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Hydrogenation and Hydrogenolysis. XVI.[1] The Reactions of Two Isomeric Enol Ethers of 3-Methylcyclohexanone over Platinum Group Metals

Shigeo NISHIMURA,* Kunihiro KAGAWA, and Nobuo SATO

Department of Industrial Chemistry, Tokyo University of Agriculture and Technology, Koganei, Tokyo 184

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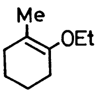
The two isomeric enol ethers of 3-methylcyclohexanone, 1-ethoxy-3-methyl-, and 1-ethoxy-5-methylcyclohexenes (**5** and **6**), have been hydrogenated in ethanol with six platinum group metals as catalysts. Palladium, rhodium, and platinum efficiently catalyzed the addition of ethanol to the enol ethers to give the corresponding acetal, while iridium and ruthenium catalyzed it only slightly. Osmium was moderately active for the acetal formation. Extensive isomerization between **5** and **6** occurred over all catalysts. In addition, isomerization to an allyl ether, 3-ethoxy-1-methylcyclohexene (**9**), was observed with **5** over the metals other than palladium. Hydrogenation of **5** and **6** with palladium gave the *trans*-ether predominantly. With the other metals, the *cis*-ether was formed in large excess from **5** and the *trans*-ether in slight excess from **6** at the initial stage of hydrogenation. Hydrogenolysis of the ethoxyl group occurred extensively over platinum but only slightly with palladium and ruthenium. These results are compared with those obtained with the corresponding dimethylcyclohexenes and allyl ether **9**.

Previously we have studied the hydrogenation of the enol ethers of 2- and 4-methylcyclohexanone **1**, **2**, and **3** with platinum group metals as catalysts.[2,3] Hydrogenation of **3** in ethanol was accompanied by formation of the corresponding acetal which depended on the catalyst metal employed. Palladium, platinum, and rhodium catalyzed the acetal formation efficiently, while ruthenium, osmium, and iridium were only poor catalysts for this reaction. Hydrogenolysis of the ethoxyl group occurred extensively over platinum, while it was very slight with palladium and ruthenium. The order of activity of the platinum metals toward hydrogenolysis has been explained in terms of the activity of ionized adsorbed hydrogen on the catalyst surface which was estimated by the activity for the acetal formation and of the strength of olefin adsorption which was assumed to increase with decreasing activity for olefin isomerization. With palladium enol ethers **1**, **2**, and **3** all gave saturated *cis*-ethers with high stereoselectivity. This stereochemistry of hydrogenation has been explained on the basis of the selective formation of the half-hydrogenated states with the adsorption bond at the carbon bearing the ethoxyl group, together with the assumption that the product-controlling step is formation of the saturated ethers. Selective formation of such half-hydrogenated states has been supported by the fact that isomerization of enol ether **1** occurred extensively to the isomeric enol ether **2** but not to an isomeric allyl ether **4**.[3)]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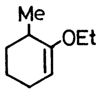
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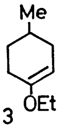
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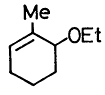
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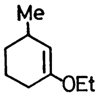
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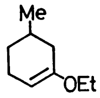
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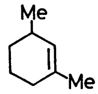
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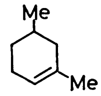
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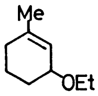
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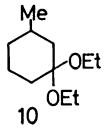
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This paper reports the hydrogenation of the two isomeric enol ethers of 3-methylcyclohexanone, 1-ethoxy-3-methyl- and 1-ethoxy-5-methylcyclohexenes (**5** and **6**) that has been studied in ethanol with six platinum group metals as catalysts. Since the enol ethers were extensively isomerized to each other during hydrogenation, characteristic behaviors of **5** and **6** were observable only at the initial stage of hydrogenation. For this reason, the selectivities of platinum metals for acetal formation, isomerization, stereochemistry of hydrogenation and hydrogenolysis are discussed on the results at the initial stage of hydrogenation which were obtained by extrapolation. Further, the results have been compared with those obtained with the corresponding dimethylcyclohexenes **7** and **8** for isomerization and stereochemistry of hydrogenation and also with those on an isomeric allyl ether **9** with respect to hydrogenolysis.

