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The vinylation of bromobiphenyls using homogeneous nickel catalysts

A.A. Kelkar

Chemical Engineering Division, National Chemical Laboratory, Pashan Road, Pune 411 088, India

T. Hanaoka, Y. Kubota and Y. Sugi [1]

National Institute of Materials and Chemical Research, AIST, Tsukuba, Ibaraki 305, Japan

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The vinylation of 4-bromo-4′-hydroxybiphenyl and ethyl acrylate was studied using the catalyst $NiCl_2 \cdot H_2O/PPh_3$ in the presence of inorganic base. Ethyl 4-(4′-hydroxyphenyl)cinnamate was formed as vinylation product with a selectivity as high as 98%. The effect of solvent, ligand and base for some halides was examined to show the applicability of the catalyst system.

Keywords: vinylation; bromobiphenyls; nickel catalyst; phosphine ligand

1. Introduction

The vinylation of organic halides is a useful reaction for the synthesis of many organic compounds. The reaction is usually carried out in the presence of a palladium catalyst, a tertiary phosphine and a base [1,2]. Although zero-valent nickel complexes readily undergo oxidative addition with organic halides [3,4], very few examples of nickel catalyzed vinylation have been described in the literature [5,6]. In both references, zinc metal was used for the reduction of the Ni(II) complex to the Ni(0) complex. These reactions using a Ni(0) complex as the catalyst gave complex mixtures of products, resulting in poor selectivity to the vinylation. Boldrini and co-workers [5] have studied the vinylation with $NiCl_2(PPh_3)_2$ as the catalyst precursor. They observed that the yield of vinylation product was in the range of 50–60%. Lebedev and co-workers [6] have modified the above catalyst system with the use of pyridine as a base. They found that vinylation proceeded with styrene as an olefin and a variety of organic halides. However, no vinylation product was

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[1] To whom correspondence should be addressed.

obtained with methyl acrylate as an olefin [6]. Thus nickel catalysts in the presence of a Ni(II) to Ni(0) reducing agent are not selective toward the vinylation and the selectivity varies depending on the type of organic halide and olefin used. In this paper, we report a highly selective vinylation of organic halides with a nickel complex catalyst without any reducing agent.

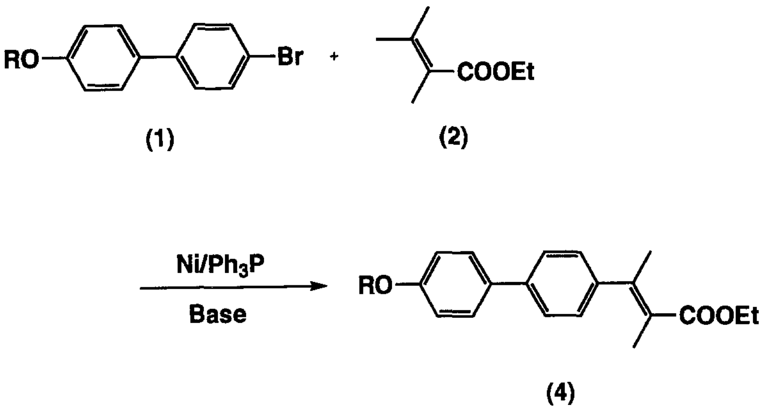
2. Experimental

Catalyst precursors, $NiCl_2{\cdot}6H_2O$, Na_2CO_3, Li_2CO_3, NaOAc, and Et_3N, were purchased from Wako Pure Chem. Inc., Osaka, Japan, and used without any purification. Ligands, Ph_3P, (*o*-tolyl)$_3$P, 1,4-bis(diphenylphosphino)propane (dppp) were obtained from Aldrich Japan Corp., Tokyo, Japan. Bromobiphenyl derivatives were donated by Sanko Chem. Co., Ltd., Osaka, Japan. Solvents, N-methyl-2-pyrrolidinone (NMP), 1,3-dimethyl-2-imidazolidinone (DMI), acetonitrile and toluene obtained from Tokyo Kasei Co., Ltd., Tokyo, Japan, were distilled before use.

