Hydrogenation and Hydrogenolysis. XIV.[1] The Hydrogenation of Ethyl *p*-Tolyl Ether over Platinum Metal Catalysts[2]

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The hydrogenation of ethyl *p*-tolyl ether (**1**) in ethanol has been studied with five unsupported platinum metals as catalysts, mainly with the purpose of estimating the yields of ethyl 4-methyl-1-cyclohexenyl ether (**2**) formed as intermediate. Except for ruthenium catalyst, the hydrogenation of **1** in ethanol was accompanied by the formation of acetal **3**, ketone **4** and alcohol **5** which seem to be related to the formation of **2**. The amounts of **2** and the related compounds which were desorbed from the catalyst surface have been estimated to be 32—33% for Ru, 32—34% for Rh, 72—76% for Pd, 3.7% for Ir and 4.7% for Pt, by application of both kinetic and extrapolation methods. A good agreement was obtained between the results from the two methods. The proportion of hydrogenolysis increased for the catalyst metals in the order $Pd < Ru \ll Rh < Ir < Pt$. With platinum catalyst a noticeable amount of toluene was formed along with methylcyclohexane. The hydrogenation of ethyl 4-methyl-3-cyclohexenyl ether (**6**), one of the other intermediates of the hydrogenation of **1**, has also been studied in ethanol. Hydrogenolysis occurred extensively with palladium and rhodium catalysts, but much less with ruthenium, iridium and platinum catalysts. The hydrogenation route of **1** and its relation to hydrogenolysis and stereochemistry of hydrogenation of **1** are discussed with reference to the formation and hydrogenation of its intermediates.

The study of catalytic hydrogenation of aromatic compounds with reference to formation of their hydrogenation intermediates has been the subject of recent investigations.[3-6] The stereochemistry of hydrogenation of aromatic compounds has been discussed on the basis of the results of the hydrogenation of their intermediates.[3,4b-d] In most cases, the amount of intermediates detectable during the course of hydrogenation is rather small, which makes it difficult to estimate the real yields of the intermediates formed on the catalyst surface and to interpret the course of hydrogenation quantitatively.[3] However, in some cases, the rate of hydrogenation of intermediates is low and these might accumulate in considerable amount during the course of hydrogenation, as with phenols,[4] where the intermediate cyclohexanones are usually hydrogenated rather slowly and the estimation of the yields of the ketones can be made quantitatively.[4d,7] In other cases, the intermediates formed on the catalyst surface are transformed into the derivatives which are hydrogenated only slowly, or they may give products which differ from those resulting from the simple hydrogenation of parent aromatic compounds. Such cases are known, for example, in the hydrogenation of aniline in acetic acid over some platinum metals where considerable amounts of *N*-phenylcyclohexylamine accumulate as intermediate[5] and in the hydrogenation of benzene with platinum or rhodium catalyst in the presence of hydrogen fluoride where the formation of phenylcyclchexane became as much as 25% by weight of the hydrogenation products.[6]

We carried out the hydrogenation of ethyl *p*-tolyl ether (**1**) in ethanol over five platinum metals. The main purpose was to estimate the yields of the enol ether **2** formed as the intermediate, the hydrogenation of which was also studied in detail and reported in the preceding paper.[1] The hydrogenation of **1** in ethanol is accompanied by the formation of the acetal **3** which probably results from the addition of ethanol to the enol ether **2** formed on the catalyst surface. The extent of the acetal formation might depend on the nature of catalyst metals.[1] Since the rate of hydrogenation of the acetal is always lower than that of the enol ether, its formation may be advantageous for an estimation of the yield of the enol ether intermediate. The hydrogenation was studied at 25 or 50°C under the atmospheric pressure of hydrogen. The hydrogenation of ethyl 4-methyl-3-cyclohexenyl ether (**6**) was also studied, since **6** may be one of the other intermediates which are susceptible to desorption from the catalyst surface on hydrogenation of **1**. It is also of interest to observe the behavior of **6**, a homoallyl ether, towards hydrogenolysis.

Experimental

Materials. Ethyl *p*-tolyl ether (**1**) was prepared according to the procedure of Vogel[8] by the reaction of ethyl iodide with sodium *p*-methylphenoxide in absolute ethanol. Bp 82°C/17 mmHg.

Ethyl 4-methyl-3-cyclohexenyl ether (**6**) was prepared by the dehydration with iodine of 4-ethoxy-1-methyl-1-cyclohex-

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[1] Part XIII: S. Nishimura, M. Katagiri, T. Watanabe, and M. Uramoto, This Bulletin, **44**, 166 (1971).

[2] Presented partly at the 25th Symposium on Catalysis, Fukuoka, October, 1969.

[3] a) S. Siegel, G. V. Smith, B. Dmuchovsky, D. Dubbel, and W. Halpern, *J. Amer. Chem. Soc.*, **84**, 3136 (1962). b) F. Hartog and P. Zwietering, *J. Catal.*, **2**, 79 (1963). c) H. Yamamoto, H. Horiguchi, K. Noda, and T. Kwan, *Chem. Pharm. Bull.* (Tokyo), **15**, 752, 1129 (1967). d) A. W. Weitkamp, *Advan. Catal.*, **19**, 360 (1968). e) S. Nishimura, F. Mochizuki, and S. Kobayakawa, This Bulletin, **43**, 1919 (1970).

