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STEREOCHEMISTRY AND MECHANISM OF CATALYTIC HYDROGENATION OF SUBSTITUTED CYCLOHEXANONES

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Abstract – Substituted alkylcyclohexanones were hydrogenated over several transition metal catalysts. The hydrogenation with freshly prepared Raney Ni gave predominantly the axial alcohols but catalyst to which sodium hydroxide was added or aged catalyst increased the stereoselectivity. In contrast to the PtO_2 hydrogenation in which the equatorial alcohols were favoured, more axial alcohols were obtained than the equatorial counterparts on Pt-black. On Pd catalyst the isomeric ratios of the cyclohexanols changed as the reaction progressed. This may be due to a decrease in the amount of hydrogen available caused by the strong adsorption of ketones on the catalyst. Rh catalyst gave more of the axial alcohols than any other catalyst used in the present study.

The stereochemistry of the hydrogenation of cyclohexanones is governed by the von Auwers-Skita hydrogenation rule[1] which states that the hydrogenation over Pt catalyst in acid medium produces predominantly the *cis* alcohols, while the *trans* alcohols are favoured in neutral or basic medium. When Ni is used as the catalyst at high hydrogen pressure and high temperature the *trans* alcohols are mainly obtained. This hydrogenation rule was modified by Barton introducing the concept of conformation[2] and gives the definition that the rapid hydrogenation in acid medium gives predominantly the axial alcohols, while in neutral medium the equatorial alcohols are preferably obtained from unhindered cyclohexanones and the axial ones from hindered cyclohexanones. But no discussion on this empirical rule has been found in the literature. This hydrogenation rule cannot be applied to the stereochemistry of the hydrogenation of cyclohexanones,[3] since many factors such as the steric structure of the substrate, metal of the catalyst, pH of the reaction medium, the activity of the catalyst, the hydrogen pressure, etc are considered to influence the steric course of the reaction.[4]

In order to investigate the mechanism of the hydrogenation of cyclohexanones and the stereochemical character of the catalysts, many alkyl-substituted cyclohexanones were hydrogenated over several kinds of transition metal catalysts.

RESULTS

Raney nickel catalyst. The hydrogenation of 2-methylcyclohexanone with a freshly prepared Raney Ni in ethanol gave 69% of the *cis* alcohol with a very small amount of hydrogenolysed product, methylcyclohexane. When the catalyst was aged for 10 days in ethanol the activity of the catalyst seemed to decrease but the stereoselectivity increased slightly. Addition of sodium hydroxide to this catalyst also increased the isomeric ratio of the *cis* alcohol to 73–80%. Similarly, the hydrogenation of alkyl-substituted cyclohexanones proceeded selectively to give cyclohexanols, the axial alcohols of which were always predominant. The addition of sodium hydroxide also increased the stereoselectivity. A similar isomer distribution was obtained in the hydrogenation over Ni-boride catalyst.

Platinum catalyst. The hydrogenation of 2-methylcyclohexanone over PtO_2 gave 52–60% of *trans* 2-methylcyclohexanol. When PtO_2 was prereduced with hydrogen, the isomeric distribution of the products did not change significantly. But by washing the used PtO_2 with water and ethanol several times the amount of the *cis* alcohol increased to 78%. When Pt-black† was used the *cis* alcohol was favoured but the addition of sodium hydroxide decreased the amount of the *cis* alcohol. These results show that the hydrogenation over PtO_2 containing an alkaline substance[5] proceeded preferably to give *trans* 2-methylcyclohexanol in ethanol. Removing the alkaline substance decreased the amount of the *trans* isomer and the *cis* was favoured. The hydrogenation over PtO_2 in ethanol with one micro drop of conc. hydrochloric acid gave ketal and ether as well as hydrocarbon as by-products and the yield of the alcohol decreased, but the *cis*/*trans* ratio increased.

