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Chemo-Selectivity of Group-VIII Metal Catalysts in Hydrogenation of Nonconjugated Enones

Jun-ichi Ishiyama,* Satoshi Maeda,[1a] Kazuhiro Takahashi,[1b] Yasuhisa Senda,† and Shin Imaizumi
Department of Engineering Science, Faculty of Engineering, Tohoku University, Aoba, Sendai 980
†Department of Chemistry, Faculty of Science, Yamagata University, Koshirakawa-cho, Yamagata 990
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The chemo-selectivity of group-VIII metal catalysts has been examined in the hydrogenation of nonconjugated enones at ambient temperature under an atmospheric pressure of hydrogen. A cobalt catalyst gave high yields of unsaturated alcohols from trialkylated olefinic ketones. Osmium showed the highest selectivity among platinum metal catalysts for the reduction of the carbonyl bond in the hydrogenation of trialkylated olefinic ketones. The hydrogenation of mono- and dialkylated olefinic ketone ordinarily proceeded with a preferential saturation of the olefinic function, regardless of the catalyst. The hydrogenation of 4-methylene- and 4-ethylidenecyclohexanone was accompanied by the formation of diethyl acetals over ruthenium, rhodium, and palladium black catalysts in an ethanol solvent. The acetals were not detected in the hydrogenation of the other enones and over the other catalysts. In addition, the chemoselectivity on the hydrogenation of acyclic enones was examined over nickel and cobalt catalysts treated with small amounts of alkali and carbon monoxide. The amount of unsaturated alcohols increased when the catalyst was treated with alkali in the case of di- and trialkylated olefinic ketones, whereas the characteristics of cobalt, which selectively reduces the ketonic function in trialkylated olefinic ketones, were completely missing when cobalt was treated with carbon monoxide.

Selective catalytic hydrogenation of nonconjugated enones to the corresponding saturated ketones is achieved easily;[2] however, a selective reduction to afford unsaturated alcohols is a formidable task. This type of compound is usually prepared from a nonconjugated enone by a non-catalytic route. However, it has also been reported that in some structural features the catalyst may have a marked effect on chemo-selectivity.[3] The ketonic function in hexahydronaphthalenedione system was reduced over Ru-on-carbon in preference to the double bond.[4] France et al. reported the preferential reduction of carbonyls in an octahydronaphthalenedione system over platinum oxide in ethanol and the preferential saturation of the double bonds over Pd-on-carbon.[5] Nishimura et al. have reported that 17-oxo group is extensively reduced in preference to Δ^5 unsaturation over unsupported osmium and ruthenium blacks in the hydrogenation of 3-hydroxyandrost-5-en-17-one (dehydroepiandrosterone).[6]

Those available data are, however, insufficient for applications to the selective reduction of the ketonic or olefinic group in unsaturated ketones; little is known about the consistent study concerning the selectivity of group-VIII metal catalysts in the hydrogenation of nonconjugated enones. Recently, we examined the catalytic hydrogenation of 7-methylenebicyclo[3.3.1]nonan-3-one (**1**) and 7-methylbicyclo[3.3.1]non-6-en-3-one (**2**) over group-VIII metals.[7,8] The olefinic bond was selectively reduced to afford 7-endo-methylbicyclo[3.3.1]nonan-3-one (**2A**) over ruthenium, rhodium, and platinum catalysts, whereas the olefinic one remained intact during the reduction of the ketone to give 6-methylbicyclo[3.3.1]non-6-en-3-endo-ol (**2B**) exclusively in the hydrogenation of **2** over a cobalt catalyst. Hydrogenation over nickel, osmium, and iridium catalysts gave mixtures of **2A** and **2B**.

Therefore, it seems of interest to more precisely study the differences for chemo-selectivity of group-VIII transition metal catalysts by an examination of the hydrogenation of simple nonconjugated aliphatic enones in comparison with their behavior under the same experimental conditions as that of **1** and **2**. The substrates which were chosen comprised the acyclic (5-hexen-2-one: **3**, 5-methyl-5-hexen-2-one: **4**, (*E*) or (*Z*)-5-hepten-2-one: **5**, 6-methyl-5-hepten-2-one: **6**) and alicyclic (4-methylenecyclohexanone: **7**, 4-ethylidenecyclohexanone: **8**) nonconjugated enones. In addition, the chemo-selectivities of the hydrogenation of **3**, **5**, and **6** were also examined using nickel and cobalt catalysts treated with small amounts of alkali and carbon monoxide.

