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Hydrogenation and Hydrogenolysis. XVII.[1] The Selectivities of Platinum Group Metals in Catalytic Hydrogenation of 2-Naphthol and Tetrahydro-2-naphthols

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Catalytic hydrogenation of 2-naphthol (NL) with the six platinum metals has been studied in *t*-BuOH at 80 °C and 4—5 MPa H_2 pressure. Selectivities for formation of 1,2,3,4- and 5,6,7,8-tetrahydro-2-naphthols (*ac*- and *ar*-TLs) have been determined by application of a kinetic equation. *ar*-TL was formed more predominantly than *ac*-TL over all the metals. The hydrogenation of *ac*- and *ar*-TLs has also been studied under the same conditions for comparison. The hydrogenation of NL and *ar*-TL was accompanied by extensive hydrogenolysis to give decalins over Os, Ir, and Pt, whereas the hydrogenolysis occurred only slightly over Ru, Rh, and Pd. In general the hydrogenolysis occurred to much lesser extents with *ac*-TL. The amounts of 2-decalone formed in hydrogenation of *ar*-TL have been determined by application of the kinetic equation. The 2-decalone was the *cis* isomer only except with Pd. For formation of the *cis* products at the ring juncture, hydrogenation of *ar*-TL was highly stereoselective with Ru, Rh, Os, and Ir, while hydrogenation of *ac*-TL was the most stereoselective with Os and Ir. The course of hydrogenolysis and the stereochemistry of hydrogenation are discussed from the comparative results on NL, *ar*-TL, and *ac*-TL.

The catalytic hydrogenation of aromatic compounds has been a subject of extensive studies not only as useful synthetic routes to alicyclic compounds but also from stereochemical and mechanistic viewpoints.[2] However, compared to a large number of studies on monocyclic aromatics, the catalytic hydrogenation of polycyclic aromatics has been investigated to rather limited extent.[3] One reason for this might be difficulties in the analysis of products that are often rather complicated. As the simplest polycyclic aromatics naphthalene and its derivatives have been hydrogenated with a variety of catalysts and conditions. Particular interests have been focused on the selectivity for formation of tetrahydro intermediates and the stereochemistry of hydrogenation in formation of decahydro derivatives.[2,3] The hydrogenation of naphthols has been interested as synthetic routes to 1,2,3,4- and 5,6,7,8-tetrahydronaphthols (abbreviated to *ac*- and *ar*-tetralols) that may be starting materials for further syntheses[4] or of therapeutic importance.[5,6] The selectivity for either *ac*- or *ar*-tetralol is known to be much influenced by the catalyst employed as well as by reaction conditions and additives.[2,7] The hydrogenation has also been studied for the stereochemistry of the resulting decahydronaphthols (abbreviated to decalols).[8—14] Among the platinum metals, platinum,[8—10] rhodium,[4,11] rhodium–platinum,[12] and ruthenium[13,14] have been used for complete hydrogenation to decalins and decalols, while palladium catalysts have been employed for selective transformation to the dihydro and tetrahydro derivatives.[6,7a,15] However, there appears to be few studies on the other platinum metals, and, to our knowledge, no comparative study on the six platinum metals with naphthols, although such a study has been reported by Weitkamp on the hydrogenation of naphthalene and its methyl derivatives.[3]

In this study the selectivities of the six platinum metals have been compared in the hydrogenation of 2-naphthol for formation of the two tetrahydro derivatives, *ac*- and *ar*-2-tetralols, for their trends towards hydrogenolysis, and for the stereochemistry in the formation of saturated compounds. The hydrogenation of *ac*- and *ar*-2-tetralols has also been studied under the same conditions for comparison.

Experimental

Materials. All the substrates hydrogenated are well documented compounds. Melting points are corrected. Their structures and purities were confirmed by NMR, IR, GC-MS, and GLC. 2-Naphthol (Wako Pure Chemical Industries) was purified by treating with Raney nickel in EtOH at 50—60 °C for 3 h to remove catalyst poisons. After removal of the catalyst, addition of water to the ethanol solution gave white crystals: mp 123 °C (lit,[16] mp 121—123 °C). *ac*- and *ar*-2-Tetralols were prepared from a mixture of them obtained by hydrogenation of 2-naphthol with Raney nickel in *i*-PrOH at 100 °C and 5—10 MPa. After removing the catalyst and solvent, the ethereal solution of the residue was extracted with 2% NaOH solution. Addition of hydrochloric acid to the extract gave crystals which were recrystallized from hexane: mp 61.5 °C (lit,[17] mp 61.5—62.5 °C). From the ethereal solution after removal of *ar*-2-tetralol, *ac*-2-tetralol was obtained by distillation at reduced pressure: bp 127 °C/6 mmHg (1 mmHg≈133.322 Pa); n_D^{25} 1.5620 (lit,[18] bp 120 °C/2 mmHg; n_D^{25} 1.5625). *trans*-Octahydro-2(1*H*)-naphthalenone (abbreviated to *trans*-2-decalone) was prepared by chromic acid oxidation of a trans-rich 2-decalol mixture obtained by isomerization of a 2-decalol mixture with Raney nickel at 160 °C and 0.2 MPa H_2. *cis*-Octahydro-2(1*H*)-naphthalenone (abbreviated to *cis*-2-decalone) was likewise obtained from a cis-rich mixture of 2-decalols. Both the *trans*- and *cis*-2-decalones were purified by a preparative GLC. *trans*-2-Decalone: n_D^{25} 1.4817 (lit,[19] n_D^{25} 1.4814); *cis*-2-decalone: n_D^{25} 1.4911 (lit,[19] n_D^{25} 1.4915). 3,4-Dihydro-2(1*H*)-naphthlenone (abbreviated to 2-tetralone) was obtained from Sigma Chemical Co. and used after distillation at reduced pressure: bp 93 °C/1 mmHg; n_D^{20} 1.5597 (lit,[20] bp 92—94 °C/1.8 mmHg; n_D^{20} 1.5594).