In acetic acid, the yield of hydrocarbon was relatively low and epimeric cyclohexanols obtained showed the composition of 64–75% *cis* and 36–

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†Pt-black is the catalyst which is prepared by the hydrogen reduction of PtO_2 and is washed well with distilled water.

25% *trans* isomer. Addition of one micro drop of conc. hydrochloric acid to the acetic acid gave a much higher stereoselectivity but acetate and others were also obtained, and sometimes the yield of the alcohol was less than 10%. The PtO_2 hydrogenation in acetic acid results in neutralisation of

Table 1. Hydrogenation of 2-methylcyclohexanone[a, b]

Entry	Catalyst[c]	Additive	Solvent[d]	The composition of the resulting mixture (%)			Cyclohexanol[e] (*cis* %)
				Starting material	Cyclohexanol	Others	
1	PtO_2	–	E	76	24	*t*[f]	48
2	PtO_2	–	E	48	52	*t*	43
3	PtO_2	–	E	40	60	*t*	40(77)[g]
4	PtO_2	–	E	13	87	*t*	42
5	PtO_2[h]	–	E	70	30	*t*	46
6	Pt-black	–	E	23	77	*t*	64
7	4 → Pt-black[i]	–	E	0	99	1	78
8	4 → Pt-black	NaOH[j]	E	0	99	1	59
9	PtO_2	HCl[k]	E	0	15	85[l]	67
10	PtO_2	–	A	2	95	3	64(70)[m]
11	PtO_2	–	A	0	100	*t*	75
12	PtO_2	HCl[k]	A	0	57	43[n]	80(93)[g]
13	Pt-black	–	A	0	90	10	69(65)[o]
14	PtO_2	–	D	17	83	*t*	38
15	PtO_2	–	H	95	5	*t*	61
16	PtO_2	–	AE	27	73	*t*	66
17	Raney Ni-A[p]	–	E	0	100	*t*	69
18	Raney Ni-A	NaOH[j]	E	0	100	*t*	73
19	Raney Ni-A	NaOH[q]	E	0	100	*t*	80
20	Raney Ni-A	NaOH[r]	E	34	66	*t*	78
21	Raney Ni-B[s]	–	E	35	65	*t*	72
22	Raney Ni-B	NaOH[q]	E	0	100	*t*	79
23	Ni-boride	–	E	75	25	*t*	72
24	Ni-boride	NaOH[q]	E	93	7	*t*	76
25	Rh-carbon	–	E	12	88	*t*	70
26	Rh-carbon[t]	–	E	39	61	*t*	55[u]
27	Pd-O[v]	–	E	57	43	*t*	68
28	Pd-carbon[w]	–	E	66	32	2	39
29	Pd-carbon	NaOH[j]	E	86	13	1	36

[a] Substrate, 10^{-3} mol.

[b] An ordinary hydrogen pressure and room temperature were employed unless otherwise indicated.

[c] Weight of catalyst (mg); Raney Ni, 100; Ni-boride, 100; PtO_2, 10; Pt-black, 7; Rh-carbon, 40; PdO, 100; Pd-carbon, 400.

[d] 5·0 ml; E, ethanol; A, acetic acid; D, dioxane; H, n-hexane; AE, ethyl acetate.

[e] Figures in parentheses are percentage appeared in the literature.

[f] Trace.

[g] W. Hückel and M. Maier, *Ann.* **616**, 46 (1958).

[h] Prereduced PtO_2.

[i] The catalyst which had been used in Entry 4 was washed with water and ethanol and then used.

[j] 2×10^{-3} mol.

[k] One micro drop.

[l] Ether and ketal as well as hydrocarbon.

[m] R. J. Wicker, *J. Chem. Soc.* 3299 (1957).

[n] Mainly 2-methylcyclohexyl acetate.

[o] W. Hückel and A. Hubele, *Ann.* **613**, 27 (1958).

[p] Freshly prepared.

[q] 5×10^{-2} mol.

