Rhodium-catalyzed Conjugate Addition of Arylstannanes to α,β-Unsaturated Ketones and Esters

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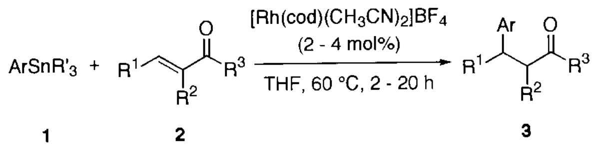
Aryltrimethylstannanes react with α,β-unsaturated ketones and esters in the presence of a catalytic amount of a cationic rhodium complex, $[Rh(cod)(MeCN)_2]BF_4$, affording the conjugate addition products in good yields.

The formation of C-C bond at the β-C atom of an α,β-unsaturated carbonyl system is generally achieved through conjugate addition of organocopper reagents generated from copper salts with organolithium or Grignard reagents.[1] Yamamoto et al. developed organocopper-Lewis acid reagents which expanded the usefulness of the organocopper reagents to previously "unreactive" substrates such as β,β-disubstituted acrylic esters, sterically highly crowded enones, and α,β-unsaturated carboxylic acids.[2] In addition to these largely applied methods, conjugate addition of organoaluminum[3] and organoboron[4] compounds have been reported. Transition metal-catalyzed 1,4-addition of main group organometallic reagents also show great promise. Thus nickel-catalyzed conjugate addition of organoaluminum,[5] organozinc,[6] and organozirconium[7] compounds to α,β-enones have been achieved. By use of palladium complexes as catalyst, Cacchi et al. effected the conjugate addition of arylmercury and arylstannane compounds to α,β-enones in an acidic two-phase system.[8] Uemura et al. reported the conjugate addition of arylantimony compounds to α,β-enones and enals catalyzed by palladium(II).[9] Recently, we demonstrated that arylstannanes add to aldehydes in the presence of a cationic rhodium complex as catalyst affording the corresponding arylated carbinols.[10] We wish to report here a rhodium-catalyzed conjugate addition of arylstannanes to α,β-unsaturated ketones and esters applying this arylation method to afford β-arylated ketones and esters in good yields under neutral conditions (Scheme 1).

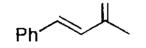
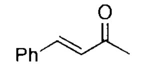
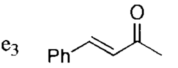
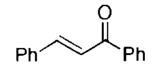
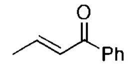
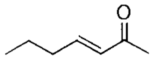
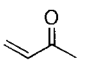
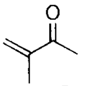
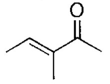
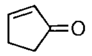
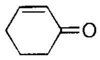
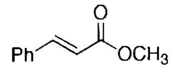
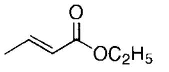
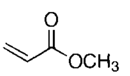
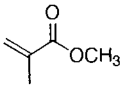


Scheme 1.

The general procedure is as follows. A mixture of 1.2 mmol of arylstannane **1**, 1.0 mmol of α,β-enones **2**, and 0.02 mmol of $[Rh(cod)(MeCN)_2]BF_4$ (cod = cycloocta-1,5-diene) in 1 ml of dried THF was stirred at 60 °C for an appropriate period of time under N_2 atmosphere in a sealed Schlenk tube. The reaction was monitored by TLC. The reaction was quenched by adding a small amount of water and then stirred for 1 h. After the solvent was removed *in vacuo*, the product was isolated by silica gel column chromatography.

The results are summarized in Table 1. The treatment of 4-phenylbut-3-en-2-one with trimethylphenylstannane in the presence of 2 mol% cationic rhodium complex $[Rh(cod)(MeCN)_2]BF_4$, afforded 4,4-diphenylbutan-2-one as the

Table 1. Conjugate addition of arylstannanes to α,β-unsaturated ketones and esters catalyzed by $[Rh(cod)(MeCN)_2]BF_4$[a]

Ently	Alyrstannane **1**	α,β-Enone and enoate **2**	Time/h	Yield/%[b]
1	$PhSnMe_3$		2	86
2	$p\text{-}FC_6H_4SnMe_3$		2	74
3	$p\text{-}MeOC_6H_4SnMe_3$		2	68
4	$PhSnMe_3$		2	94
5[c]	$PhSnMe_3$		2	60
6[c]	$PhSnMe_3$		2	82
7	$PhSnMe_3$		20	18
8	$PhSnMe_3$		20	38
9	$PhSnMe_3$		20	13
10[c]	$PhSnMe_3$		5	30
11[c]	$PhSnMe_3$		2	77
12[c]	$PhSnMe_3$		2	91
13[c]	$PhSnMe_3$		20	64
14	$PhSnMe_3$		20	2
15[c]	$PhSnMe_3$		2	76

[a] A mixture of 1 (1.2 mmol), 2 (1.0 mmol), and $[Rh(cod)(MeCN)_2]BF_4$ (0.02 mmol) in THF (1 ml) was stirred under N_2 atmosphere. [b] Isolated yield based on 2. [c] 0.04 mmol of $[Rh(cod)(MeCN)_2]BF_4$ was used.