Results and Discussion

Since the reaction of a substrate with a solvent over metal catalysts occurs because of the reactivity of the carbonyl and hydroxy functions when methanol or ethanol is used as a solvent for ketone hydrogenation,[9] the chemo-selectivity of group-VIII metal catalysts in the hydrogenation of nonconjugated enones was examined in a cyclohexane solvent at ambient temperature and approximately atmospheric pressure. Cobalt and nickel catalysts were prepared from Raney alloys using a W-4 method[10] or by reducing the corresponding metal oxides, and platinum metal catalysts by reducing the corresponding metal oxides or hydroxides.[11] The products are saturated ketone (**A**), unsaturated alcohol (**B**), and saturated alcohol (**C**).

Although the hydrogenation of all substrates used here showed chemo-selectively the saturated ketones over ruthenium, rhodium, palladium,[12] platinum, and iridium[13] catalysts, osmium catalyst showed different chemo-selectivities from that of other platinum metals. Osmium gave unsaturated alcohols together with saturated ketones and saturated alcohols in the hydrogenation of trialkylated ones (**2**, **6**, and **8**). A nickel catalyst showed a similar chemo-selectivity to osmium. The initial chemo-selectivity for unsaturated alcohols of osmium and nickel catalysts are listed in Table 1. Since hydrogenation products increased linearly until 50% of reaction conversion of the substrates, the values shown in Tables give the initial chemo-selectivity of catalysts at 50% conversion. Cobalt catalysts gave high yields of unsaturated alcohols from trialkylated olefinic ketones, and **2B**, 6-methyl-5-hepten-2-ol (**6B**), and 4-ethylidenecyclohexanol (**8B**) were exclusively produced (Table 2).

Table 1. Initial Selectivity for Unsaturated Alcohol(**B**) of Osmium and Nickel Catalysts a)

Enone	**B**/(**A**+**B**+**C**) b)	
	Os c)	Ni d)
1, 3, 4, 5, 7	0	0
2	0.24	(0.26) e)
6	0.15	0.05
8	0.24	0.45

a) Substrate, 0.5 mmol; solvent(cyclohexane), 5 ml. Enones were hydrogenated at ambient temperature under atomospheric pressure. Values are the ratio when 50% of substrate was consumed. b) **A** = Saturated ketone, **B** = unsaturated alcohol, **C** = saturated alcohol. Selectivity for the formation of unsaturated alcohol to all products. c) A 5 mg of catalyst was used. d) A weighed sample of catalyst (500 mg for Raney Ni under wet conditions; 200 mg as NiO for Ni-black) was used. e) Value in parentheses indicates the product ratio over Ni-black catalyst.

Table 2. Hydrogenation of Enones over Cobalt Catalyst a)

Enone	Product b)/mol%		
	A	**B**	**C**
1	(64) c)	(0)	(4)
2	(0)	(100)	(0)
3	100	0	0
4	50	8	42
5	34	12	54
6	0	100	0
7	56 (56)	22 (44)	22 (0)
8	0 (0)	100 (100)	t d) (0)

a) See footnote a in Table 1 except for the weight of catalyst. A weighed sample of catalyst (500 mg for Raney Co under wet conditions; 1000 mg as CoO for Co-black) was used. Values in parentheses indicate the product ratios over Co-black catalyst. b) See footnote b in Table 1. c) 1-Adamantanol (26%) and 1-methyl-2-oxa-adamantane (6%) were also detected. d) Trace.