[4] a) H. A. Smith and B. L. Stump, *J. Amer. Chem. Soc.*, **83**, 2739 (1961). b) P. N. Rylander and D. R. Steele, *Engelhard Ind. Tech. Bull.*, **3**, 125 (1965). c) F. Zymalkowsky and G. Strippel, *Arch. Pharm.*, **297**, 727 (1964). d) Y. Takagi, S. Nishimura, and K. Hirota, *J. Catal.*, **12**, 214 (1967); This Bulletin, **43**, 1846 (1970).

[5] K. Ikedate, T. Suzuki, and S. Suzuki, *Nippon Kagaku Zasshi*, **88**, 972 (1967); *ibid.*, **89**, 90 (1968); K. Ikedate and S. Suzuki, *ibid.*, **90**, 92 (1969).

[6] B. F. Dannels and A. F. Shepard, *J. Catal.*, **15**, 106 (1969).

[7] F. Coussemant and J. C. Jungers, *Bull. Soc. Chim. Belges*, **59**, 295 (1950).

[8] A. I. Vogel, *J. Chem. Soc.*, **1948**, 616.

Table 1. Hydrogenation of ethyl *p*-tolyl ether (**1**) with ruthenium catalyst in ethanol[a]

Reac. time (hr)	Composition of reaction mixture, mol %									*cis/trans* ratio of **7**	Selectivity for formation of **2** and related compounds[b] (mol %)
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**		
0.08	90.0	3.1	—	—	—	0.6	5.8	—	0.6	6.3	31.0
0.22	68.0	8.8	0.1	—	—	0.8	20.0	—	2.3	4.9	27.8
0.37	52.8	11.1	0.1	—	—	0.7	32.3	—	3.0	4.8	23.7
0.55	44.4	11.6	0.1	—	—	0.6	39.0	—	4.3	4.0	21.0
0.77	32.6	11.8	0.2	—	—	0.5	49.2	—	5.8	3.7	17.8
1.25	17.8	9.4	0.2	—	—	0.3	64.9	—	7.5	3.3	
3.78	0.0	0.0	0.2	—	—	0.0	90.2	—	9.6	2.9	

a) **1** (0.2 m*l*) was hydrogenated in 10 m*l* ethanol with 25 mg of ruthenium catalyst at 25°C under the atmospheric pressure of hydrogen.

b) Given by 100 × mol (**2**+**3**+**4**+**5**)/mol (100−**1**).

anol which was obtained by the addition of methylmagnesium iodide to 4-ethoxycyclohexanone. Bp 170°C; n_D^{20} 1.4530. The structure of **6** was confirmed by the NMR spectrum obtained on a JNM-C-60HL spectrometer (Japan Electron Optics Laboratory, Co.) at 60 MHz: τ 4.75 (1H, m, vinyl proton), 6.52 (2H, q, $O\underline{CH_2}CH_3$), 6.30—6.75 (1H, m, $C\underline{H}$ adjacent to oxygen), 7.5—8.5 (6H, broad m, saturated ring protons other than at C-1), 8.36 (3H, s, 4-$C\underline{H_3}$), 8.82 (3H, t, $OCH_2\underline{CH_3}$).

Catalysts. Unsupported ruthenium, rhodium, palladium, iridium and platinum catalysts were prepared by the methods descibed in the preceding paper.[1)]

Solvent. The S. S. G. ethanol of the Wako Pure Chemical Industries was further dehydrated by refluxing with sodium metal and diethyl phthalate.[9)]

Hydrogenation. The substrate (0.2 m*l*) was hydrogenated as usual with 25—50 mg of the catalyst in 10 m*l* ethanol at 25 or 50°C under the atmospheric pressure of hydrogen. The catalyst was shaken with hydrogen for about 10 min before the addition of the substrate.

Analysis of Reaction Mixture. The reaction mixture was taken into a microsyringe through a silicone rubber stopper during the course of hydrogenation and subjected to gas chromatography. For most analyses a column of 10% PEG 20M on Chromosorb W (3 mm × 3.75 m) was used at the temperature programmed in 2°C/min for 36—100°C and in 4°C/min for 100—160°C. Under these conditions, the peaks of unsaturated ethers **2** and **6** were not separated. Since in most cases the amount of **6** in the reaction mixture was extremely small, the peak corresponding to **2** and **6** was regarded to be that of **2**. When separation of **2** and **6** was needed, a column consisting of PEG 20M and Apiezon L was used. However, complete separation of the reaction mixture was also difficult even with this column. Accordingly, a complete analysis of the reaction mixture was carried out by superposing the two gas chromatograms obtained using the two columns described above.

Results

*Hydrogenation of **1** with Ruthenium Catalyst.* Table 1 shows the change in composition of the reaction mixture during the hydrogenation of **1** with ruthenium catalyst in ethanol at 25°C. A noteworthy feature of the ruthenium-catalyzed hydrogenation is that the enol ether **2**, formed as intermediate, is hydrogenated to saturated ether **7** with little formation of acetal **3**. This result was not unexpected as addition of ethanol to **2** occurred only very slowly during the hydrogenation of **2** with ruthenium catalyst in ethanol.[1)] In Fig. 1 the varying amounts of **2** and **3** during the course of hydrogenation are plotted *versus* the conversion of **1**. The maximum amount was 12.0% at 67.4% conversion of **1**. The amount of intermediates desorbed from the catalyst surface can be calculated by means of the following equation (deduced on the reaction scheme shown below)[10)] to be 32.6% [f=0.326 in Eq. (1)].[11)]

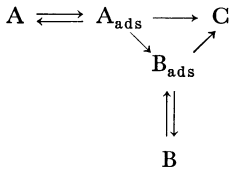
$$C_B = \frac{f}{K-1}(C_A - C_A{}^K) \qquad (1)$$

C_A: concentration of aromatic compound A when the initial concentration of A is unity.