[r] 10^{-2} mol.

[s] Aged for 10 days.

[t] 20 mg.

[u] Initial hydrogen pressure was 70 atm.

[v] Prereduced PdO.

[w] Method-B: *Org. Syntheses*, 1955, 3, 686.

Table 2. Hydrogenation of methylcyclohexanone in ethanol[a]

Entry	Cyclohexanone	Catalyst (Weight, mg)	Reaction Time (hr)	Conversion[b] (%)	Axial Alcohol (%)
30	2-Me-	PdO(100)	5	7	24
			13	11	43
31	2-Me-	$PtO_2(10)$	0·5	5	44
			2	46	43
			13	56	43
32	2-Me-	Pt-black	0·5	9	80
		(7)	1	37	80
			1·5	50	82
			5	100	81
33	2-Me-	Raney Ni[c]	0·75	20	62
		(100)	1·5	43	63
			5	100	63
34	4-Me-	PdO(100)[d]	4	15	38
			13	44	49
35	4-Me-	PdO(250)[d]	3	43	77
			14	85	77

[a] Substrate, 10^{-3} mol; solvent, 5·0 ml.
[b] Percent of methylcyclohexanol in the resulting mixture.
[c] Freshly prepared.
[d] Prereduced PdO.

Table 3. Hydrogenation of substituted cyclohexanones[a]

Entry	Cyclohexanone[b]	Catalyst[c]	Additive[d]	Solvent[e]	Conversion[f]	Axial Alcohol[g] (%)
36	4-Me-	Raney Ni-A[h]	–	E	100	65
37		Raney Ni-A	NaOH	E	100	80
38		Raney Ni-B[i]	–	E	31	80
39		Ni-boride	–	E	68	77
40		Ni-boride	NaOH	E	98	72
41		Rh-carbon	–	E	100	84
42		Rh-carbon	–	E	100	60[j](54)[k]
43		Rh-carbon	NaOH	E	37	52
44		Pt-black	–	E	100	53
45		Pt-black	–	A	100	53
46		PtO_2	–	E	100	34(26)[l]
47		PtO_2	–	A	100	49(47)[m]
48		PdO[n]	–	E	43(12)	77
49		Pd-carbon[o]	–	E	98(68)	44
50		Pd-carbon	NaOH	E	100	23
51	4-t-Bu-	Raney-Ni-A	–	E	100	74
52		Raney Ni-A	NaOH	E	100	88
53		Raney Ni-B	–	E	100	92
54		Ni-boride	–	E	100	85
55		Ni-boride	NaOH	E	100	73
56		Rh-carbon	–	E	100	94
57		Rh-carbon	–	E	90	58[p]
58		Rh-carbon	NaOH	E	95	63
59		Pt-black	–	E	100(60)	57
60		Pt-black	–	A	100(70)	68

Table 3. (*continued*)

