CHEMISTRY LETTERS, pp. 1243-1244, 1983. © The Chemical Society of Japan 1983

CATALYTIC HYDROGENATION OF 7-METHYLBICYCLO[3.3.1]NON-6-EN-3-ONE. ANOMALOUSLY HIGH SELECTIVITIES ON Pd AND Co BLACK CATALYSTS

Jun-ichi ISHIYAMA,* Yasuhisa SENDA, and Shin IMAIZUMI
Department of Engineering Science (Chemistry), Faculty of
Engineering, Tohoku University, Aoba, Sendai 980

Anomalously high selectivities on Pd and Co black catalysts were observed in the catalytic hydrogenation of 7-methylbicyclo[3.3.1]non-6-en-3-one. Unexpected products, 1-adamantanol and 6-methylbicyclo[3.3.1]non-6-en-3-endo-ol were exclusively produced over Pd and Co, respectively.

It is well-known that PtO_2, Pd/C, and Raney Ni catalysts are efficient in the hydrogenation of olefinic bond in non-conjugated enones.$^{1)}$ However, little is known about the consistent study concerning the selectivity of the group VIII transition metal catalysts in the hydrogenation of non-conjugated enones. Different selectivities were observed depending on the catalysts used in the hydrogenation of 7-methylenebicyclo[3.3.1]nonan-3-one (1) over a variety of the group VIII transition metal black catalysts. A novel reductive cyclization occurred selectively to give 1-adamantanol (5) over Pd catalyst.$^{2)}$ We present here the anomalously high selectivities in the hydrogenation of 7-methylbicyclo-[3.3.1]non-6-en-3-one (2) which is derived by the double bond migration of 1 using Pd and Co catalysts (Fig.1). Table 1 shows the product ratios after 50% of reaction conversion of 2.

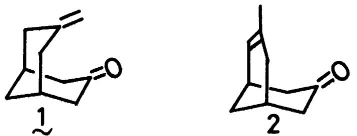
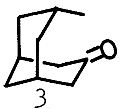
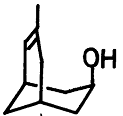
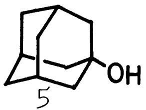


Fig.1.

The hydrogenation of 2 over Ru and Pt catalysts gave only 7-endo-methylbicyclo-[3.3.1]nonan-3-one (3). The hydrogenation over Ni, Os and Ir gave 10–60% of 7-methylbicyclo[3.3.1]non-6-en-3-endo-ol (4) with 3. The hydrogenation of 2 over Pd gave exclusively the cyclic product (5) similar to 1. Only 3 was formed over Rh catalyst in cyclohexane similar to Ru and Pt while 5 which was obtained over Pd was also detected in ethanol. Ni and noble metal catalysts except Pd gave 40–100% of 3. Alternative to other catalysts, Co gave exclusively 4, which is formed by the introduction of hydrogens to the carbonyl moiety.

On the basis of the obtained results, it is confirmed that the hydrogenation over the group VIII transition metal catalysts except Pd and Co occurs preferentially on the trialkyl substituted olefinic bond as well as the dialkyl substituted one rather than the carbonyl moiety.$^{2)}$ Only 5 was formed in the hydrogenation of 2 over Pd. Since it is not likely for 5 to be produced directly

Table 1. Hydrogenation of 7-methylbicyclo[3.3.1]non-6-en-3-one (**2**)[a]

Products Catalysts	 **3**	 **4**	 **5**
Co-black	0(0)[b]	100(100)	0(0)
Ni-black	74(56)	26(44)	0(0)
Ru-black	100(100)	0(0)	0(0)
Rh-black	100(76)	0(0)	0(24)
Pd-black	0(0)	0(0)	100(100)
Os-black	76(40)	24(60)	0(0)
Ir-black	90(89)	10(11)	0(0)
Pt-black	100(100)	0(0)	0(0)

a) The substrate (0.5 mmol) was hydrogenated in 5 ml cyclohexane at 25°C and atmospheric pressure using a weighed sample catalyst (noble metals : 5 mg, Co: 1000 mg, Ni: 200 mg). Values are the composition (%) when 50 % of **2** was consumed.

b) Values in parentheses indicate the product ratios in ethanol.

from **2**, and Pd catalyst has the very high isomerizing activity, we envisage that **5** was obtained from **1** which is derived from **2** by the double bond migration (Fig.2). The olefinic moiety of **1** is adsorbed on the Pd surface and the electrons are back-donated from the catalyst to the π^*-orbital of the olefinic bond. Then, the through-space charge transfer to the positively charged carbonyl carbon occurs smoothly to form the cyclic product (**5**). The hydrogenation of **1** gave 42∼62 % of **3** over Co,[2] while **4** was formed exclusively from **2** over Co. These results show that the reactivity of the carbonyl moiety over Co is lower than the dialkyl substituted olefinic linkages but is much higher than the trialkyl substituted ones in non-conjugated enones.

This is one of the good examples that the intramolecular through-space charge transfer determines the selectivity of the heterogeneous hydrogenation.[3] It is important in organic synthesis that only the unsaturated alcohol is obtained from non-conjugated enones in the hydrogenation over Co catalyst.

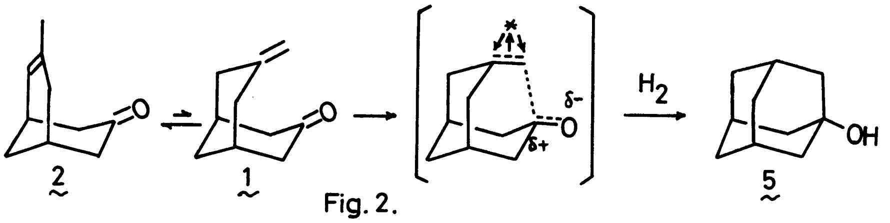


Fig. 2.

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(Received June 14, 1983)