Reactions were carried out in a 100 cm^3 SUS316 autoclave equipped with a variable speed magnetic agitator. A typical procedure is as follows: 4-bromo-4′-hydroxybiphenyl (**1**) (10 mmol), ethyl acrylate (**2**) (12.5 mmol), Na_2CO_3 (12.5 mmol), $NiCl_2{\cdot}6H_2O$ (0.1 mmol), Ph_3P (0.2 mmol) and NMP as a solvent (15 ml) were introduced into the reactor. The contents were flushed twice with N_2, and the reactor was heated to 160°C. Reaction was started by switching on the stirrer. The reaction was continued for 19 h, after which the reactor was cooled to room temperature. 2-methylnaphthalene was added as an internal standard for the analysis of products. The reaction mixture was analyzed using a Hewlett Packard GC (model 5890) with FID and helium as a carrier gas. Gas chromatographic analysis was carried out using a capillary column, Ultra 1 (crosslinked methyl silicone), 25 m × 0.2 mm × 0.3 μm, supplied by Hewlett Packard. Products formed were identified by GC-MS analysis and NMR spectroscopy. The selectivities were calculated on the basis of an internal standard added just after the reaction. Side products other than **3**, **4**, and **5** were not found by GC analysis.

3. Results and discussion

Preliminary experiments showed that the vinylation reaction was feasible with the $NiCl_2{\cdot}6H_2O/Ph_3P$ complex as the catalyst system with 4-bromo-4′-hydroxy-biphenyl (**1**) and ethyl acrylate (**2**) as substrates to yield ethyl 4-(4′-hydroxyphenyl)cinnamate (**3**). The side products formed were 4-hydroxybiphenyl (**4**) and ethyl cinnamate (**5**). **5** was formed by the cleavage of a phenyl group from Ph_3P, and it was formed in trace quantities in all the reactions with Ph_3P as a ligand.



(1)

The effect of solvent, ligand, base, aryl halide, $Ph_3P/NiCl_2{\cdot}6H_2O$ (P/Ni) ratio and temperature on the activity and the selectivity was studied. The average activity is defined as

$$\text{average activity} = \frac{\text{consumed aryl halide (mol)}}{NiCl_2{\cdot}6H_2O\ (g) \times \text{time (h)}} .$$

The effect of solvent on the activity and the selectivity was studied (table 1). Amide solvents such as NMP and DMI gave high activity as well as selectivity for the vinylation. With acetonitrile and toluene, the conversion was poor, and the selectivity for **3** was low due to the formation of side products (not identified). In all the reactions, the formation of reduction product **4** was negligible. Since the highest activity and selectivity were obtained with NMP as a solvent, further work was carried out using NMP as solvent. Although $NiCl_2{\cdot}6H_2O$ alone was active for the vinylation, the activity of the catalyst was enhanced in the presence of aryl phosphine ligands, and the highest activity was observed with Ph_3P as a ligand (table 2). With isoquinoline as a ligand, the average activity was very low (7.54), and no activity was observed with dppp as a ligand.

The effect of P/Ni ratio on average activity was studied at 140°C, and results are summarized in table 3. The activity was observed at P/Ni ratio lower than 2. No catalytic activity was observed at a ratio of 4 and higher. For the catalyst with

Table 1
Effect of solvents in nickel catalyzed vinylation of **1** [a]

Run	Solvent	Average activity	Conversion (%)	Selectivity (%)	
				3	4
1	NMP	15.1	69	98	1
2	DMI	10.8	49	75	2
3	acetonitrile	1.3	6	40	5
4	toluene	6.4	29	55	0

[a] Reaction conditions: **1**, 10 mmol; **2**, 12.5 mmol; Na_2CO_3, 12.5 mmol; solvent, 15 ml; $NiCl_2{\cdot}6H_2O$, 0.1 mmol; Ph_3P, 0.2 mmol; reaction temperature: 160°C; reaction time, 19 h.