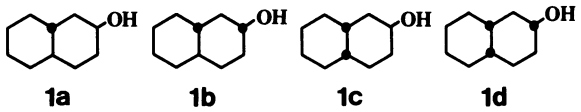
Catalysts. Unsupported metal catalysts were prepared by reducing the corresponding metal hydroxides (Ru, Rh, Ir) or oxides (Pt, Os) with hydrogen in water at atmospheric or elevated pressure.[21,22] Care was taken to remove

alkaline or acidic impurities with repeated reductions and washings. Pd-C catalyst (5% Pd) was obtained from Nippon Engelhard Co. and used throughout this study, since unsupported palladium was liable to deactivation during hydrogenation.

Solvent. *t*-Butyl alcohol (Wako Pure Chemical Industries) was distilled with addition of a small amount of sodium and stored in a refrigerator.

Hydrogenation. All hydrogenations were performed in a 40 ml stainless steel autoclave with a stirrer driven magnetically. The autoclave was immersed in an oil bath maintained at 80 °C during hydrogenation. The catalyst, the amount of which varied with metal, was pretreated with hydrogen at 80 °C and 5 MPa H_2 (15 min for Pd-C, 30 min for Rh, Ir, Os, and Pt, and 1 h for Ru). After the pretreatment the solvent was replaced by a new portion of *t*-butyl alcohol and then the substrate, dissolved in a small amount of the solvent, was added, the combined amount of the solvent being 16 ml. The mixture was hydrogenated at 80 °C and 4—5 MPa H_2 pressure.

Analysis of the Reaction Mixture. The reaction mixture was analyzed by GLC with 2-methoxynaphthalene as an internal standard. For the analysis of *cis*- and *trans*-decalins and tetralin, the reaction mixture was subjected directly to GLC, using a glass capillary column of OV-17 (0.3 mmϕ×30 m) at 70—130 °C programmed at 1 °C/min and with N_2 at 0.075 MPa. The retention times were 5.4 min (*trans*-decalin), 6.4 min (*cis*-decalin), 8.8 min (tetralin), and 33.9 min (2-methoxynaphthalene). For the analysis of four stereoisomeric 2-decalols, *ar*-2-tetralol, and 2-naphthol, the reaction mixture, after removal of the solvent, was trimethylsilylated and then subjected to GLC, using the same glass capillary column mentioned above under the same conditions. The retention times were 13.3 min (*trans,trans*-2-decalol (**1a**)), 16.9 min (*trans, cis*-2-decalol (**1b**)), 18.5 min (*cis,trans*-2-decalol (**1c**)), 19.3 min (*cis,cis*-2-decalol (**1d**)), 33.9 min (2-methoxynaphthalene), 35.5 min (*ar*-2-tetralol), and 38.8 min (2-naphthol). For the analysis of *ac*-2-tetralol, *trans*- and *cis*-2-decalones, and 2-tetralone, the trimethylsilylated products were subjected to GLC, using a DEGS column (3 mmϕ×3 m) at 170 °C and with N_2 at 0.09 MPa. The retention times were 13.2 min (*ac*-2-tetralol), 19.8 min (*trans*-2-decalone), 25.4 min (*cis*-2-decalone), 62.7 min (2-tetralone), and 65.3 min (2-methoxynaphthalene).



Results

Hydrogenation of 2-Naphthol to ar- *and* ac-*2-Tetralols.* Hydrogenation of 2-naphthol gives *ar*- and *ac*-2-tetralols as the intermediates leading to decalins and 2-decalols. In order to know the selectivities for the two tetralols, 2-naphthol was hydrogenated in *t*-butyl alcohol at 80 °C and 4—5 MPa of hydrogen pressure over the six platinum metals as catalysts. In

