Selective Hydrogenation of Cyclic Diolefins to Monoolefins Catalyzed by a Nickel Complex

Mutsuji Sakai,* Fumiya Harada, Yasumasa Sakakibara, and Norito Uchino
Department of Fiber Chemistry, Kyoto Technical University, Matsugasaki, Sakyo-ku, Kyoto 606

(Received July 29, 1981)

Synopsis. Cyclic diolefins were hydrogenated selectively to monoolefins with a nickel catalyst prepared from bis(acetylacetonato)nickel(II), triethyldialuminium trichloride, and triphenylphosphine at 40 °C under an atmospheric hydrogen pressure.

The hydrogenation of olefins using homogeneous Ziegler catalysts has been studied.[1] We found that the nickel catalyst prepared from bis(acetylacetonato)-nickel(II), triethyldialuminium trichloride, and triphenylphosphine (mole ratio, $Ni(acac)_2:Al_2Et_3Cl_3:PPh_3=1:10:5$) catalyzed the selective hydrogenation of conjugated diolefins.[2] In the preceding paper[3] the selective hydrogenation of 2,3-dimethyl-1,3-butadiene to monoenes with the nickel catalyst was studied kinetically. This paper reports that cyclic diolefins were hydrogenated selectively to monoolefins with the nickel catalyst under mild conditions (40 °C, 1 atm H_2).

Results and Discussion

1,4-Cyclohexadiene was hydrogenated to produce cyclohexene alone in a high yield of 81%. Trace amounts of benzene (disproportionation product) were detected in the hydrogenation. Under nitrogen 1,4-cyclohexadiene neither isomerized to 1,3-diene nor disproportionated to benzene and cyclohexene with the catalyst, remaining unchanged. On the contrary, a Ziegler-type nickel catalyst, $Ni(II)–AlEt_3$, has been reported to be active for the disproportionation.[4)]

Substituted cyclic 1,4-diene, such as 1-methyl- and 1,2-dimethyl-1,4-cyclohexadiene, were hydrogenated selectively to similar extents, as shown in Table 1. In the case of 1-methyl-1,4-cyclohexadiene the hydrogenation products were 1-methyl-1-cyclohexene (yield, 67%) and a mixture of 3- and 4-methyl-1-cyclohexene (yield, 7%). Under the conditions used, however, the resulting latter two methylcyclohexenes isomerized very rapidly to thermodynamically more stable 1-methyl-1-cyclohexene. The equilibrium composition consisted of 90% of 1-methyl-1-cyclohexene and 10% of a mixture of 3- and 4-methyl isomers. Thus, the alkyl substituted 1,4-dienes may be hydrogenated selectively to the corresponding thermodynamically more stable monoolefins.

In the case of 1,3-cyclohexadiene polymerization occurred exclusively. However, 1,3-cyclohexadiene was hydrogenated selectively to cyclohexene by adding the 1,3-diene dropwise to the catalyst system. The order and rate of addition played a significant role in the hydrogenation of the 1,3-diene. 1,3-Cyclooctadiene was hydrogenated selectively without requiring its slow addition, while 1,5-cyclooctadiene isomerized quantitatively to bicyclo[3.3.0]oct-2-ene. 1,5,9-Cyclododecatriene also was hydrogenated to cyclododecene. 2,5-Norbornadiene and 4-vinyl-1-cyclohexene polymerized with the catalyst.

The nickel catalyst is thus useful for the selective hydrogenation of cyclic diolefins.

Experimental

Materials. 1-Methyl-1,4-cyclohexadiene and 1,2-dimethyl-1,4-cyclohexadiene were prepared by Birch reduction.[5)] The other reagents were commercially available. Solvents were distilled over sodium and diolefins were distilled freshly before use.

Hydrogenation. To a 200 ml flask fitted with a hydrogen buret, a septum inlet, and a magnetic stirrer were added

Table 1. Hydrogenation of cyclic diolefins by a nickel complex catalyst
Diolefin 11 mol, $Ni(acac)_2$, 0.11 mol, $Ni:Al_2:P=1:10:5$,
solvent 100 ml, temp 40 °C, H_2 1 atm.

Diolefin	Solvent	Time / h	Conv. / %	Product (Select/%)
1,4-Cyclohexadiene	Toluene	6	100	Cyclohexene(81) Cyclohexane(0)
1-Methyl-1,4-cyclohexadiene	Toluene	8	100	1-Methyl-1-cyclohexene(67) 3- and 4-Methyl-1-cyclohexene(7) 1-Methylcyclohexane(2)
1,2-Dimethyl-1,4-cyclohexadiene	Ethylbenzene	22	100	1,2-Dimethylcyclohexene(73) 1,2-Dimethylcyclohexane(0)
1,3-Cyclohexadiene	Toluene	1	99	Cyclohexene(4) Cyclohexane(0)
1,3-Cyclohexadiene	Toluene	5[a)]	93	Cyclohexene(74) Cyclohexane(6)
1,3-Cyclooctadiene	Ethylbenzene	3	100	Cyclooctene(89) Cyclooctane(0)
1,5-Cyclooctadiene	Ethylbenzene	(10 min)	100	Cyclooctene(0) Cyclooctane(0) Bicyclo[3.3.0]oct-2-ene(100)
1,5,9-Cyclododecatriene	Toluene	30[b)]	70	Cyclododecene(48) Cyclododecane(0)

a) 1,3-Cyclohexadiene was added dropwise over a period of 5 h. b) 50 °C.

Ni(acac)$_2$ (0.11 mmol) and PPh$_3$ (0.55 mmol) in toluene. After the atmosphere had been replaced with hydrogen the diolefin (11 mmol) in toluene was added. The hydrogenation reaction was started by the addition of Al$_2$Et$_3$Cl$_3$ (1.1 mmol) in toluene. The mixture became a homogeneous solution. The solution was stirred with a magnetic stirrer and kept in a thermostated bath. An aliquot (2 ml) 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.

Analysis. The gas chromatographic analyses were made by a Yanagimoto G-80 apparatus using columns of bis(2-cyanoethyl) ether, poly(ethylene glycol) 20 M, and 1,2,3-tris(2-cyanoethoxy)propane.

References

1) B. R. James, "Homogeneous Hydrogenation," John Wiley & Sons, New York (1973), pp. 363—383, and references cited therein.

2) Y. Sakakibara, H. Hisaki, M. Sakai, and N. Uchino, *Nippon Kagaku Kaishi,* **1976,** 1893.

3) Y. Sakakibara, S. Yagi, M. Sakai, and N. Uchino, *Nippon Kagaku Kaishi,* **1980,** 240.

4) C. B. Hanson, *Tetrahedron Lett.,* **21,** 1581 (1980).

5) T. Yamaguchi, T. Ono, K. Nagai, and C. C. Sin, *Kogyo Kagaku Zasshi,* **73,** 727 (1970).