The hydrogenation of **1** and **2** was examined over a variety of group-VIII transition metals in order to evaluate how an intramolecular orbital interaction operates regarding the selectivity of an addition reaction.[7,8,14] Different selectivities were observed depending on the catalysts used in the hydrogenation of **1** and **2**. A novel reductive cyclization occurred to give 1-adamantanol (**2E**) over cobalt, nickel, rhodium, and palladium catalysis in the hydrogenation of **1**,[7] and to give selectively **2E** over palladium in the hydrogenation of **2**.[8] However, reductive cyclization could not be observed in the hydrogenation of acyclic nonconjugated enones (**5** and **6**). We envisage that the proximity between two π-orbitals is closely associated with the formation of reductive cyclization products.[15]

Figure 1 shows the product ratios of unsaturated alcohols (**2B**, **6B**, **7B**, and **8B**) when 50% of the enones were consumed over cobalt, nickel, and osmium catalysts. The high-selectivity to the unsaturated alcohol formation was observed when a carbonyl moiety was associated with a relative hindered olefinic bond. In the case of trialkylated olefinic ketones (**2**, **6**, and **8**), the unsaturated alcohols (**2B**, **6B**, and **8B**) were exclusively produced over cobalt catalyst; however, the formation of **7B** decreased to 22% yield in the case of dialkylated olefinic ketone (**7**). These results show that the reactivity of the carbonyl moiety over cobalt is a little lower than the dialkyl-substituted olefins but is much higher than the trialkyl-substituted ones in nonconjugated enones. This trend was also observed over nickel and osmium catalysts. The hydrogenation

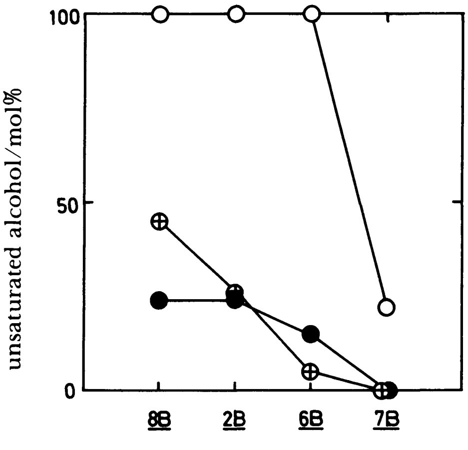

Fig. 1. Product ratios of unsaturated alcohols (**2B**, **6B**, **7B**, and **8B**) when 50% of substrates were consumed over Co, Ni, and Os catalysts. ○: Co, ⊕: Ni, ●: Os.

of **2**, **6**, and **8** gave 5—45% of **B** over those catalysts, while **7B** was rarely formed in that of **7**. An osmium catalyst showed the highest selectivity for the reduction of the carbonyl bond in platinum metals. Osmium might be expected to be the most suited for reducing the carbonyl function of nonconjugated enones among the platinum metats in this sense.

The selectivity of the reduction of trialkylated olefinic ketones to unsaturated alcohols declined in the series Co≫Ni, Os≫Ir, Ru, Rh, Pd, Pt. This tendency may be attributed to the fact that nickel, osmium, and especially cobalt catalysts have a stronger affinity for the carbonyl moiety than the other catalysts.[16] It is important in organic syntheses that the unsaturated alochol is selectively obtained from trialkylated olefinic ketones during hydrogenation over a cobalt catalyst. The hydrogenation of **2**, **6**, and **8** over cobalt gave those corresponding unsaturated alcohols in 98% yield after absorption of one equivalent of hydrogen. A Raney cobalt catalyst was also remarkably chemoselective in the competitive hydrogenation of a mixture of 6-methyl-2-heptanone (**6A**) and 6-methyl-5-hepten-2-ol (**6B**). The carbonyl moiety of **6A** was completely reduced before the double bond of **6B** was saturated, whereas **6A** and **6B** were converted with a comparable rate over a Raney nickel catalyst (Fig. 2).

Hydrogenations were also carried out in an ethanol solvent. Although the proportion of saturated alcohols decreased according to the catalysts used, the chemo-selectivity of metal catalysts in ethanol showed a similar trend of that in cyclohexane as a whole. Diethyl acetals were rapidly formed in addition to the hydrogenated products by the use of **7** and **8** as nonconjugated enones over ruthenium, rhodium, and palladium catalysts in ethanol. The acetals were a mixture of 4-alkylidenecyclohexanone diethyl acetal (**F**), 4-alkyl-3-cyclohexenone diethyl acetal (**G**), 4-alkylcyclohexanone diethyl acetal (**H**) (Fig. 3). The acetal formation relative to the hydrogenation increased in the order Rh<Ru<Pd. Those were not detected at all during the hydrogenation of the other enones, and were not observed over the other catalysts.

