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Disproportionation of Cyclohexadienes Catalyzed by Metallic Nickel

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Cyclohexadienes, 1,3-cyclohexadiene (**1**) and 1,4-cyclohexadiene (**2**), disproportionated to benzene (**3**) and cyclohexene (**4**) in the presence of catalytic amounts of metallic nickel prepared from nickel halides and zinc powder in *N,N*-dimethyformamide (DMF) under nitrogen.

In the preceding paper, the authors pointed out that a small amount of benzene was formed in the hydrogenation of 1,4-cyclohexadiene by a $Ni(acac)_2$–$Al_2Et_3Cl_3$–PPh_3 catalyst.[1] Recently, it has been reported that Ziegler catalysts prepared from Co(II) or Ni(II) alkanoates and alkylaluminiums are active for the disproportionation of cyclohexadienes to benzene and cyclohexene.[2] Homogeneous catalysts (Cr,[3] Zr,[4] Ru,[5] Rh,[6] and Ir[7] compounds) are known for the disproportionation of cyclic dienes. In many cases, isomerization took place simultaneously. Catalytic reactions involving disproportionation and dehydrogenation are also noted with heterogeneous metal calalysts (Ni,[8] Rh,[9] and Pd[10] catalysts). We have found that metallic nickel (colloidal state) prepared from anhydrous nickel halides and zinc powder was active for the disproportionation of cyclohexadienes. Compared with other metal catalysts, advantages of the metallic nickel catalyst are negligible isomerization and dehydrogenation, and easy access to the reagents. The utility of metallic nickel for catalytic reactions will be further extended.

$$\text{Cyclohexadiene} \xrightarrow[\text{under } N_2]{NiBr_2\text{–}Zn,\ \text{in DMF}} \underset{(\mathbf{3})}{\text{Benzene}} + \underset{(\mathbf{4})}{\text{Cyclohexene}}$$

$$\left(\begin{array}{l}\text{1,3-Cyclohexadiene, } \mathbf{1}\\ \text{1,4-Cyclohexadiene, } \mathbf{2}\end{array}\right)$$

Experimental

Materials. Metal halides, metal powders, and alkylaluminium compounds were commercially available and used without further purification. Solvents and dienes were dried and distilled under nitrogen before use. $[NiBr_2(PPh_3)_2]$ was prepared according to the literature.[11]

Procedure. A typical reaction of **1** is as follows. To a 50 cm³ flask fitted with a septum inlet and a magnetic stirrer were added anhydrous nickel bromide (44 mg, 0.2 mmol) and zinc powder (65 mg, 1.0 mmol) in *N,N*-dimethylformamide (DMF) (15 cm³). After the atmosphere was replaced with nitrogen the catalyst was allowed to stand overnight at room temperature. The mixture became a black solution containing fine metallic nickel. To the mixture was added **1** (400 mg, 5 mmol) in DMF (5 cm³), and the mixture was stirred with a magnetic stirrer and kept in a thermostated bath. The reaction was stopped by adding a dilute hydrochloric acid solution and the aqueous mixture was shaken with toluene. The toluene extract was washed with water, dried over anhydrous calcium chloride, and subjected to GLC analysis.

Analysis. The gas chromatographic analyses were performed on a Shimadzu GC-8A instrument with a TC detector and helium carrier gas using a 3 m column of 20% bis(2-cyanoethyl) ether on Celite 545. The amounts of products were determined by the peak areas of chromatogram using *p*-xylene as an internal standard.