Entry	Cyclohexanone[b]	Catalyst[c]	Additive[d]	Solvent[e]	Conversion[f]	Axial Alcohol[g] (%)
61		PtO_2	–	E	100	38(35)[q]
62		PtO_2	–	A	98(40)	46(35)[r]
63		PdO[n]	–	E	34(20)	72
64		Pd-carbon	–	E	100(36)	44
65		Pd-carbon	NaOH	E	40	23
66	3-Me-	Raney Ni-A	–	E	100	52
67		Raney Ni-A	NaOH	E	96	67
68		Raney Ni-B	–	E	17	82
69		Ni-boride	–	E	100	65
70		Rh-carbon	–	E	100	88
71		Rh-carbon	–	E	100	57[s]
72		Rh-carbon	NaOH	E	25	43
73		Pt-black	–	E	100(80)	44
74		PtO_2	–	E	77(76)	23
75		PtO_2	–	A	100(96)	44(38)[t]
76		PdO[j]	–	E	71	55
77		Pd-carbon	–	E	100	40
78		Pd-carbon	NaOH	E	73	30
79	3-t-Bu-	Raney Ni-A	–	E	100	64
80		Raney Ni-A	NaOH	E	100	73
81		Ni-boride	–	E	98	56
82		Rh-carbon	–	E	100	94
83		Rh-carbon	–	E	100	56[u]
84		Rh-carbon	NaOH	E	100	52
85		Pt-black	–	E	72(65)	52
86		PtO_2	–	E	62	41
87		PtO_2	–	A	99(67)	60
88		PdO	–	E	96(17)	84
89		Pd-carbon	–	E	100(40)	45
90		Pd-carbon	NaOH	E	17	25
91	3-Phenyl-	Raney Ni-A	–	E	100	60
92		Raney Ni-A	NaOH	E	100	66
93		Pt-black	–	E	93(65)	42
94		PtO_2	–	E	100(92)	20
95		PtO_2	–	A	100(7·5)	55
96	3,3,5-Trimethyl-	Raney Ni-A	–	E	91	97
97		Raney Ni-A	NaOH	E	100	97
98		Rh-carbon	–	E	100	99
99		Rh-carbon	–	E	66	97[s]
100		Rh-carbon	NaOH	E	58	97
101		Pt-black	–	E	96	99
102		PtO_2	–	E	16	97(93)[v]
103		Pd-carbon	–	E	100(76)	99
104	2-Et-	Raney Ni-A	–	E	100(76)	72
105		Raney Ni-A	NaOH	E	100(84)	79
106		Pt-black	–	E	92(83)	76
107		PtO_2	–	E	95(84)	50
108		PtO_2	–	A	100(84)	65
109	2-i-Pr-	Raney Ni-A	–	E	100	88
110		Rh-carbon	–	E	15	94
111		Pt-black	–	E	95	86
112		PtO_2	–	E	95	76

Table 3. (*continued*)

Entry	Cyclohexanone[b]	Catalyst[c]	Additive[d]	Solvent[e]	Conversion[f]	Axial Alcohol[g] (%)
113	2-Cyclohexyl-	Raney Ni-A	–	E	48	88
114		Raney Ni-A	NaOH	E	95	92
115		Ni-boride	–	E	14	88
116		Rh-carbon	–	E	100	87
117		Pt-black	–	E	94(88)	92
118		Pt-black	NaOH	E	15	89
119		PtO_2	–	E	15(14)	65
120		PtO_2	–	A	100	87
121		PdO	–	E	3	93
122	2-Phenyl-	Raney Ni-A	–	E	90	88
123		Raney Ni-A	NaOH	E	98	95
124		Pt-black	–	E	50(36)	83
125		Pt-black	NaOH	E	100	66
126		PtO_2	–	E	100	57
127		PtO_2	NaOH	E	100	71
128	2-t-Bu-	Raney Ni-A	–	E	95	90
129		Raney Ni-A	–	E	100	92[s]
130		Rh-carbon	–	E	5	97
131		Pt-black	–	E	75	100[j,w]
132		Pt-black	–	E	70	78[j,x]

[a] An ordinary hydrogen pressure and room temperature were employed unless otherwise indicated.

[b] Substrate, 10^{-3} mol.

[c] Weight of catalyst (mg); Raney Ni, 100; Ni-boride, 100; PtO_2, 10; Pt-black, 7; Rh-carbon, 40; Pd-carbon, 400.

[d] NaOH, 5×10^{-2} mol.

[e] 5·0 ml; E, ethanol; A, acetic acid.

[f] Figures in parentheses are percentage of cyclohexanols in the resulting mixture.

[g] Figures in parentheses are percentage appeared in the literature.

[h] Freshly prepared.

[i] Aged for 10 days.

[j] Initial hydrogen pressure 80 atm.

[k] Initial hydrogen pressure 70 atm; P. N. Rylander and D. R. Steele, *Engelhard Ind. Tech. Bull.* 3, 125 (1963).