Experimental

*1-Ethoxy-3-methyl- and 1-Ethoxy-5-methylcyclohexenes (**5** and **6**).* A mixture of **5** and **6** was prepared by heating 3-methylcyclohexanone diethyl acetal with a catalytic amount of ammonium dihydrogenphosphate.[4)] Bp 171.5—172.5 °C. Pure **5** and **6** were obtained by purification on a preparative GLPC employing a column of PEG 20M. Enol ether **5**: n_D^{25} 1.4533; ^{1}H NMR (60 MHz, CCl_4), $\delta=0.93$ (d, 3H, $>CHC\underline{H}_3$), 1.19 (t, 3H, $OCH_2C\underline{H}_3$), 1.33—2.33 (m, 7H, saturated ring protons), 3,52 (q, 2H, $OC\underline{H}_2CH_3$) and 4.27 ppm (d, 1H, olefinic proton). Enol ether **6**: n_D^{25} 1.4514; ^{1}H NMR (60 MHz, CCl_4), $\delta=0.93$ (d, 3H, $>CHC\underline{H}_3$), 1.19 (t, 3H, $OCH_2OC\underline{H}_3$), 1.33—2.33 (m, 7H, saturated ring protons), 3.52 (q, 2H, $OC\underline{H}_2CH_3$) and 4.38 ppm (t, 1H, olefinic proton). The structures of **5** and **6** were determined from their NMR specta: the olefinic proton of **5** showed a doublet at a higher field (4.27 ppm) while that of **6** gave a triplet at a lower field (4.38 ppm). The structures thus assigned were supported by the occurrence of the isomerization of **5** to the allyl ether **9** and its absence with **6** during hydrogenation, and also by the similarities in stereochemistry of hydrogenation of **5** and **6** to the corresponding dimethylcyclohexenes **7** and **8**, respectively, as observed over the metals of low isomerization (Ru, Os, Ir, Pt) (see Table 3).

*1,3- and 1,5-Dimethylcyclohexenes (**7** and **8**).* **8** was obtained by purification on a preparative GLPC of a mixture of **7** and **8** prepared by dehydrating 1,3-dimethylcyclohexanol with iodine.[5] **7** was prepared by pyrolysis of 2,6-dimethylcyclohexanol acetate at 400 °C[6] followed by purification on a preparative GLPC.

*3-Ethoxy-1-methylcyclohexene (**9**).* This is a known compound and was prepared by the method of Spangler and Hennis[7] followed by purification on a preparative GLPC.

All the compounds described above were obtained in greater than 99% purity by GLPC analysis.

Solvent. S. S. G. ethanol of Wako Pure Chemical Industries was dehydrated by refluxing with sodium metal and diethyl phthalate.[8]

Catalysts. All the catalysts used in this study were unsupported metals and prepared by reducing the corresponding metal hydroxides (Ru, Rh, Pd, Ir, Pt) or oxide (Os) with hydrogen in water at atmospheric or high pressure.[2,9] Great care was taken to remove traces of alkaline or acidic substances with repeated reductions and washings.[9]

Hydrogenations. All hydrogenations were carried out in a small glass bottle at 25 °C and atmospheric pressure. A high purity hydrogen gas (Nippon Sanso Co.) was used without further purification. The catalyst (1.5—4 mg) was shaken with hydrogen in ethanol (2 ml) for the time which differed with the catalyst metal used (15—20 min for Pd, Pt, and Rh; 1 h for Ir and Os; 2 h for Ru), and then the substance to be hydrogenated (0.04 ml) was added with a microsyringe through a silicone rubber stopper.

Product Analysis. The reaction mixture was taken into a microsyringe through the silicone rubber stopper during the course of hydrogenation and subjected to GLPC analysis (column: PEG 20 M, programmed at 2°C/min in the temperature range of 50 to 160 °C for the products from **5**, **6**, and **9**; TXP at 60 °C for the products from **7** and **8**). The peaks of *cis*- and *trans*-1-ethoxy-3-methylcyclohexanes were identified by comparison with those of a *cis*-rich sample of the ethers which was obtained by ethylating a *cis*-rich 3-methylcyclohexanol with sodium hydride and ethyl iodide in tetrahydrofuran.[10] The peak at a longer retention time was found to be that of the *cis* isomer. Other peaks were identified by comparison of their retention times with those of authentic samples.