Results and Discussion

Cyclohexadienes (**1** and **2**) disproportionated to **3** and **4** by metallic nickel. The results are shown in Table 1. The catalyst prepared from anhydrous nickel chloride or bromide and zinc powder was most effective for the disproportionation reaction. Bis(acetylacetonato)nickel, nickel acetate, nickel sulfate, nickel hydroxide, and cobalt bromide have little activity for the reaction. Zinc powder was more effective as a reductant than magnesium and manganese powders. Three times amounts of zinc powder to nickel bromide were sufficient to reduce nickel(II). When sodium borohydride was used as a reductant, the hydrogenation of **1** took place predominantly to give **4**. Table 2 shows the effect of solvent. DMF, hexamethylphosphoric triamide (HMPA), and methanol were good solvents for the disproportionation. However, little disproportionation reaction occurred in dimethyl sul-

TABLE 1. NICKEL CATALYSTS FOR THE DISPROPORTIONATION OF **1**[a)]

Catalyst	Solvent	Temp	Time	Composition/mol%				Total
		°C	h	**1**	**2**	**3**	**4**	yield/%
$NiBr_2$–Zn(powder)	DMF	60	2	Trace	0	46	54	95
$NiCl_2$–Zn(powder)	DMF	60	2	2	0	46	52	98
$NiBr_2$–Mn(powder)	DMF	60	2	66	0	15	20	94
$NiBr_2$–Mg(powder)	DMF	60	2	79	0	9	12	98
$Ni(acac)_2$–Zn(powder)	DMF	60	2	99	0	1	Trace	96
$NiBr_2$–$NaBH_4$	DMF	60	2	81	0	1	17	98
$Ni(acac)_2$–$AlEt_3$	Toluene	20	10 min	1	1	41	57	98
$Ni(acac)_2$–$Al_2Et_3Cl_3$	Toluene	20	2	100	0	0	Trace	95

a) **1**, 5 mmol; Ni compound, 0.2 mmol; reductant, 1.0 mmol; solvent, 20 cm³.

foxide (DMSO), acetonitrile, tetrahydrofuran (THF), and toluene. Under a nitrogen atmosphere, the mixture consisting of nickel bromide and zinc powder in DMF turned black after stirring for 5 h at room temperature. Resulting nickel did not precipitate and could not be separated by filtration. The catalyst mixture containing colloidal nickel was used as it was. It was not deteriorated over a long period and stable to water; however, it was air sensitive. An active species for the disproportionation may be metallic nickel since the reaction was retarded significantly by the addition of triphenylphosphine, as shown in Table 3. The disproportionation of **1** was studied in the temperature range from 0 to 100 °C, as shown in Fig. 1. At 100 °C the catalyst was satisfactorily active.[12] Table 4 shows that the 1,3-diene disproportionated faster than the 1,4-diene did. Little isomerization of cyclohexadienes was observed. 1-Methyl-1,4-cyclohexadiene (**5**), 1,3-cyclooctadiene (**6**), and 1,5-cyclooctadiene (**7**) did not react and remained unchanged under similar reaction conditions.

In Scheme 1 the most probable mechanism of the disproportionation of **1** is illustrated and metallic nickel is represented as Ni(0) (one atom). Nickel(II) is reduced to nickel(0) by zinc. Nickel(0) is colloidal and so fine that it has large surface area and many reaction sites. The diene **1** is activated by coordination (adsorption) on the active site of nickel(0). The cleavage of allylic C–H bond of **1** by nickel(0) (oxidative addition) gives a nickel hydride intermediate, followed by insertion reaction, β-hydrogen elimination, and reductive elimination to give **3** and **4**. No disproportionation of **4** occurs, probably because of its weak coordination. The diene **2** also disproportionated with nickel(0) under the conditions, but much more

Table 2. Effect of solvent[a)]

Solvent	Time	Composition/mol%				Total
	h	**1**	**2**	**3**	**4**	yield/%
DMF	2	Trace	0	46	54	95
HMPA	2	1	0	46	53	98
Methanol	2	0	0	47	53	87
DMSO	30	96	0	2	2	97
Acetonitrile	30	99	0	1	0	86
THF	30	99	0	0	1	95
Toluene	30	99	0	1	0	91

a) **1**, 5 mmol; $NiBr_2$, 0.2 mmol; Zn, 1.0 mmol; solvent, 20 cm^3; temp, 60 °C.