[l] In methanol; R. J. Wicker, *J. Chem. Soc.* 3299 (1957); Wicker reported that at 70 atm. 4-methylcyclohexanone gives 74% *cis*.

[m] R. J. Wicker, *J Chem Soc.* 3299 (1957).

[n] Prereduced PdO.

[o] Prepared by the method-B: *Org. Syntheses*, 1955, 3, 686.

[p] Initial hydrogen pressure 80 atm.

[q] M. Muhlstädt and R. Borodorf, *Tetrahedron Letters* 1879 (1966).

[r] E. L. Eliel and R. S. Ro, *J Am. Chem. Soc.* 79, 5992 (1957).

[s] Initial hydrogen pressure 85 atm.

[t] W. Hückel and J. Kurz, *Ber.* 91, 1290 (1958).

[u] Initial hydrogen pressure 110 atm.

[v] In methanol, R. J. Wicker, *J. Chem. Soc.* 3299 (1957).

[w] Temp, 100°C.

[x] Temp, 120°C.

alkaline substance in the catalyst. The addition of mineral acid to the reaction system gave an increased percentage of the *cis* alcohol but the formation of hydrocarbon, ester or ketal and ether were also likely.

The hydrogenation of 2-alkylcyclohexanones on Pt-black gave preferably the axial alcohols, while cyclohexanones which have the alkyl substituent at the 3 or 4 position showed no appreciable stereoselectivity. On Pt-black catalyst to which sodium hydroxide was added or on PtO_2 which contains an alkaline substance, the reaction proceeded preferably to give the equatorial alcohols with very small amounts of by-products. In the hydrogenation of cyclohexanones with a bulky substituent at the 2-position and 3,3,5-trimethylcyclohexanone, the axial alcohols were always favoured.

Rhodium catalyst. Rh-carbon was the most stereoselective catalyst to form the axial alcohol in the present study. When sodium hydroxide was added, 2-substituted cyclohexanone was not hydrogenated at all under the conditions employed but 3- and 4-substituted compounds have the cyclohexanols with less stereoselectivity.

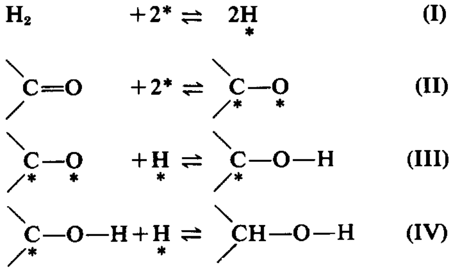
Palladium catalyst. Cyclohexanones over Pd catalyst seemed to be less reactive than over any other catalyst used in the present study. When a large amount of catalyst was used, the reaction proceeded slowly and the ratio of the *cis* to *trans* alcohol changed with the progress of the hydrogenation. On PdO hydrogenation of 2-methylcyclohexanone the *trans* isomer was favoured at an early stage of the reaction but the percentage of the *cis* isomer increased later. In contrast, when the PdO was thoroughly prereduced with hydrogen and the substrate was added without the catalyst contacting the air, the *cis* isomer was preferably obtained even at the early stage of the hydrogenation. Similar trends were also observed in the hydrogenation of 4-methylcyclohexanone. The equatorial alcohols were always preferred on Pd-carbon which contains a small amount of alkaline substance except in the case of the hydrogenation of 3,3,5-trimethylcyclohexanone.

The results of the hydrogenation of 2-methylcyclohexanone over various catalysts are tabulated in Table 1.

In Table 2 the results indicate the change of isomer distribution with the progress of the hydrogenation. The hydrogenation results of other substituted cyclohexanones are summarized in Table 3.

