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Studies on Hydrogenation by Nickel Complexes. 5. The Selective Hydrogenation of 1,4-Cyclohexadienes to Cyclohexenes Catalyzed by a Nickel Complex

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1,4-Cyclohexadiene was hydrogenated selectively to cyclohexene with a nickel catalyst generated from bis(acetylacetonato)nickel(II), triethyldialuminium trichloride, and triphenylphosphine at 40 °C under an atmospheric pressure of hydrogen. The hydrogenation of eleven kinds of alkyl-substituted 1,4-cyclohexadienes gave the corresponding cyclohexenes in good yields by the nickel catalyst. The structural factors of the alkyl substituent on the diolefin are shown to affect the hydrogenation rate. The homogeneous nickel catalyst system, in which a nickel hydride complex $NiH(PPh_3)(AlCl_4)$ is supposed to be an active species, was effective for the selective hydrogenation of the diolefin to the olefin. A plausible pathway involving π-allylnickel complexes for the hydrogenation is proposed.

Homogeneous hydrogenation has been extensively investigated.[1-3] Concerning nickel catalysts used for selective hydrogenation of diolefins, nickel-based Ziegler catalysts are known to be effective for the hydrogenation of diolefins[4,5] and unsaturated fats.[6,7] The catalyst systems are complicated (homogeneous and/or heterogeneous system) and poorly understood. Phosphine-coordinated nickel catalysts also are active for the hydrogenation of diolefins.[8,9] In many cases, however, less satisfactory results for selective hydrogenation are obtained. We used a homogeneous nickel catalyst generated from $Ni(acac)_2$, $Et_3Al_2Cl_3$, and PPh_3, and found that diolefins were hydrogenated selectively in good yields with the nickel catalyst in a series of studies reported.[10-13]

In this paper, we examine closely the selective hydrogenation of cyclic diolefins by the nickel catalyst under mild conditions and will complete the aspect of the catalytic hydrogenation.

Experimental

Materials. 1,4-Cyclohexadiene and methylcyclohexenes were commercially available. Alkyl-substituted 1,4-cyclohexadienes were prepared from the corresponding alkylbenzenes by Birch reduction.[14-16] Solvents were distilled over sodium. The other reagents were commercially available and used without purification.

General Procedure. Hydrogenation: To a 200 cm^3 flask fitted with a hydrogen buret, a septum inlet, and a magnetic stirring bar were added $Ni(acac)_2$ (0.11 mmol) and PPh_3 (0.55 mmol) in toluene. After the air was replaced with hydrogen the diolefin (11 mmol) in toluene was added. The hydrogenation was started by the addition of $Et_3Al_2Cl_3$ (1.1 mmol) in toluene. The solution was stirred with a magnetic stirrer and kept in a thermostated bath. An aliquot (2 cm^3) of the solution was taken and treated with a methanol-aqueous hydrochloric acid mixture. The organic layer was separated, washed with water, and subjected to GLC analysis.

Competitive Hydrogenation: The mixture of equimolar amounts of two diolefins was hydrogenated by the same procedure. An aliquot of the solution was worked up similarly. The initial rates for disappearance of diolefin were measured and relative rates were calculated, estimating the disappearance rate of 1,4-cyclohexadiene as 1.0.

Isomerization: Under an atmosphere of nitrogen methylcyclohexene was treated with the nickel catalyst under conditions similar to those of hydrogenation. The same work-up was done.

Analysis. The gas chromatographic analyses were made by a Yanaco G-80 apparatus with a TC detector and herium carrier gas using a 3 m column of bis(2-cyanoethyl) ether. ^{1}H NMR spectra were recorded on a Varian T-60A spectrometer using tetramethylsilane as an internal standard. The composition of methylcyclohexenes was determined by the NMR analyses, in which the relative areas of the characteristic signals for 3- and 4-methylcyclohexene were calculated.

Results and Discussion

Hydrogenation of 1,4-Cyclohexadienes. Under mild conditions 1,4-cyclohexadiene and alkyl-substituted homologs were hydrogenated selectively to cyclohexenes with a nickel catalyst generated from $Ni(acac)_2$, $Et_3Al_2Cl_3$, and PPh_3. The results are shown in Table 1. 1,4-Cyclohexadiene was hydrogenated selectively to produce cyclohexene in a high yield of 81%. Trace amounts of benzene (disproportionation product)[17] were detected. Cyclohexene was hydrogenated very slowly to cyclohexane with the nickel catalyst. In the case of 1,3-cyclohexadiene polymerization predominated over hydrogenation under the same conditions. However, 1,3-cyclohexadiene also was hydrogenated selectively to cyclohexene by adding the 1,3-diene dropwise to the catalyst system.[12] Mono- and dialkyl-substituted 1,4-cyclohexadienes gave the corresponding cyclohexenes in good yields. However, the compositions of alkyl-substituted cyclohexene isomers, except methylcyclohexenes, could not be determined exactly by GLC and NMR analyses because the isomers overlapped each other on the signals.