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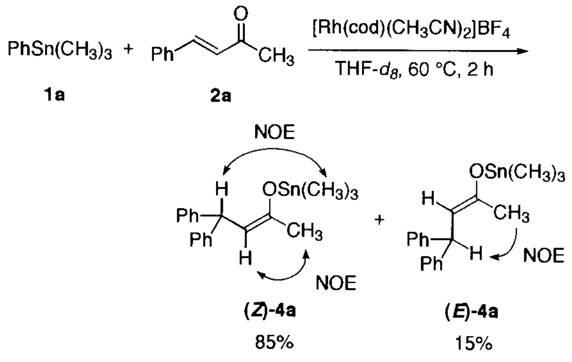
conjugate adduct in 86% isolated yield (entry 1). Since NMR examination of the reaction mixture prior to quenching the reaction by adding water indicated the formation of the corresponding enol stannyl ether, the hydrolysis of the enol ether must take place during the work-up. NOE experiment of the resulting mixture in THF-d_8 showed the preferential formation of the *Z*-isomer of the enol stannyl ether ((**Z**)-**4a**, Scheme 2).[11]



Scheme 2.

Heck type product of 4,4-diphenylbut-3-en-2-one was not produced. Addition of phosphine ligands such as PPh_3 to $[Rh(cod)(MeCN)_2]BF_4$ inhibited the reaction. The reaction of *p*-fluorophenyltrimethylstannane and *p*-methoxyphenyltrimethylstannane with 4-phenylbut-3-en-2-one also proceeded smoothly, affording the corresponding conjugate adducts in good yields (entries 2 and 3). Reactions of trimethylphenylstannane and several α,β-unsaturated ketones and esters were then examined. The product yield was greatly dependent on the substitution pattern of the substrates. α,β-Unsaturated ketones having 1,2-disubstituted olefinic part afforded the corresponding conjugate adducts in good yields (entries 4 to 6). On the contrary, the reactions of methyl vinyl ketone having monosubstituted olefinic part, 3-methylbut-3-en-2-one having 1,1-disubstituted olefinic part, and 3-methylpent-3-en-2-one having 1,1,2-trisubstituted olefinic part afforded the adducts in poor yields (entries 7 to 9). The reaction of cyclopentenone gave the adduct in moderate yield, while the reaction of cyclohexenone gave the adduct in good yield (entries 10 and 11). α,β-Unsaturated esters having 1,2-disubstituted olefinic part and methyl methacrylate also reacted with trimethylphenylstannane affording the corresponding conjugate adducts in good yields (entries 12, 13, and 15), although the reaction of methyl acrylate proceeded only scarcely (entry 14). In order to develop the scope, the reaction of α,β-unsaturated aldehyde was also investigated using cinnamaldehyde as the probe. Unfortunately, the reaction with trimethylphenylstannane was complicated since the 1,2-addition of the trimethylphenylstannane also took place to both the starting aldehyde and the 1,4-addition product resulting the desired product in a poor yield.

Although the mechanism is not clear, an arylrhodium species could be assumed as an active species, which would be generated by transmetallation between an arylstannane and $[Rh(cod)(MeCN)_2]BF_4$[10].

The reaction reported herein represents a new method for conjugate addition of arylstannanes to α,β-unsaturated ketones and esters affording β-arylated ketones and esters under neutral conditions using a catalytic amount of the cationic rhodium complex. Further work is now in progress to obtain the full scope of this reaction.

References and Notes

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11 (**Z**)-**4a**: ^1H NMR (400 MHz, THF-d_8) δ 0.35 ($J_{^{119}Sn\text{-}H}$ = 61.8 Hz, $J_{^{117}Sn\text{-}H}$ = 59.2Hz, 9H), 1.74 (s, 3H), 4.72 (d, *J* = 8.9 Hz, 1H), 5.20 (d, *J* = 8.9 Hz, 1H), 7.10 - 7.35 (m, 10H). (**E**)-**4a**: ^1H NMR (400 MHz, THF-d_8) δ 0.43 ($J_{^{119}Sn\text{-}H}$ = 61.6 Hz, $J_{^{117}Sn\text{-}H}$ = 59.4Hz, 9H), 1.76 (s, 3H), 4.62 (d, *J* = 9.4 Hz, 1H), 4.76 (d, *J* = 9.4 Hz, 1H), 7.10 - 7.35 (m, 10H).