

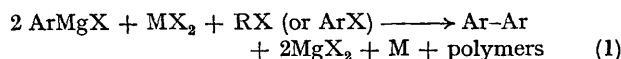
Activation of Grignard Reagents by Transition-metal Complexes. A New and Simple Synthesis of *trans*-Stilbenes and Polyphenyls

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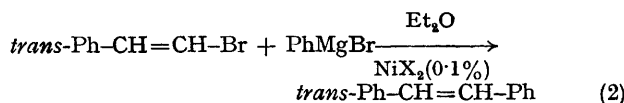
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Summary A rapid, efficient method for the synthesis of stilbenes and terphenyls is described *via* reaction between olefinic or aromatic halides and aromatic Grignard reagents activated by a nickel catalyst.

THE effect of metal halides on the reaction between Grignard reagents with organic halides has received attention in the past¹⁻³ 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).

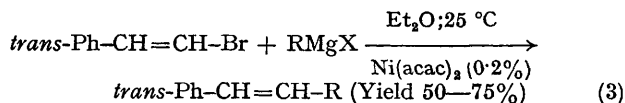


We have examined the coupling reactions between aromatic Grignard reagents and olefinic halides. Thus, *trans*-stilbene was prepared (70%) from *trans*- β -bromostyrene, on treatment with phenylmagnesium bromide, at room temperature, in the presence of a catalytic amount of nickel halide.



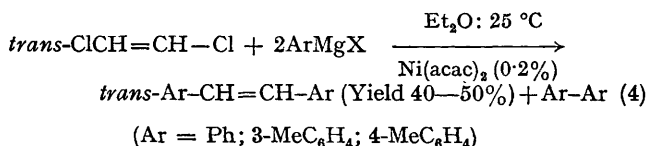
In order to find the most effective catalyst, several nickel and cobalt salts were used [NiCl_2 , $\text{Ni}(\text{acac})_2$, $(\text{PPh}_3)_2\text{NiCl}_2$, CoCl_2]. Nickel(II) acetylacetonate seemed to be the most effective when used in the proportion of 0.1–0.5% with respect to Grignard reagent.

The reaction was then extended to substituted aromatic Grignard reagents.

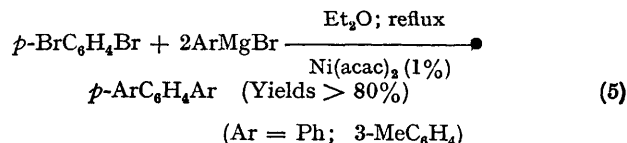


[R = 4-MeO-C₆H₄; 4-MeC₆H₄; 3-MeC₆H₄; 4-BrC₆H₄; 2,4-di-Me-C₆H₄; α -naphthyl; α -thienyl.]

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).



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



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