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A NOVEL PALLADIUM-CATALYZED PREPARATIVE METHOD OF α,β-UNSATURATED KETONES AND ALDEHYDES FROM SATURATED KETONES AND ALDEHYDES VIA THEIR SILYL ENOL ETHERS

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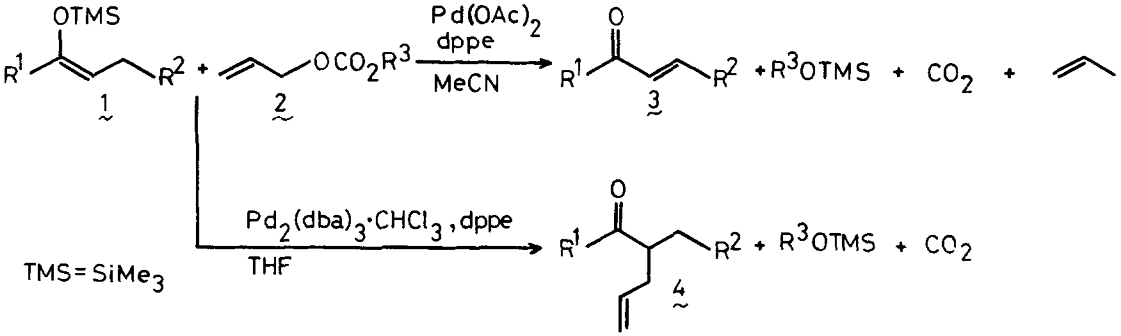
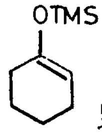
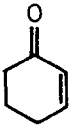
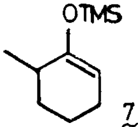
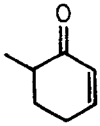
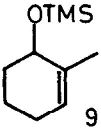
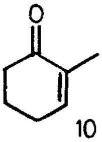
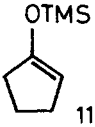
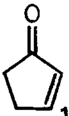
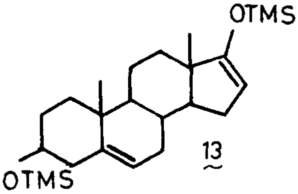
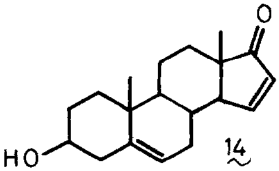
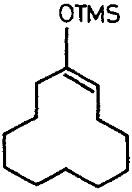
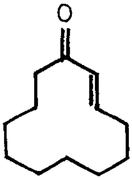
Summary: Silyl enol ethers prepared from saturated ketones and aldehydes can be converted to α,β-unsaturated ketones and aldehydes by the reaction of allyl carbonate in the presence of palladium-phosphine complexes as a catalyst. The selection of solvent is crucial and nitriles are most effective as the solvent.

Conversion of saturated ketones and aldehydes to the corresponding α,β-unsaturated compounds is an important synthetic method. Established methods are based on introduction of heteroatoms (halogen, S, and Se) at the α-position, and their elimination with β-hydrogen.[1-3] We now wish to report a novel catalytic method to introduce α,β-unsaturation into saturated ketones and aldehydes via their silyl enol ethers. Silyl enol ethers, prepared easily from ketones and aldehydes,[4] are known as very useful intermediates for organic synthesis.[5] We found that silyl enol ethers 1 can be converted in one step in good yields to α,β-unsaturated carbonyl compounds 3 by the reaction of allyl carbonates 2 using a palladium-phosphine complex as a catalyst. The reaction can be expressed by the following equation.



In this reaction, the selection of solvent is crucial. The enone and enal formation proceeds satisfactorily only in nitriles, and MeCN is used most conveniently. In some cases, PhCN gives better results. For example, the cyclopentanones were the main products from the silyl enol ethers 11 and 13 in MeCN, while the desired cyclopentenones 12 and 14 were obtained in satisfactory yields in PhCN. The enone formation is competitive with the allylation. When the reaction was carried out in THF or other solvents, the α-allyl ketones 4, instead of enones, were obtained.[6] As the ligand, 1,2-bis(diphenylphosphino)ethane (dppe) gives good results.

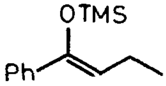
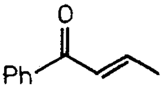
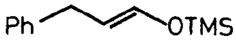
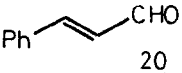
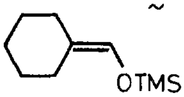
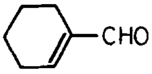
Table Formation of enones and enals by the reaction of silyl enol ethers with diallyl carbonate.

Silyl enol ether	Solvent	Product	Yield(%)$^{a)}$
 5	MeCN	 6	(87)
 7	MeCN	 8	(87)
 9	MeCN	 10	(100)$^{b)}$
 11	PhCN	 12	(69)
 13	PhCN	 14	52
 15	MeCN	 16	78

a) Isolated yield. GLC yield in parenthesis.

b) A mixture of 9 and 7 (77:23) was used and the product consisted of 10 and 8 (75:25).