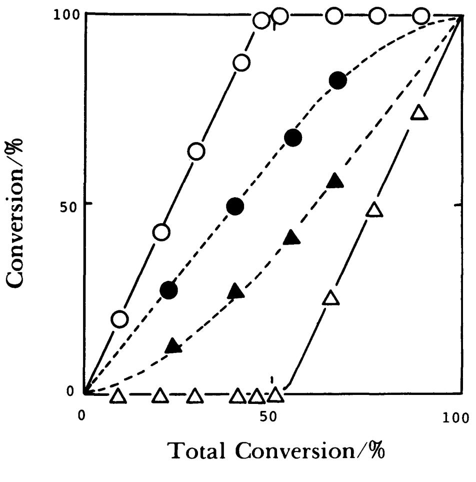

Fig. 2. Conversion of 6-methyl-2-heptanone (**6A**: ○, ●) and 6-methyl-5-hepten-2-ol (**6B**: △, ▲) versus total conversion. Raney Co (○, △: ——), Raney Ni (●, ▲: ------).

Since **7** and **8**, which have olefinic and carbonyl functions at 1 and 4 positions on a cyclohexane ring, take a rigid and flat chair conformation compared with the other simple nonconjugated enones, it is suggested that the neighborhood of the carbonyl moieties of **7** and **8** is hindered less sterically than that of the other enones. The effect of such steric factors is associated with the formation of diethyl acetals. 4-Ethylidenecyclohexanone diethyl acetal (**8F**) is found to be the most abundant among acetals in the hydrogenation of **8**; it is contemplated that acetal formation occurs faster than a reduction of the olefin. The varying composition of the reaction mixture at the initial stage of the hydrogenation over a Pd catalyst in ethanol is shown in Fig. 4 as an example. Palladium, rhodium, and ruthenium catalysts are the ones which efficiently hydrogenate olefins. It is,

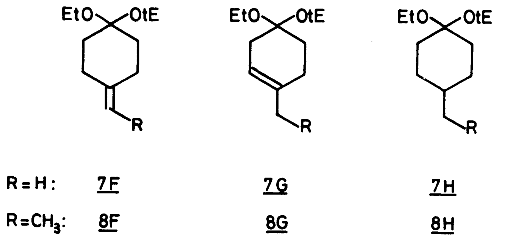

Fig. 3

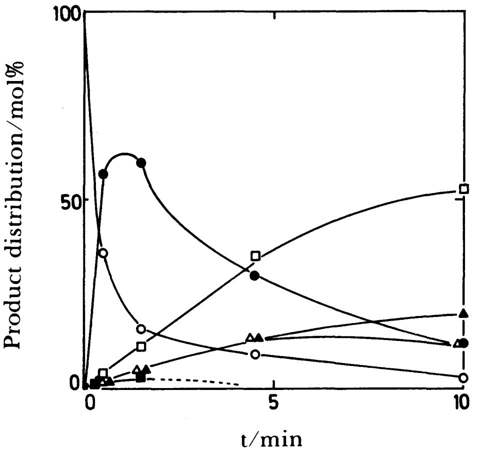

Fig. 4. Product distribution in hydrogenation of 4-ethylidenecyclohexanone (**8**) over Pd catalyst in ethanol. ○: **8**, ▲: 4-ethylcyclohexanone (**8B**), ■: 4-ethyl-3-cyclohexenone (**8D**), ●: 4-ethylidenecyclohexanone diethyl acetal (**8F**), △: 4-ethyl-3-cyclohexenone diethyl acetal (**8G**), □: 4-ethylcyclohexanone diethyl acetal (**8H**).

nevertheless, interesting that the formation of the acetal occurs faster than the hydrogenation of the olefin. Acetal formation is an acid-catalyzed reaction; therefore it may be considered that palladium, rhodium, and ruthenium black catalysts tend to have ionized hydrogens on the surfaces of these metals.[9]

