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Preliminary communication

Stereochemistry of the nickel-catalyzed cross-coupling reaction of Grignard reagents with olefinic halides: stereospecific *versus* nonstereospecific-stereoselective reactions

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SUMMARY

The nickel-catalyzed cross-coupling reactions of Grignard reagents with monohaloolefins proceed stereospecifically, while with 1,2-dihaloethylenes they proceed nonstereospecifically to form *cis*-olefins stereoselectively in many cases.

Recently, Corriu and Masse[1], and we[2, 3] reported the selective cross-coupling reaction of Grignard reagents with olefinic and aromatic halides in the presence of nickel-phosphine complexes as catalysts. In our first communication[2] we briefly pointed out the formation of an isomeric mixture of stilbene in the reaction of *cis*- or *trans*-dichloroethylene with a phenyl Grignard reagent in the presence of Ni(Dpe)Cl_2[*] as catalyst. Corriu and Masse's results[1] revealed that the reactions of *trans*-β-bromostyrene and *trans*-dichloroethylene with aryl Grignard reagents in the presence of Ni $(Acac)_2$ formed *trans*-diarylethylenes. No mention has been made of the formation of the *cis* compounds.

We have now investigated systematically the stereochemistry of the cross-coupling reactions in the presence of nickel(II) catalysts with various phosphine ligands, and found that with monohaloolefins the reaction takes place stereospecifically with retention of configuration, while with *cis*- and *trans*-dihaloethylenes the reaction proceeds nonstereospecifically but stereoselectively to give *cis*-olefins in many cases (Table 1). In the latter case, strong evidence has been obtained to show that an elimination-addition mechanism is operative on nickel.

Cis- and *trans*-β-bromostyrene were treated with phenylmagnesium bromide in the presence of a nickel-phosphine catalyst to form, with retention of configuration of olefin carbon, *cis*- and *trans*-stilbene, respectively. The stereochemistry is invariant with the nature of ligands in the catalyst. Similar stereochemistry has been found in the reaction of these halides with methylmagnesium bromide. On the other hand, in the reactions of *cis*- and

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[*] Abbreviation Dpe, Dpp, Dmpe and *cis*-Dpen are used for $Ph_2P(CH_2)_2PPh_2$, $Ph_2P(CH_2)_3PPh_2$, $Me_2P(CH_2)_2PMe_2$ and *cis*-$Ph_2PCH{=}CHPPh_2$, respectively.

TABLE I

YIELDS AND ISOMER RATIOS OF STILBENE FORMED FROM THE REACTION OF HALOOLEFINS WITH PhMgBr IN THE PRESENCE OF NiL_2Cl_2[a]

L_2 in NiL_2Cl_2	From *trans*-PhCH=CHBr[b] *Yield(%) (cis/trans)*[d]	*cis*-PhCH=CHBr[c] *Yield(%) (cis/trans)*[d]	*trans*-CHCl=CHCl *Yield(%) (cis/trans)*[d]	*cis*-CHCl=CHCl *Yield(%) (cis/trans)*[d]
Dpp[e]	88(7/93)	100(93/7)	93(26/74)	91(33/67)
Dpe[e]	74(10/90)	–	100(80/20)	92(90/10)
Dmpe[e]	80(8/92)	–	100(99/1)	95(100/0)
cis-Dpen[e]	–	–	98(74/26)	100(83/17)
$2Ph_3P$	87(8/92)	–	37(30/70)	19(84/16)

[a] Grignard reagent/one carbon–halogen bond/NiL_2Cl_2 ∿1.2/1/10^{-2}. To a mixture of the halide and the catalyst in ether was added phenyl Grignard solution at 0°. The reaction mixture was stirred at room temperature for 2 h, hydrolyzed, and then analyzed by GLC. [b] The isomeric purity was about *trans/cis* ∿ 92/8 (GLC area ratio). [c] The isomeric purity was about *cis/trans* = ∿ 95/5 (GLC area ratio). [d] Determined by GLC using an internal standard. [e] For the abbreviations, see footnote of the text.

trans-1,2-dichloroethylene with a phenyl Grignard reagent in the presence of Ni (Dpe)Cl_2, Ni (Dmpe)Cl_2, or Ni (*cis*-Dpen)Cl_2, the isomer ratios of the stilbene formed were essentially the same for each catalyst, and the thermodynamically less stable *cis* isomer has the preponderance over the *trans* isomer. The Ni (Dpp)Cl_2 catalyst offers an exceptional case in which *trans*-stereoselectivity is observed. With Ni $(PPh_3)_2Cl_2$ as catalyst the reaction occurred with low stereospecificity. Similar stereochemical results were obtained from the reaction with dibromoethylene, but in considerably decreased total yield.