C_B: concentration of intermediate B when the initial concentration of A is unity.

f: fraction of A that leaves the catalyst surface as B during hydrogenation.

K: a constant which depends on the relative reactivity of A and B.



The amount can also be obtained by extrapolating the varying selectivity for formation of **2** and **3** during

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[9)] L. F. Fieser, "Experiments in Organic Chemistry," 3rd Ed., Heath and Company, Boston (1955), p. 285.

[10)] Equation (1) is obtained by assuming that the hydrogenation is of first order and the function of hydrogen is the same, for A and B. For the derivation, see Ref. 7 which deals with the case where A is all transformed into C through the intermediate B and the establishment of adsorption-desorption equilibria is fast. It was shown by de Boer and van der Borg that Eq. (1) is also widely applicable to other cases [J. H. de Boer and R. J. A. M. van der Borg, *Actes Congr. Intern. Catal.*, 2ᵉ, *Paris*, 1960, p. 919 (Editions Technip, Paris, 1961)].

[11)] Approximate values of f and K can be obtained from the maximum concentration of B, $(C_B)_{max}$, and the corresponding concentration of A, $(C_A)_m$, using the following relations obtained by differentiating Eq. (1) with respect to C_A and putting the resulting expression equal to zero:

$$(C_A)_m = K^{1/1-K}; \ (C_B)_{max} = f \times K^{K/1-K}$$

The values of f and K thus obtained were corrected graphically to represent the experimental results better throughout the course of hydrogenation.

hydrogenation to the initiation, as also shown in Fig. 1. By this method we obtain a 32% yield of **2** and **3** which is in excellent accord with the value obtained above by the kinetic method. Detectable amounts of the intermediate **6** were very small, the maximum amount being only 0.8% in 32% conversion of **1** (see Fig. 1). Application of Eq. (1) to the change in the amount of **6** during hydrogenation gives the amount of **6** which leaves the catalyst surface to be 6%. The *cis*/*trans* ratio of saturated ether **7** formed decreases during the course of hydrogenation from 6.3 at an initial stage to 2.9 at an almost complete hydrogenation. The degree of hydrogenolysis is rather small with ruthenium catalyst (9.6%), but somewhat greater than that with palladium catalyst.

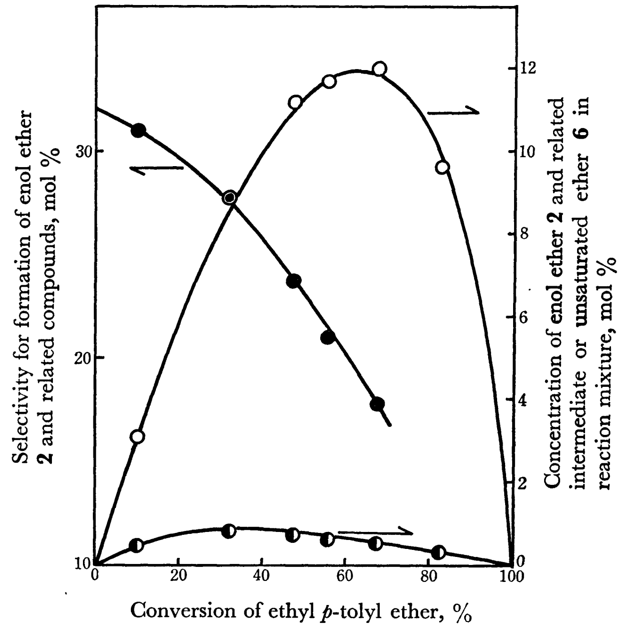
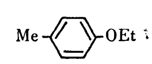


Fig. 1. Hydrogenation of ethyl *p*-tolyl ether with ruthenium catalyst in ethanol at 25°C and the atmospheric pressure of hydrogen.

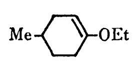
● : Selectivity for formation of enol ether **2** and related compound (see Table 1).

○ : Concentration of enol ether **2** and related intermediate in the reaction mixture. The full line shows the theoretical curve given by Eq. (1) when $K=1.0$ and $f=0.326$.

◐ : Concentration of unsaturated ether **6** in reaction mixture. The full line shows the theoretical curve given by Eq. (1) when $K=5.0$ and $f=0.060$.