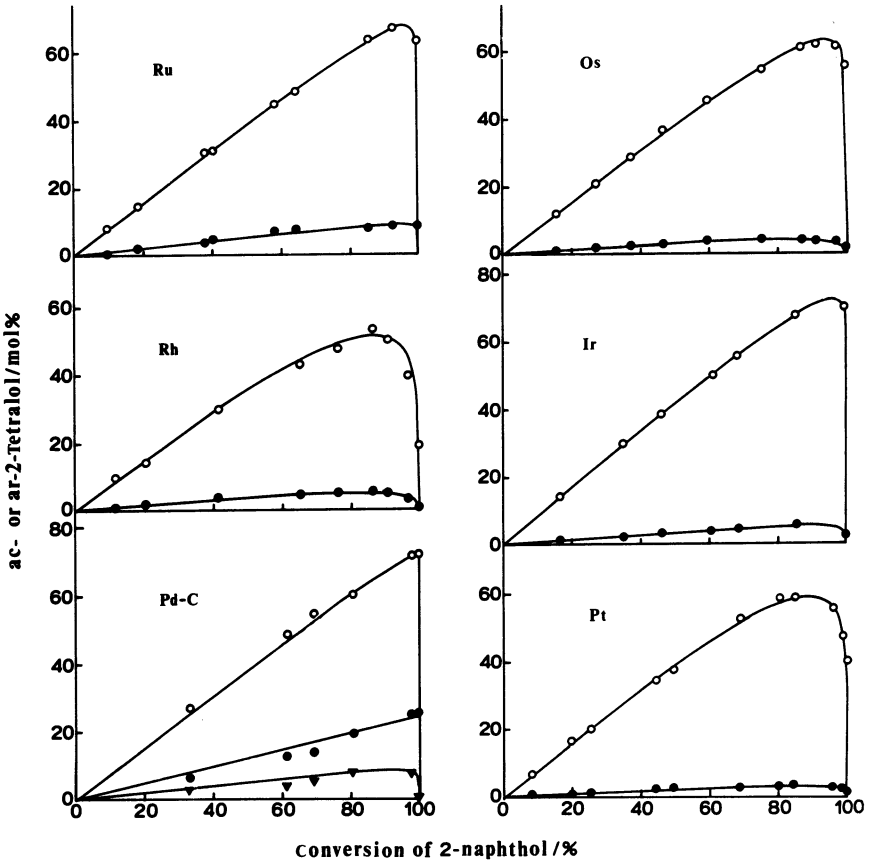
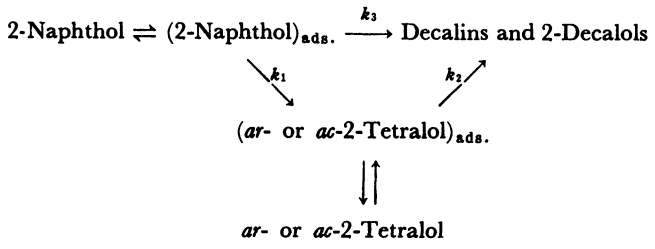


Fig. 1. Hydrogenation of 2-naphthol: formation of *ar*- and *ac*-2-tetralols. ○: *ar*-2-tetralol, ●: *ac*-2-tetralol (2-tetralone+*ac*-2-tetralol for Pd-C), ▼: 2-tetralone. The results show a set of separate experiments with varying conversions of 2-naphthol. The full lines show the theroretical curves given by Eq. 1. For the values of f and K, see Tables 1 and 8, respectively.

Fig. 1 are shown the variations in amount of the two tetralols during the course of hydrogenation as a function of 2-naphthol conversion. The selectivity for either *ar*- or *ac*-2-tetralol has been determined by application of Eq. 1 which is derived on the basis of the reaction pathways shown in Scheme 1.[23] C_{NL} and C_{TL} represent the concentrations of 2-naphthol and *ar*- or *ac*-2-tetralol, respectively, when the initial concentration of 2-naphthol is taken as unity. f is the fraction of 2-tetralol which leaves the catalyst surface and given by $k_1/(k_1+k_3)$ where k_1 and k_3 are the rate constants for the respective reaction pathways shown in Scheme 1. K is a constant which depends on the relative reactivity of 2-tetralol to 2-naphthol. The circles in Fig. 1 show the results of a set of experiments done separately for varying conversions of 2-naphthol. The full lines in Fig. 1 present the theoretical curves given by Eq. 1 when an appropriate set of values of f and K are selected to

$$C_{TL} = \frac{f}{K-1}(C_{NL} - C_{NL}^{K}) \quad (1)$$



Scheme 1. Hydrogenation pathways of 2-naphthol.

represent best the variations in concentration of *ar*- or *ac*-2-tetralol throughout the course of the hydrogenation. With palladium 2-tetralone was formed together with the tetralols (see Fig. 1). Since 2-tetralone has been converted nearly quantitatively to *ac*-2-tetralol over palladium,[24] the sum of *ac*-2-tetralol and 2-tetralone is plotted in Fig. 1. The selectivities for the products other than the tetralols were obtained by extrapolating the varying selectivities with the conversion of 2-naphthol to the initiation of hydrogenation. The composition of the products at the initial stage of hydrogenation thus obtained by application of Eq. 1 and the extrapolation method is summarized in Table 1.

Hydrogenation of ar-*2-Tetralol.* Since *ar*-2-tetralol has been the predominant intermediate in the hydrogenation of 2-naphthol over all the catalyst metals investigated, the hydrogenation of *ar*-2-tetralol has also been studied in detail. Table 2 summarizes the composition of the products obtained on complete hydrogenation. Analysis of the reaction mixture during hydrogenation indicated that 2-decalone is formed as an intermediate, the amount of which depended on the catalyst metal used, as shown in Fig. 2. Hydrogenation with osmium, however, gave no detectable amount of 2-decalone. The selectivity for 2-decalone has been determined by application of Eq. 1 to the varying concentrations of the ketone with the conversion of *ar*-2-tetralol. The selectivity for iridium was evaluated by extrapolation method since the amounts of 2-decalone found were too small to apply Eq. 1. It is noteworthy

