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Palladium(II)-Catalyzed Hydroarylation of α,β-Unsaturated Aldehydes and Ketones with Triarylstibines in the Presence of Silver Acetate

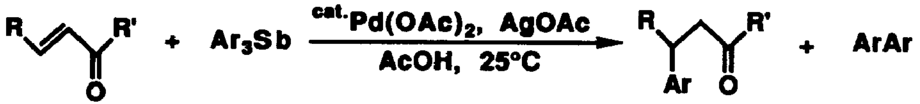
Chan Sik Cho, Koichiro Tanabe, and Sakae Uemura*

Division of Energy and Hydrocarbon Chemistry, Graduate School of Engineering, Kyoto University, Sakyo-ku, Kyoto 606-01 (Japan)

Abstract: Triarylstibines react with α,β-unsaturated aldehydes and ketones in acetic acid at 25°C in the presence of silver acetate and a catalytic amount of palladium(II) acetate to afford the hydroarylation products by conjugate addition in good yields.

Synthetic applications of organoantimony compounds are rapidly increasing,[1] and yet a clear-cut example of the conversion of a C-Sb bond to a C-C bond seems to be limited to the palladium(II) salt-mediated self-coupling of Ar_3Sb[2] and Heck-type reaction of Ph_3Sb[3] and the reactions of pentaorganylstiboranes with aldehydes, acyl chlorides and ketones.[4] We now disclose that triarylstibines work as reagents for hydroarylation of α,β-unsaturated ketones and aldehydes (conjugate addition) in the presence of palladium(II) acetate as a catalyst. The reaction did not almost occur with other compounds of group 15 elements such as triphenylphosphine, triphenylarsine and triarylbismuthines.

Scheme 1



(R' = H, Me)

1

a; Ar = Ph
b; Ar = 4-MeC_6H_4
c; Ar = 4-MeOC_6H_4
d; Ar = 4-ClC_6H_4
e; Ar = 3-ClC_6H_4
f; Ar = $4\text{-CF}_3C_6H_4$
g; Ar = 1-naphthyl

Treatment of triphenylstibine (1 mmol) with an equimolar amount of 2-butenal (croton aldehyde) in acetic acid in the presence of a catalytic amount of palladium(II) acetate (10 mol%) and silver acetate (2 mol equiv.) at 25°C for 24 h afforded 3-phenylbutanal (conjugate addition product) and biphenyl in 61% and 63% yield (GLC yield based on triphenylstibine)[5] respectively, whereas none of 3-phenyl-2-butenals (Heck-type reaction products[6]) were produced. The hydroarylation reaction did not proceed at all using other silver(I) salts such as nitrate, chloride and sulfate in place of acetate. Here, the coexistence of palladium(II) acetate and silver acetate was revealed to be necessary since hydroarylation did not proceed at all in the absence of either of them. From other easily available α,β-unsaturated aldehydes the corresponding conjugate addition products were also formed in good yields. This reaction system could also be applied to many α,β-unsaturated ketones as well as various triarylstibines (Scheme 1). Several representative results are summarized in Table 1. Interestingly, under completely the same reaction conditions, Heck-type reaction leading to phenylated alkenes occurred almost exclusively with some other alkenes such as styrene, allyl acetate, methyl acrylate, methyl cinnamate and acrylonitrile.[7]

Although the exact nature of the reaction is not yet clear, we presume Scheme 2 as one of the most plausible reaction pathways. Arylpalladium acetate [ArPdOAc], initially formed *in situ,* adds to enones or enals to produce an alkylpalladium(II) species **2** where some antimony compounds coordinate to the carbonyl oxygen. The coordination may accelerate the heterolytic fission of the palladium-carbon bond to give the enolate **3** leading to hydroarylation products **4** faster than β-hydride *syn*-elimination leading to Heck-type products. Electron-donating nature of R' in the intermediate **2** (R' = MeO>H>Me) might give more chance toward the β-elimination by preventing the transformation of **2** to **3**. The role of silver acetate is still obscure and the studies for clarifying its actual role as well as the application to other organoheteroatom compounds are in progress.

Scheme 2

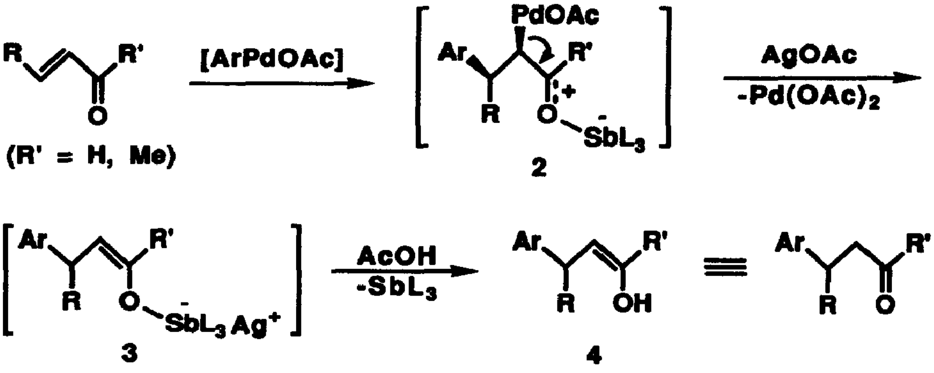
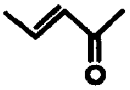
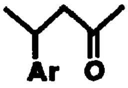
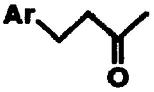
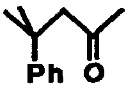
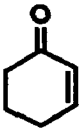
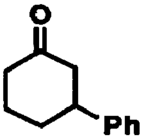
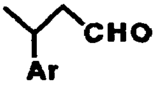
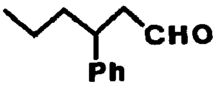
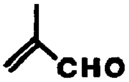
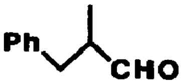


Table 1. Palladium-catalyzed hydroarylation of enones and enals with triarylstibines[a]

Enone or enal	Triarylstibine	Isolated yield (%)[b]	
	1a		41
	1b		44
	1c		57
	1d		68
	1e		74
	1f		72[c]
	1a		80[d]
	1g		53[e]
	1a		42[d]
	1a		14
	1a		43
	1a		50
	1b		46
	1d		52
	1a		55
	1a		100[d]
	1a		35

[a] Carried out with enone or enal (1 mmol), Ar_3Sb (1 mmol), $Pd(OAc)_2$ (0.1 mmol), and AgOAc (2 mmol) in AcOH (20 ml) at 25°C for 24 h. [b] Based on enone or enal unless otherwise mentioned. [c] Other product; 4-[(4-trifluoromethyl)phenyl]-3-penten-2-one (12%). [d] GLC yield. [e] Other product; 4-(1-naphthyl)-3-buten-2-one (26%).

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5. Under similar reaction conditions without 2-butenal, biphenyl was produced in 53-58% yield.
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7. For example, when triphenylstibine was subjected to react with methyl acrylate under the conditions similar to those described above, methyl 3,3-diphenylpropanoate, a conjugate addition product derived from the initially formed methyl cinnamate, was obtained only in 4% yield, while Heck-type vinylic substitution products, methyl cinnamate and methyl 3,3-diphenylpropanoate, were predominantly produced in 53% and 35% yields, respectively. Similar treatment of methyl cinnamate afforded methyl 3,3-diphenylpropenoate in 83% yield together with methyl 3,3-diphenylpropanoate (2%).

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