(1)



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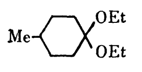

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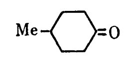

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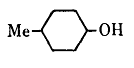

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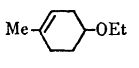

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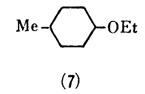

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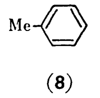

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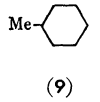

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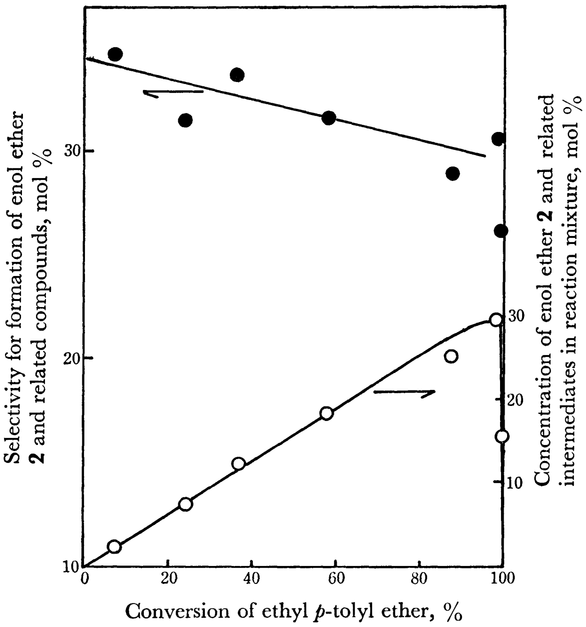

Fig. 2. Hydrogenation of ethyl *p*-tolyl ether with rhodium catalyst in ethanol at 25°C and the atmospheric pressure of hydrogen.

● : Selectivity for formation of enol ether **2** and related compounds (see footnote b in Table 1).

○ : Concentration of enol ether and related intermediates in reaction mixture. The full line shows the theoretical curve given by Eq. (1) when $K=0.02$ and $f=0.32$.

TABLE 2. HYDROGENATION OF ETHYL *p*-TOLYL ETHER(**1**) WITH RHODIUM CATALYST IN ETHANOL[a]

Reac. time (hr)	Composition of reaction mixture, mol %[b]									*cis*/*trans* ratio of **7**	Selectivity for formation of **2** and related compounds[c] (mol %)
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**		
0.12	92.5	0.9	1.4	0.3	—	—	1.5	—	3.4	21.0	34.7
0.28	75.8	1.0	5.2	1.4	—	—	5.7	—	10.9	19.3	31.4
0.67	63.2	0.7	9.0	2.7	—	—	9.2	—	15.2	14.9	33.7
1.2	41.9	1.2	13.0	4.0	0.1	—	13.6	—	26.2	12.8	31.5
1.5	12.2	1.6	18.0	5.5	0.3	—	20.1	—	42.3	11.8	28.9
1.9	0.7	2.1	20.8	6.7	0.8	—	24.4	—	44.5	11.3	30.6
2.5	0.0	0.5	6.0	1.6	17.8	—	26.3	—	48.0	9.8	25.9

a) **1** (0.2 m*l*) was hydrogenated in 10 m*l* ethanol with 25 mg of rhodium catalyst at 25°C under the atmospheric pressure of hydrogen.

b) The amount of **6** was very small and included in **2** because of incomplete separation on gas chromatography (see Experimental).

c) See footnote b, Table 1.

Table 3. Hydrogenation of ethyl *p*-tolyl ether(**1**) with palladium catalyst in ethanol[a)]

Reac. time (hr)	Composition of reaction mixture, mol %[b)]									*cis*/*trans* ratio of **7**	Selectivity for formation of **2** and related compounds[c)] (mol %)
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**		
0.7	95.9	0.3	1.5	1.1	0.1	—	1.0	—	0.3	8.6	73.2
1.4	90.0	0.6	3.7	2.1	0.1	—	2.7	—	0.8	7.3	65.0
2.4	82.8	0.8	4.6	3.6	0.1	—	7.1	—	1.0	11.0	52.9
3.4	78.8	0.9	4.6	4.6	0.1	—	9.4	—	1.6	9.4	48.1
5.4	64.8	1.1	4.9	6.2	0.1	—	20.6	—	2.3	11.2	34.9
6.4	59.3	1.0	5.0	6.5	0.1	—	25.4	—	2.7	11.4	27.7
7.6	54.1	1.1	4.8	6.2	0.1	—	30.8	—	2.9	12.2	
9.2	44.0	0.9	4.4	5.5	0.1	—	41.6	—	3.3	14.1	
10.9	36.2	0.6	4.1	5.2	0.1	—	50.4	—	3.4	14.2	

a) **1** (0.2 m*l*) was hydrogenated in 10 m*l* ethanol with 50 mg of palladium catalyst at 50°C under the atmospheric pressure of hydrogen.
b) See footnote b, Table 2.
c) See footnote b, Table 1.

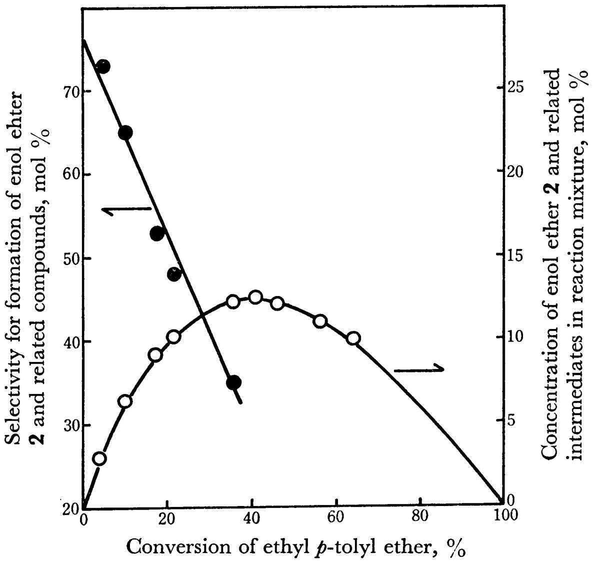

Fig. 3. Hydrogenation of ethyl *p*-tolyl ether with palladium catalyst in ethanol at 50°C and the atmospheric pressure of hydrogen.
● : Selectivity for formation of enol ether and related compounds (see footnote b, Table 1).
○ : Concentration of enol ether **2** and related intermediates in reaction mixture. The full line shows the theoretical curve given by Eq. (1) when $K=3.5$ and $f=0.72$.