Results and Discussion

In Figs. 1 and 2 are shown the changes in composition of reaction mixture during the course of hydrogenation of enol ethers **5** and **6** in ethanol. All hydrogenations were performed at 25 °C and atmospheric pressure with unsupported metals as catalysts. Although ethanol used as the solvent had been carefully dehydrated, some amounts of a hydrolysis product, 3-methylcyclohexanone, was formed together with the acetal **10** over rhodium and palladium and to a lesser extent over platinum. Since the hydrolysis is considered to be related to the acetal formation,[2,11] the ketone formed is included in the acetal in the figures. Usually hydrogenation of the acetal proceeded very slowly and did not go to completion.

Acetal Formation. As seen in Figs. 1 and 2, the extent of the acetal formation greatly depends on the catalyst metal used and to some extent on the enol ether hydrogenated as well. Table 1 summarizes the ratios of the acetal formed to the enol ether hydrogenated at initial stage of hydrogenation. The tendency of the platinum metals for the acetal formation is consistent in both the enol ethers. Thus palladium, rhodium and platinum are definitely more active for the acetal formation than the other platinum

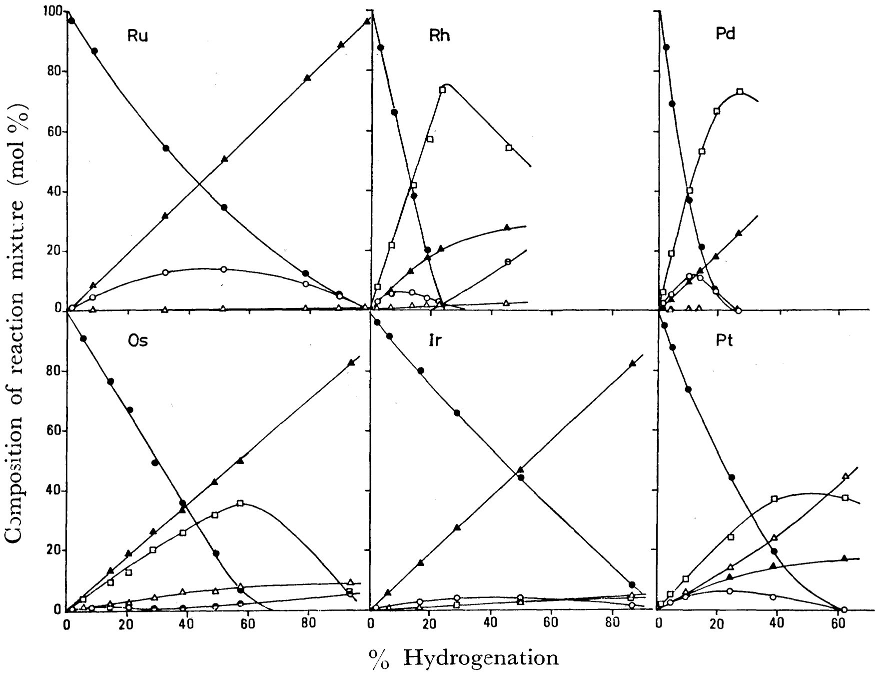


Fig. 1. Hydrogenation of enol ether **5** in ethanol.
●: Enol ether **5**, ○: enol ether **6**, ▲: saturated *cis*- and *trans*-ether, △: methylcyclohexane, □: acetal **10** and 3-methylcyclohexanone, ⊖: 3-methylcyclohexanol.

