CHEMISTRY LETTERS, pp. 1377-1378, 1977. Published by the Chemical Society of Japan

SELECTIVE HYDROGENATION OF 1,3-BUTADIENE CATALYZED BY COBALT(I)-BIPYRIDYL COMPLEXES

Nobuyuki YAMAMOTO, Hiroyoshi KANAI, and Kimio TARAMA
Department of Hydrocarbon Chemistry, Kyoto University, Sakyo-ku,
Kyoto 606

1,3-Butadiene was selectively hydrogenated to *cis*-2-butene by cobalt(I)-bipyridyl complexes. The order of the addition of butadiene to cobalt complexes determined the distribution of products. The catalytic activity was affected by the bipyridyl/cobalt ratio and halide anions.

Many transition metal complexes are known to catalyze the selective hydrogenation of dienes to monoenes.$^{1-4)}$ $[Co(bipy)(PR_3)_2]^+$ $^{1)}$ and $CoBr(PPh_3)_3$-$BF_3OEt_2$$^{2)}$ are selective catalysts for the hydrogenation of 1,3-butadiene to 1-butene. Using cyanocobaltate complexes 1-butene is mainly produced at CN/Co > 5, while *trans*-2-butene is formed at CN/Co $\leq$ 5.$^{3)}$ However, there are few catalysts which produce mainly *cis*-monoenes in the hydrogenation of dienes.$^{4)}$ We have found that cobalt(I)-bipyridyl complexes prepared *in situ* from cobalt(II) halides, bipyridyl, and zinc in THF and EtOH were active for the selective hydrogenation of 1,3-butadiene to *cis*-2-butene under ambient temperature and pressure.

A typical experimental procedure was as follows. A dry ethanol solution (5 ml) of cobalt(II) halide (0.44 mmol) was added to a dry THF solution (15 ml) of 2,2'-bipyridyl (0.44 $\sim$ 1.32 mmol) including zinc powder (ca.4 mmol), and 1,3-butadiene was introduced at the same time. When the solution was stirred, the solution changed from yellow-brown to dark blue, which showed characteristic of cobalt(I).$^{5)}$ Hydrogen was introduced into the flask with vigorous stirring under atmospheric pressure at 25°C and hydrogen pressure was kept constant. The rate of hydrogenation was followed by hydrogen-uptake. Hydrogenation products were analyzed by gas chromatography.

Hydrogen was not absorbed before 1,3-butadiene was added. Induction periods were observed. The rate of hydrogenation was determined from the linear uptake of hydrogen after the induction period. The rates of the hydrogenation are summarized in the table. 1,3-Butadiene was selectively hydrogenated to butenes. Main product was *cis*-2-butene. After the diene had been consumed, 1-butene was hydrogenated slowly, and butenes were isomerized much more slowly. The bipyridyl/cobalt ratio and halide anions gave the same distribution of products but affected the rate of hydrogenation. A maximum activity is commonly observed for a bipyridyl/cobalt ratio of about 2. Hydrogenation rates decreased in the order I > Br > Cl. When 1,3-butadiene was introduced to the THF-EtOH solution after cobalt(II)-bipyridyl complex was reduced to cobalt(I), 1-butene was formed preferably in the early stage of the reaction but *cis*-2-butene

Table. Hydrogenation of 1,3-butadiene with Cobalt(I)-bipyridyl Complexes[a]

CoX_2-nbipy-Zn		Reac. time	Conv.	Composition of products (%)				Induction period	Rate
						trans-	cis-		
X	n	(min)	(%)	$n-C_4H_{10}$	$1-C_4H_8$	$2-C_4H_8$	$2-C_4H_8$	(min)	(ml/min)
I[b]	1.0	129	38.2	0.0	18.9	2.3	78.8	50	0.66
I[b]	1.5	143	46.2	0.0	17.0	1.6	81.4	65	1.10
I[b]	2.1	65	35.5	0.0	16.5	2.0	81.5	19	1.29
I[c]	2.1	77	10.3	trace	24.0	5.0	71.0	40	0.69
I[b]	2.5	150	31.7	0.0	19.8	2.6	77.6	70	0.50
I[b]	3.1	174	37.8	0.0	16.6	3.2	80.2	60	0.28
Br[b]	2.0	152	43.3	0.0	17.2	1.4	81.4	75	0.56
Br[c]	2.1	75	11.5	2.1	45.0	15.7	37.2	12	0.48
Br[c]	2.1	136	32.3	1.3	32.7	9.3	56.7	12	0.48
Cl[b]	2.1	169	32.6	0.0	17.0	3.0	80.0	60	0.48
Cl[c]	2.0	99	31.7	1.7	53.1	17.9	27.3	4	0.33

a) A catalyst solution was prepared from adding an ethanol (5 ml) solution of cobalt(II) halide (0.44 mmol) to a THF (15 ml) solution of bipyridyl and zinc. 1,3-Butadiene; 4 mmol, P_{H_2}; 580 Torr. 25°C.

b) Butadiene was added before cobalt(II)-bipyridyl complexes were reduced to cobalt(I).

c) Butadiene was added after cobalt(II) was reduced to cobalt(I).

increased gradually as the time elapsed. When butadiene is added before the reduction of cobalt complex, butadiene-cobalt(I) complex may be formed in a chelate structure, and hydrogen presumably adds to butadiene by 1,4-addition to give *cis*-2-butene. However, when butadiene is added after the reduction of cobalt complex, π-olefinic complex of butadiene is formed, and hydrogen adds to butadiene by 1,2-addition to give 1-butene.

Cobalt complexes with o-phenanthroline instead of 2,2'-bipyridyl as ligand showed the similar selectivity in the hydrogenation of 1,3-butadiene.

Acknowlegement. The author (H.K.) acknowleges to the Ministry of Education for grant in aid.

References

1) A. Camus, C. Cocevar, and G. Mestroni, J. Organometal. Chem., 39, 355 (1972).
2) K. Kawakami, T. Mizoroki, and A. Ozaki, Chem. Lett., 1976, 847.
3) J. Kwiatek, I. L. Madov, and J. K. Seyler, Adv. Chem. Ser., 37, 201 (1963).
4) a) E. N. Frankel and R. O. Butterfield, J. Org. Chem., 34, 3930 (1969).
b) Y. Tajima and E. Kunioka, J. Cat., 11, 83 (1968).
5) G. M. Waind and B. Martin, J. Inorg. Nucl. Chem., 8, 551 (1958).

(Received August 27, 1977)