Table 1. Hydrogenation of 2-naphthol to *ar*- and *ac*-2-tetralols: selectivity for each product at initial stage[a]

Catalyst	Amount / mg	Selectivity/mol%[b]					
		DN	TN	DL	TO	*ac*-TL	*ar*-TL
Ru	4	0.7	0.5	10.5	0.0	10.6	77.7
Rh	4	0.7	0.6	11.9	0.0	8.6	78.2
Pd-C	150	0.0	0.0	0.1	8.5	15.4	76.0
Os	10	3.1	1.1	11.0	0.0	7.2	77.6
Ir	4	2.0	1.3	6.0	0.0	7.2	83.5
Pt	10	3.8	1.4	6.0	0.0	4.9	83.9

a) 2-Naphthol (600 mg) was hydrogenated in *t*-BuOH (16 ml) at 80 °C and 4—5 MPa H_2 pressure. b) DN: *cis*- and *trans*-decalins; TN: tetralin; DL: 2-decalols; TO: 2-tetralone; *ac*-TL: *ac*-2-tetralol; *ar*-TL: *ar*-2-tetralol.

Table 2. Hydrogenation of *ar*-2-tetralol: the composition of products at complete hydrogenation[a]

Catalyst	Amount / mg	Reac. time / h	Product composition/mol%[b]					
			t-DN	*c*-DN	*t,t*-DL	*t,c*-DL	*c,t*-DL	*c,c*-DL
Ru	6	2.5	0.1	0.5	0.4	0.6	28.2	70.2
Rh	4	1.1	0.1	1.0	0.9	2.9	17.4	77.7
Pd-C	300	12	0.1	0.1	9.5	21.8	10.5	58.0
Os	20	4.0	0.7	27.8	0.2	0.6	12.0	58.7
Ir	10	2.0	1.3	34.7	0.2	0.7	10.4	52.7
Pt	20	2.5	9.9	31.7	1.5	1.4	12.3	43.2

a) *ar*-2-Tetralol (617 mg) was hydrogenated in *t*-BuOH (16 ml) at 80 °C and 4—5 MPa H_2 pressure. b) For the notation of the compounds, see footnote b) in Table 1; *t* and *c* represent trans and cis.

that, except with palladium, the 2-decalone found was the cis isomer only and no trans isomer was observed. The amounts of 2-decalones thus determined are summarized in Table 3. Table 4 shows the results of the hydrogenation of *cis*-2-decalone with the six platinum metals and of *trans*-2-decalone with palladium catalyst.

Hydrogenation of ac-*2-Tetralol.* *ac*-2-Tetralol is another important intermediate of the hydrogenation of 2-naphthol, although it was found always in lesser amounts than *ar*-2-tetralol. In Table 5 is presented the composition of the products obtained at complete hydrogenation of *ac*-2-tetralol. Isomerization of *ac*-2-

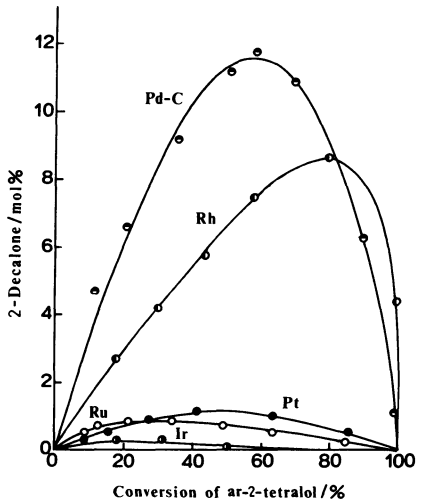


Fig. 2. Hydrogenation of *ar*-2-tetralol: formation of 2-decalone. The circles show a set of experiments with varying conversions of *ar*-2-tetralol. The full lines show the theoretical curves given by Eq. 1. For the values of f, see Table 3. The values of K are 7.2 for Ru, 0.37 for Rh, 1.33 for Pd-C, and 2.0 for Pt.

TABLE 3. HYDROGENATION OF *ar*-2-TETRALOL: AMOUNTS OF 2-DECALONES AS DESORBED INTERMEDIATES

Catalyst	2-Decalone/mol%	
	Trans	*Cis*
Ru	0.0	8.9
Rh	0.0	15.6
Pd-C	13.3	23.8
Os	0.0	0.0
Ir	0.0	3.5
Pt	0.0	4.4

TABLE 4. HYDROGENATION OF 2-DECALONES[a]

Catalyst	2-Decalone	Product composition/mol%		
		c-DN	*c,t*-DL	*c,c*-DL
Ru	Cis	0.0	38.0	62.0
Rh	Cis	0.6	50.2	49.2
Pd-C	Cis	0.0	15.1	84.9
Os	Cis	0.1	33.8	66.1
Ir	Cis	0.1	39.9	60.0
Pt	Cis	4.1	22.2	73.7
		t-DN	*t,t*-DL	*t,c*-DL
Pd-C	Trans	0.0	19.8	80.2

a) 2-Decalone (630 mg) was hydrogenated in *t*-BuOH (16 ml) under the same conditions as for *ar*-2-tetralol (see Table 2).