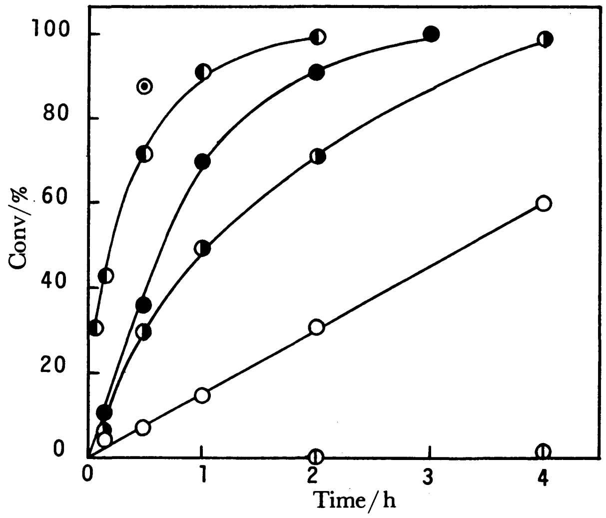


Fig. 1. Effect of temperature.
1, 5 mmol; $NiBr_2$, 0.2 mmol; Zn, 0.6 mmol; DMF, 20 cm^3; temperature (°C) —⦶: −30, ○: 0, ◑: 20, ●: 40, ◐: 60, ⊙: 100.

Table 3. Effect of additive[a)]

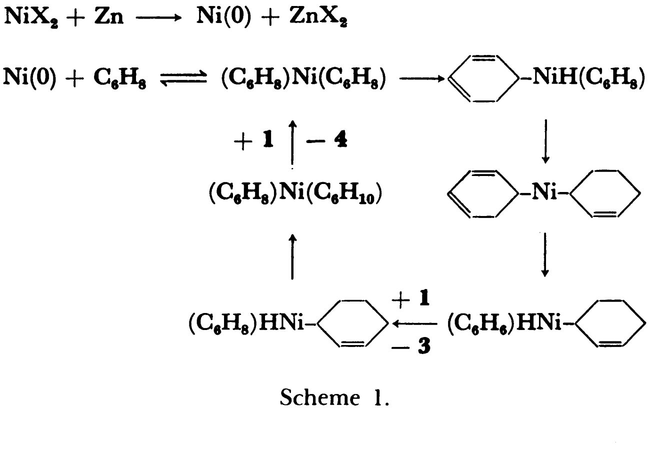
Catalyst	Additive	Conv	Composition/mol%				Total
	(mmol)	%	**1**	**2**	**3**	**4**	yield/%
$NiBr_2$–Zn	—	100	Trace	0	46	54	95
$NiBr_2$–Zn	PPh_3(0.4)	5	95	0	2	3	97
$NiBr_2(PPh_3)_2$–Zn	— (0.4)	11	89	0	5	6	98
$NiBr_2$–Zn	H_2O(100)	95	5	0	41	54	89

a) **1**, 5 mmol; Ni compound, 0.2 mmol; Zn, 1.0 mmol; DMF, 20 cm^3; temp, 60 °C; time, 2 h.

Table 4. Effect of substrate[a)]

Substrate	Time	Composition/mol%				Total
(mmol)	h	**1**	**2**	**3**	**4**	yield/%
1(5)	2	Trace	0	46	54	95
1(18)	2	47	Trace	26	27	98
	6	1	Trace	48	51	92
2(5)	2	0	30	31	38	93
	6	0	19	37	44	90
1(2)+**2**(3)	2	0	30	33	38	93
4(5)	30	0	0	1	99	95[b)]
5(5)	50	No Reaction				
6(5)	50	No Reaction				
7(5)	50	No Reaction				

a) $NiBr_2$, 0.2 mmol; Zn, 1.0 mmol; DMF, 20 cm^3; temp, 60 °C. b) Trace amounts of cyclohexane were detected.



Scheme 1.

slowly. Triphenylphosphine occupies the active site of nickel(0) and blocks the coordination of diene.

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12) A homogeneous nickel catalyst prepared from Ni(acac)$_2$–Al$_2$Et$_3$Cl$_3$–PPh$_3$, being effective for the selective hydrogenation of **2**, was deactivated at 90 °C.