Pergamon

Tetrahedron Letters, Vol. 38, No. 46, pp. 8113-8116, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)10122-8

The Vinylation of Aryl and Vinyl Halides Catalyzed by Copper Salts

Suresh Iyer*, Chinnasamy Ramesh, Anjana Sarkar, Prakash P. Wadgaonkar

Organic Chemistry Division (Synthesis), National Chemical Laboratory
Pune 411 008 (India)

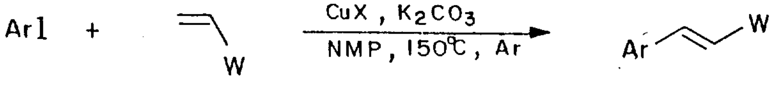
Abstract : Copper (I) bromide and copper (I) iodide catalyzed the vinylation of aryl and vinyl iodides to give the corresponding vinylated products in good to high yields. © 1997 Elsevier Science Ltd.

The development of new catalysts for C-C bond formation reactions is a challenging area in organic synthesis. Such activities are directed towards the development of more active, selective and cheaper catalysts. The vinylation of aryl and vinyl halides, called the Heck reaction, is extensively used in organic synthesis.[1] Pd salts are extremely active catalysts for this reaction. In recent years there have been a few reports on the use of Ni complexes for the Heck reaction.[2]

We have been studying the use of various low valent metal complexes for the catalysis of the vinylation of aryl halides. The reaction of various aryl halides with acrylates and styrene was catalyzed by Co(I), Rh (I) (Wilkinson's catalyst), and Ir(I) (Vaska's complex) complexes and gave the coupled products in high yields.[3] Further investigations in this area have revealed some very interesting and useful heterogeneous catalysts for the Heck reaction.[4]

Copper salts are well known to catalyze the reaction of aryl halides with various carbon and heteroatom nucleophiles.[5] Reactions of copper acetylides with aryl halides has also been reported.[6] Copper oxide has been found to mediate the reaction of o-iodo phenols with alkynes to give benzofurans.[7] Most of these reactions involve stoichiometric amount of the copper catalyst. Copper salts are also known to catalyse the Meerwein reaction viz. the vinylation of aryl diazonium salts.[8] There have also been some reports on the preparation of highly activated copper which undergoes very facile oxidative addition to aryl, vinyl and alkyl halides.[9] The reaction of the so formed organocopper species with alkyl and acyl halides has been reported.

SCHEME- I



W : COOMe , Ph

Miura and coworkers have reported the facile CuI catalyzed reaction of aryl and vinyl iodides with alkynes and other carbon nucleophiles like cyano ethylacetate and acetoacetates.[10] We report here the first use of copper salts for the catalysis of the reaction of aryl and vinyl iodides with olefins (Heck reaction). The results of our experiments are summarized in Table 1. The reaction of iodobenzene with methyl acrylate was catalyzed by CuBr to give methyl cinnamate in good yield (Scheme I).

Table - 1: Vinylation of Aryl and Vinyl Halides

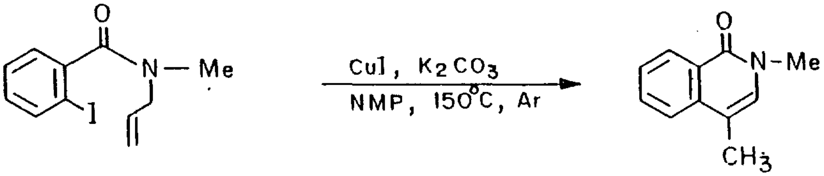
S. No.	ARYL IODIDE	OLEFIN	TIME	YIELD %		
			h	A	B	C
1	PhI	$CH_2CHCOOMe$	24	75	75	-
2	2-ClPhI	$CH_2CHCOOMe$	24	56	50	-
3	4-ClPhI	$CH_2CHCOOMe$	24	75	75	-
4	4-MeOPhI	$CH_2CHCOOMe$	24	85	78	-
5	4-MeOPhI	$PhCHCH_2$	30	-	-	80
4	4-MeOPhI	$CH_2CHCOOEt$	24	-	-	78
5	PhI	$PhCHCH_2$	24	67	60	-
6	$4\text{-}NO_2PhI$	$PhCHCH_2$	24	60	-	-
7	4-MeOPhI	C_8H_{14}	20	NR		
8	4-MeOPhI	$CH_2CMeCOOMe$	51	-	-	31
9	4-MeOPhI	$CH_2CMeCHO$	34	-	-	40
10	4-MeOPhI	$PhCHCH_2$	30			
11	PhCHCHBr	$PhCHCH_2$	28	-		46
12	PhCHCHBr	$CH_2CHCOOEt$	28	-		75
13	$2\text{-}IPhCONMeC_3H_5$	-	48	-	54^a	54^a
14	$2\text{-}IPhCOOC_3H_5$	-	18	-	51^b	53^b

A: CuBr; B: CuI; C: Stoichiometric CuI; a: Cyclized Product, b: Dehalogenated, deallylated Product; Reaction Conditions: ArI/Olefin/K_2CO_3/Catalyst = 1/2/2/0.1; NMP, 150 °C, 24 h, Yields based on Aryl Iodide; All products were characterized by IR and ^1H NMR.

In a typical reaction, the aryl halide (2 mmol), methyl acrylate (4 mmol), K_2CO_3 (4 mmol) and the catalyst (0.2 mmol) were placed in a round bottom flask. 1-Methylpyrrolidinone (5 mL) was used as solvent and the reaction mixture heated to 150 °C for 24 h. After the usual workup, the reaction product was purified by passing through a column of silica gel.

Different aryl iodides reacted with methyl acrylate to give the corresponding trans cinnamates in good yields. Under similar conditions, iodobenzene also reacted with styrene to form stilbene in good yield. Interestingly, phosphine and other ligands were not required for the reaction. Styryl bromide reacted with styrene and ethyl acrylate to give the corresponding dienes in good yields. All these reactions gave the trans olefins. The cyclization of N-methyl-N-allyl-2-iodobenzamide to give N-methyl-4-methylisoquinolone also proceeded in moderate yields (54%) in the presence of CuI (Scheme II). The reaction of 2-iodoallylbenzoate led to dehalogenation and deallylation giving benzoic acid (53%).

SCHEME-II



CuI being inexpensive and readily available, we also investigated the effect of stoichiometric amounts of the catalyst on this reaction (CuI may preferably be recrystallized and stored in a vial covered with aluminium foil).[11] The reactions were also carried out in new round bottom flasks using clean stirring bars to eliminate the possibility of poisoning (in a reverse way for eg. with Pd or Ni, which might catalyze the reaction) with other metal catalysts.[12] The reactions between different aryl and vinyl halides with various olefins proceeded to give the corresponding vinylated products in good to high yields. Methyl methacrylate and methacrolein gave low yields (31 and 40 %) of the substituted products. No reaction was observed with cyclooctene. With catalytic amount of CuI or CuBr, no reaction was observed with methylmethacrolein and methyl methacrylate.

Bromobenzene and chlorobenzene did not react under these conditions. Similarly, aliphatic halides also did not undergo the reaction. In summary, CuBr and CuI were found to catalyze the vinylation of aryl iodides in good yields. Further studies are underway to investigate the mechanism and the effect of ligands and more active copper species on this reaction.

Acknowledgements: We thank DST for a research grant and CSIR for a fellowship to C. Ramesh.

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(*Received in UK* 19 *August* 1997; *revised* 11 *September* 1997; *accepted* 12 *September* 1997)