In anticipation of a more preferential reduction of the ketone group of the nonconjugated enones, we also examined the hydrogenation of **5** and **6** over Raney nickel, cobalt, and cobalt black catalysts treated with alkali and carbon monoxide (Table 3). Selectivity to the unsaturated alcohols varied greatly with the additives over cobalt and nickel catalysts. When the catalysts were treated with alkali, the amount of **5B** over Raney cobalt and of **6B** over Raney nickel increased compared with that over the untreated catalysts, respectively. However, the treatment of carbon monoxide for catalysts indicated an opposite and marked effect to that of alkali. The double bond of **6** was selectively reduced to give **6A** over Raney nickel treated with carbon monoxide. When cobalt was treated with carbon monoxide in the hydrogenation of **6**, the characteristics of cobalt, which proceed with the preferential reduction of the ketone group, was completely missing.

Since alkali has a promoting effect on the ketone reduction, the hydrogenation of **3** was examined over Raney cobalt and nickel catalysts which were treated with sodium and potassium hydroxides. However, the chemo-selectivity for **3** was not altered by the treatment of alkali. Gradeff and Formica achieved a preferential reduction of the ketone group in trialkylated olefinic ketones. They have obtained the corresponding unsaturated alcohol using a chromium-promoted Raney nickel catalyst in the presence of a strong inorganic base, triethylamine, and small amounts of water in methanol solvents.[17] The amounts of **5B** and **6B** increased similarly to the results of Gradeff and Formica when the catalysts were treated with alkali (Table 3). The function of alkali in the promotion on the ketone reduction is not always obvious. It may increase the enol content, or change the product-determining step by altering the adsorbability of the substrate.[18]

Table 3. Effect of Modification of Cobalt and Nickel Catalysts in Hydrogenation of Enones **5** and **6**[a]

Enone	Catalyst	Modification (mmol)	Product[b]/mol% A	B	C
5	Co	——	61	22	17
	Co	NaOH (1)[c]	59	30	11
	Co	KOH (1)	42	42	16
	Ni	——	100	0	0
6	Co	——	(2)[d]	(96)	(2)
	Co	NaOH (0.1)[e]	(0)	(100)	(0)
	Co	CO (0.001)	(100)	(0)	(0)
	Ni	——	61	10	29
	Ni	NaOH (0.1)	34	37	29
	Ni	NaOH (1)	6	88	6
	Ni	NaOH (2)	5	74	21
	Ni	Reflux (CO)[f]	94	2	4

a) Substrate, 0.5 mmol; Raney Ni and Co, 500 mg; Co-black, 1000 mg; Solvent(ethanol), 5 ml. Values are the composition (mol.%) 50% of substrate was consumed. Enones were hydrogenated in ethanol in terms of modification of catalyst. b) See footnote b in Table 1. c) Added ca. 60% solution of NaOH or KOH in water then stirred for 0.5 h at ambient temperature under hydrogen atmosphere. d) Values in parentheses indicate the product ratios over Co-black catalyst. e) Introduced CO, then stirred under the same conditions as alkali. f) Refluxed in ethanol for 2 h under nitrogen atmosphere; when Ni is refluxed in ethanol, CO is adsorbed over catalyst.

Carbon monoxide has no promoting effect on ketone reduction, and the apparent rate of the hydrogenation over a catalyst treated with carbon monoxide decreases compared to an unmodified catalyst. When Raney nickel refluxed in ethanol was used in the hydrogenation of **6**, **6A** increased in a similar manner as a cobalt catalyst treated with carbon monoxide. Ethanol is decomposed to carbon monoxide and methane by refluxing over Raney nickel.[19] It has been known that the amount of the adsorbed hydrogen on nickel pretreated with carbon monoxide is larger than that on an unpoisoned catalyst.[20] Similarly, the adsorption of pyridine on nickel–silica can be promoted if nickel is pretreated with carbon monoxide.[21] Sheets and Hansen considered that if a strong electron withdrawing species like carbon monoxide is already present on the surface of a catalyst, the formation of a coordinated pyridine can be promoted owing to the electron defficiency of the catalyst surface.[22] This suggests that the absorbed state on cobalt and nickel catalysts treated with carbon monoxide is different from that on untreated ones; it may be responsible for the disappearance of the characteristics proceeding with the preferential reduction of the ketone group.