GLC analysis showed that methylcyclohexenes formed in the hydrogenation of 1-methyl-1,4-cyclohexadiene consisted of 1-methylcyclohexene (yield, 67%) and the mixture (7%) of 3- and 4-methylcyclohexene.

Table 1. The Hydrogenation of 1,4-Cyclohexadienes Catalyzed by a Nickel Complex[a]

Diolefin	Solvent	Time h	Conv. %	Product (Yield/%)
1,4-Cyclohexadiene[b]	Toluene	6	100	Cyclohexene (81) Cyclohexane (0)
1-Methyl-1,4-cyclohexadiene[b]	Toluene	8	100	1-Methylcyclohexene (67) 3- and 4-Methylcyclohexene (7) Methylcyclohexane (2)
1-Ethyl-1,4-cyclohexadiene	Ethylbenzene	8	91	Ethylcyclohexenes (80) Ethylcyclohexane (0)
1,2-Dimethyl-1,4-cyclohexadiene[b]	Ethylbenzene	22	100	Dimethylcyclohexenes (73) 1,2-Dimethylcyclohexane (0)
1,5-Dimethyl-1,4-cyclohexadiene	Ethylbenzene	22	97	Dimethylcyclohexenes (68) 1,3-Dimethylcyclohexane (0)
1,4-Dimethyl-1,4-cyclohexadiene	Ethylbenzene	28	82	Dimethylcyclohexenes (56) 1,4-Dimethylcyclohexane (6)

a) Reaction conditions: Diolefin 11 mmol; $Ni(acac)_2$ 0.11 mmol; $Ni:Al_2:P=1:10:5$; solvent 100 cm^3; temp 40 °C; H_2 1 atm. b) Data are derived from the Ref. 12.

Table 2. The Hydrogenation of 1-Methyl-1,4-cyclohexadiene Catalyzed by a Nickel Complex[a]

Time	Conv.	Select/%	
h	%	Methylcyclohexene (Composition/%)[b]	Methylcyclohexane
1	15	77 (59/41)	0
2	34	74 (58/42)	0
4	63	75 (61/39), (61/17/22)[c]	0
6	87	78 (63/37)	1
8	100	74 (90/10)	2
10	100	72 (90/10)	2

a) Reaction conditions: Diolefin 8 mmol; $Ni(acac)_2$ 0.1 mmol; $Ni:Al_2:P=1:10:5$; toluene 100 cm^3; temp 40 °C; H_2 1 atm. b) The ratio of methylcyclohexene isomers (1-methylcyclohexene/3- and 4-methylcyclohexene) by GLC analysis. c) The ratio of methylcyclohexene isomers (1-methylcyclohexene/3-methylcyclohexene/4-methylcyclohexene) by NMR analysis.

Table 3. The Isomerization of Methylcyclohexenes Catalyzed by a Nickel Complex[a]

Methylcyclohexene	Time	Product/mmol (Composition/%)[b]	
	min	1-Methylcyclohexene	3- and 4-Methylcyclohexene
1-Methylcyclohexene	0	8.97	Trace
	1	7.91 (90)	0.88 (10)
	150	7.86 (89)	0.94 (11)
4-Methylcyclohexene	0	0.71 (8)	8.11 (92)
	1	7.42 (90)	0.88 (10)
	180	7.41 (90)	0.82 (10)

a) Reaction conditions: $Ni(acac)_2$ 0.2 mmol; $Ni:Al_2:P=1:10:5$; toluene 100 cm^3; temp 40 °C; under N_2.
b) The composition of methylcyclohexene/% by GLC analysis.

At the initial stage of hydrogenation primary products were three kinds of methylcyclohexene, 1-, 3-, and 4-methylcyclohexene, in the ratio of 61 : 17 : 22, as shown in Table 2. After the diolefin was consumed the composition of the products was 90% of 1-methylcyclohexene and 10% of 3- and 4-methyl isomer. The above results suggest a subsequent isomerization occurred.