TABLE 5. HYDROGENATION OF *ac*-2-TETRALOL: THE COMPOSITION OF PRODUCTS AT COMPLETE HYDROGENATION[a]

Catalyst	Amount	Reac. time	Product composition/mol%[b]					
	mg	h	*t*-DN	*c*-DN	*t,t*-DL	*t,c*-DL	*c,t*-DL	*c,c*-DL
Ru	6	2	0.1	0.4	2.7	9.2	34.9	52.7
Rh	4	2	0.3	1.3	3.1	9.5	28.1	57.7
Pd-C	400	24	0.8	0.8	18.0	30.2	22.3	27.9
Os	20	2	0.2	5.1	0.9	3.8	26.6	63.4
Ir	10	2	0.1	3.1	0.7	4.0	28.0	64.1
Pt	20	3	1.6	5.6	1.9	10.3	22.7	57.9

a) *ac*-2-Tetralol (617 mg) was hydrogenated in *t*-BuOH (16 ml) at 80 °C and 4—5 MPa H_2 pressure. b) For the notations of compounds, see footnote b) in Table 2.

TABLE 6. HYDROGENATION OF 2-NAPHTHOL TO DECALINS AND DECALOLS[a]

Catalyst	Amount	Reac. time	Product composition/mol%[b]					
	mg	h	*t*-DN	*c*-DN	*t,t*-DL	*t,c*-DL	*c,t*-DL	*c,c*-DL
Ru	6	2	0.2	1.9	0.6	1.7	26.1	69.5
Rh	4	2	0.5	2.7	1.0	3.4	21.6	70.8
Pd-C	400	24	0.1	0.1	9.9	24.3	12.8	52.8
Os	20	4	1.0	34.0	0.2	0.8	11.0	53.0
Ir	10	2	1.2	31.8	0.2	1.0	12.0	53.8
Pt	20	3	8.3	28.6	2.1	2.3	14.2	44.5

a) 2-Naphthol (600 mg) was hydrogenated in *t*-BuOH (16 ml) at 80 °C and 4—5 MPa H_2 pressure. b) For the notations of compounds, see footnote b) in Table 2.

tetralol to *ar*-2-tetralol during hydrogenation was not found under the present conditions, although such an isomerization was observed by Weitkamp in the hydrogenation of methyltetrahydronaphthalenes.[3]

Hydrogenation of 2-Naphthol to Decalins and 2-Decalols. Table 6 summarizes the composition of the products obtained when 2-naphthol was hydrogenated completely to give decalins and 2-decalols.

Discussion

The Selectivity for Formation of ar- *and* ac-*2-Tetralols.* 2-Naphthol may be hydrogenated by way of either *ar*- or *ac*-2-tetralol as the intermediate leading to decalins and 2-decalols. The results in Table 1, however, indicate that, except over palladium, some 10—15% of 2-naphthol is hydrogenated apparently not through the tetralols and gives directly decalins and 2-decalols. Hydrogenation with palladium is an exception in that all naphthol is hydrogenated *via* either *ar*- or *ac*-2-naphthol and no other hydrogenation pathway was found on this metal. On the basis of the amounts of *ar*- and *ac*-2-tetralols determined, the selectivity ratios for hydrogenation of the unsubstituted ring (the benzene ring) to the substituted ring (the phenol ring) are shown in Table 7. The corresponding results on 2-methylnaphthalene obtained by Weitkamp[3] are also listed in the table for comparison. It is seen that the preferential hydrogenation of the unsubstituted ring is a common trend for both the compounds over all the catalysts. However, this trend is more pronounced in the hydrogenation of 2-naphthol than in 2-methylnaphthalene. Since the steric effect of the substituent against adsorption to catalyst is considered to be greater for the methyl group than for the hydroxyl group,[25] it would be difficult to explain the results by the steric effect of the substituent alone. Another explanation for the relative unreactivity of the phenol ring might be a great energy of resonance stabilization in the phenol ring that is estimated to be 22 kJ mol^{-1} greater than that in the benzene ring. A loss of the energy accompanying the activated adsorption would cause a difficulty in hydrogenation and this effect is considered to be greater in the phenol ring with a greater resonance energy.[2a] It is of interest that, in line with the results on methylnaphthalenes, the selectivity ratio is the smallest with palladium. As suggested by Weitkamp,[3] over palladium the product-controlling step may be different from those on the other metals, just as in the palladium-catalyzed hydrogenation of cycloolefins, where Siegel has proposed such a difference in product-controlling step between palladium and platinum.[27] The fact that with palladium no pathway other than the hydrogenations through the two tetralols was found indicates that an adsorption-desorption equilibrium has been established during hydrogenation with respect to 2-naphthol and the intermediate tetralols and gives a support for the suggestion made above. Such a complete establishment of adsorption-desorption equilibrium has also been observed in the palladium-catalyzed hydrogenation of isomeric cresols where the formation of methylcyclohexanones as intermediates has been shown to be quantitative.[28]

Table 7. Selectivity ratio for hydrogenation of the unsubstituted ring to the substituted ring

Catalyst	2-Naphthol	Catalyst	2-Methyl-naphthalene[a]
Ru	7.0	0.6% $Ru-Al_2O_3$	4.0
Rh	8.5	0.6% $Rh-Al_2O_3$	3.7
Pd-C	3.2	0.6% $Pd-Al_2O_3$	1.3
Os	9.3	5% Pd-C	3.0
Ir	9.8		
Pt	13.3		

a) Data based on the results in Fig. 11 by A. W. Weitkamp, *Adv. Catal.*, **18**, 1 (1968). 2-Methylnaphthalene was hydrogenated at 100 °C and *ca.* 7 MPa H_2 pressure.

