Palladium-promoted Vinylic Hydrogen Substitution of Alkenes by Grignard Reagents. Stoicheiometric and Catalytic Reactions

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Summary Arylation of styrene by Grignard reagents has been performed in the presence of stoicheiometric or catalytic amount of palladium chloride.

VINYLIC hydrogen substitution is a useful reaction in organic synthesis. It is well known that direct alkylation of alkenes can be brought about catalytically by organomercury compounds[1] or by aryl halides[2] in the presence of palladium salts. Recently, styrene was methylated by methyl-lithium provided that stoicheiometric amounts of $Pd(OAc)_2$ or $Pd(acac)_2$ (acacH = acetylacetone) were added; only poor yields were obtained with $PdCl_2$.[3] The availability of Grignard reagents makes their use in organic synthesis attractive, but so far attempts to use them as alkylating agents in this type of reaction have failed;[1,4] only very poor yields of alkylated alkenes were obtained. We now report that by a suitable choice of solvent and base, Grignard reagents can be quite efficient arylating agents for vinylic hydrogen substitution of alkenes, using a stoicheiometric or catalytic amount of palladium chloride.

trans-Stilbene was obtained by treatment of phenylmagnesium bromide with styrene in the presence of palladium chloride, lithium chloride, and tri-n-butylamine (or potassium carbonate) at room temperature, under nitrogen [equation (1)]. This transformation most probably proceeds through a mechanism similar to that proposed by Heck, involving the formation of a reactive σ organopalladium species from the Grignard reagent and palladium salt [equation (2)], and an alkene insertion followed by a β hydrogen elimination with formation of the arylated alkene and a palladium hydride species. Tri-n-butylamine or potassium carbonate are present in order to prevent Grignard reagent decomposition by HCl (or HBr) formed from the palladium hydride.

$$PhMgBr + PhCH{=}CH_2 \xrightarrow[NBu^n_3 \text{ or } K_2CO_3]{PdCl_2,\ LiCl} PhCH{=}CHPh + HBr \quad (1)$$

$$RMgX + PdCl_2 \longrightarrow RPdCl \quad (2)$$

Reactions with stoicheiometric amounts of palladium salt were first investigated. As shown in the Table, the yields of arylated alkene were strongly solvent dependent, the best yields being obtained with acetonitrile. Moreover, at least in that solvent, potassium carbonate appears to be a better base. A similar base effect has already been observed in the Pd-catalysed vinylic hydrogen substitution by aryl halides.[5]

TABLE. Reaction of styrene with phenylmagnesium bromide in the presence of stoicheiometric or catalytic amounts of palladium chloride, at room temperature for 1 h.

Solvent	Molar ratio ($PhMgBr/PdCl_2$)	Base	%Yield of *trans*-stilbene[a]
$PhCH{=}CH_2$	1·1	NBu^n_3	10
o-$Cl_2C_6H_4$	1·1	,,	10
CH_2Cl_2	1·1	,,	15
THF[b]	1·1	,,	35
MeCN	1·1	,,	55
,,	1·1	K_2CO_3	75
,,	2	NBu^n_3	90
,,	2	K_2CO_3	98
,,	10	NBu^n_3	125
,,	20	K_2CO_3	1000

[a] Based on $PdCl_2$. [b] Tetrahydrofuran.

Under catalytic conditions ($CuCl_2$ was used to reoxidize the Pd° formed in the reaction) poor yields were obtained with tri-n-butylamine. This could be due to incomplete neutralization of HCl by the amine as proposed by Chalk and Magennis;[5] it also may be attributed to competitive complexation of $CuCl_2$ by NBu^n_3, so affecting the regeneration of the reactive Pd^{II} by oxidation of Pd^0. The use of potassium carbonate can overcome these disadvantages and make the catalytic reaction feasible.

These reactions (stoicheiometric or catalytic) are much more rapid than arylation by organomercury compounds[1] or by lithium compounds[3] as yields are maximum after 1 h or less. In comparison with Pd-catalysed vinylic hydrogen substitution by aryl halides[2] reaction times are shorter and conditions (room temperature) are much milder. These reactions should be extendable to other alkenes, and applications to functionalized alkenes are currently being investigated.

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