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HYDROGENATION OF 7-METHYLENEBICYCLO[3.3.1]NONAN-3-ONE OVER GROUP VIII METAL CATALYSTS. NOVEL REDUCTIVE CYCLIZATION

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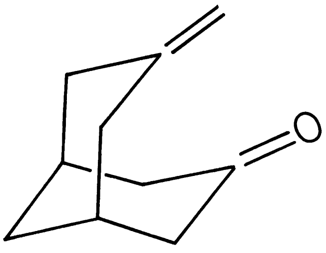
The products of novel reductive cyclization, 1-adamantanol and 1-methyl-2-oxa-adamantane, were obtained in the hydrogenation of 7-methylenebicyclo[3.3.1]nonan-3-one over group VIII metal black catalysts in ethanol or cyclohexane. 1-Adamantanol was produced over Pd, Rh, Co and Ni catalysts, and 1-methyl-2-oxa-adamantane only over Co catalyst in cyclohexane.

As a part of the study on the intramolecular orbital interaction, we previously reported that 7-methylenebicyclo[3.3.1]nonan-3-one (**1**), both π-electron moieties of which are on the same plane of symmetry and face each other, exists in the double-chair conformation. Carbon-13 n.m.r. chemical shifts of this compound indicate the presence of the intramolecular through-space interaction between two π-orbitals (Fig. 1).1) We have discussed the correlation between the intramolecular orbital interaction and the stereochemistry of the catalytic hydrogenation.2) To evaluate how such an interaction operates on the selectivity of the addition reaction, the catalytic hydrogenation of **1** was examined over a variety of group VIII transition metals.



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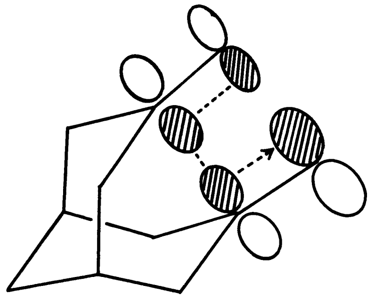
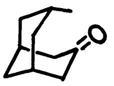
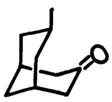
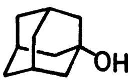
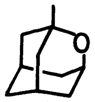
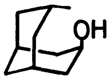
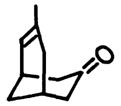


Fig. 1

Table 1. Hydrogenation of 7-methylenebicyclo[3.3.1]nonan-3-one (1)[a)]

Products / Catalysts	 2a	 2b	 4	 5	 6	 7
Co	62(42)[b)]	2(0)	26(28)	6(0)	4(30)	0(0)
Ni	78(54)	t(0)	2(24)	0(0)	0(0)	20(22)
Ru	80(76)	2(0)	0(0)	0(0)	0(0)	18(24)
Rh	30(34)	2(0)	0(14)	0(0)	0(0)	68(52)
Pd	0(0)	0(0)	18(26)	0(0)	0(0)	82(74)
Os	94(90)	2(0)	0(0)	0(0)	0(0)	4(10)
Ir	94(70)	6(0)	0(0)	0(0)	0(0)	0(30)
Pt	76(60)	t(0)	0(0)	0(0)	0(0)	24(40)

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 1 was consumed.

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

The product ratios at 50 % conversion of 1 are shown in Table 1. The Co and Ni catalysts were prepared from those metal oxides by the reduction at 350°C in hydrogen flow. Noble metal catalysts were prepared according to the procedure described by Tanaka et al.[3)] The hydrogenation of 1 on Co, Ni, Ru, Os, Ir and Pt catalysts gave predominantly 7-endo-methylbicyclo[3.3.1]nonan-3-one (2a). 7-Methylbicyclo[3.3.1]non-6-en-3-one (7) was the major product over Rh and Pd catalysts. 2a was not obtained at all over the latter. The products of novel reductive cyclization, 1-adamantanol (4) and 1-methyl-2-oxa-adamantane (5), were formed over particular metal catalysts. 4 was produced over Pd, Rh, Co and Ni, while 5 was slightly formed only over Co in cyclohexane. Although aldolization and coupling reaction have been observed in the hydrogenation of cyclic diketones,[4)] little is known about the cyclization between the carbonyl and the olefinic moiety. It was surprising that 4 was exclusively obtained, when the hydrogenation over Pd catalyst was continued till 1 equiv. of hydrogen