DISCUSSION

The hydrogenation of the CO group is considered similar as that of olefin and the following scheme has been postulated in terms of the Horiuti-Polanyi mechanism[6] (Scheme 1).



$$\mathrm{H_2} + 2^* \rightleftharpoons 2\underset{*}{\mathrm{H}} \qquad \text{(I)}$$

$$\rangle\mathrm{C{=}O} + 2^* \rightleftharpoons \rangle\underset{*}{\mathrm{C}}\!-\!\underset{*}{\mathrm{O}} \qquad \text{(II)}$$

$$\rangle\underset{*}{\mathrm{C}}\!-\!\underset{*}{\mathrm{O}} + \underset{*}{\mathrm{H}} \rightleftharpoons \rangle\underset{*}{\mathrm{C}}\!-\!\mathrm{O}\!-\!\mathrm{H} \qquad \text{(III)}$$

$$\rangle\underset{*}{\mathrm{C}}\!-\!\mathrm{O}\!-\!\mathrm{H} + \underset{*}{\mathrm{H}} \rightleftharpoons \rangle\mathrm{CH}\!-\!\mathrm{O}\!-\!\mathrm{H} \qquad \text{(IV)}$$

SCHEME 1

Cyclohexanone which has a steric structure similar to methylenecyclohexane may be adsorbed on the catalyst in a chair conformation[7] in which the substituent prefers the equatorial position. A possible reaction course is shown in Scheme 2 which is discussed in terms of a modified Horiuti-Polanyi mechanism.[8] Taking account of the concept of catalyst hindrance, it is easier for the ketone to be adsorbed from the equatorial side (**2a**) than from the axial side of the molecule (**2b**).[9]

Therefore, the adsorption states to give the *cis* alcohols for 2- or 4-substituted cyclohexanones and the *trans* alcohols for 3-substituted cyclohexanones are more stable than the alternatives. In consequence, the hydrogenation of cyclohexanones over Raney Ni will give preferably the axial alcohols. Considering with the fact that similar results were obtained on Ni-boride catalyst the adsorption of the substrate on the catalyst may be the product determining step over Ni similar to the hydrogenation of cycloolefin.[10] The reaction proceeded to give more axial alcohol on aged Raney Ni or if sodium hydroxide was added than if freshly prepared catalyst was used. This infers that the difference in the free energies of activation to form two epimeric adsorbed species becomes significant on such a catalyst.

The hydrogenation of cyclohexanones on Pt-black which does not contain an alkaline substance proceeded preferably to give the axial alcohols. Siegel and Smith reported that the product determining step of the hydrogenation of olefins on Pt catalyst is the hydrogen transfer to the adsorbed species.[11]

Felkin *et al.* suggested that the complex metal hydride reduction of cyclohexanones have a reactant-like transition state.[12] If it is possible to extend the above assumption to the hydrogenation, the transition state of the hydrogen transfer to the adsorbed species may be reactant-like and the relative stabilities of the two epimeric adsorbed states (**2′a** and **2′b**) reflect on those of the transition states (**3a** and **3b**). Consequently, the axial alcohol will be preferred to the equatorial alcohol. In the presence of alkaline substance, the equatorial alcohols were favoured other than the cases of hindered cyclohexanones. It may be that the hydrogenolysis of the oxygen-metal bond is restricted owing to the decrease of the amount of hydrogen available which is controlled by the presence of alkaline substance on the catalyst surface.* Therefore, the reaction step III and IV in Scheme 1, the hydrogen transfer from the catalyst surface to the adsorbed species and the half-hydrogenated one, will be