*Hydrogenation of **1** with Rhodium Catalyst.* Table 2 indicates the change in composition of the reaction mixture during hydrogenation of **1** with rhodium catalyst in ethanol at 25°C. It is seen that the intermediates accumulate mostly as acetal **3** along with small amounts of enol ether **2** and ketone **4**. The ketone **4** probably is the product of the hydrolysis of **2** or **3** during hydrogenation, in spite of the fact that carefully dehydrated solvent was used. It is noteworthy that **2**, **3**, and **4** formed are scarcely hydrogenated during the hydrogenation of **1** and their sum increases almost linearly with the conversion of **1** (Fig. 2). By assuming that **3** and **4** were all formed through **2** which was produced on the catalyst surface, the amount of **2** which left the catalyst surface as itself or its derivatives can be calculated to be 32% by means of Eq. (1) (Fig. 2). Application of the extrapolation method gives a 34% yield of **2** and related compounds, as also shown in Fig. 2. When the amount of unreacted **1** approaches almost zero, hydrogenation of the accumulated intermediates seems to begin and the main product is the alcohol **5**, as indicated by a definite increase of **5** over saturated ether **7** and methylcyclohexane (Table 2).[12)] The *cis*/*trans* ratio of **7** formed is very high at the initial stage, but decreases to about 10 towards the end of hydrogenation. Hydrogenolysis occurs rather extensively with rhodium catalyst (about 45% at 58.1% conversion of **1**) and constitutes the most important hydrogenation pathway of **1**.

*Hydrogenation of **1** with Palladium Catalyst.* **1** was hydrogenated at 50°C in ethanol, the results being shown in Table 3. The main intermediates are acetal **3** and ketone **4** and they are hydrogenated further to give ether **7** as the major product. Change in the sum of **2**, **3**, and **4** during hydrogenation is shown in Fig. 3. The amount of **2** and the related intermediates which left the catalyst surface was estimated to be 72% by the kinetic method. The value of 76% was obtained for that amount by the extrapolation method (Fig. 3). Alcohol **5** was formed only slightly with palladium catalyst although the ketone was produced in considerable amount during the course of hydrogenation. This might be due to the fact that with palladium catalyst in ethanol ketone **3** is hydrogenated mostly to give **7**, rather than alcohol **5**.[13)] The *cis*/*trans* ratio of ether **7** formed is about 8 at initial stages of hydrogenation and then increases gradually to about 14 towards later stages. It is to be noted that the yield of *cis*-ether is the greatest with palladium catalyst among the platinum metals investigated. Another noteworthy feature of the palladium-catalyzed hydrogenation is that hydrogenolysis occurred only to the extent of 5.3% which is smaller than any of those obtained by the other platinum metals.

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12) The alcohol was also the main product of hydrogenation of acetal **3** with rhodium catalyst in ethanol.[1)]

13) S. Nishimura, T. Itaya, and M. Shiota, *Chem. Commun.*, **1967**, 422.

TABLE 4. HYDROGENATION OF ETHYL *p*-TOLYL ETHER(**1**) WITH IRIDIUM CATALYST IN ETHANOL[a]

Reac. time (hr)	Composition of reaction mixture, mol %[b]									*cis*/*trans* ratio of **7**	Selectivity for formation of **2** and related compounds (mol %)[c]
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**		
0.2	90.9	0.1	0.1	—	0.1	—	3.8	—	5.0	10.1	3.3
1.2	74.6	0.1	0.4	—	0.1	—	10.9	0.7	13.3	7.9	2.4
2.1	64.6	0.1	0.4	—	0.2	—	13.9	1.1	19.7	8.0	2.5
4.7	52.5	—	0.4	—	0.4	—	20.8	0.7	25.3	7.6	1.7
8.3	45.9	—	0.2	—	0.6	—	21.4	0.7	31.3	6.4	1.5

a) **1** (0.2 m*l*) was hydrogenated in 10 m*l* ethanol with 50 mg of iridium catalyst at 50°C under the atmospheric pressure of hydrogen.
b) See footnote b, Table 2.
c) See footnote b, Table 1.

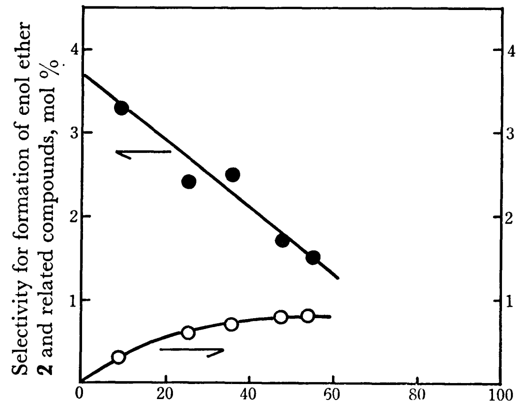

Fig. 4. Hydrogenation of ethyl *p*-tolyl ether with iridium catalyst in ethanol at 50°C and the atmospheric pressure of hydrogen.
● : Selectivity for formation of enol ether **2** and related compounds (see footnote b, Table 1).
○ : Concentration of enol ether **2** and related compounds in the reaction mixture.

