CHEMISTRY LETTERS, pp. 847-848, 1976. Published by the Chemical Society of Japan

SELECTIVE HYDROGENATION OF DIOLEFINS CATALYZED BY HALOGENOTRIS(TRIPHENYLPHOSPHINE)COBALT(I)-LEWIS ACID

Kiyoshi KAWAKAMI, Tsutomu MIZOROKI, and Atsumu OZAKI
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Ohokayama, Meguro-ku, Tokyo 152

Hydrogenation of diolefins to monoenes is highly selectively catalyzed by halogenotris(triphenylphosphine)cobalt(I) in the presence of Lewis acid in bromobenzene. Internal double bonds are reduced more rapidly than terminal ones.

Many transition metal complexes such as $PdCl_2(PPh_3)_2$[1], $PtCl_2(PPh_3)_2$[2], $Ru(CO)_2Cl_2(PPh_3)_2$[3], $Ir(CO)Cl(PPh_3)_2$[4], and $(C_6H_6)Cr(CO)_3$[5], have been reported to catalyze the selective hydrogenation of polyene to monoene under elevated pressure. $K_3Co(CN)_5$[6] and $Co_2(CO)_6(PPh_3)_2$[7] are also fairly active for the selective hydrogenation under ambient temperature and pressure. We report here that halogenotris(triphenylphosphine)cobalt(I) complex activated with Lewis acid, which is active for the selective dimerization of ethylene[8], also catalyzes effectively the hydrogenation of conjugated diene to monoene in bromobenzene.

To a dry bromobenzene solution (20 ml) of halogenotris(triphenylphosphine)cobalt (I) (0.2 mmol) in a two necked flask (100 ml) was added boron trifluoride etherate (0.44 mmol) and diolefine (3.0 mmol). Hydrogen was introduced into the flask with vigorous stirring under atmospheric pressure at 0°C, and the hydrogen pressure was kept constant. The rate of hydrogen consumption was followed by a gas burette. Hydrogen gas was taken up almost linearly with time accompanying no induction period. Hydrogenation products were quantitatively determined by gas chromatography.

Typical results are shown in Table 1. Main products were 1-butene, 3-methyl-1-butene, 1-pentene, 1-pentene and 1-hexene from butadiene, isoprene, 1,3-pentadiene, 1,4-pentadiene and 1,3-hexadiene respectively. Hydrogenation rates were in the order isoprene $>$ 1,3-pentadiene $>$ 1,3-hexadiene $>$ butadiene. One of the characteristics of this catalyst is that 1,3-pentadiene and 1,3-hexadiene give mainly 1-pentene and 1-hexene respectively. Namely, the internal double bonds are reduced more rapidly than the terminal ones. When the dienes are mostly hydrogenated, the monoenes formed are rapidly isomerized and very slowly hydrogenated to alkanes. This is the reason why the selectivities to monoenes (almost 100%) are all exceedingly high.

In the hydrogenation of butadiene, the rate is nearly proportional to the hydrogen pressure, and the rate was 1.6 times larger than that with deuterium ($r_H/r_D = 1.6$). Main deuteration products of butadiene was 3,4-dideutero-1-butene, which was identified by mass spectrometry and ^2D-[^1H] NMR. These results indicate

Table 1 Hydrogenation of Diolefins Catalyzed by $CoBr(PPh_3)_3$

Reactant	Reac. time (min)	Conv. (%)	Selectivity to monoene (%)			Rate (ml/min)
Butadiene	90	28	1-Butene (89)	trans-2-Butene (-)	cis-2-Butene (11)	0.19
Isoprene	30	96	3-Methyl-1-butene (86)	2-Methyl-1-butene (4.5)	2-Methyl-2-butene (9.1)	1.83
1,3-Pentadiene	60	83	1-Pentene (56)	trans-2-Pentene (21)	cis-2-Pentene (23)	0.97
1,3-Pentadiene	15*	68	1-Pentene (74)	trans-2-Pentene (19)	cis-2-Pentene (7)	2.1
1,4-Pentadiene**	260	37	1-Pentene (65)	trans-2-Pentene (12)	cis-2-Pentene (23)	0.11
1,3-Hexadiene	60	53	1-Hexene (61)	trans-3-Hexene (18)	cis-3-Hexene (22)	0.45

$CoBr(PPh_3)_3$ 0.2 mmol, BF_3OEt_2 0.44 mmol, PhBr 20 ml, React. temp. 0°C, Diolefins 3.0 mmol, P_{H_2} 76 cmHg. * $AlCl_3$ (0.16 mmol) was used instead of BF_3OEt_2. The induction time is excluded. ** No detection of 1,3-pentadiene in the product.

that the hydrogenation takes place via 1,2-hydrogen addition to butadiene.

Hydrogenations of other alkenes, such as methyl vinyl ketone, vinyl cyclohexene, methyl acrylate, n-buthyl vinyl ether and styrene were not observed even under enforced conditions. Only vinyl acetate was found to be hydrogenated to ethyl acetate under 40 kg/cm^2 of hydrogen pressure at room temperature (ca 65% conversion for 2 hr).

Aluminum trichloride (* in Table 1) was more effective than boron trifluoride etherate, but some induction period was observed.

References

1) H.Itatani and J.C.Bailar, J. Am. Oil. Chemists Soc., 44, 147 (1967).
2) J.C.Bailar and H.Itatani, J. Amer. Chem. Soc., 89, 1592 (1967).
3) D.R.Fahey, J. Org. Chem., 38, 80 (1973).
4) J.E.Lyons, J. Catal., 30, 490 (1973). C.U.Pittman,Jr., S.E.Jacobson, and H.Hiramoto, J. Amer. Chem. Soc., 97, 4774 (1975).
5) E.N.Frankel, R.O.Butterfield, J. Org. Chem., 34, 3930 (1969).
6) J.Kwiatek, I.L.Mador, and J.K.Seyler, J. Amer. Chem. Soc., 84, 304 (1962).
7) A.Misono, Y.Uchida, T.Saito, and K.M.Song, Chem. Commun. (London), 1967, 419.
8) K.Kawakami, T.Mizoroki, and A.Ozaki, Chem. Lett., 1975, 903.

(Received June 29, 1976)