The Rates of Hydrogenation of 2-Naphthol and 2-Tetralols. The relative rates of hydrogenation of *ar*- or *ac*-2-tetralol to 2-naphthol are given by the values of K in Eq. 1. The values were evaluated on the basis of the results shown in Fig. 1 and are summarized in Table 8. The rate constants in individual hydrogenation for 2-naphthol and *ar*-2-tetralol (k_{NL} and $k_{ar\text{-}TL}$) are also shown in Table 8. By assuming the relationship: K(*ar*-TL/NL)=($k_{ar\text{-}TL}/k_{NL}$)($b_{ar\text{-}TL}/b_{NL}$),[23] where K (*ar*-TL/NL) represents the relative reactivity of *ar*-2-tetralol to 2-naphthol and $b_{ar\text{-}TL}$ and b_{NL} are the adsorption coefficients for *ar*-2-tetralol and 2-naphthol, we can evaluate the relative ratio of the adsorption coefficients for *ar*-2-tetralol and 2-naphthol. These are also given in Table 8. The results in Table 8 clearly show that the low reactivities of *ar*-2-tetralol in the

Table 8. Rate data for the hydrogenation of 2-naphthol and 2-tetralols[a]

Catalyst	K(*ac*-TL/NL)	K(*ar*-TL/NL)	$10^3 k_{NL}$ (mol min^{-1} g $metal^{-1}$)	$10^3 k_{ar\text{-}TL}$ (mol min^{-1} g $metal^{-1}$)	$k_{ar\text{-}TL}/k_{NL}$	$b_{ar\text{-}TL}/b_{NL}$
Ru	0.050	0.046	19.9	6.51	0.33	0.14
Rh	0.305	0.205	22.4	20.5	0.92	0.22
Pd-C	0	0.01	9.98	0.562	0.056	0.18
Os	0.33	0.074	4.32	2.50	0.58	0.13
Ir	0.12	0.046	9.65	6.31	0.65	0.07
Pt	0.24	0.16	3.66	2.88	0.79	0.20

a) K is the relative reactivity of *ac*- or *ar*-2-tetralol to 2-naphthol (see Eq. 1); k is a rate constant in individual hydrogenation; b represents the adsorption coefficient for 2-naphthol or *ar*-2-tetralol.

presence of 2-naphthol, as expressed by the small values of K (*ar*-TL/NL), result from a strong adsorption of 2-naphthol over *ar*-2-tetralol. Although the values of K for *ac*-2-tetralol are larger than those for *ar*-2-tetralol except over palladium, the situation would be similar for *ac*-2-tetralol as well. Hydrogenation with palladium is noteworthy in that the values of K are extremely small for both *ar*- and *ac*-2-tetralols, and in contrast to the other metals, the value of $k_{ar\text{-TL}}/k_{NL}$ is also very small (0.056). Thus it is concluded that in the palladium-catalyzed hydrogenation of 2-naphthol the difference in the rates between 2-naphthol and *ar*-2-tetralol plays a more important role than the difference in the strengths of adsorption for the selective formation of *ar*-2-tetralol. It will be possible that this situation affects the product controlling step over palladium to be different from those on the other metals, as suggested in the preceding discussion. On the other hand, with rhodium catalyst the rate constants in individual hydrogenation are almost of the same magnitude for 2-naphthol and *ar*-2-tetralol and the selectivity is mostly controlled by a difference in strength of adsorption between the two compounds.

The Ketones as Intermediates. It is well documented that cyclohexanones are formed as intermediates in the hydrogenation of phenols.[2] With Raney nickel[29] and palladium[28] the formation of the ketone intermediates has been shown to be quantitative in hydrogenation of phenol and cresols, respectively. With ruthenium and rhodium some 50—70% of methylcyclohexanones are formed in hydrogenation of cresols, while the detectable amounts of the ketones are very small over the 3rd row platinum metals (Os, Ir, Pt).[28,30] In the hydrogenation of 2-naphthol, the formation of 2-tetralone was observed over palladium to the extent of 8.5% as an intermediate to *ac*-2-tetralol (see Table 1). However, the ketone was not formed in detectable amounts over the other metals. It will be possible that the ketone is also formed over the metals other than palladium, but is hydrogenated without leaving the catalysts, because it is presumed that the benzene ring in 2-tetralone may contribute to a strong adsorption and/or a high reactivity of the ketone. On the other hand, the formation of 2-decalone was observed over the metals except osmium with *ar*-2-tetralol (Fig. 2). It should be noted that, except with palladium, the 2-decalone found was the cis isomer only (see Table 3). It seems that this is related to the high stereoselectivities of ruthenium and rhodium for formation of the cis products at the ring juncture, as will be discussed later. In general, the amounts of 2-decalone given in Table 3 are considerably smaller than those of methylcyclohexanones reported in the hydrogenation of cresols.[28,30] Probably the use of *t*-butyl alcohol as solvent has decreased the detectable amounts of 2-decalone since hydrogenation of *m*-cresol in *t*-butyl alcohol has also decreased the amounts of 3-methylcyclohexanone formed during hydrogenation, compared to the hydrogenation without solvent.[31]