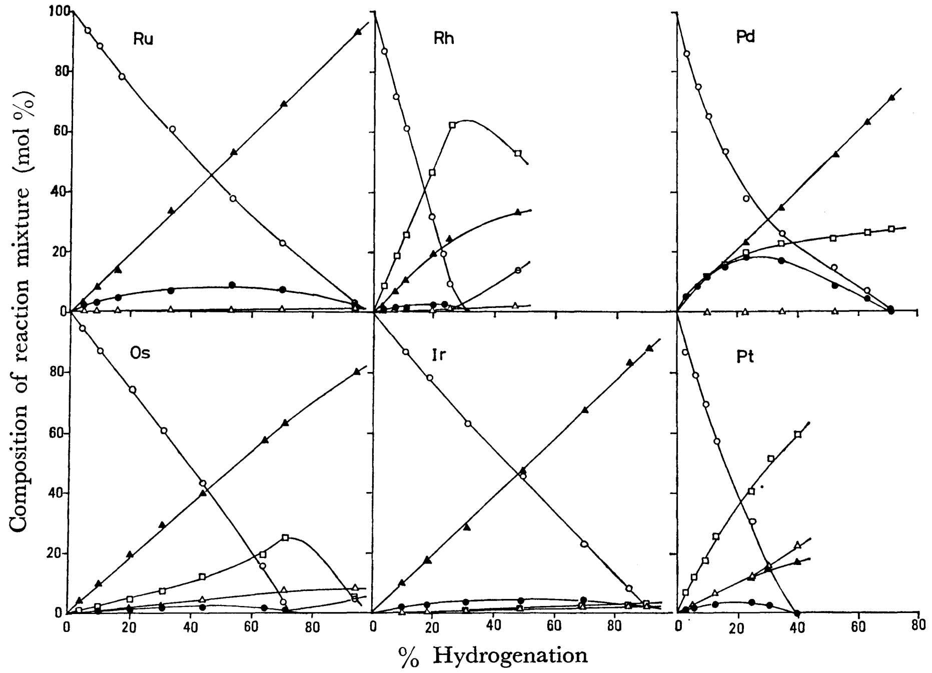


Fig. 2. Hydrogenation of enol ether **6** in ethanol. For indications, see the footnotes in Fig. 1.

Table 1. Initial ratio of acetal formation to hydrogenation with enol ethers **5** and **6**a)

Catalyst	Enol ether **5**	 **6**
Ru	0	0
Rh	3.0	2.5
Pd	4.5	2.0
Os	0.70	0.25
Ir	0.05	0.06
Pt	1.2	2.4

a) Hydrogenation including hydrogenolysis.

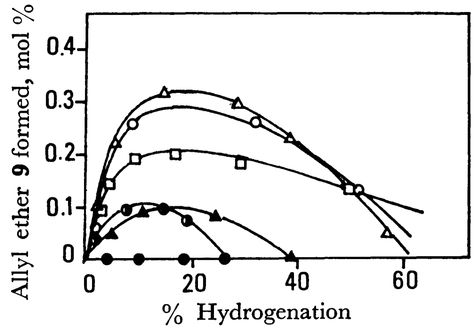


Fig. 3. Isomerization of enol ether **5** to allyl ether **9**. △: Os, ○: Ru, □: Ir, ◐: Rh, ▲: Pt, ●: Pd.

metals. Iridium and ruthenium cause little or no acetal formation. Osmium is moderately active for this reaction and lies between the two extreme groups of the metals. The acetal formation is very sensitive to the preparations of catalyst metals, and therefore great care was taken to remove traces of alkaline or acidic substances according to the procedures described previously.9) The trend of the platinum metals shown in Table 1, however, is in good agreement with that reported previously with enol ether **3** except in a few cases. The acetal formation is an acid-catalyzed reaction and therefore it is considered that the high activity of palladium, rhodium, and platinum results from the presence of ionized hydrogen on the surfaces of these metals, as discussed previously.2,11)

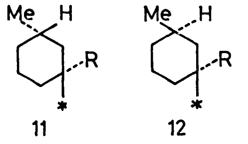
Isomerization. As previously shown with enol ethers **1** and **2**, isomeric enol ethers are very liable to isomerization to each other.3) Enol ethers **5** and **6** also isomerized extensively to each other as seen in Figs. 1 and 2. In addition, with enol ether **5** the isomerization to an isomeric allyl ether **9** was observed over the metals other than palladium (see Fig. 3), although it was much less extensive than the isomerization to the isomeric enol ether. The isomerization of an enol ether to an allyl ether as observed here could not be detected previously in the hydrogenation of enol ether **1**.3) The initial ratios of isomerized product to enol ether hydrogenated are summarized in Table 2. The comparable data obtained with the corresponding cycloolefins **7** and **8** are also included in Table 2. Although the observed isomerization of enol ethers might be decreased by the acetal formation, it is seen that isomerization occurs much more extensively in the enol ethers than in the cycloolefins. With palladium, however, isomerization in the cycloolefins was as much or even more extensive. It is to be noted that isomerization occurs more easily from **5** to **6** than from **6** to **5**. Similar trend is also seen with cycloolefins **7** and **8**. It appears that more isomerization in **5** and **7** than in **6** and **8** may be related to the stereochemistry of hydrogenation of these compounds. As will be described later, with most catalysts both **5** and **7** give much greater amounts of *cis* isomers than **6** and **8**. If isomerization between **5** and **6** or **7** and **8** occurs *via* the

