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ALLYLATION OF KETONES VIA THEIR ENOL ACETATES CATALYZED BY PALLADIUM-PHOSPHINE COMPLEXES AND ORGANOTIN COMPOUNDS

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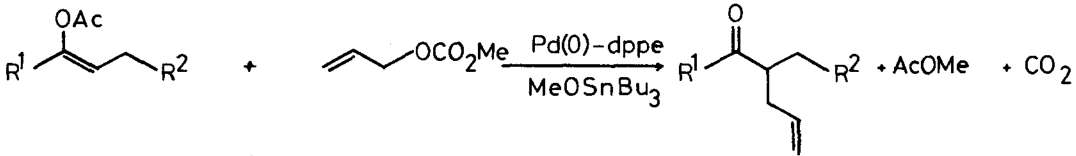
Summary: Enol acetates are converted to allyl ketones by the reaction of allylic carbonates in the presence of palladium-phosphine complex and tin alkoxide as bimetallic catalysts.

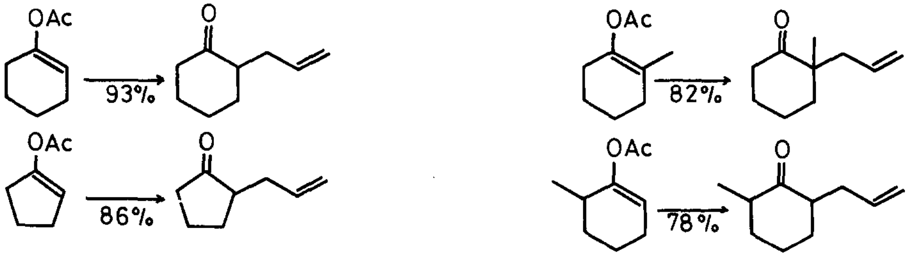
We have reported the regioselective allylation of ketones by the palladium-catalyzed rearrangement of allyl β-keto carboxylates$^{1)}$ and alkenyl allyl carbonates.$^{2)}$ We now wish to report that enol acetates can be converted to allyl ketones by the reaction of allylic carbonates by the catalyses of palladium-phosphine complex and tributyltin methoxide as expressed by the following scheme.

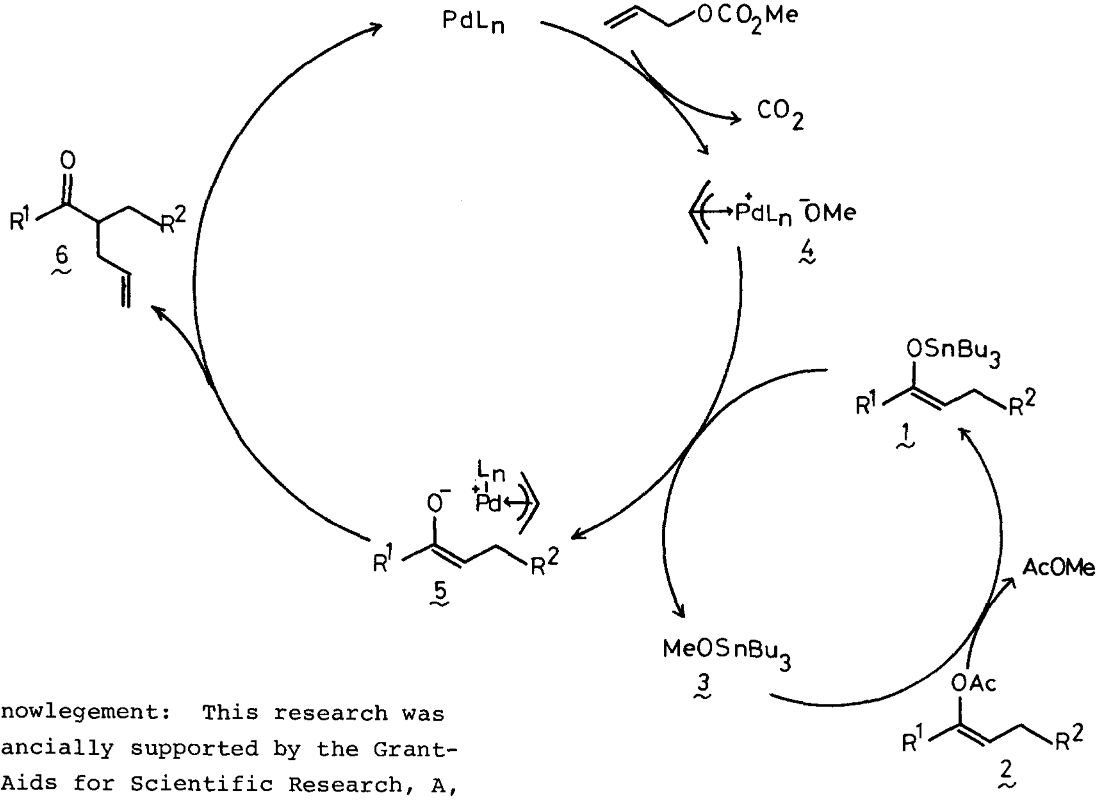


In this reaction, both palladium and tin compounds are necessary as the catalysts. Bis(diphenylphosphino)ethane (dppe) is the most suitable ligand of palladium. In a typical example, a solution of enol acetate (1 mmol), allyl methyl carbonate (2 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (0.05 mmol) and dppe (0.1 mmol) in dry dioxane (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 10-12 h. The allyl ketone was isolated by the usual work-up. Some results are shown in the table.

This unique bimetallic catalysis can be explained by the following mechanism. The *in situ* formation of tin enolates 1 by the reaction of enol acetates 2 with tin aldoxide 3 is known.$^{3)}$ The transmetallation of tin enolates 1 with π-allylpalladium complex 4, formed by the oxidative addition of allyl carbonate to Pd(0) complex, give π-allylpalladium enolates 5. Regeneration of the tin alkoxide 3 makes the reaction catalytic. Finally the reductive coupling of 5 gives the allyl ketones 6.

The *in situ* formation of tin enolates from the reaction of tin methoxide with enol acetates, followed by the palladium-catalyzed reaction with alkenyl and aryl halides to give 2-alkenyl or 2-aryl ketones has been reported.$^{4,5)}$ However, in these cases, stoichiometric amounts of tin methoxide were consumed.





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