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1-ALKENYLATION ON α-POSITION OF KETONE: PALLADIUM-CATALYZED REACTION OF TIN ENOLATES AND 1-BROMO-1-ALKENES

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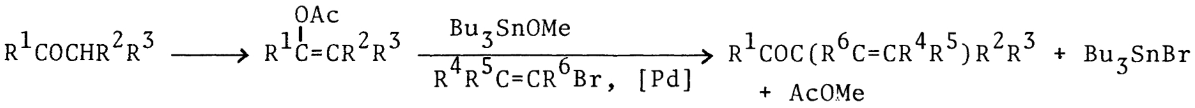
The reaction of tributyltin enolates, prepared from tributyltin methoxide and enol acetates *in situ,* with 1-bromo-1-alkenes in the presence of a catalytic amount of $PdCl_2(o\text{-}tolyl_3P)_2$ was found to give the derivatives of allyl ketone in good yields.

Vinyl halides are usually unreactive toward nucleophilic displacement reactions and thus fail to react with metal enolates under ordinary conditions.¹⁾ Generation of a number of vinyl cation equivalents and their reactions have been recently reported,²⁾ but they all require special reagents or multistep operations.

This communication describes a palladium-catalyzed substitution of 1-alkenyl bromides with tin enolates, under the conditions similar to those for the reaction of aryl bromides,³⁾ giving allylic ketones in good yields.



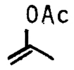
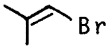
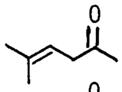
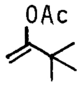
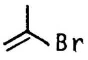
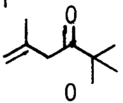
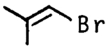
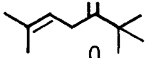
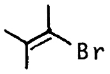
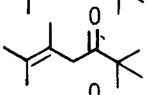
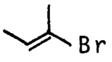
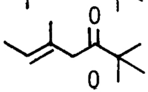
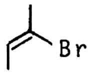
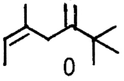
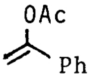
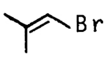
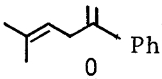
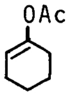
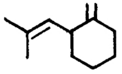
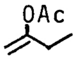
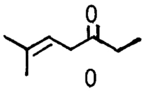
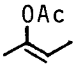
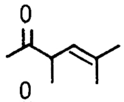
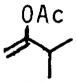
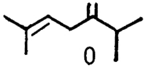
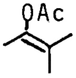
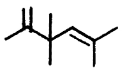
$$R^1COCHR^2R^3 \longrightarrow R^1\overset{OAc}{\overset{|}{C}}=CR^2R^3 \xrightarrow[R^4R^5C=CR^6Br,\ [Pd]]{Bu_3SnOMe} \underset{+\ AcOMe}{R^1COC(R^6C=CR^4R^5)R^2R^3} + Bu_3SnBr$$

The reaction of tributyltin enolates, prepared from tributyltin methoxide and enol acetates *in situ,* with 1-bromo-1-alkenes in the presence of a catalytic amount of $PdCl_2(o\text{-}tolyl_3P)_2$ was found to give the derivatives of allyl ketone in good yields. Since enol acetates can be derived from the corresponding ketones,⁴⁾ 1-alkenylation on the α-position of the starting ketones can be attained through two steps.

Typical procedure was as follows: a stirred solution of tributyltin methoxide (30 mmol), enol acetate (30 mmol), 1-bromo-1-alkene (20 mmol), and $PdCl_2(o\text{-}tolyl_3P)_2$ (0.2 mmol) in toluene (10 ml) was heated at 100°C under argon. After the palladium was deposited (ca. 30 min), the product was isolated by distillation under reduced pressure. Results are shown in Table 1.

The reaction seems sensitive to steric hindrance caused by substituents on enol acetate. The reaction of enol acetates bearing terminal methylene gave the 1-alkenylated ketones generally in high yields, while lower yields were obtained for the substrates having substituents on the reaction site. Number and position of substituents on 1-alkenyl bromide seem not to give serious effect on the product yield. Moreover, it is noteworthy that the configuration of vinyl bromide was completely retained. The reaction of acetophenone gave allyl ketone as a major product, but together with isomerized conjugated enones. Thus the present reaction is particularly effective for 1-alkenylation of methyl group of methyl alkyl ketones.

Table 1. Pd-Catalyzed 1-Alkenylation on α-Position of Ketone *via* Tin Enolates

Entry	Enol Ester	Bromide	Product	Yield(%)[a]	Bp (°C/mmHg)
1				62	43-45/17
2				53	62-63/34
3				81	72-73/19
4				86	79-80/16
5		(E) 	(E) 	76	70-71/15
6		(Z) 	(Z) 	90	67-69/14
7			[b]	74	130-132/17
8				32	95-97/15
9				(53)	
10				35	56-58/20
11				74	69-71/20
12				(8)	

a) Isolated yield based on bromide (GLC yield in parentheses).

b) α,β-Unsaturated ketone was detected by NMR. (ca. 5%).

References

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