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PALLADIUM-CATALYZED ALLYLATION OF KETONES AND ALDEHYDES WITH ALLYLIC CARBONATES VIA SILYL ENOL ETHERS UNDER NEUTRAL CONDITIONS

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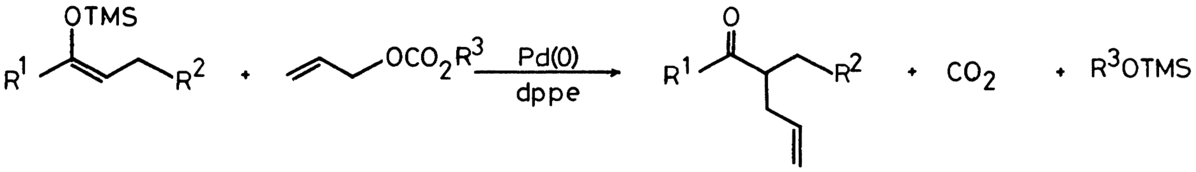
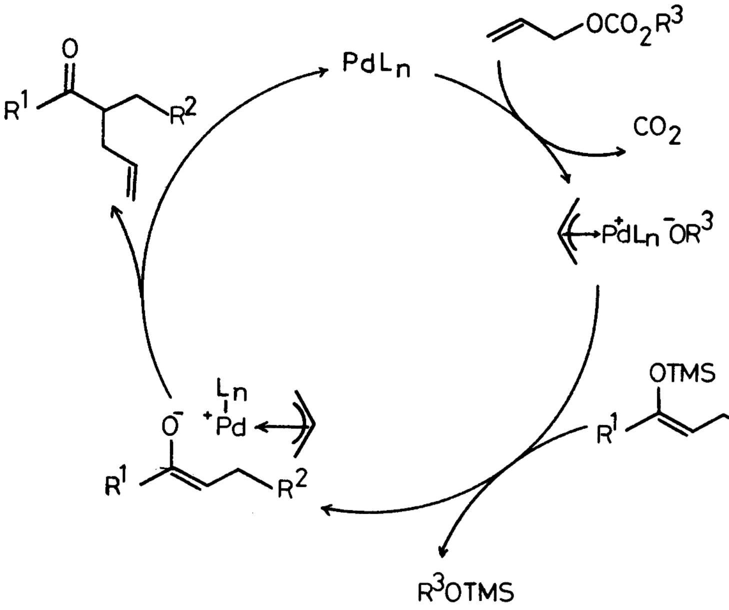
Silyl enol ethers are converted to 2-allyl ketones and aldehydes by the reaction with allylic carbonates in the presence of a palladium-phosphine catalyst.

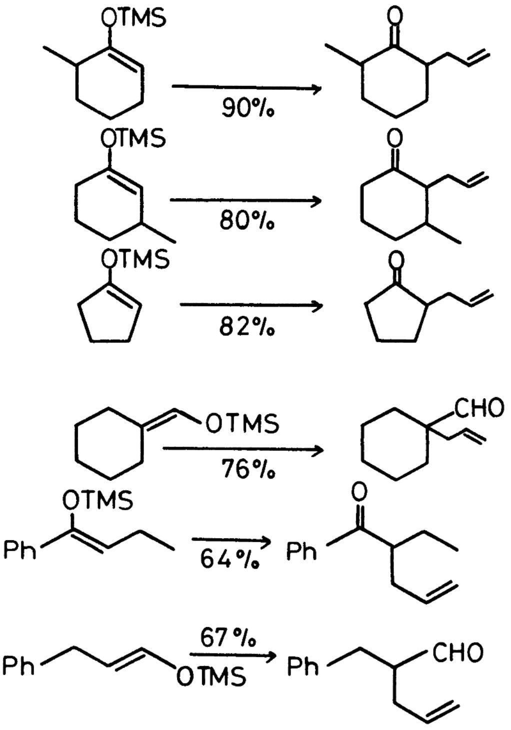
Silyl enol ethers are easily prepared from ketones and aldehydes, and used extensively in organic synthesis as reactive enolate equivalents, particularly for aldol condensation and Michael addition reaction in the presence of Lewis acids or other promoters.[1)] The usefulness of silyl enol ethers would be greatly enhanced if their alkylation is possible. So far a few examples are known. For example, intramolecular reaction of allylic acetate with silyl enol ether promoted by an organoaluminum reagent,[2)] and fluoride-, or Lewis acids-promoted reactions[3,4)] have been reported. Now we wish to report the palladium-catalyzed facile allylation reaction of silyl enol ethers with allylic carbonates expressed by the following scheme.

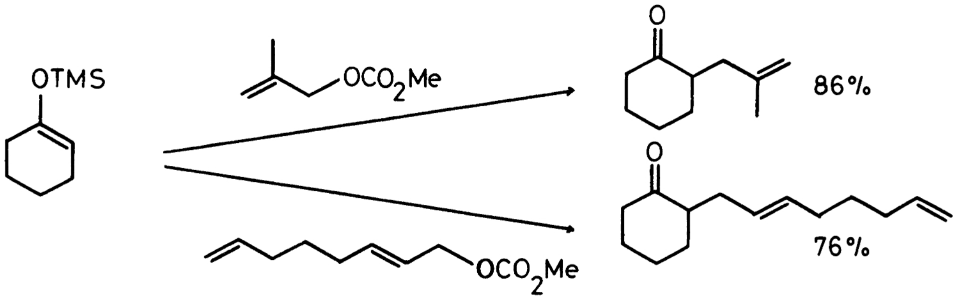


The palladium-catalyzed allylation reaction of active methylene compounds is a well established reaction.[5)] But satisfactory allylation of simple ketones is not possible.[6)] Also it is known that attempted palladium-catalyzed allylation of silyl enol ethers with allyl acetate[7)] or allyl ammonium salt[8)] gave poor results. In our continuous effort to carry out the palladium-catalyzed allylation of various compounds under neutral conditions, we found that allylic carbonates react with silyl enol ethers to give allylated ketones in high yields. Some results are shown in Table. Bis(diphenylphosphino)ethane (dppe) is the most suitable ligand, and PPh_3 is inferior to dppe. The reaction is applicable to cyclic and acyclic ketones and aldehydes. This reaction proceeds under neutral conditions, and hence no proton transfer takes place. Thus, regioselective allylation of silyl enol ethers derived from unsymmetrical ketones is possible. In a typical example, a solution of $Pd_2(dba)_3 \cdot CHCl_3$ (0.05 mmol), dppe (0.1 mmol), silyl enol ether (1 mmol) and diallyl carbonate (2 mmol) in dry THF (5 cm^3) was refluxed for 10-12 h under argon. The allylated product was isolated by the usual work-up.

When the reaction was carried out in MeCN, the enone formation rather than the allylation was observed. The enone formation will be reported separately.







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