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Selective Hydrogenation of Alkynes Catalyzed by Metallic Nickel and Modifier[1]

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Synopsis. Under an atmospheric pressure of hydrogen alkynes were successively hydrogenated to give alkanes via (*Z*)-alkenes with the metallic nickel catalyst, which was easily prepared by reaction of nickel bromide with zinc powder. Phosphines and diamines as catalyst modifiers were effective for the partial hydrogenation of alkynes.

The partial hydrogenation of alkynes has become of interest in recent years. Various metal catalysts such as Ca,[2] Fe,[3] Pd,[4—6] and Pt[7,8] are used for the partial hydrogenation of alkynes. Heterogeneous nickel catalysts for hydrogenation were usually made by the reduction of nickel salts with molecular hydrogen,[9] metal,[10—12] alkali metal hydride,[13] and sodium borohydride.[14—16] The catalytic activities were occasionally changed by the combination of nickel salts, reductants, and solvents. In the preceding papers, it has been reported that metallic nickel (colloidal state) prepared from nickel halides and zinc powder was active for the hydrogen transfer reaction (disproportionation) of cyclohexadienes[17] and for the hydrogenation of styrene homologs.[18] The present work has been studied to determine how alkynes are hydrogenated to give (*Z*)-alkenes selectively by the catalyst consisting of metallic nickel and modifier. The effect of modifiers on the selective hydrogenation is examined. The advantage of this procedure is the easy and economical access to the reagents.

Experimental

Materials. *N*,*N*-Dimethylformamide (DMF) was refluxed with calcium hydride and distilled under reduced pressure. Other reagents were commercially available and used without purification.

General Procedure of Hydrogenation. A typical procedure for the hydrogenation of alkynes was as follows. To a 100 cm^3 flask fitted with a condenser, a septum inlet, and a stir bar were added anhydrous nickel bromide (0.2 mmol), zinc powder (1 mmol), and DMF (15 cm^3). After the atmosphere was replaced with nitrogen the catalyst mixture was allowed to stand overnight at room temperature. The mixture became a black solution containing fine metallic nickel. A hydrogen buret was connected to the flask and the atmosphere was replaced with hydrogen. To the mixture 1-phenyl-1-propyne (**1**) (6 mmol) and 1,2-bis(diphenylphosphino)ethane (DIPHOS) (0.8 mmol) in DMF (5 cm^3) were added. The mixture was stirred with a magnetic stirrer at 800 revolutions per minute and kept in a thermostated bath. The reaction mixture (0.5 cm^3) was picked up and shaked in the air, and it was extracted with hexane (0.5 cm^3)–saturated brine (0.5 cm^3). The organic layer was subjected to GC analysis.

Analysis. The gas chromatographic analyses were made by the use of a Shimadzu GC-8A apparatus with a TC detector and helium carrier gas using a 3 m column of PEG-20M, Silicone DC-200, or EGS, and by the use of a Shimadzu GC-14A apparatus with a FI detector and nitrogen carrier gas using a 25 m capillary column of PEG-20M Bonded or OV-1701 Bonded.

Results and Discussion

Colloidal metallic nickel was obtained by reducing nickel(II) bromide with zinc powder in a solvent. The most favorable solvent for the reaction was DMF.[18] In comparison with Raney nickel, the metallic nickel (colloidal state) has advantages; safety and a simple preparation and treatment of the catalyst. It was not deteriorated over a long period and stable to water; however, it was air sensitive and catched no fire on exposure to air.

Under an atmospheric pressure of hydrogen **1** was successively hydrogenated to give propylbenzene via (*Z*)-1-phenyl-1-propene with a slight amount of (*E*)-isomer in the presence of metallic nickel. (*Z*)-1-Phenyl-1-propene was obtained in a 94% yield at 3.5 h and propylbenzene was done in a 98% yield at 6 h, as shown in Table 1 and Eq. 1.

$$\underset{\text{alkyne}}{\mathrm{R^1C{\equiv}CR^2}} \xrightarrow[\text{under } \mathrm{H_2} \text{ atmosphere}]{\mathrm{NiBr_2}\text{-Zn in DMF}} \underset{(Z)\text{-alkene}}{\mathrm{R^1HC{=}CHR^2}}$$

$$\xrightarrow{\qquad\qquad} \underset{\text{alkane}}{\mathrm{R^1CH_2CH_2R^2}} \qquad (1)$$

The successive hydrogenation of alkynes were catalyzed by the metallic nickel catalyst. In the first stage of hydrogenation alkynes were exclusively hydrogenated to give (*Z*)-alkenes with small amounts of (*E*)-isomer. The second hydrogenation gave alkanes as fast as the first hydrogenation did alkenes.

