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Antimony(III) Chloride as an Efficient Catalyst for Palladium-Catalyzed Hydrophenylation of α,β-Unsaturated Ketones and Aldehydes

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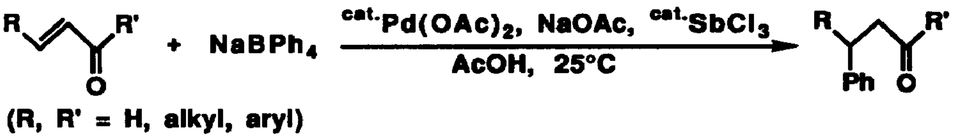
Abstract: A remarkable catalytic effect of antimony(III) chloride was disclosed in palladium-catalyzed hydrophenylation of α,β-unsaturated ketones and aldehydes (Michael-type conjugate addition) with sodium tetraphenylborate in acetic acid at 25°C.

Although a characteristic catalytic nature of bismuth(III) chloride has been recently disclosed in several carbon-carbon bond forming reactions such as allyl unit addition to aldehydes,[1] aldol and Michael reactions,[2,3] and Knoevenagel condensation,[4] there seems to be only one report[3b] on the use of antimony(III) chloride, the salt of the same group 15 elements, for such a reaction (aldol reaction; less effective than $BiCl_3$) to the best of our knowledge. Recently, we found that sodium tetraphenylborate reacted with alkenes to give the corresponding phenylated alkenes (Heck-type products) in the presence of $Pd(OAc)_2$(cat.) and NaOAc,[5] while triarylstibines worked as reagents for hydroarylation of enones and enals (conjugate addition products) in the presence of $Pd(OAc)_2$(cat.) and AgOAc.[6] Consideration of the role of antimony in the latter reaction led us to attempt the former reaction in the presence of some antimony compounds. Eventually, it was disclosed that the addition of only a catalytic amount of $SbCl_3$ resulted in formation of the corresponding hydroarylation products in high yields from α,β-unsaturated ketones and aldehydes. We here report the first clear-cut example of a remarkable catalytic effect of $SbCl_3$ for a carbon-carbon bond forming reaction.

Scheme 1



(R, R' = H, alkyl, aryl)

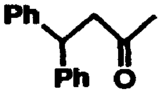
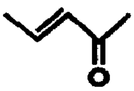
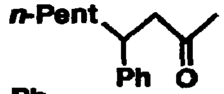
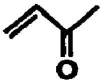
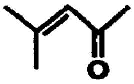
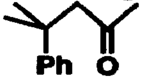
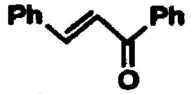
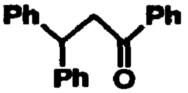
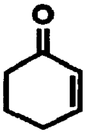
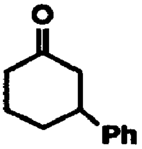
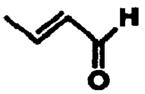
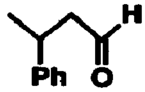
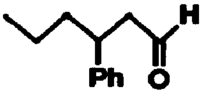
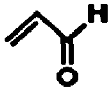
Treatment of equimolar amounts of $NaBPh_4$ and 4-phenyl-3-buten-2-one in acetic acid in the presence of a catalytic amount of palladium(II) acetate (10 mol%) and sodium acetate (2 mol equiv.) at 25°C for 24 h afforded 4,4-diphenylbutan-2-one (conjugate addition product) and 4,4-diphenyl-3-buten-2-one (Heck-type product) in 87% yield (the former/the latter = 24/76) together with biphenyl (4%). However, when a catalytic amount of antimony(III) chloride (10 mol%) was added to the above reaction system, the conjugate addition product was obtained nearly as a sole product (90% yield, ratio = 98/2). Although it is well-known that organoboranes react with enones and enals to afford 1,4-addition products even in the absence of palladium catalyst,[7] the reaction with $NaBPh_4$ did not proceed at all without the catalyst, only benzene being formed. Among the chloride of other group 15 elements examined, arsenic(III) chloride was moderately effective, but bismuth(III) chloride was almost ineffective for this hydrophenylation reaction. The reaction system could also be applied to many α,β-unsaturated ketones and aldehydes (Scheme 1), several representative results being summarized in Table 1.