Table 2
Effect of ligands in nickel catalyzed vinylation of **1** [a]

Run	Ligand	Average activity	Conversion (%)	Selectivity (%)	
				3	**4**
1	no ligand	11.0	50	77	1
2	Ph_3P	15.1	69	98	1
3	$(o\text{-tolyl})_3P$	12.6	58	90	1
4	dppp	0.0	0	0	0
5	isoquinoline	7.5	34	98	1

[a] Reaction conditions: **4**, 10 mmol; **5**, 12.5 mmol; Na_2CO_3, 12.5 mmol; NMP, 15 ml; $NiCl_2{\cdot}6H_2O$, 0.1 mmol; ligand, 0.2 mmol; reaction temperature: 160°C; reaction time, 19 h.

Ph_3P/Ni ratio higher than 3 or with dppp, nickel-phosphine complex may be too stable for the reduction or for the coordination of substrates, leading to catalytic inactivity. These results show that the moderate coordination of phosphine and substrates to nickel is important for catalysis with nickel complexes.

The effect of temperature on the activity was studied in the range of 120–180°C (fig. 1). Reaction did not take place at 120°C indicating that a certain minimum temperature above 140°C was required for the catalysis. The catalytic activity was very good at 180°C, but the selectivity to the vinylation product was low due to formation of some polymeric products. The highest selectivity was obtained at 160°C and most of the further work was carried out at 160°C.

Some bases were screened for their activity; the results are presented in table 4. With inorganic bases, good activity and selectivity to the vinylation product were observed, while with triethylamine as a base, the activity as well as the selectivity of the vinylation were poor. The main reason for this poor selectivity was the reduction of **1** to **4** in a similar manner as described for palladium catalysts [2]. The highest activity was obtained with potassium acetate as a base. High efficiency or inorganic bases may be due to facile removal of hydrogen bromide formed during product elimination step. The reason for the high selectivity to vinylation is that inorganic bases have no releasable hydrogen source for the reduction of aryl

Table 3
Effect of $Ph_3P/NiCl_2$ ratio in nickel catalyzed vinylation of **1** [a]

Run	P/Ni ratio	Average activity	Conversion (%)	Selectivity (%)	
				3	**4**
1	0	3.6	17	98	2
2	2	4.9	22	88	3
3	4	0.0	0	0	0
4	10	0.0	0	0	0

[a] Reaction conditions: **1**, 10 mmol; **2**, 12.5 mmol; Na_2CO_3, 12.5 mmol; NMP, 15 ml; $NiCl_2{\cdot}6H_2O$, 0.1 mmol; reaction temperature, 140°C; reaction time, 19 h.

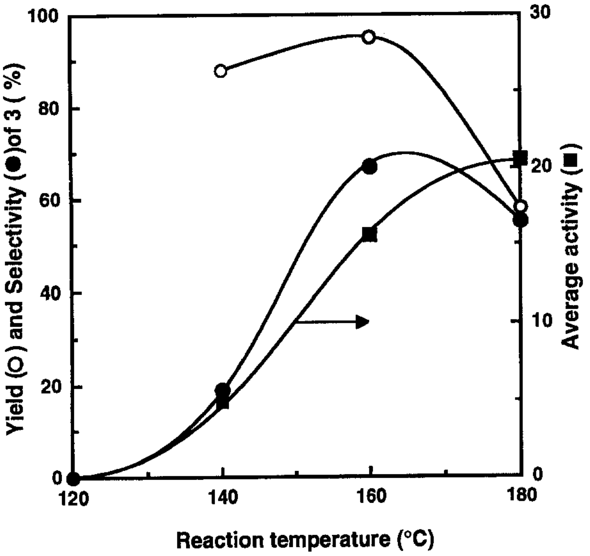


Fig. 1. The effect of temperature on the nickel catalyzed vinylation of **1**. Reaction conditions: **1**, 10 mmol; **2**, 12.5 mmol; Na_2CO_3, 12.5 mmol; NMP, 15 ml; $NiCl_2 \cdot 6H_2O$, 0.1 mmol; Ph_3P, 0.2 mmol; reaction time, 19 h.

halides. Thus, inorganic bases were found to be superior to triethylamine for this reaction with a nickel complex catalyst.