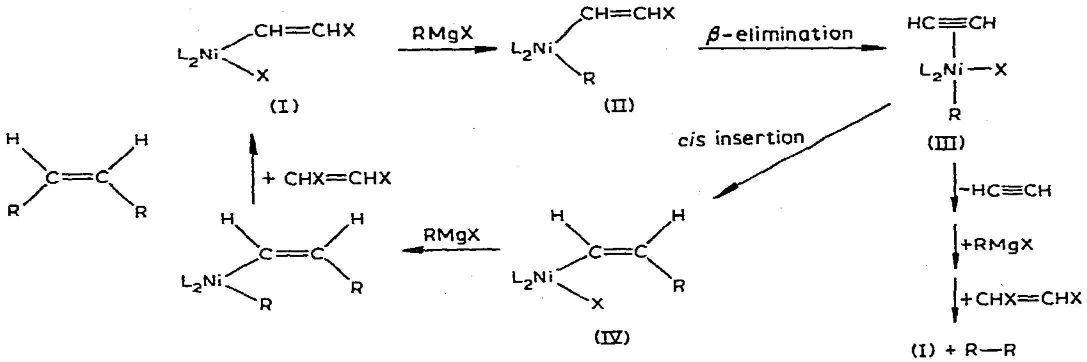
Control experiments indicated that the starting dichloroethylene neither did react with a Grignard reagent in the absence of a nickel catalyst nor isomerize under the present reaction conditions.

Stereospecific reaction of monohaloolefins seems consistent with the oxidative addition of (*E*)- and (*Z*)-1,2-dichlorodifluoroethylene to nickel(0) complexes[4], and the homo coupling reaction of *trans*-propenyl groups on nickel[5], both proceeding with retention of configuration.

The high *cis*-stereoselectivity observed with dihaloethylenes strongly suggests that an elimination-addition mechanism[6] is operative on nickel. A plausible mechanism is illustrated in Scheme 1.

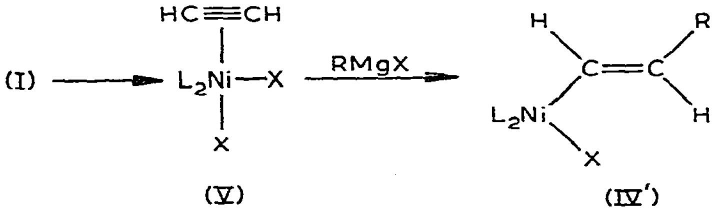
The evolution of acetylene during the course of the cross-coupling reaction provides strong evidence for the elimination-addition mechanism. For example, the reaction of an isomeric mixture of 1,2-dibromoethylene with phenylmagnesium bromide in the presence of Ni (Dpe)Cl_2 at 0° for 30 min proceeded with evolution of gas (15% yield based on the halide) consisting of acetylene and ethylene (85/15), and afforded diphenyl (14.0%), *cis*-stilbene (60.6%) and *trans*-stilbene (7.6%). Treatment of the reaction mixture with trimethylchlorosilane gave only 0.4% yield of bis(trimethylsilyl)acetylene[7]. Acetylene was characterized by GLC (silica gel/alumina, 20ft, 200°) and IR spectrum of its acetone solution [ν (CH) 3210 cm^{-1}].

Scheme 1



Furthermore, this sequence can be supported by some related reactions described in the literature, *e.g.*, the facile decomposition of *trans*-bromo-(*trans*-β-bromovinyl) bis-(diphenylmethylphosphine) platinum(II) to the corresponding dibromodiphosphineplatinum-(II) and acetylene[8], the *cis* insertion of acetylenic compounds to a transition metal–carbon bond[9, 10], and the recent isolation[11] of some platinum complexes of the type $PtClMe(L_2)(CF_3C{\equiv}CCF_3)$, where L stands for tertiary phosphines, arsines, and stibines, analogous to our hypothetical acetylene-nickel intermediate (III).

Although the *trans*-stereoselectivity observed with Ni (Dpp)Cl_2 as catalyst is not fully elucidated at the present time, we propose another possibility of the elimination-addition mechanism, in which the intermediate (I) undergoes β-elimination to form the corresponding acetylene complex (V) before (I) reacts with a Grignard reagent to give (II). In such a five coordinate intermediate (V) the nickel center may well be blocked by the coordinating acetylene molecule from the attack of a Grignard reagent. Consequently, the nucleophilic attack of the Grignard reagent could occur on the acetylene carbon atom from the outside instead of on the nickel atom, resulting in the formation of a *trans*-vinyl complex (IV′) (*cf.* ref. 9).



It seems interesting to correlate these stereochemical changes with the differences in structure between Ni (Dpe)X_2 and Ni (Dpp)X_2 in solution[12]. Studies are underway to obtain additional evidence for these mechanisms.

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