Experimental

All boiling points are uncorrected. ^{1}H and ^{13}C NMR spectra were obtained with either a JEOL JNM-MH100 or a JEOL-JNM-FX100 spectrometer. The frequency was 100 MHz for ^{1}H NMR and 25 MHz for ^{13}C NMR spectra. All IR spectra were obtained with a JASCO A-3 spectrometer as neat samples. Mass spectra were taken at 70 eV on a JEOL JMS-D300 GC/MS spectrometer.

Materials. 5-Hexen-2-one (**3**) and 6-methyl-5-hepten-2-one (**6**) were commercially available: **3** and **6** were obtained from Tokyo Kasei Kogyo and used after distillation: **3**, bp 126 °C/755 mmHg (1 mmHg=133.322 Pa); **6**, bp 73 °C/18 mmHg. The preparation of 5-methyl-5-hexen-2-one (**4**) is described hereinafter. By use of the method of Jones and Sondheimer,[23] 25 g of 2,5-hexanediol, 164 ml of dry pyridine, 84 g of benzoyl chloride, and 400 ml of dry chloroform gave a 48% yield of 2,5-hexanediol monobenzoate: bp 143—147 °C/1.8 mmHg. The monobenzoate (44.4 g) was oxygenized by pyridinium chlorochromate (PCC) in dichloromethane,[24] affording a 79% yield of 5-benzoyloxy-2-hexanone: bp 130 °C/0.65 mmHg; IR (neat) 1720 (s), 1605 (w), 1590 (w), 1495 (w), 1455 (w), 1320 (m), 1280 (s), 1030 (m), 715 (s). 5-Benzoyloxy-2-methyl-1-hexene was prepared by the Wittig reaction of 5-benzoyloxy-2-hexanone using methylsulfinylmethanide (yield: 70%),[25] a following hydrolysis gave a 50% yield of 5-methyl-5-hexen-2-ol (**4B**). 5-Benzoyloxy-2-methyl-1-hexene: bp 150—155 °C/20 mmHg; IR (neat) 1720 (s), 1650 (w), 1600 (w), 1585 (w), 1450 (m), 1315 (m), 1275 (s), 1115 (m), 1030 (m), 890 (m), 710 (s). **4B**: bp 68—69 °C/20 mmHg; IR (neat) 3350 (s, br), 1650 (m), 1378 (m), 890 (m). A 70% yield of **4** was obtained by the oxidation of **4B** using PCC. **4**: bp 60—62 °C/20 mmHg; IR (neat) 1720 (s), 1660 (m), 1360 (m), 1162 (m), 895 (m); ^{1}H NMR ($CDCl_3$) δ=1.72 (3H, s), 2.15 (3H, s), 2.40 (4H, m), 4.69 (2H, dd); ^{13}C NMR ($CDCl_3$) δ=22.57, 29.77, 31.59, 41.86, 110.17, 144.34, 207.92; MS *m/z* 112 (M^+, 13), 97 (42), 69 (81), 55 (28), 43 (100), 41 (98) 39 (35), 28 (25). Found: C, 74.90; H, 10.81. Calcd for $C_7H_{12}O$: C, 74.95; H, 10.78.

5-Hepten-2-one (**5**) was prepared by the method of Schechter, Green, and LaForge.[26] **5** was a mixture of cis and trans isomers (cis:trans=14:86). **5**: bp 140—150 °C/755 mmHg (yield: 54%); IR (neat) 1720 (s), 1360 (m), 1165 (m), 980 (m); ^{13}C NMR ($CDCl_3$, trans isomer) δ=17.85, 26.89, 29.88, 43.50, 125.81, 129.51, 208.18; MS *m/z* 112 (M^+, 50), 97 (43), 69 (46), 58 (36), 55 (68), 43 (100), 41 (98), 39 (44), 28 (36).