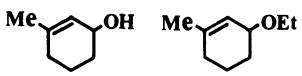
Hydrogenolysis. The proportion of hydrogenolysis obtained in hydrogenation of 2-naphthol and *ac*- and *ar*-2-tetralols is summarized in Table 9. It is clearly seen from the results in Table 9 that the hydrogenolysis occurs far more extensively over the 3rd row platinum metals (Os, Ir, Pt) than over the 2nd row metals (Ru, Rh, Pd). This characteristics is much pronounced in the hydrogenation of *ar*-2-tetralol and 2-naphthol. A similar trend of the platinum metals have also been observed in the hydrogenation of cresols.[30] The degree of the hydrogenolysis, however, is much higher with 2-naphthol and *ar*-2-tetralol than with cresols. Such an extensive hydrogenolysis in a phenol ring has also been reported in the hydrogenation of 2,5-dimethylphenol with an iridium catalyst.[32] Hydrogenolysis occurs to much lesser extents with *ac*-2-tetralol which is a homobenzyl-type alcohol. The proportion of hydrogenolysis which occurs in the pathway not *via ac*- and *ar*-2-tetralols is unusually high with ruthenium and rhodium, compared to the results with *ar*-2-tetralol and 2-naphthol. It is presumed that unsaturated alcohols, rather than unsaturated ketones, are concerned as intermediates with the high degree of hydrogenolysis in the pathway leading to direct formation of decalins and 2-decalols. This consideration comes from the fact that hydrogenation of *ar*-2-tetralol gives only slight hydrogenolysis with ruthenium and rhodium, where formation of the intermediates leading to 2-decalone may be significant and the hydrogenation through this pathway may be accompanied by little hydrogenolysis.

Table 9. Proportion of hydrogenolysis in the hydrogenation of 2-naphthol and *ac*- and *ar*-2-tetralols

Catalyst	Proportion of hydrogenolysis/mol%				
	ac-TL	*ar*-TL	Pathway not via *ac*- and *ar*-TL	NL	
				Calcd	Obsd
Ru	0.5	0.6	10.3	1.7	2.1
Rh	1.6	1.1	9.8	2.2	2.1
Pd-C	1.6	0.2	—	0.5	0.2
Os	5.3	28.5	27.6	26.6	35.0
Ir	3.2	36.0	35.5	33.6	33.0
Pt	7.2	41.6	46.4	40.5	36.9

From the amounts of hydrogenolysis for *ar*- and *ac*-2-tetralols, and for the pathway not *via* the tetralols, together with the selectivities for the respective pathways, we can calculate the amounts of hydrogenolysis that would occur in the hydrogenation of 2-naphthol. In Table 9 the amounts of hydrogenolysis thus calculated are compared with those obtained in the complete hydrogenation of 2-naphthol (see Table 6). It is seen that agreements between the calculated and observed values are generally satisfactory. With osmium, however, a considerably greater amount of hydrogenolysis was obtained with 2-naphthol, although the reason for that is not certain.

Possible intermediates that may lead to the extensive hydrogenolysis over the 3rd row metals are not clear from the knowledge now available. Both allyl- and enol-type intermediates must be taken into consideration. It seems that the extensive hydrogenolysis is difficult to explain by the allyl-type intermediates alone, because, as presumed from the results on an allyl alcohol

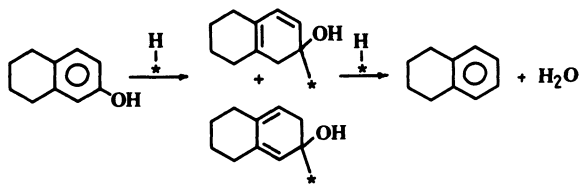


2 3

2 and its ethyl ether **3**,[1,30,33] allyl-type compounds are hydrogenolyzed not so extensively over the 3rd row metals as to be able to explain the present results. Rather, the high degree of hydrogenolysis over the 3rd row metals is a characteristics of an enol-type compounds towards hydrogenolysis as has been shown previously.[1,21] If this is the case, the intermediates leading to the extensive hydrogenolysis are presumed to be the adsorbed enols that are hydrogenated without being isomerized to the corresponding ketones, because 2-decalone, and possibly its precursors as well, should be hydrogenated with only slight hydrogenolysis even over the 3rd row metals, as shown in Table 4. The metals of low olefin isomerization activity such as the 3rd row metals may have a strong affinity for the olefinic bonds of the adsorbed enols and thus may activate the carbon–oxygen bond to be susceptible to hydrogenolysis, as has been discussed previously.[1,21]

The hydrogenolysis to give tetralin has also been observed at initial stages of the hydrogenation of 2-naphthol and *ar*-2-tetralol. The tetralin formation amounted to 7.2% with platinum in the hydrogenation of *ar*-2-tetralol. With the other metals, however, the amounts of tetralin detected were small and the route through tetralin will not be significant for the formation of decalins. The hydrogenolysis leading to tetralin is considered to occur through the half-hydrogenated states derived from *ar*-2-tetralol (an unsaturated enol), as shown in Scheme 2. This type of hydrogenolysis has previously been observed in the hydrogenation of *p*-ethoxytoluene in ethanol where toluene was formed to an extent of 8% over platinum.[33]