Table 2. Initial ratio of isomerization to hydrogenation with enol ethers **5** and **6**[a] and with corresponding cycloolefins **7** and **8**

Catalyst	Enol ether			Cycloolefin	
	5		**6**	**7**	**8**
	Isomer to **6**	Isomer to **9**	Isomer to **5**	Isomer to **8**	Isomer to **7**
Ru	0.52	0.044	0.34	0.052	0.026
Rh	1.05	0.025	0.20	0.18	0.044
Pd	2.2	0.0	1.8	3.0	1.9
Os	0.16	0.051	0.046	0.035	0.028
Ir	0.34	0.038	0.29	0.043	0.022
Pt	0.76	0.010	0.29	0.055	0.010

a) Hydrogenation including hydrogenolysis.

common half-hydrogenated states **11** and **12**, the one which will lead to the formation of *cis* isomers on further hydroegnation (**11**) is considered to be more unstable than that which will give rise to *trans* isomers (**12**), as presumed from the conformations shown in Fig. 4. Accordingly, the reversal of the half-hydrogenated states leading to isomerization may be expected to occur more easily in **11** than in **12**. More isomerization in **5** and **7** than in **6** and **8** may be accounted for by considering a more significant contribution of the half-hydrogenated state **11** in **5** and **7**.



R = OEt or Me

The ratio of the isomerizations **5** to **6** and **5** to **9** is informative on the nature of catalyst metals. It increases in the order: Os (3.1)<Ir (8.9)<Ru (12)≪ Rh (42)<Pt (76)<Pd (∞). It is pointed out that the metals which are active for acetal formation (Rh, Pt, Pd) isomerize **5** very selectively to the isomeric enol ether **6**. It is further noted that isomerization to **6** is three times more extensive than isomerization to **9** even over osmium which causes the latter isomerization more extensively than any other metals investigated. The selective isomerization of enol ethers is probably directed by the electron-releasing ethoxyl group which will force to form the half-hydrogenated state with an adsorption bond at the carbon bearing the ethoxyl group. The fact that the selectivity is especially high with platinum and palladium is consistent with the observation by Teratani and Takagi[12,13] that deuteration of 4-*t*-butyl-1-methoxycyclohexene gave the exchanged products with deuterium atoms at C_2 and C_6 but no deuterium at C_3 and C_5 in the cases of platinum and palladium.

Stereochemistry of Hydrogenation. Initial *cis*/*trans* isomer ratios of the saturated ether from hydrogenation of **5** and **6** are shown in Table 3, in comparison with those obtained with the cycloolefins **7** and **8**.

Table 3. Initial *cis*/*trans* isomer ratio of saturated product from hydrogenation of enol ethers **5** and **6** and corresponding cycloolefins **7** and **8**

Catalyst	Compound hydrogenated			
	5	**6**	**7**	**8**
Ru	5.3	0.69	11	0.70
Rh	1.4	0.26	3.0	0.85
Pd	0.26	0.18	5.2	4.2
Os	12	0.89	12	0.80
Ir	9.0	0.72	8.2	0.73
Pt	3.0	0.58	4.2	0.81

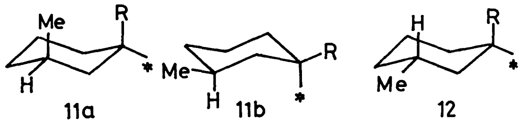


Fig. 4. Conformations of the half-hydrogenated states **11** and **12** (R=OEt or Me).

The results with palladium are characteristic in that both **5** and **6** give the *trans*-ether predominantly and, in contrast, the *cis* isomer is formed from both **7** and **8** with high selectivity. Previously it was shown that hydrogenation of the enol ethers **1**, **2**, and **3** with palladium give the *cis*-ethers with high stereoselectivity. The results have been explained on the basis of the preferential formation of the half-hydrogenated states with adsorption bonds at the carbons carrying the ethoxyl group, together with the assumption that the product-controlling step is formation of the saturated ethers. Application of the same explanation to the hydrogenation of enol ethers **5** and **6** expects a predominant formation of the *trans*-ether from both **5** and **6**, since the half-hydrogenated state leading to the *trans*-ether (**12**, R=OEt) will be more stable than that producing the *cis*-ether (**11**, R=OEt). The results shown in Table 3 are in accord with this expectation and may give further support for the explanation made previously for the stereochemistry of hydrogenation of enol ethers **1**, **2**, and **3**.