4-Methylenecyclohexanone (**7**) and 4-ethylidenecyclohexanone (**8**) were prepared by a modification of the synthetic method of **4**.[23—25] **7**: bp 65 °C/27 mmHg; IR (neat) 1720 (s), 1650 (w), 1440 (m), 1142 (m), 900 (m), 792 (w); ^{1}H NMR ($CDCl_3$) δ=2.48 (8H, bs), 4.89 (2H, s); ^{13}C NMR ($CDCl_3$) δ=33.14, 41.57, 110.73, 144.34, 210.65; MS *m/z* 110 (M^+, 100), 82 (85), 81 (71), 68 (51), 55 (38), 54 (98), 53 (61), 41 (48), 40 (31), 39 (82), 28 (62). Found: C, 76.53; H, 9.21. Calcd for $C_7H_{10}O$: C, 76.32; H, 9.15. **7B**: bp 78 °C/16 mmHg; IR (neat) 3350 (s. br), 1650 (m), 1070 (m), 895 (m); ^{13}C NMR ($CDCl_3$) δ=31.88, 35.87, 68.98, 107.70, 147.74. **8**: bp 78 °C/20 mmHg; IR (neat) 1720 (s), 1442 (m), 1150 (m), 950 (w), 825 (w), 780 (w), 700 (w); ^{1}H NMR ($CDCl_3$) δ=1.65 (3H, d), 2.43 (8H, bs), 5.41 (1H, q); ^{13}C NMR ($CDCl_3$) δ=13.12, 25.77, 34.14, 40.69, 41.77, 119.36, 134.50, 211.73; MS *m/z* 124 (M^+, 87), 82 (39), 81 (35), 68 (27), 67 (100), 54 (37), 41 (32), 39 (38), 28 (26). Found: C, 77.41; H, 9.74. Calcd for $C_8H_{12}O$: C, 77.37; H, 9.74. **8B**: bp 83—87 °C/14 mmHg: ^{13}C NMR ($CDCl_3$) δ=12.83, 24.57, 33.47, 35.40, 36.40, 69.89, 116.33, 137.70; MS *m/z* 126 (M^+, 7), 108 (50), 93 (79), 79 (100), 67 (38), 41 (32), 39 (26).

Catalysts. Unsupported metal catalysts were prepared by reducing the corresponding metal hydroxides (Ru, Rh, Pd, Ir) or oxides (Pt, Os) with hydrogen in water at atmospheric or elevated pressure using a method which is similar to that described by Nishimura[27] and Tanaka.[11] Care was taken to removal alkaline or acidic impurities with reductions and washings. W-4 Raney Ni and Co were prepared as described earlier.[10] Reduced Ni and Co were prepared by the reduction of NiO and CoO which were obtained from $Ni(NO_3)_2$ and $Co(NO_3)_2$ in hydrogen atmosphere at 350 °C.

Hydrogenation. All hydrogenations were carried out in a 50 ml round glass bottle with a silicone rubber stopper at room temperature (20—25 °C) and approximately atmospheric pressure (1—1.05 atm). A high purity hydrogen gas was used without further purification. In the reaction vessel a weighed sample of catalyst (5 mg for noble metals; 500 mg for Raney Ni and Co under wet conditions; 200 mg as NiO for Ni-black; 1000 mg as CoO for Co-black) was placed along with 5 ml of purified cyclohexane or 99% ethanol, and then the vessel was flushed with hydrogen. The catalyst was stirred magnetically with hydrogen in a solvent for 0.5—1 h; the substrate (0.5 mmol) to be hydrogenated was then added with a microsyringe through a silicone rubber stopper.

Product Analysis. The reaction was followed volumetrically by measuring the hyrogen consumption and also followed gas-chromatographically by analyzing aliquots of the reaction mixture at appropriate time intervals. The reaction mixture was taken into a microsyringe through the silicone rubber stopper during the course of hydrogenation. The gas chromatography was performed on Hitachi F-6 and 164 instruments equipped with a flame ionization detector using nitrogen as the carrier gas. The products were analyzed on a 45 m×0.25 mm Goley column of PEG 400 at 60 °C for **3**, and on a 45 m×0.25 mm Goley column of PEG 4000 at 80—90 °C for **4**, **5**, and **6** or at 120—140 °C for **7** and **8**. The peaks were identified by a comparison of their retention times with those of authentic samples.

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12) A 37% of 5-methyl-4-hexen-2-one (**4D**) and a 27% of 4-methyl-3-cyclohexenone (**7D**) were formed besides saturated ketones from **4** and **7** over Pd at the 50% of conversion. **4D** was also present in trace amounts over Ru, Rh, and Pt.

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