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One Step Synthesis of α -Substituted α , β -Unsaturated Aldehydes

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One Step Synthesis of α -Substituted α , β -Unsaturated Aldehydes

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The conversion of carbonyl compounds into homologated α,β -unsaturated aldehydes ("formylolefination") is a highly useful transformation in organic synthesis. A large number of methods have been reported for effecting such a chain lengthening. These proceed mainly via silylated intermediates or via phosphorylated reagents. The "phosphonate-strategy" has found widespread use, but leads exclusively to α,β -unsaturated aldehydes, non-substituted in the α -position.

We now describe a simple and efficient procedure to convert a carbonyl compound into an α -substituted α,β -unsaturated aldehyde starting from an alkylphosphonate, with the possibility of not isolating any of the intermediates. The key step of this method is the formation of a stabilized lithiated adduct resulting from the addition, in the presence of a two-fold excess of metallating agent (n-BuLi + LDA), of an α -phosphorylated carbanion on the readily available ethyl N-phenylformimidate.

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$$(Et0)_{2} P^{-CH}_{2} = \frac{1}{2} \frac{1}{Et0-CH=N\emptyset} \frac{1}{Et0} \frac{1}{2} P^{-C}_{1} P^{-C}_{2} P^{-C}_{2} P^{-C}_{2} P^{-C}_{3} P^{-C}_{4} P^{-C}_$$