α-Phenylation of Ketones *via* Tin Enolates Catalysed by a Palladium Complex

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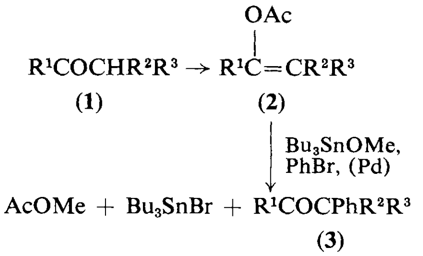
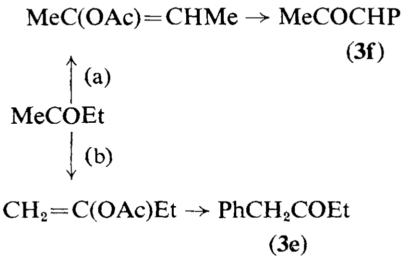
The reaction of tributyltin enolates, prepared from tributyltin methoxide and enol acetates *in situ*, with bromobenzene in the presence of a catalytic amount of $PdCl_2(o\text{-tolyl}_3P)_2$ was found to give α-phenyl ketones in good yields with essentially complete retention of the acetate regiochemistry.

Even though the α-arylation of ketones has received much attention recently,[1] there is still a need for a simple and regio-controlled procedure for this conversion. We have previously reported the palladium-catalysed arylation of acetone *via* acetonyltributyltin,[2] and we now report a similar reaction for the simple and regio-controlled α-arylation of unsymmetrical ketones, exemplified by the α-phenylation of several simple ketones shown (Scheme 1). The first step has been investigated thoroughly, including its regiochemistry.[3] *E.g.* treatment of butan-2-one with keten gave 2-acetoxybut-2-ene (route a), and treatment with triphenylmethyl-lithium followed by



$$\underset{(1)}{R^1COCHR^2R^3} \rightarrow \underset{(2)}{R^1\overset{\displaystyle OAc}{\overset{|}{C}}{=}CR^2R^3} \xrightarrow{Bu_3SnOMe,\ PhBr,\ (Pd)} AcOMe + Bu_3SnBr + \underset{(3)}{R^1COCPhR^2R^3}$$

Scheme 1



Scheme 2

acetic anhydride (route b) produced 2-acetoxybut-1-ene, both as major products. Fractional distillation gave the acetates with >95% purity (Scheme 2). The second step is a 'one-pot' procedure involving tributyltin enolates prepared *in situ* from the enol acetates and tributyltin methoxide.[2]

Reactions were carried out as follows: a stirred solution of tributyltin methoxide (15 mmol), the appropriate enol acetate (15 mmol), bromobenzene (10 mmol), and $PdCl_2(o\text{-tolyl}_3P)_2$ (0.1 mmol) in toluene (5 ml) was heated under argon at 100 °C for 5 h. After evaporation to remove the solvent and methyl acetate, column chromatography of the residue (silica gel; cyclohexane followed by diethyl ether as eluants) provided the α-phenyl ketone from the ethereal eluate following distillation under reduced pressure. The results are in Table 1.

The isolated yields were reasonably high, indicating that the reaction can be used for the preparation of α-phenyl ketones with complete retention of the acetate regiochemistry. Thus, 2-acetoxybut-1-ene and -2-ene gave exclusively 1-phenyl- and 3-phenyl-butanones, respectively. Low yields for the substrates bearing methyl substituents on the reaction site [particularly (**3h**)] may be due to steric hindrance. $PdCl_2(o\text{-tolyl}_3P)_2$ was the best catalyst among the various complexes examined so far.

Table 1. Pd-catalysed α-phenylation of ketones (**1**) *via* tin enolates (**2**) to provide the ketones (**3**).

				(3)	
	R^1	R^2	R^3	% Yield[a]	B.p., t/°C (p/mmHg)
a	Me	H	H	78	88—92 (15)
b	Bu^t	H	H	86	110—111 (18)
c	Ph	H	H	90	115—117 (1)
d	$-[CH_2]_4-$		H	54	M.p. 58—59
e	Et	H	H	(67)	—
f	Me	H	Me	60	94—95 (14)
g	Pr^i	H	H	87	114—115 (25)
h	Me	Me	Me	33 (38)	99—101 (17)

[a] Isolated yield based on PhBr (g.l.c. yield in parentheses).

M. K. thanks the Ministry of Education, Science and Culture, Japan, for a Grant-in-Aid.

Received, 24th January 1983; Com. 106

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