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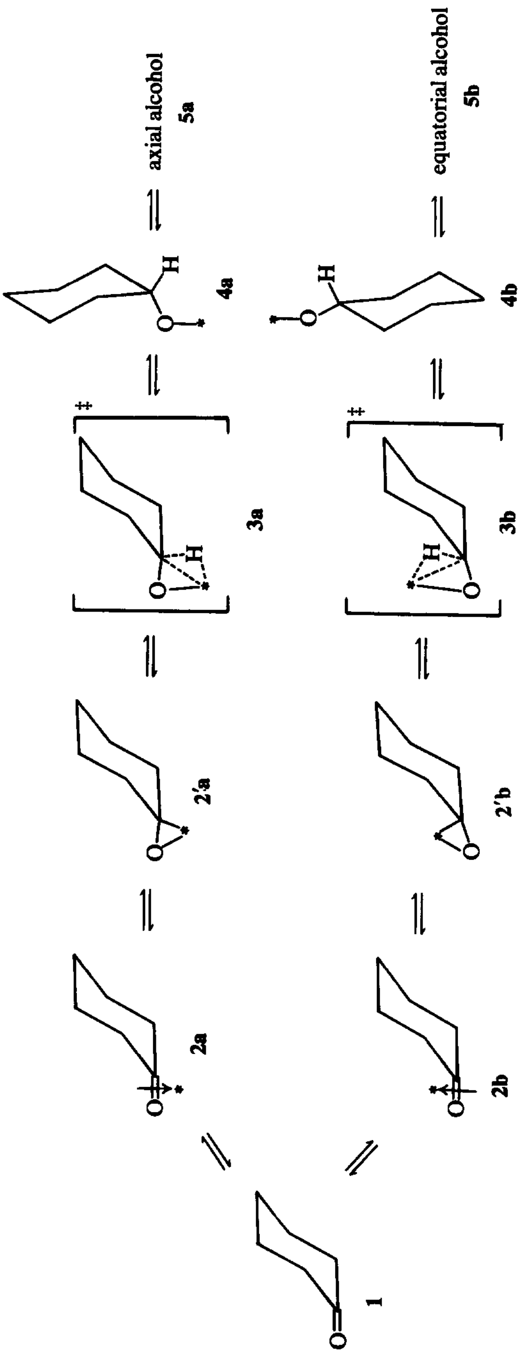
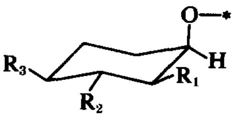
*We presumed that the hydrogenolysis of carbon-metal bond is also restricted owing to the decrease of the amount of hydrogen available but the relative stabilities between the carbon-metal bond and the oxygen-metal bond infers that the hydrogenolysis of the former bond will be more affected than that of the latter.

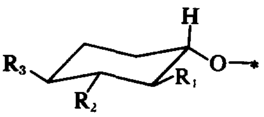

1
2a
2b
2'a
2'b
3a
3b
4a
4b
axial alcohol
5a
equatorial alcohol
5b
O
H
*
‡

Scheme 2

affected. Step IV may be particularly affected and this step will participate in the determination of the product distribution. In other words, the half-hydrogenated intermediates should tend to become equilibriated with one another. A consideration of the energy states of the two epimeric half-hydrogenated intermediates of substituted cyclohexanones supplies a rationale for these results. The structure **A** is of much higher energy and is less likely, while **B** is of lower energy and is more favoured. Consequently, the *trans* alcohol for 2- or 4-substituted cyclohexanone or the *cis* for 3-substituted cyclohexanone was favoured as the more stable of the two possible half-hydrogenated intermediates.



A



B

2-Substituted cyclohexanone; R_2, R_3; H
3-Substituted cyclohexanone; R_1, R_3; H
4-Substituted cyclohexanone; R_1, R_2; H

Rh catalyst gave more of the axial alcohol than any other catalyst used in the present study. Since the results of the Rh-carbon hydrogenation of cycloolefins suggested that its stereospecificity lies between Ni and Pt,[13] both the adsorption of the substrate on the catalyst (Step II) and the hydrogen transfer to the adsorbed species (Step III) may contribute to the determination of the product distribution.

The hydrogenation over PdO showed that the equatorial alcohols were favoured at an early stage of the reaction but axial/equatorial ratio gradually increased as the hydrogenation progressed. On the other hand, when a large amount of PdO was stirred with hydrogen before the substrate was added, the axial alcohol was preferably obtained even at an early stage of the hydrogenation. This fact may mean that the amount of hydrogen on the catalyst surface affects the product distribution.

