Pergamon

Tetrahedron Letters, Vol. 38, No. 49, pp. 8533-8536, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)10240-4

Ni(0) Catalyzed Reactions of Aryl and Vinyl Halides with Alkenes and Alkynes

Suresh Iyer*, Chinnasamy Ramesh, A. Ramani

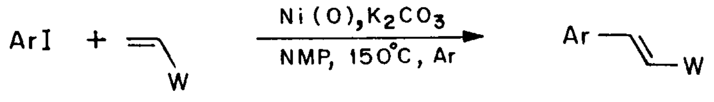
Organic Chemistry Division (Synthesis), National Chemical Laboratory
PUNE 411 008 (INDIA)

Abstract : $Ni[P(OPh)_3]_4$ and $Ni[P(OEt)_3]_4$ catalyze the reaction of aryl and vinyl halides with olefins (Heck reaction) and alkynes. © 1997 Elsevier Science Ltd.

The formation of C-C bonds by the reaction of aryl halides with olefins (Heck reaction) in presence of palladium catalysts is a well studied reaction.[1] We have been investigating the use of other metal catalysts for this reaction based on the known mechanism of the Pd catalyzed vinylation reaction. The key step in the reaction mechanism is the oxidative addition of a low valent coordinatively unsaturated metal complex to the aryl halide followed by olefin coordination, migratory insertion and reductive elimination. We have reported the use of Co(I), Rh (I) (Wilkinson's Catalyst) and Ir(I) (Vaska's complex) successfully based on this rationale.[2]

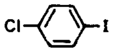
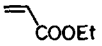
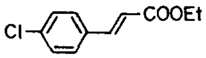
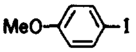
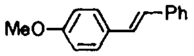
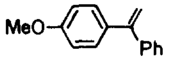
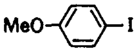
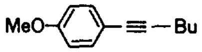
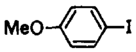
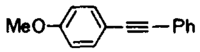
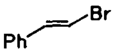
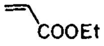
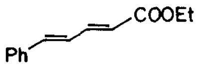
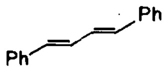
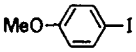
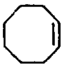
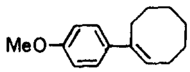
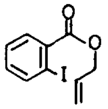
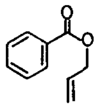
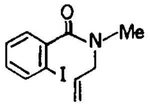
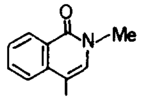
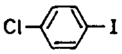
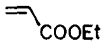
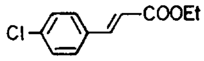
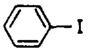
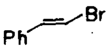
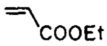
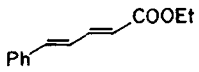
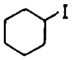
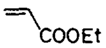
We decided to investigate other new catalysts for the Heck reaction based on the reaction mechanism viz. a metal complex capable of oxidative addition reductive elimination and undergoing ligand dissociation and association. $NiCl_2(PPh_3)_2$ is known to catalyze the reaction of aryl and aliphatic halides with olefins in the presence of Zn dust to give mixtures of addition and substitution products.[3] But it is not a very useful catalyst for the Heck reaction because it gives different types of products with ethylacrylate (addition product) and styrene (substitution product). The highly active and air sensitive complex, $Ni(PPh_3)_4$, generated in situ by the action of Et_3Al on $Ni(acac)_2$, has been used for the intramolecular reaction of aryl halides with olefins to form indoles.[4] $Ni[P(OPh)_3]_4$ and $Ni[P(OEt)_3]_4$ are stable metal complexes of Ni(0) and are well known to undergo ligand dissociation, oxidative addition and reductive elimination reactions and have been used to catalyze the reaction of allyl acetates with nucleophiles.[5] We report here, the first use of these stable Ni(0) metal complexes, for the activation of aryl halides for reaction with olefins (Heck reaction) and alkynes.

SCHEME-I



W: CO_2Me, Ph etc.