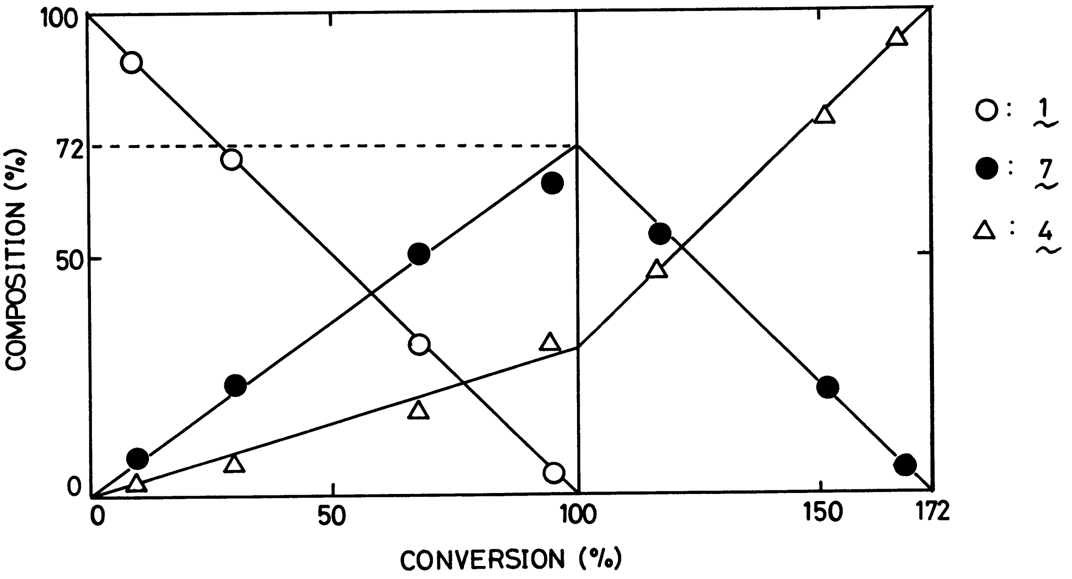
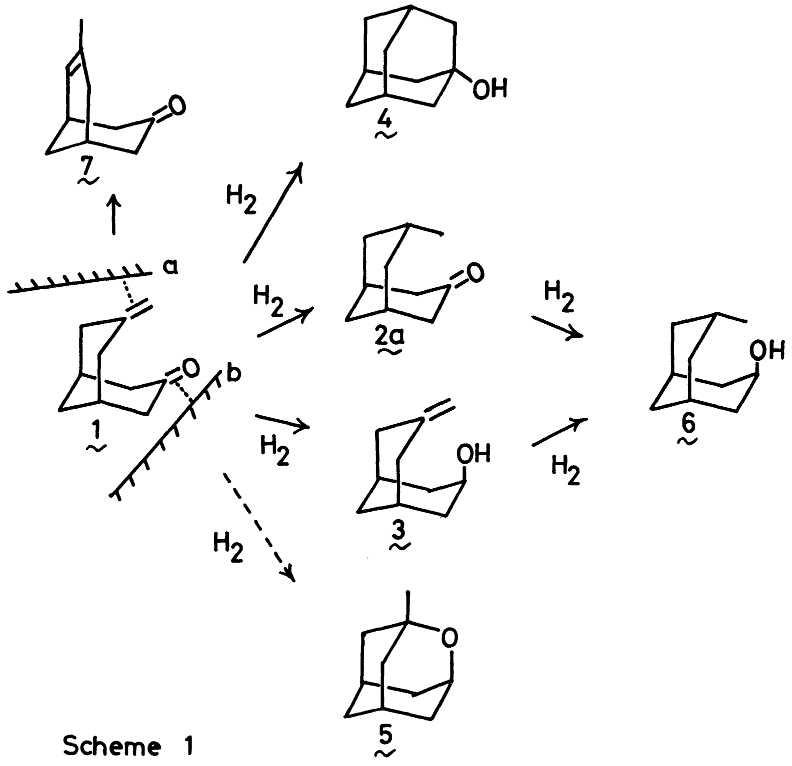


Fig. 2. Product distribution over Pd in ethanol

had been absorbed in ethanol (Fig. 2).

Since steric environment of both unsaturated bonds of **1** (a- or b-side) is much the same, **1** is a suitable substrate to examine the chemoselectivity between the olefinic and carbonyl moieties. We tentatively presume that the reaction proceeds as shown in Scheme 1. No 7-methylenebicyclo[3.3.1]nonan-3-endo-ol (**3**), which should be produced by the reduction of the carbonyl moiety of **1**, was detected over any catalyst. Taking into account the results obtained here (Table 1), it is confirmed that the addition of hydrogen over the group VIII transition metal catalysts occurs selectively from the olefinic side (a-side) rather than the carbonyl side (b-side). The formation of **5** and 7-endo-methylbicyclo[3.3.1]nonan-3-endo-ol (**6**) as well as **2a** and **4** in cyclohexane, suggests that the affinity of Co to the carbonyl moiety is stronger than that of the other catalysts.5) 7-exo-Methylbicyclo[3.3.1]nonan-3-one (**2b**) was not obtained in ethanol. The population of **4** increased over Co, Ni, Rh and Pd, while that of **7** increased over the other catalysts in ethanol. Such a solvent effect may be due to the promotion of the intramolecular through-space interaction by the hydrogen bonding between ethanol and the oxygen of carbonyl moiety.

It is particularly interesting that Pd and Co catalysts show the different selectivity to other transition metals in the hydrogenation of **1** which has the intramolecular through-space interaction. We believe that the proximity between two π-orbitals of 1 is closely associated with the formation of products of novel reductive cyclization, **4** and **5**.6) Further investigation are in progress to elucidate the reaction mechanism of **4** and **5**.



Scheme 1

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