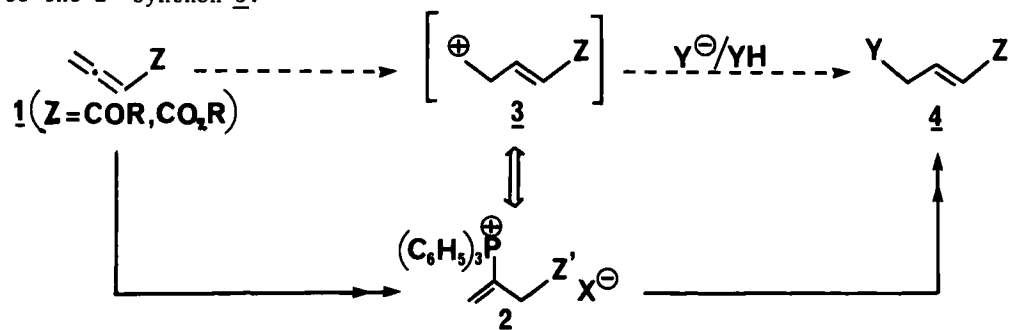
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Umpolung of α -Allenic Ketones and Esters by Phosphorus Groups

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Change in the regioselectivity of the addition of nucleophilic compounds YH (ROH, RSH, RNH₂) on α -allenic ketones and esters can be achieved by using the triphenylphosphonio group as an umpolung agent¹⁾. 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 characterized by a functional vinylphosphonium salt **2** as a synthetic equivalent of the α^4 -synthon **3**.



The Umpolung method can also be applied, in a α^4 - α^3 diaddition process, to binucleophilic compounds HY—Y'H as a new synthesis for functional 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 still in progress by investigating a new auxiliary protection (using trimethylsiloxy group) of the carbonylfunction, and by using α^4 - α^3 diaddition to have access to various heterocycles.

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