The Stereochemistry of Hydrogenation. In Table 10 are compared the amounts of the cis products at the ring juncture from hydrogenation of 2-naphthol and *ac*-and *ar*-2-tetralols. It is seen that, except with palladium and platinum, the selectivities for the cis products are very high for 2-naphthol and *ar*-2-tetralol. With *ac*-2-tetralol the selectivities decrease with ruthenium and rhodium to 88.0 and 87.1%, respectively. The high stereoselectivities of osmium and iridium are in accord with the results previously obtained with *o*-xylene and 1,2-dimethylcyclohexene.[34] However, the high stereoselectivities of ruthenium and rhodium as observed with 2-naphthol and *ar*-2-tetralol appear rather unusual, compared to the results on *ac*-2-tetralol as well as *o*-xylene and 1,2-dimethylcyclohexene.[2c] The unusually high selectivities of ruthenium and rhodium are probably related to the stereoselective formation of *cis*-2-decalone on the catalyst surface, because, as presumed from the results on cresols that the ketones are formed in the amounts of 50—70%, the hydrogenation through a ketone may be a significant pathway in hydrogenation of phenolic compounds over ruthenium and rhodium, although estimated amounts of 2-decalone were not so great (Table 3). The tendency of palladium to produce the trans products is in agreement with the results reported on aromatic hydrocarbons and related cycloolefins.[2c,3,27] A considerable amount of the trans isomer was also found in the 2-decalones formed from *ar*-2-tetralol over palladium. These results support the suggestion that the product controlling step over palladium differs from those on the other metals.



Scheme 2. Hydrogenolysis of *ar*-2-tetralol leading to the formation of tetralin.

TABLE 10. SELECTIVITY FOR THE CIS PRODUCTS AT RING JUNCTURE IN HYDROGENATION OF 2-NAPHTHOL AND *ac*- AND *ar*-2-TETRALOLS

Catalyst	Cis products/mol%		
	2-NL	*ac*-TL	*ar*-TL
Ru	97.5	88.0	98.9
Rh	95.1	87.1	96.1
Pd-C	65.7	51.0	68.6
Os	98.0	95.1	98.5
Ir	97.6	95.2	97.8
Pt	87.3	86.2	87.2

Table 11 shows the selectivities for formation of *cis*-2-decalols (cis,cis and cis,trans isomers) and *cis,cis*-2-decalol in the decalol mixture. It is seen that the high selectivities for *cis*-2-decalols from 2-naphthol and *ar*-2-tetralol considerably decrease for *cis,cis*-2-decalol. The decrease is particularly pronounced in the case of ruthenium (from 99.0% to 70.6% with *ar*-2-tetralol). These results suggest that a stepwise hydrogenation is occurring in the course to saturated products even over those metals that give high yields of the cis products at the ring juncture. It is noted that the yields of *cis*-2-decalols and *cis,cis*-2-decalol in hydrogenation of 2-naphthol and *ar*-2-tetralol are much higher with ruthenium (95.6 and 69.5% for 2-naphthol; 98.4 and 70.2% for *ar*-2-tetralol) and with rhodium (92.4 and 70.8% for 2-naphthol; 95.1 and 77.7% for *ar*-2-tetralol)

TABLE 11. STEREOCHEMISTRY OF THE FORMATION OF 2-DECALOLS IN HYDROGENATION OF 2-NAPHTHOL AND *ac*- AND *ar*-2-TETRALOLS

Catalyst	Cis isomers[a] and cis,cis isomer in 2-decalols /mol%					
	NL		*ac*-TL		*ar*-TL	
Ru	97.7	71.0	88.0	53.0	99.0	70.6
Rh	95.5	73.1	87.2	58.6	96.2	78.6
Pd-C	65.7	52.9	51.0	28.4	68.7	58.1
Os	98.5	81.5	95.0	66.9	98.9	82.1
Ir	98.2	80.3	95.1	66.2	98.6	82.3
Pt	93.0	70.5	86.9	62.4	95.0	74.0

a) *cis,cis*- and *cis,trans*-2-Decalols.

than with the 3rd row metals because of the occurrence of extensive hydrogenolysis with the latter metals. In accord with the results in the literature,[4,11,12] the highest yield of the cis,cis isomer was obtained in the hydrogenation of *ar*-2-tetralol with rhodium catalyst. The yield further increased to 85.4% in the hydrogenation at 30 °C and 10 MPa of hydrogen pressure. The selectivities for the cis,cis isomer is generally much lower with *ac*-2-tetralol, as would be expected, because *ac*-2-tetralol can be adsorbed to the catalyst to afford the cis,trans isomer as equally as to give the cis,cis isomer. It is noteworthy that in the hydrogenation of *ar*-tetralol the proportion of *cis,cis*-2-decalol in *cis*-2-decalols is the greatest with palladium (84.6%) and the value is very close to that obtained in the hydrogenation of *cis*-2-decalone (84.9%) (see Table 4). This is in line with the findings that the hydrogenation through a ketone may be the exclusive pathway in the palladium-catalyzed hydrogenation of phenols.[28] The reason for the high stereoselectivity of palladium in the formation of the cis,cis isomer from *cis*-2-decalone is not certain. Since the conformation of *cis*-2-decalone is accepted not to be fixed, the stereochemistry of hydrogenation of *cis*-2-decalone would be not simply interpreted, as discussed by Hückel and coworkers.[35]

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