*Hydrogenation of **1** with Iridium Catalyst.* Table 4 shows the results of the hydrogenation of **1** in ethanol at 50°C with iridium as a catalyst. The iridium-catalyzed hydrogenation is characteristic in that the detectable amount of **2**, **3**, **4**, and **5** is extremely small, their sum being less than 1% at maximum. The amount of **2** and related compounds was estimated to be 3.7% by the extrapolation method as shown in Fig. 4. The *cis*/*trans* ratio of **7** formed decreases slightly during hydrogenation from about 10 to 6.4. Hydrogenolysis occurred more extensively than with rhodium (59% at 54.1% conversion of **1**) and a small amount of toluene (1.1% at 35.4% conversion of **1**) was formed along with methylcyclohexane.

*Hydrogenation of **1** with Platinum Catalyst.* The results of the hydrogenation of **1** in ethanol at 50°C

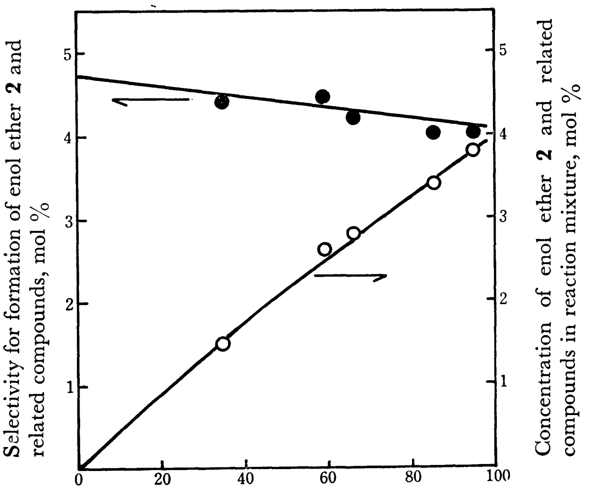

Fig. 5. Hydrogenation of ethyl *p*-tolyl ether with platinum catalyst in ethanol at 50°C and the atmospheric pressure of hydrogen.
● : Selectivity for formation of enol ether **2** and related compounds (see footnote b, Table 1).
○ : Concentration of enol ether **2** and related compounds in the reaction mixture.

TABLE 5. HYDROGENATION OF ETHYL *p*-TOLYL ETHER(**1**) WITH PLATINUM CATALYST IN ETHANOL[a]

Reac. time (hr)	Composition of reaction mixture, mol %[b]									*cis*/*trans* ratio of **7**	Selectivity for formation of **2** and related compounds[c] (mol %)
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**		
1.9	65.7	0.1	1.2	0.2	—	—	11.7	2.9	18.1	8.5	4.4
3.5	41.2	0.2	2.0	0.4	—	—	20.0	3.7	32.5	8.5	4.4
4.5	33.8	0.2	2.3	0.3	—	—	23.5	3.8	36.0	8.8	4.2
7.3	14.7	0.1	3.0	0.3	—	—	27.9	2.7	51.3	8.9	4.0
10.3	5.2	0.1	3.5	0.2	—	—	31.1	1.8	58.2	9.9	4.0

a) **1** (0.2 m*l*) was hydrogenated in 10 m*l* ethanol with 30 mg of platinum catalyst at 50°C under the atmospheric pressure of hydrogen.
b) See footnote b, Table 2.
c) See footnote b, Table 1.

TABLE 6. HYDROGENATION OF ETHYL 4-METHYL-3-CYCLOHEXENYL ETHER (**6**) WITH PLATINUM METAL CATALYSTS[a]

Catalyst	Amount (mg)	Reac. time (hr)	Reac. temp. (°C)	Composition of reac. mixture, mol %				*cis*/*trans* ratio of **7**	Proportion of hydrogenolysis[b] (mol %)
				6	**7**	**8**	**9**		
Ruthenium	25	1.0	25	0.0	97.0	—	3.0	3.0	3.0
Rhodium	25	1.0	25	0.0	76.4	—	23.6	4.0	23.6
Palladium	30	1.9	50	27.3	27.2	4.0	41.5	2.0	62.6
Iridium	25	1.7	50	0.0	96.1	0.2	3.7	4.4	3.9
Platinum	10	1.0	50	0.0	93.0	0.6	6.5	5.2	7.1

a) **6** (0.2 m*l*) was hydrogenated in 10 m*l* ethanol under the atmospheric pressure of hydrogen.
b) Given by mol 100 × mol(**8**+**9**)/mol(**7**+**8**+**9**)

are given in Table 5. The formation of acetal **3** and related compounds is small, although they are hydrogenated only with difficulty and increases almost linearly with hydrogenation. The amount of **2** and the related compounds was estimated to be 4.7% by the extrapolation method as shown in Fig. 5. The *cis*/*trans* ratio of ether **7** formed was 9.9 near the end of hydrogenation and it did not vary much during hydrogenation. It is noticeable that of the platinum metals investigated hydrogenolysis occurred to the greatest extent with platinum (about 63%). The platinum-catalyzed hydrogenation is also characteristic in that a noticeable amount of toluene is formed along with methylcyclohexane (about 4% at 72.5% conversion) and the toluene formed is hydrogenated rather slowly in the presence of **1**.[14] By applying Eq. (1) to the change in the amount of toluene during hydrogenation, the amount which left the surface was estimated to be 9.5% [f=0.095, K=0.9 in Eq. (1)].