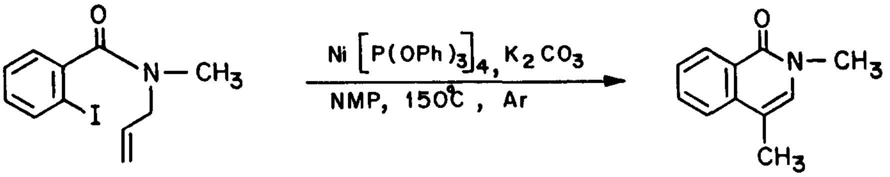
Table-1: Reaction of Aryl and Vinyl Halides with Olefins and Alkynes

Sr.No.	Aryl/Vinyl Halide	Olefin/Alkyne	Time,h	Product	Yield,%
1			24		87[a]
2			24	 (85)  (15)	95[a]
3		nBuC≡CH	23		55[a]
4		PhC≡CH	24		67[a]
5			24		64[a]
6			24		44[a]
7			24		55[a]
8		——	23		16[a]
9		——	48		79[a]
10			12		85[b]
11		PhC≡CH	12	Ph—C≡C—Ph	69[b]
12			12		76[b]
13			24	NR	—

a : Ni $[P(OPh)_3]_4$; b : Ni $[P(OEt)_3]_4$

Reaction conditions: ArI / Olefin / K_2CO_3/Catalyst = 1/1-2 /2 /0·1 ; NMP, 150°C, 12-24 h ; All products were characterized by IR and ^1H NMR

SCHEME : II



The Heck reaction of aryl iodide with styrene and ethyl acrylate in the presence of Ni[P(OPh)$_3$]$_4$ and Ni[P(OEt)$_3$]$_4$ gave high yields of the corresponding trans cinnamates and stilbenes (Scheme I). Unlike the NiCl$_2$(PPh$_3$)$_2$ catalyzed reactions reported earlier, the Ni(0) catalyzed reactions gave only the substitution products in high yields. Reaction with terminal alkynes also gave good yields of the substitution products, but no reaction was observed with ethyl cyanoacetate and diethyl malonate under different conditions. Succinimide also gave no substitution product. Intramolecular cyclization reaction with 2-Iodo-N-Methylallylbenzamide gave good yield (79%) of the isoquinolone as the cyclized product, while allyl-2-iodo benzoate gave the dehalogenated product (Scheme II).

In a typical reaction, the aryl halide (1 mMol), olefin (2-4 mMol), K$_2$CO$_3$ (2.5 mMol) and the catalyst (0.1 mMol) were taken in a round bottom flask. 1-methylpyrrolidinone (5 mL) was added and the reaction mixture heated to 150 °C for 24 h. The reaction was monitored by TLC and at the end of the reaction (disappearance of aryl halide) the reaction mixture was poured into 10% HCl and extracted with ethyl acetate. The ethyl acetate extracts was washed thouroughly with brine, dried and concentrated. Usual chromatographic purification on silica gel gave the pure products in high yields (yields based on aryl halide).

Unsubstituted olefins like cyclooctene, also reacted to give the aryl cyclooctene in moderate yield. Reaction of 4-MeOPhI with styrene gave the 2 isomers (Stilbene:1,1-Diphenylethylene) in 85:15 ratio (Table - 1). Styryl bromide reacted with ethyl acrylate and styrene to give the trans dienes in moderate yields. Aliphatic halides did not undergo the reaction.

These reactions were catalyzed by both Ni[P(OPh)$_3$]$_4$ and Ni[P(OEt)$_3$]$_4$. The rate of reaction was faster with Ni[P(OEt)$_3$]$_4$ as catalyst. The use of PPh$_3$ as ligand increased the rate even more (reaction of aryl iodide with ethyl acrylate was over in 3-5 h).

Novel and stable Ni(0) catalysts have been found for the activation of aryl halides and further study is in progress on the application of these and other transition metal complexes for the activation of aryl, vinyl and alkyl halides.

Acknowledgements: We thank DST for a research grant and CSIR for fellowships to C. Ramesh and A. Ramani.

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(*Received in UK* 10 *September* 1997; *accepted* 26 *September* 1997)