The predominant formation of the *cis* isomer in the cycloolefins **7** and **8** with palladium is consistent with the results by other investigators.[14)] In these cases the stereochemistry of hydrogenation has been explained by assuming that the stability of the half-hydrogenated states decreases with increasing steric requirement at the adsorbed carbon.[14,15)]

As in the case of palladium, the selective formation of the half-hydrogenated states **11** and **12** from **5** and **6** may also be considered over the other metals, as has been indicated by the extensive isomerization between **5** and **6**. However, in contrast to palladium, the stereochemistry of hydrogenation is not similar for **5** and **6**. In general the *cis*-ether is formed in large excess from **5** while the *trans*-ether is produced in slight excess from **6**. Further it should be noted that the stereochemistry is very similar for **5** and **7** and for **6** and **8**. These results suggest that the product-controlling step may be the same for the enol ethers and the cycloolefins, probably it being either adsorption of the substrates or formation of half-hydrogenated

TABLE 4. INITIAL AMOUNT OF HYDROGENOLYSIS WITH ENOL ETHERS **5** AND **6** AND WITH ALLYL ETHER **9** (mol %)[a]

Catalyst	Compound hydrogenated		
	5	**6**	**9**
Ru	0.4	1.2	1.6
Rh	6.5	4.4	9.8
Pd	3.0	0.2	18
Os	13	8.1	4.5
Ir	6.0	2.7	2.5
Pt	50	43	21.5

a) Proportion of hydrogenolysis in mol % in hydrogenation and hydrogenolysis.

states.[16)] The stereoselective formation of *cis* isomers from **5** and **7** may be a result of a steric interaction between the methyl group at the allylic position and the catalyst surface, because the methyl group is considered to be in a quasi-axial conformation and may increase the addition of hydrogen from the opposite side to the methyl group.[17)] The *cis*/*trans* product ratios from **5** and **6** are rather small in the case of rhodium, although greater than with palladium. This is indicative that the rhodium catalyzed hydrogenation of enol ethers has some aspect similar to the hydrogenation with palladium.

Hydrogenolysis. The hydrogenation of enol ethers is accompanied by the hydrogenolysis of alkoxyl group which depends largely on the catalyst metal and solvent.[2)] The initial amounts of the hydrogenolysis products with **5** and **6** in ethanol are summarized in Table 4, together with the results obtained with an isomeric allyl ether **9** for comparison.

In agreement with the previous results on enol ether **3**,[2)] platinum is definitely more active for the hydrogenolysis than the other platinum metals. On the other hand, palladium and ruthenium show the least tendency toward the hydrogenolysis. Osmium, iridium and rhodium are intermediately active in this reaction. The order of the platinum metals in catalyzing the hydrogenolysis of an enol ether has previously been explained in terms of two factors: the activity of ionized adsorbed hydrogen and the strength of olefin adsorption. The former factor was estimated from the activity of catalyst metal for acetal formation in the presence of adsorbed hydrogen and for the latter it has been assumed that the strength of olefin adsorption increases with decreasing tendency of catalyst metal for olefin isomerization. On the basis of this explanation, the extremely high activity of platinum toward the hydrogenolysis can be accounted for by its high activity for acetal formation and its low activity for olefin isomerization. Only small amounts of hydrogenolysis with palladium is attributed to its extremely high acitivity for olefin isomerization which may surpass its high activity for acetal formation. Differences in the amounts of hydrogenolysis between osmium and iridium might result from their differences in acetal formation activity, rather than in olefin isomerization activity.

The factors that control the hydrogenolysis of an allyl ether appear not the same as in the hydrogenolysis of an enol ether. As seen in Table 4, the metals which are active for the hydrogenolysis of allyl ether **9** (platinum, palladium, and rhodium) are all those which are active for acetal formation (see Table 1). This result suggests that the action of ionized hydrogen may be the most important factor in the hydrogenolysis of an allyl ether. This consideration is also consistent with the fact that the hydrogenolysis of allyl and benzyl ethers is greatly promoted by the presence of acid.[18)]

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