Hydrogenation of **6** *with Platinum Metal Catalysts.* Table 6 summarizes the results of the hydrogenation of **6** in ethanol with the five platinum metals as catalysts. It is seen that hydrogenolysis occurs rather extensively with palladium and rhodium catalysts, but not so with ruthenium, iridium and platinum catalysts. In general, the *cis*-ether is formed in larger amounts than the *trans*-ether.[15]

Discussion

It is seen that the results of estimation of enol ether **2** and related compounds by the kinetic and extrapolation methods were in good agreement. Thus the amount of enol ether and related compounds which leaves the catalyst surface during hydrogenation has been estimated to be 32—33% for ruthenium, 32—34% for rhodium, 72—76% for palladium, 3.7% for iridium and 4.7% for platinum. If we assume that acetal, ketone and alcohol are all formed through enol ether **2**, the values obtained above are considered to show the amount of **2** which left the catalyst surface. Since it is not certain whether these values indicate the real yields of the enol ether intermediate formed on the catalyst surface, they might be considered to be the minimum values of the amount of the intermediate formed in hydrogenation of **1**.[17]

TABLE 7. AMOUNT OF ENOL ETHER OR KETONE INTERMEDIATE WHICH LEAVES THE CATALYST SURFACE DURING THE COURSE OF HYDROGENATION OF ETHYL *p*-TOLYL ETHER OR *p*-CRESOL

Catalyst	Amount of the intermediate, mol %	
	Enol ether in hydrogenation of ethyl *p*-tolyl ether	Ketone in hydrogenation of *p*-cresol[a]
Ru	33,[b] 32[c]	60[b]
Rh	32,[b] 34[c]	54[b]
Pd	72,[b] 76[c]	100[b]
Ir	— 3.7[c]	20[b]
Pt	— 4.7[c]	—[d]

a) Data from Ref. 4d and Y. Takagi, *Sci. Pap. Inst. Phys. Chem. Res.* (Tokyo), **64**, 39 (1970).
b) Estimated by kinetic method.
c) Estimated by extrapolation method.
d) Not estimated accurately. The maximum amount of ketone detected was only 2—2.5%.

When the present results are compared with those obtained previously on the ketone intermediate formed in hydrogenation of *p*-cresol (Table 7), it is obvious that there exists a common tendency in the selectivity of the catalyst metals for the formation of the intermediates, although the yield of enol ether is always smaller than that of ketone over the same metal. Thus, the palladium-catalyzed hydrogenation of **1** proceeds to a greater part through enol ether as intermediate, and *p*-cresol is hydrogenated quantitatively *via* the ketone intermediate over the same metal. Ruthenium and rhodium catalysts are very similar in the way they give nearly the same yield of enol ether or ketone in hydrogenation of **1** or *p*-cresol. Both iridium and platinum catalysts are characteristic in that detectable amounts of the intermediates are small in hydrogenation.

The extent of hydrogenolysis also depends on the nature of the catalyst metals and increases in the order

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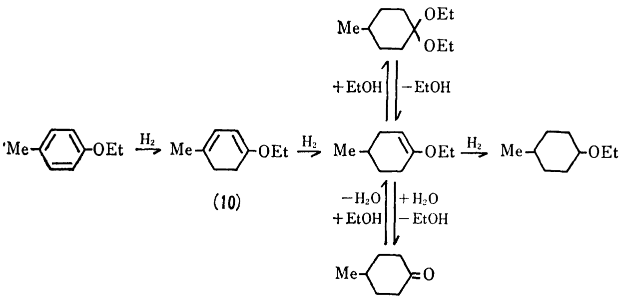
[14] Formation of toluene in as much as 21% was observed in hydrogenation of ethyl *m*-tolyl ether with platinum catalyst under the same conditions as for the hydrogenation of **1** (the results presented at the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1970).

[15] It should be noted that 1,4-dimethylcyclohexene is reported to give the product of much smaller *cis*/*trans* ratios (1.56, 0.39, 1.33 for Rh, Pd, Pt catalysts, respectively, in acetic acid at 25°C and 1 atm).[16]

[16] A. S. Hussey, T. A. Schenach, and R. H. Baker, *J. Org. Chem.*, **33**, 3258 (1968).

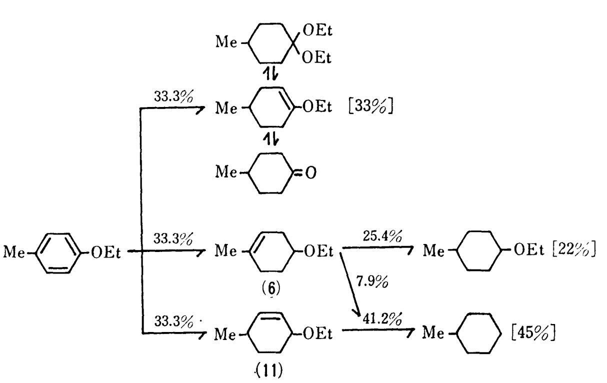
[17] Acetal formation is adventageous for the estimation of enol ether formed on the catalyst surface. As an example, the largest amount of enol ether **2** during hydrogenation was only 1.2% at 35.4% conversion on hydrogenation of **1** with rhodium catalyst in *t*-butyl alcohol in which an acetal is not formed.