Isomerization. As shown in Table 3, the treatment of methylcyclohexenes with the nickel catalyst under nitrogen atmosphere resulted in the same composition with that of hydrogenation, 90% of 1-methylcyclohexene and 10% of 3- and 4-methyl isomer. It was found that each of methylcyclohexenes isomerized very rapidly by the nickel catalyst and the reaction mixture attained thermodynamically to equilibrium. The nickel catalyst was an excellent catalyst for the isomerization of the olefins.

On the other hand, 1,4-cyclohexadiene and 1-methyl-

Table 4. Relative Rates for the Competitive Hydrogenation of Substituted 1,4-Cyclohexadienes[a)]

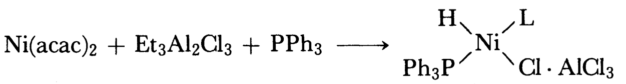
Substituent group on 1,4-cyclohexadiene	Reference diolefin[b)]	Solvent[c)]	Relative rate[d)]
1-Methyl	A	E	0.45
1-Ethyl	B	E	0.36
1-Propyl	C	T	0.32
1-Isopropyl	C	E	0.28
1-Butyl	B	E	0.27
1-Isobutyl	A	T	0.19
1-*t*-Butyl	C	T	0.15
1,2-Dimethyl	B	E	0.28
1,5-Dimethyl	B	E	0.085
1,4-Dimethyl	B	E	0.054

a) Reaction conditions: Each diolefin 5 mmol; Ni(acac)$_2$ 0.1 mmol; Ni:Al$_2$:P=1:10:5; solvent 100 cm^3; temp 60 °C; H_2 1 atm. b) Reference diolefin: A 1,4-cyclohexadiene; B 1-methyl-1,4-cyclohexadiene; C 1-ethyl-1,4-cyclohexadiene. c) Solvent: E ethylbenzene; T toluene. d) The disappearance rate of 1,4-cyclohexadiene was estimated as 1.0.

1,4-cyclohexadiene hardly isomerized and the 1,3-dienes were detected in trace amounts.

Competitive Hydrogenation. A mixture of equimolar amounts of two diolefins was hydrogenated. The initial rates for disappearance of diolefins were measured and the relative rates were calculated by estimating the disappearance rate of 1,4-cyclohexadiene as 1.0. Table 4 shows that the steric effect of alkyl substituents on the hydrogenation rate. The rate slowed down in the order of the chain length and branching of the alkyl substituent; H(1.0)>Me(0.45)>Et(0.36)>*n*-Pr(0.32)>*n*-Bu(0.27), *n*-Pr(0.32)>*i*-Pr(0.28), and *n*-Bu(0.27)>*i*-Bu(0.19)>*t*-Bu(0.15). Moreover, the number of substituent has a significant influence on the rate, and the order was H(1.0)>1-Me(0.45)>1,2-Me$_2$(0.28)>1,5-Me$_2$(0.085)>1,4-Me$_2$(0.054).

Hydrogenation Pathway. It has been proposed that a nickel hydride complex **1** is the active species for hydrogenation, as represented in the equation.[10,11,18)]

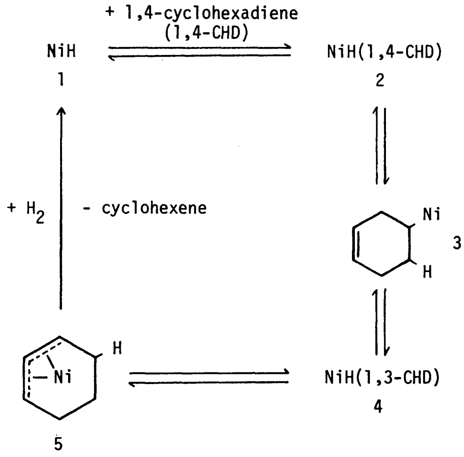


$$Ni(acac)_2 + Et_3Al_2Cl_3 + PPh_3 \longrightarrow (H)(L)Ni(PPh_3)Cl\cdot AlCl_3$$