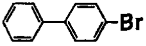
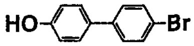
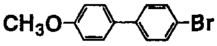
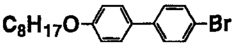
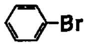
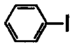
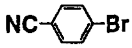
To know the applicability of nickel catalyzed vinylation, the reactions of various aryl halides with **2** were examined. For biphenyl derivatives, it was observed that the average activity was increased by the presence of electron donating groups such as –OH, $-OCH_3$, and $-OC_8H_{17}$ (table 5). The selectivity to vinylation was very high in all the cases. Bromobenzene and iodobenzene also reacted in the same manner to give vinylation products with selectivity higher than 94%. The activity with iodobenzene was higher than that with bromobenzene. However, the activity of the catalyst was reduced considerably in the reaction of 4-cyanobromobenzene because of the –CN group in para position. The selectivity to vinylation was ca. 70%, however, the side products could not be identified.

Table 4
Effect of bases in nickel catalyzed vinylation of **1** [a]

Run	Base	Average activity	Conversion (%)	Selectivity (%)	
				3	**4**
1	Et_3N	4.7	21	26	74
2	Li_2CO_3	9.1	42	80	2
3	Na_2CO_3	15.1	69	98	1
4	NaOAc	14.7	67	86	2
5	KOAc	21.8	100	88	1

[a] Reaction conditions: **1**, 10 mmol; **2**, 12.5 mmol; base, 12.5 mmol; NMP, 15 ml; $NiCl_2 \cdot 6H_2O$, 0.1 mmol; Ph_3P, 0.2 mmol; reaction temperature, 160°C; reaction time, 19 h.

Table 5
Nickel catalyzed vinylation of aryl halides [a]

Run	Aryl halide	Average activity	Conversion (%)	Selectivity (%)	
				vinylation	dehalogenation
1		15.3	70	82	1
2		15.7	71	95	1
3		19.5	89	99	0
4		18.5	84	99	1
5		17.8	81	95	1
6		21.9	100	98	0
7		5.2	24	69	0

[a] Reaction conditions: aryl halide, 10 mmol; **2**, 12.5 mmol; Na_2CO_3, 12.5 mmol; NMP, 15 ml; $NiCl_2 \cdot 6H_2O$, 0.1 mmol; Ph_3P, 0.2 mmol; reaction temperature, 160°C; reaction time, 19 h.

The reaction mechanism for nickel catalyzed vinylation is probably similar to the generally accepted mechanism with palladium catalysts [1,2]. They involve the oxidative addition of aryl halide to the Ni(0) complex, the insertion of olefin, the elimination of the vinylation product, and the regeneration of the Ni(0) complex by the removal of hydrogen halide with base. The reduction of the Ni(II) complex to Ni(0) is required for the formation of active catalytic species. The active species of the nickel complex described by Boldrini and co-workers was produced by the reduction with reducing agents such as zinc metal. However, our system does not involve a reducing agent. The reduction of the nickel complex in our system probably occurs via hydrogen transfer from the solvent, because amide solvents such as NMP gave the best results for the vinylation. Amides such as NMP should be dehydrogenated more easily than actonitrile or toluene. The reduction of the Ni(II) complex by an organic molecule occurs at higher temperature than in the case of reduction by a reducing agent. This may be the reason why the reaction with our system requires a temperature as high as 160°C for high catalytic activity. The absence of catalytic activity with excess triphenylphosphine ligand or with chelated phosphine such as dppp indicates that the phosphine ligand is important for the activation of organic halide because these nickel complexes are too stable for the reduction or for the coordination of substrates. The high selectivity for the vinylation using ethyl acrylate by our catalytic system is due to the absence of reducing agent. In the presence of an organic base with easily releasable hydrogen, such as triethylamine, promotes the reduction of aryl halide as is the case for palladium catalysts [2]. These catalyst systems are not adequate for vinylation. Our catalyst system with inorganic base gives a high selectivity to vinylation with moderate activity.

The present work has shown that nickel is a potential catalyst for the vinylation of aromatic halides with high selectivity. Further work is necessary to improve the activity of the catalysts and also to study the active catalytic species.

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