

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

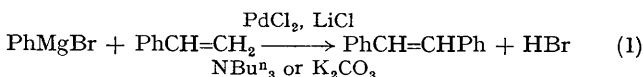
By NGOC-TUYET LUONG-THI and HENRIETTE RIVIERE

(Groupe de Recherche no. 12, C.N.R.S., 2—8 Rue H. Dunant, 94320, Thiais, France)

Summary Arylation of styrene by Grignard reagents has been performed in the presence of stoichiometric 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 compounds¹ or by aryl halides² in the presence of palladium salts. Recently, styrene was methylated by methyl-lithium provided that stoichiometric amounts of Pd(OAc)₂ or Pd(acac)₂ (acacH = acetylacetonone) were added; only poor yields were obtained with PdCl₂.³ 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 stoichiometric 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 pro-



ceeds 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.

Reactions with stoichiometric 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 stoichiometric or catalytic amounts of palladium chloride, at room temperature for 1 h.

| Solvent | Molar ratio (PhMgBr/PdCl ₂) | Base | % Yield of <i>trans</i> -stilbene ^a |
|---|--|--------------------------------|---|
| PhCH=CH ₂ | 1·1 | NBu ₃ ^a | 10 |
| <i>o</i> -Cl ₂ C ₆ H ₄ | 1·1 | " | 10 |
| CH ₂ Cl ₂ | 1·1 | " | 15 |
| THF ^b | 1·1 | " | 35 |
| MeCN | 1·1 | " | 55 |
| " | 1·1 | K ₂ CO ₃ | 75 |
| " | 2 | NBu ₃ ^a | 90 |
| " | 2 | K ₂ CO ₃ | 98 |
| " | 10 | NBu ₃ ^a | 125 |
| " | 20 | K ₂ CO ₃ | 1000 |

^a Based on PdCl₂. ^b Tetrahydrofuran.

Under catalytic conditions (CuCl₂ was used to reoxidize the Pd⁰ 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 CuCl₂ by NBu₃, so affecting the regeneration of the reactive Pd^{II} by oxidation of Pd⁰. The use of potassium carbonate can overcome these disadvantages and make the catalytic reaction feasible.

These reactions (stoichiometric or catalytic) are much more rapid than arylation by organomercury compounds¹ or by lithium compounds³ as yields are maximum after 1 h or less. In comparison with Pd-catalysed vinylic hydrogen substitution by aryl halides² 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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⁴ H. Okada and H. Hashimoto, *Kogyo Kagaku Zasshi*, 1967, **70**, 2152.

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