Since $NaBPh_4$ may react with solvent acetic acid to give triphenylboron (Ph_3B) (Scheme 2) it might be conceivable that Ph_3B is the real reactive species. In fact, we observed in a separate experiment that the reaction of triphenylboron (1 mmol) with an equimolar amount of 2-cyclohexenone under the above reaction conditions in the presence of 10 mol% $SbCl_3$ afforded 3-phenylcyclohexanone and 3-phenyl-2-cyclohexenone[8] in 93% and 5% yields, respectively, together with benzene (0.91 mmol). Treatment of $NaBPh_4$ (1 mmol) in place of Ph_3B afforded similar yields of both phenylated products together with more benzene (2.21 mmol). These results support the assumption that triphenylboron is the actual phenylating reagent. Although the details of the reaction scheme are not yet clear, a plausible pathway is presented in Scheme 3. Phenylpalladium borane [$PhPdBPh_2$], initially formed *in situ* by oxidative addition of a carbon-boron bond to palladium(0),[9] adds to enones or enals to produce an alkylpalladium(II) species **1**. Antimony(III) chloride, as a weak Lewis acid, coordinates to the carbonyl oxygen of this intermediate **1** to give the species **2** where the heterolytic palladium-carbon bond fission occurs to lead to hydrophenylation products **3** faster than β-hydride *syn*-elimination leading to Heck-type products.

Scheme 2

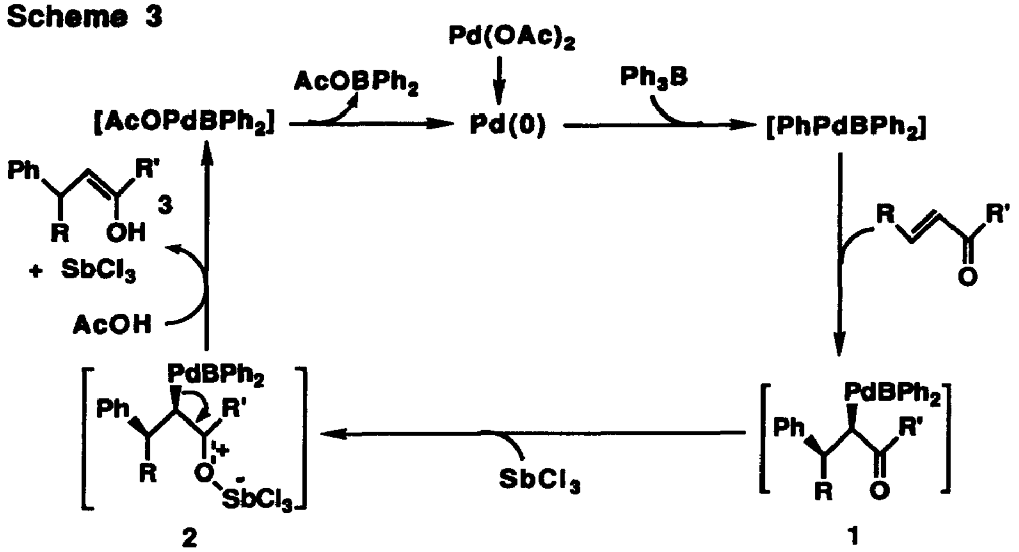
$$NaBPh_4 + AcOH \longrightarrow Ph_3B + PhH + NaOAc$$

Table 1. Antimony(III) chloride catalysis in palladium-catalyzed hydrophenylation of enones and enals with sodium tetraphenylborate[a]

Enone or enal	MCl_3 (mmol)	Reaction time (h)	Isolated yield (%)[b]	
	$SbCl_3$(0.1)	24		88
	$AsCl_3$(0.1)	24		64[c]
	$BiCl_3$(0.1)	24		26[c]
	$SbCl_3$(0.1)	24		65
	$SbCl_3$(0.1)	24		47
	$SbCl_3$(0.1)	24		32[c,d]
	$SbCl_3$(0.1)	24		39
	$SbCl_3$(0.1)	24		84
	$SbCl_3$(0.1)	24		91[e]
	$SbCl_3$(0.1)	24		31
	$SbCl_3$(0.3)	20		47
	$SbCl_3$(0.5)	5		63
	$SbCl_3$(0.3)	6		60
	$SbCl_3$(0.1)	20		31[c,f]

[a] Carried out with enone or enal (1 mmol), $NaBPh_4$ (1 mmol), $Pd(OAc)_2$ (0.1 mmol), and NaOAc (2 mmol) in AcOH (20 ml) at 25°C. [b] In all cases, biphenyl (<10%), Heck-type products (2~5%), and a large amount of benzene, even if not determined, were always formed. [c] GLC yield. [d] Other product; *trans*-4-phenyl-3-buten-2-one (20%). [e] Other products; 3-phenyl-2-cyclohexenone (3%), benzene (2.21 mmol). [f] Other product; *trans*-cinnamaldehyde (8%).

Scheme 3



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