The effect of modifier on the hydrogenation of **1** is shown in Table 1. The addition of DIPHOS, triphenylphosphine, ethylenediamine, 1,3-diaminopropane, 1,4-diaminobutane, or 2,2′-dipyridyl depressed the second hydrogenation. As catalyst poisons for the selective hydrogenation, however, quinoline, pyridine, and aniline were not so good modifiers as compared with phosphines and diamines. It was observed that the rate of the second hydrogenation in the presence of phosphine or diamine was slower than that of the first hydrogenation. This suggests that the phosphine and the diamine were more strongly adsorbed on metallic nickel

Table 1. Effect of Modifier on the Hydrogenation of **1** Catalyzed by Metallic Nickel[a)]

Modifier (mmol)	Time	Yield/%		
	h	(*Z*)-Alkene	(*E*)-Alkene	Alkane
None	3	93	0	1
	6	0	0	98
DIPHOS (0.8)	4	92	1	1
	15	90	2	2
Triphenylphosphine (0.8)	4	81	2	3
	12	90	5	5
Triphenylphosphine (6)	4	93	2	3
Ethylenediamine (0.2)	8	79	7	11
Ethylenediamine (0.4)	8	96	0	3
Ethylenediamine (0.8)	8	92(75)[b)]	Trace	Trace
	24	93	0	2
Ethylenediamine (1.6)	8	78	0	1
1,3-Diaminopropane (0.8)	8	91	Trace	Trace
1,4-Diaminobutane (0.8)	8	90	Trace	Trace
2,2′-Dipyridyl (0.8)	5	94	2	3
	8	95	2	3
Quinoline (0.8)	4	91	2	9
	12	66	7	22
Quinoline (6)	4	95	2	2

a) Reaction conditions; alkyne 6 mmol, $NiBr_2$ 0.2 mmol, Zn 1 mmol, DMF 20 cm^3, temp 50 °C, H_2 1 atm. b) Isolated yield.

Table 2. Selective Hydrogenation of Alkynes Catalyzed by Metallic Nickel and Diamine[a)]

Alkyne	Modifier (mmol)	Time	Conv.	Yield/%		
		h	%	(*Z*)-Alkene	(*E*)-Alkene	Alkane
Phenylacetylene	None	6	100	0	—	98
	Ethylenediamine (0.8)	6	95	87	—	0
Diphenylacetylene	None	10	100	0	3	96
	Ethylenediamine (0.8)	24	100	95	0	2
	2,2′-Dipyridyl (0.8)	24	59	57	0	0
2-Octyne	None	8	100	32	21[c)]	43
	Ethylenediamine (0.8)	8	100	96	Trace	1
	2,2′-Dipyridyl (0.8)	8	98	96	Trace	Trace
	DIPHOS (0.8)	8	100	94	Trace	2
1-Octyne	None	10	100	4[b)]	5[c)]	74
	Ethylenediamine (0.8)	8	100	63[d)]	Trace[c)]	13
3-Phenyl-2-propyn-1-ol	None	20	100	10	13	73
	Ethylenediamine (0.4)	20	63	62	Trace	Trace
	Ethylenediamine (0.8)	20	46	41	0	0
Methyl 2-butynoate	None	8	100	0	0	99
	Ethylenediamine (0.8)	8	98	70	5	8
Ethyl phenylpropiolate	None	10	100	0	8	91
	Ethylenediamine (0.8)	21	95	76	Trace	13
	2,2′-Dipyridyl (0.8)	12	83	73	3	9

a) Reaction conditions; alkyne 6 mmol, $NiBr_2$ 0.2 mmol, Zn 1 mmol, DMF 20 cm^3, temp 50 °C, H_2 1 atm. b) Yield of 1-octene (1%) and (*Z*)-2-octene (3%). c) Yield of (*E*)-2-octene. d) Yield of 1-octene.

than the alkene, and the order of the strength of adsorption (coordination) on the surface of the metallic nickel is as follows; alkyne > bidentate diphosphine ligand, diamine > monodentate phosphine ligand > alkene, monoamine. After the alkyne was consumed in the reaction system, the alkene resulted was adsorbed weakly on the catalyst and was successively hydrogenated to give alkane. It was found that the selectivity for hydrogenation was significantly affected by the amount of modifier added (mole ratio, modifier/nickel=0.8/0.2), and slightly by the modification time between the modifier and the catalyst. The rate of the second hydrogenation decreased with an increase in the amount of the modifier. The improvement methods for the selective hydrogenation of alkynes were obtained by the addition of amines as a catalyst modifier to the catalyst system,[1,7,12,14] as exemplified by the most well-known Lindlar catalyst (Pd/$CaCO_3$/quinoline).[19] For the selective hydrogenation ethylenediamine is very useful and practical in the laboratory because it can be extracted with water from the organic alkene at the workup operation. By the catalysis of the metallic nickel and modifier the alkyne was hydrogenated to give the corresponding alkene in a high selectivity under similar reaction conditions using Lindlar catalyst; **1** was hydrogenated to afford (*Z*)-alkene (95% yield) with the Lindlar catalyst.

The selective hydrogenation of several alkynes with the metallic nickel and modifier is listed in Table 2. In the case of the hydrogenation of octynes the migration of a double bond and (*E*),(*Z*)-isomerization of alkenes formed were inhibited by the addition of ethylenediamine. Acetylenic esters and an alkynol were hydrogenated to give the corresponding olefins in moderate to good yields.

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