Activation of Grignard Reagents by Transition-metal Complexes. A New and Simple Synthesis of *trans*-Stilbenes and Polyphenyls

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Summary A rapid, efficient method for the synthesis of stilbenes and terphenyls is described *via* reaction between olefinic or aromatic halides and aromatic Grignard reagents activated by a nickel catalyst.

The effect of metal halides on the reaction between Grignard reagents with organic halides has received attention in the past[1-3] and also recently.[4-9] In particular, it has been shown that aromatic Grignard reagents undergo coupling reactions when treated with organic halides in the presence of small quantities (3—10 mole %) of halides of nickel, iron, cobalt, manganese, or chromium. Biaryl compounds are obtained according to reaction (1).

$$2\,\mathrm{ArMgX} + \mathrm{MX_2} + \mathrm{RX}\ (\text{or ArX}) \longrightarrow \mathrm{Ar{-}Ar} + 2\mathrm{MgX_2} + \mathrm{M} + \text{polymers} \tag{1}$$

We have examined the coupling reactions between aromatic Grignard reagents and olefinic halides. Thus, *trans*-stilbene was prepared (70%) from *trans*-β-bromostyrene, on treatment with phenylmagnesium bromide, at room temperature, in the presence of a catalytic amount of nickel halide.

$$\textit{trans}\text{-Ph-CH=CH-Br} + \mathrm{PhMgBr} \xrightarrow[\mathrm{NiX_2}(0{\cdot}1\%)]{\mathrm{Et_2O}} \textit{trans}\text{-Ph-CH=CH-Ph} \tag{2}$$

In order to find the most effective catalyst, several nickel and cobalt salts were used [$\mathrm{NiCl_2}$, $\mathrm{Ni(acac)_2}$, $\mathrm{(PPh_3)_2NiCl_2}$, $\mathrm{CoCl_2}$]. Nickel(II) acetylacetonate seemed to be the most effective when used in the proportion of 0·1—0·5% with respect to Grignard reagent.

The reaction was then extended to substituted aromatic Grignard reagents.

$$\textit{trans}\text{-Ph-CH=CH-Br} + \mathrm{RMgX} \xrightarrow[\mathrm{Ni(acac)_2}\,(0{\cdot}2\%)]{\mathrm{Et_2O};25\ ^\circ\mathrm{C}} \textit{trans}\text{-Ph-CH=CH-R}\ (\text{Yield } 50\text{—}75\%) \tag{3}$$

[R = $4\text{-MeO}{\cdot}\mathrm{C_6H_4}$; $4\text{-MeC}_6\mathrm{H}_4$; $3\text{-MeC}_6\mathrm{H}_4$; $4\text{-BrC}_6\mathrm{H}_4$; 2,4-di-Me-$\mathrm{C_6H_4}$; α-naphthyl; α-thienyl.]

When *trans*-dichloroethylene was used as the organic halide, symmetric *trans*-stilbenes were obtained (40—50%) with some (20—30%) of the corresponding biaryl compounds, according to equation (4).

$$\textit{trans}\text{-ClCH=CH-Cl} + 2\mathrm{ArMgX} \xrightarrow[\mathrm{Ni(acac)_2}\,(0{\cdot}2\%)]{\mathrm{Et_2O}:\ 25\ ^\circ\mathrm{C}} \textit{trans}\text{-Ar-CH=CH-Ar}\ (\text{Yield } 40\text{—}50\%) + \mathrm{Ar{-}Ar} \tag{4}$$

(Ar = Ph; $3\text{-MeC}_6\mathrm{H}_4$; $4\text{-MeC}_6\mathrm{H}_4$)

Finally, we found that the *p*-dibromobenzene reacted similarly, allowing the synthesis of *para*-terphenyls in good yields.

$$p\text{-BrC}_6\mathrm{H_4Br} + 2\mathrm{ArMgBr} \xrightarrow[\mathrm{Ni(acac)_2}\,(1\%)]{\mathrm{Et_2O};\ \text{reflux}} p\text{-ArC}_6\mathrm{H_4Ar}\ \ (\text{Yields} > 80\%) \tag{5}$$

(Ar = Ph; $3\text{-MeC}_6\mathrm{H}_4$)

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