Novel Stereoselective Alkenyl–Aryl Coupling *via* Nickel-catalysed Reaction of Alkenylalanes with Aryl Halides

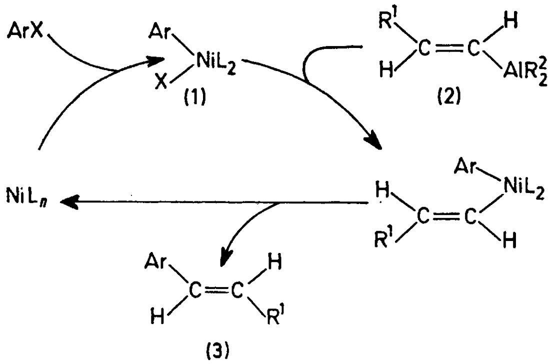
By Ei-ichi Negishi* and Shigeru Baba

(*Department of Chemistry, Syracuse University, Syracuse, New York* 13210)

Summary *trans*-Alkenylalanes, readily obtainable *via* hydroaluminiation of acetylenes, react readily with aryl bromides and iodides in the presence of catalytic amounts of nickel complexes, such as tetrakis(triphenylphosphine)-nickel, to produce arylated alkenes in high yields, the stereochemistry of the products being >99% *trans*.

Stereoselective generation of *trans*-alkenylaluminium compounds *via* hydroaluminiation of acetylenes followed by transfer of the stereodefined alkenyl group to electrophilic carbon has provided some of the simplest routes to *trans*-alkenes.[1] This approach, however, is limited by the inertness of the alkenylaluminium intermediates toward aryl, alkenyl, or alkynyl halides.

We have found that alkenylalanes can be activated towards aryl bromides and iodides by certain nickel complexes, such as $Ni(PPh_3)_4$, so as to form arylated *trans*-alkenes in high yields (Table). The reaction is catalytic with respect to the nickel reagent used. Bromo-1-naphthylbis(triphenylphosphine)nickel (**1a**), obtainable as an isolable species *via* oxidative addition of 1-bromonaphthalene to $Ni(PPh_3)_4$, reacts with an equimolar amount of *trans*-hex-1-enyldi-isobutylalane to form the cross-coupled product in 65% yield within 1 h at 25 °C. Under otherwise comparable conditions the corresponding catalytic reaction using 5 mole % of $Ni(PPh_3)_4$ requires 12—24 h for completion.



Scheme

It is therefore likely that (**1a**) is an intermediate in this reaction. As in other related nickel-catalysed cross-coupling reactions,[2] the reaction reported here presumably proceeds as shown in the Scheme. The present procedure offers a distinct advantage over the existing alkenyl-aryl coupling procedures which involve the use of copper,[3] nickel,[2] and palladium[4] in that it permits a convenient and stereoselective conversion of acetylenes into arylated *trans*-alkenes which does not require isolation and/or purification of any intermediates, such as alkenyl halides. The following representative procedure indicates the simplicity of the present method.

To $Ni(PPh_3)_4$ (0·25 mmol), prepared by the reaction of anhydrous $Ni(acac)_2$ (0·25 mmol) (acacH = $MeCOCH_2CO$-Me) with $HAlBu^i_2$ (0·25 mmol) in the presence of PPh_3 (1·0 mmol) in tetrahydrofuran (THF) (5 ml), were added sequentially *trans*-hex-1-enyldi-isobutylalane (10 mmol) in hexane (10 ml) and 1-bromonaphthalene (5 mmol) at 25 °C. The mixture was stirred for 3 h, 3N-HCl was added, and the quenched mixture was analysed by g.l.c. *trans*-Hex-1-enylnaphthalene was obtained in 93% yield (based on 1-bromonaphthalene). The stereochemistry of the product in each case was ≥99% *trans*, as judged by g.l.c., and ^1H and ^{13}C n.m.r. and i.r. spectroscopy. The procedure is critically dependent on various conditions.

Table

ArX	R^1 of (**2**; $R^2 = Bu^i$)	(**2**; $R^2 = Bu^i$) : ArX	Reaction time/h[a]	Yield[b] (%) of (**3**)
PhI	Bu^n	2 : 1	12	89
PhBr	Bu^n	2 : 1	3[c]	85
		2 : 1	24[d]	89[d]
p-MePhBr	Bu^n	2 : 1	24	84
p-MePhBr	Cyclohexyl	2 : 1	24[c]	75
p-NCPhBr	Bu^n	1 : 1	1	64
1-Naphthyl bromide	Bu^n	1 : 1	12	73
		2 : 1	3[c]	93

[a] Unless otherwise mentioned, $Ni(PPh_3)_4$ (5 mole %) was used as a catalyst, and the reaction temperature was 25 °C. [b] Based on ArX and determined by g.l.c. The isolated products were adequately characterized by n.m.r. and i.r. spectroscopy. [c] Reaction temperature 50 °C. [d] $Pd(PPh_3)_4$ was used instead of $Ni(PPh_3)_4$, and the mixture was heated under reflux in THF–hexane.

Whereas $Ni(PPh_3)_4$ is a satisfactory catalyst to the cross-coupling reaction, other Ni^0 complexes, such as bis(cyclooctadiene)nickel, are not, indicating that use of a phosphine is essential. Palladium complexes, such as $Ph(PPh_3)_4$ and $Pd(acac)_2$, also catalyse the alkenyl–aryl coupling. However, the palladium-catalysed reaction is much slower than the corresponding nickel-catalysed reaction and does not appear to offer any advantage over the latter. The reaction of the alanate complex derived from *trans*-hex-1-enyldi-isobutylalane and n-butyl-lithium with iodobenzene (25 °C; 12 h) produced *trans*-hex-1-enylbenzene in only 19% yield along with a few unidentified products formed in comparable yields. Alkenylboranes and their 'ate' complexes have failed to undergo the desired cross coupling.

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