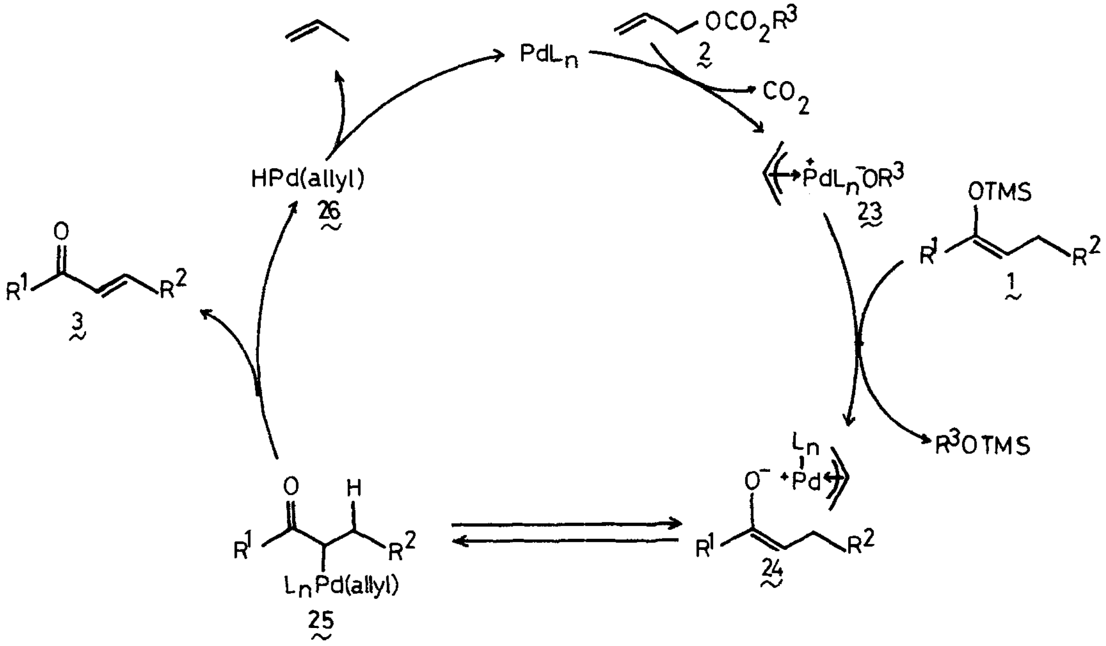
(table continued)

 17	MeCN	 18	66
 19	MeCN	 20	80
 21	MeCN	 22	(74)

Unless otherwise stated, the reaction is carried out in the following way. A solution of $Pd(OAc)_2$ (11 mg, 0.05 mmOl) and dppe (20 mg, 0.05 mmol) in dry MeCN (1 mL) is heated under argon. As soon as the solution begins to reflux, a mixture of silyl enol ether (1 mmol) and diallyl carbonate (2 mmol) in MeCN (4 mL) is added in one portion. The mixture is refluxed for 1 h. After the usual work-up, the unsaturated product is isolated by distillation or column chromatography. Results of the reaction of various silyl enol ethers with diallyl carbonate are shown in the table. All products were identified by comparing their NMR, IR spectra, and TLC and GLC analyses with those of authentic samples. In this reaction, alkyl allyl carbonates such as allyl methyl carbonate can be used as well as diallyl carbonate. As for the catalyst, only 1 mol% of $Pd(OAc)_2$-dppe gives the enones in good yield, although the reaction is slower. For example, reaction of 5 (5 mmol) and diallyl carbonate (7 mmol) with $Pd(OAc)_2$-dppe (0.05 mmol) for 30 h gave 6 in 95% yield.

The reaction is regioselective. From 2-methylcyclohexanone, two silyl enol ethers 7 and 9 were prepared and they were converted to 6-methyl-2-cyclohexenone (8) and 2-methyl-2-cyclohexenone (10) respectively with high regioselectivity.

The enone formation can be explained by the following mechanism. Oxidative addition of the allyl carbonate 2 to Pd(0) and subsequent decarboxylation afford the π-allylpalladium complex 23. Then transmetallation of palladium with silicon gives the allylpalladium enolate complex 24, which is in equilibrium with the carbon-bonded complex 25. Then the enone is formed by the elimination of Pd-H species from 25. Finally the reductive elimination of the allylpalladium hydride complex 26 produces propene and regenerates the Pd(0) catalyst. The last part of this mechanism is closely related to that of the palladium-catalyzed enone formation from allyl β-keto carboxylates[7)] and allyl alkenyl carbonates.[8)] The conversion of ketones to α,β-unsaturated ketones via their silyl enol ethers by using Pd(II) salts has been reported,[9)] but the latter reaction requires the use of Cu(II) salt as a cocatalyst to reoxidize the Pd(0) to make the reaction catalytic. Thus the truly catalytic reaction reported here offers the more convenient and useful method.



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