Tetrahedron Letters,Vol.24,No.50,pp 5639-5640,1983 0040-4039/83 $3.00 + .00
Printed in Great Britain

ONE-STEP SYNTHESIS OF α,β-UNSATURATED KETONES BY THE REACTION OF ENOL ACETATES WITH ALLYL METHYL CARBONATE CATALYZED BY PALLADIUM AND TIN COMPOUNDS

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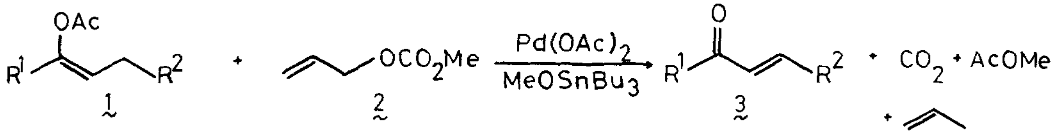
Summary: Enol acetates derived from saturated ketones are converted to α,β-unsaturated ketones by heating with allyl methyl carbonate in MeCN by bimetallic catalysis of palladium-phosphine complex and tin methoxide.

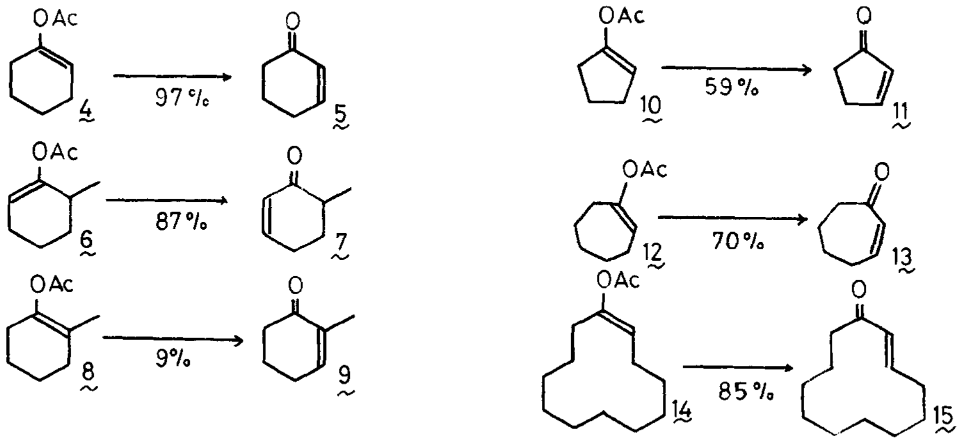
Conversion of saturated ketones to corresponding α,β-unsaturated ketones is an important synthetic method. Established methods are based on introduction of hetero atoms (Cl, Br, S, Se) at the α-position, and their elimination with β-hydrogen.[1,2,3] We have reported before that enones are formed by the palladium-catalyzed decarboxylation-dehydrogenation of allyl β-keto carboxylates[4] and alkenyl allyl carbonates.[5] Also silyl enol ethers can be converted to enones by the palladium-catalyzed reaction of allylic carbonates.[6] We now wish to report a novel catalytic method for enone formation from enol acetates by the reaction of allyl methyl carbonate using $Pd(OAc)_2$ and tin methoxide as a bimetallic catalyst as expressed by the following scheme.

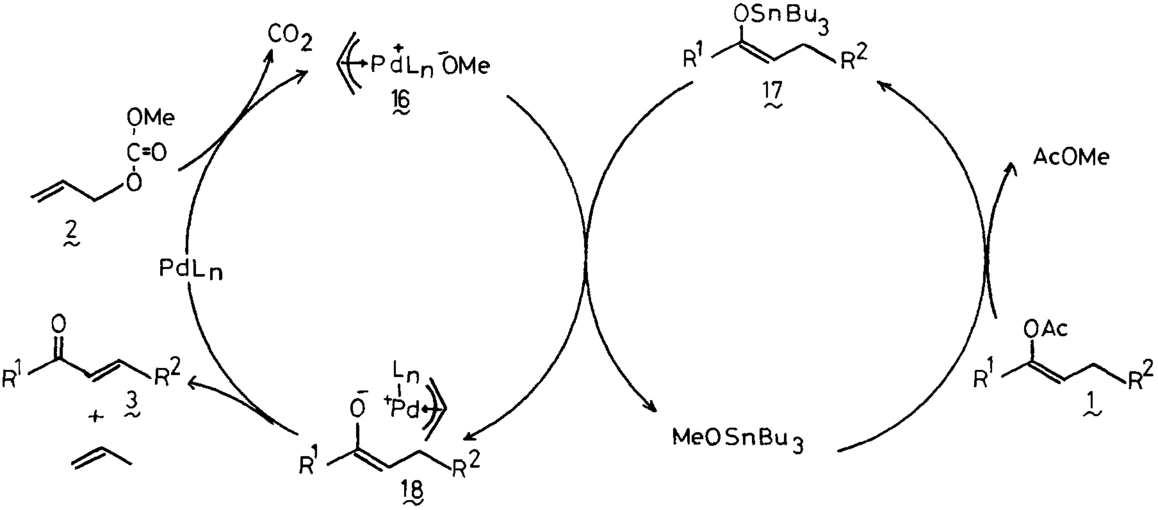


We found that enol acetates are converted to allyl ketones by the Pd-Sn catalyzed reaction of allylic carbonates.[7] In this reaction we found a very crucial effect of solvent. When the reaction was carried out in MeCN, enol acetates were converted to enones rather than α-allyl ketones. Use of other easily available solvents afforded α-allyl ketones. In a typical example, a solution of enol acetate (1 mmol), allyl methyl carbonate (2 mmol), $Pd(OAc)_2$ (0.05 mmol) and bis(diphenylphosphino)ethane (0.05 mmol) in dry MeCN (5 mL) was stirred at room temperature for 10 min under argon. Then tributyltin methoxide (0.2 mmol) was added and the mixture was refluxed for 10 h. The enone was isolated by the usual work-up. Some results are given in the table. As one limitation of this reaction, substituted enol acetates such as 8 gave allyl ketones as a major product.

This unique bimetallic catalysis can be explained by the following mechanism. The *in situ* generation of the tin enolate 17 by the reaction of enol acetate 1 with tin alkoxide is known.[8] Transmetallation of the tin enolate 17 with the π-allylpalladium complex 16, formed by the oxidative addition of allyl carbonate 2 to Pd(0) complex, gives the palladium enolate 18, and regenerates the tin alkoxide, making the reaction catalytic with the tin compound. Finally, the elimination of β-hydrogen from 18 affords the enone and regenerates Pd catalyst.

Table. Conversion of Enol Acetates to α,β-Unsaturated Ketones





It is known that some enol acetates can be converted to enones by electrochemical anodic oxidation.[9]

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(Received in Japan 25 August 1983)