Pd<Ru≪Rh<Ir<Pt. The very small amount of hydrogenolysis observed with palladium catalyst suggests that the yields of the allyl and homoallyl ether intermediates are also small, because these ethers are expected to be susceptible to extensive hydrogenolysis in further hydrogenation when produced on the catalyst surface (Table 6). This is in line with the fact that the enol ether intermediate is formed in a large yield, since enol ether is known to be hydrogenolyzed only to a slight extent with palladium catalyst.[1] The hydrogenation of **1** over palladium catalyst is fairly stereospecific, the *cis*-ether being formed in a selectivity of 93%. This result may also be related to the production of enol ether or acetal in large yield since they are known to give the saturated ether of a high *cis*/*trans* ratio.[1,18] Thus, it is suggested that the predominant hydrogenation route of ethyl *p*-tolyl ether over palladium catalyst will be the one shown in Scheme 1. The selective hydrogenation of the dihydro intermediate **10** to the enol ether **2** can be expected from similar examples.[19]



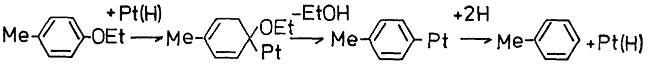
Scheme 1. Hydrogenation pathway of ethyl *p*-tolyl ether with palladium catalyst in ethanol.

It is of interest that the selectivity of ruthenium and rhodium catalysts for the formation of the enol ether intermediate is similar, and its estimated yield is very close to the value 33.3% based on the assumption that all tetrahydro derivatives of **1** are formed in equal probability. This assumption was proposed by Siegel and his coworkers[3a] for an explanation of the results of stereochemistry of the hydrogenation of isomeric xylenes with platinum catalyst. If the other two tetrahydro intermediates, the allyl and homoallyl ethers (**11** and **6**), are also produced equally in 33.3% yield according to the above assumption and the allyl ether is assumed to be hydrogenolyzed completely over rhodium catalyst, we can calculate the amount of hydrogenolysis which will occur in hydrogenation of **1**, using the value in Table 6 for the homoallyl ether. Thus the proportion of hydrogenolysis over rhodium catalyst may be evaluated to be 41.2% as shown in Scheme 2. It is seen that the value obtained experimentally (45%) is fairly close to the calculated one. Over ruthenium catalyst, the hydrogenation pathways leading to the tetrahydro derivatives may be similar to those given in Scheme 2. The small amount of hydrogenolysis over this catalyst will probably be due to its poor activity towards the hydrogenolysis of the allyl and homoallyl ethers.



Scheme 2. Hydrogenation pathways of ethyl *p*-tolyl ether over rhodium catalyst in ethanol: figures in parentheses indicate the observed composition of the reaction mixture.

The large extent of hydrogenolysis taking place with iridium and platinum catalysts must result from the formation of the allyl and enol ether intermediates, because the homoallyl ether **6** is hydrogenolyzed only to a small extent over these metals (see Table 6). With platinum the hydrogenolysis of **1** to give toluene is also responsible for the extensive hydrogenolysis. It was shown that enol ether **2** is extensively hydrogenolyzed with platinum catalyst in ethanol.[1] Since **1** is also considered to be an enol type ether, this type of hydrogenolysis is also expected to occur according to the mechanism suggested for the hydrogenolysis of **2** as shown in Scheme 3.[1] On the other hand, the saturated ether **7** formed with platinum catalyst on hydrogenation of **1** may be supposed to be formed mostly through the homoallyl ether intermediate.



Scheme 3. Hydrogenolysis of ethyl *p*-tolyl ether with platinum catalyst.

With respect to the stereochemistry of hydrogenation of **1**, the fairly high stereospecificity of palladium catalyst has been discussed. Among the other platinum metals, rhodium and platinum catalysts also give the saturated ether of rather high *cis*/*trans* ratio, as compared with the hydrogenation of *p*-xylene.[20] This is probably due to the fact that homoallyl ether **6** gives the saturated *cis* isomer in much greater yield than does 1,4-dimethylcyclohexene in the hydrogenation with these catalysts.[21] A lower yield of saturated *cis*-ether with ruthenium catalyst can also be explained in relation to the stereochemistry of hydrogenation of the intermediate unsaturated ethers, since both **2** and **6** give a saturated ether of rather small *cis*/*trans* ratio (1.45 for **2** and 3.0 for **6**).

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[18] Hydrogenation of ethyl *m*-tolyl ether in ethanol with palladium catalyst gives *trans*-ether predominantly. Similarly, 3-methylcyclohexanone diethyl acetal as well as the enol ethers derived from it also give the *trans*-ether predominantly under the same conditions (the results partly presented at the 23rd Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1970).

[19] a) J. M. Bell, R. Garrett, V. A. Jones, and D. G. Kubler, *J. Org. Chem.*, **32**, 1307 (1967). b) W. S. Johnson, *J. Amer. Chem. Soc.*, **78**, 6278 (1956).

[20] Hydrogenation of *p*-xylene with rhodium and platinum catalysts in isopropyl alcohol at 25°C under 1 atm gave the product of *cis*/*trans* ratio 2.4 and 2.3, respectively (unpublished results). *Cf.* also Ref. 3a.

[21] See Ref. 15 and Table 6.