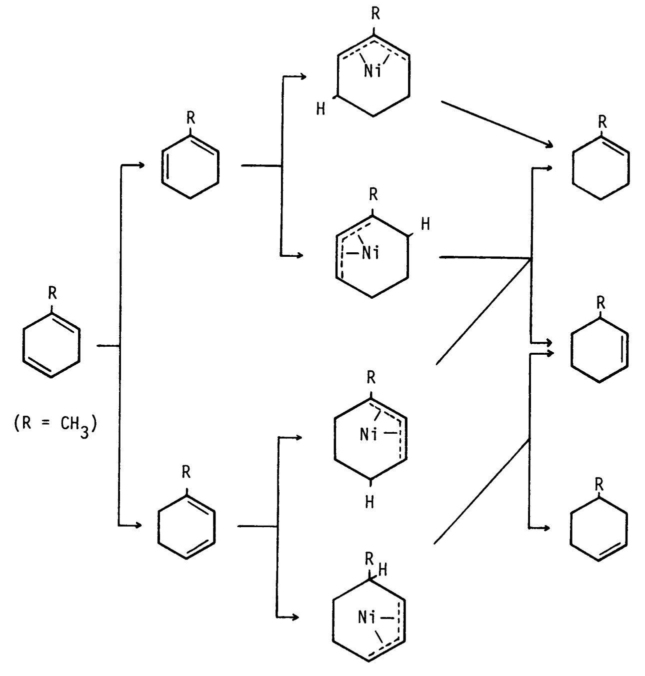
1 (L; solvent)

Scheme 1 shows a plausible pathway for the selective hydrogenation of 1,4-cyclohexadiene catalyzed by **1**. 1,4-cyclohexadiene coordinates to **1** and an insertion reaction of coordinated diolefin **2** produces a cyclohexenylnickel complex **3**. Its *β*-hydrogen elimination leads to the isomerization of 1,4-diene to 1,3-diene and then a *π*-allylnickel complex **5** is formed via an insertion reaction from the complex **4**. These four steps are reversible. The oxidative addition of hydrogen to **5** and the reductive elimination of cyclohexene regenerate **1**, which continues the catalytic cycle.

It has been reported that complexes such as **1** are most probably planar[19,20)] and the fragment of AlCl$_3$ strengthens the protonic character[21,22)] of hydrogen and promotes a ligand exchange.[23,24)] The use of five equimolar amounts of PPh$_3$ and a large excess of Et$_3$Al$_2$Cl$_3$ was favorable for the hydrogenation of 1,4-cyclohexadiene. It is suggested that appropriate amounts of the phosphine is necessary to form **1** and a second phosphine coordinates to **1** to form NiH(PPh$_3$)$_2$(AlCl$_4$), an inactive species, in a large excess of the phosphine. The complex **1** would have an excellent catalytic ability for isomerization of olefins and a good catalytic ability for selective hydrogenation of diolefins. Methylcyclohexenes isomerized very rapidly, while, 1,4-cyclohexadiene hardly did. The formation of a *π*-allylnickel complex[25)] from **4** is suggested by the products in the case of the hydrogenation of 1-methyl-1,4-cyclohexadiene. At the initial stage of the hydrogenation of 1-methyl-1,4-cyclohexadiene primary products were three kinds of cyclohexene,[26)] 1-, 3-, and 4-methylcyclohexene. These cyclohexenes isomerized very rapidly each other in the absence of the diolefin since the strength of coordination of diolefin to **1** is much stronger than that of olefins and the product attained to equilibrium. The formation of three isomers of methylcyclohexene is shown in Scheme 2. 1-Methyl-1,4-cyclohexadiene isomerizes to thermodynamically stable 1,3-isomers. Insertion reactions of coordinated 1,3-diolefin to **1** produce four types of *π*-allylnickel complex. In these complexes less steric crowding and thermodynamically stable *π*-allylnickel



Scheme 1.



Scheme 2.

complexes appear to be preferred.[25] β-Hydrogen eliminations from the complexes formed by oxidative addition of hydrogen to π-allylnickel complexes yield three kinds of methylcyclohexene, 1-, 3-, and 4-methylcyclohexene. It is reported that β-hydrogen eliminations tend to give internal olefins in the hydrogenation of 1,3-diolefins.[11] Thus, it is expected that 1-methylcyclohexene is a major product in the hydrogenation of 1-methyl-1,4-cyclohexadiene. However, little information on the interconversion between π- and σ-allylnickel complexes, and on the direction of β-hydrogen elimination was obtained from the results.

Although the oxidative addition of hydrogen to **5** may be the slow step in the hydrogenation of diolefins,[11] the steric factors of alkyl-substituted 1,4-cyclohexadienes gave a significant effect on hydrogenation rate. The hydrogenation rate slowed down in proportion to the bulkiness of the substrate coordinated (Table 1). This suggests that the equilibrium shown in Scheme 1 lies so far to the left (coordination side). In the isomerization of linear olefins by the nickel catalyst the insertion of olefin into **1** is assumed to be the slow step.[27]

In conclusion, it is presented that the nickel complex generated from $Ni(acac)_2$, $Et_3Al_2Cl_3$, and PPh_3 is a good catalyst for selective hydrogenation of diolefins and the hydrogenation proceeds via π-allylnickel complexes.

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