Rylander *et al.* reported that Pd was ineffective when the ketone was added all at once to the catalyst. Such a failure of Pd to hydrogenate the aliphatic ketone might be attributed to exceptionally strong adsorption of the ketone. If the ketone was added dropwise to the Pd in solvent, hydrogenation would proceed at a slow but tolerable rate.[14]

Keeping in mind the above assumption, the change in the ratio of the epimeric products when ketone is added, is due to the prevention of hydrogen adsorption on the catalyst by the strong adsorption of the ketone, so that the reaction step IV, the hydrogen transfer to the half-hydrogenated species, which is more affected by the hydrogen concentration on the catalyst surface than that to the adsorbed species becomes product determining. With the progress of the hydrogenation ketone concentration in the reaction system decreases and the hydrogen is easily supplied from the catalyst surface to the intermediates. Therefore, the product determining step shifts to other reaction steps.

Coker *et al.* reported that in the hydrogenation of α-pinene over Pd-carbon, an increase of temperature resulted in an increase of *trans*-pinane. They gave the following plausible reasons: (a) Thermal deformation of the α-pinene molecule might allow shift of equilibrium between α and β-face adsorbed species toward the latter. (b) At higher temperature another mechanism employing a differently adsorbed species might assume prominence so as to give *trans*-pinane by thermodynamic control of the reaction. They had not studied the mechanism of these reactions.[15] We consider that this result infers that at high temperature the amount of hydrogen available decreases and the reaction step IV becomes product determining. Two possible half-hydrogenated species, therefore, should tend to establish the equilibrium with one another and *trans*-pinane will be favoured.

On Pd-carbon which contains alkaline substance the equatorial alcohols were preferably obtained from cyclohexanones. This is similar to the case on Rh or Pt catalyst with sodium hydroxide.

The hydrogenation of 3,3,5-trimethylcyclohexanone gave selectively the axial alcohol irrespective of the catalysts and of reaction conditions. This is because of the large catalyst hindrance of the axial Me group at the 3 position making the adsorption of the substrate from the axial side very difficult.

We concluded that the distribution of the stereoisomeric alcohols depends not only on the structure of the substrates and the kind of the catalyst metal but on the change of the amount of hydrogen available. No significant influence of the presence of alkaline substance in the reaction system was observed in the hydrogenation of methylenecycloalkanes[8,16] and cyclohexenes.[17] In the hydrogenation of ketones over Rh, Pd or Pt the amount of hydrogen available which is affected by the presence of alkaline substance or the strong adsorption of the ketone on the catalyst participates in the distribution of epimeric alcohols, so that the hydrogen transfer to the half-hydrogenated states becomes product determining. On Raney Ni the presence of alkaline substance shows the opposite trend of the isomeric ratio of the products to the hydrogenation on Rh, Pd or Pt. This would indicate that the product determining step of this reaction is not the hydrogen transfer to the substrate but the adsorption of the substrate on the catalyst.

EXPERIMENTAL

Material. Methylcyclohexanone (2-, 3- and 4-substituted), 2-ethylcyclohexanone, 2-isopropylcyclohexanone and t-butylcyclohexanone (2-, 3- and 4-substituted) were prepared by the oxidation ($Na_2Cr_2O_7$ and H_2SO_4 or CrO_3 in AcOH) of the corresponding cyclohexanols which were obtained by the Raney Ni hydrogenation of phenolic compounds at 160° and 150 atm of H_2. Phenylcyclohexanones were prepared by the Pd-C hydrogenation of corresponding substituted cyclohexenols[18] followed by the CrO_3 oxidation in AcOH. 3,3,5-Trimethylcyclohexanone was prepared by the Pd-C hydrogenation of commercial isophorone. 2-Cyclohexylcyclohexanone was prepared by published method.[19] All cyclohexanones agreed in physical constants with samples earlier prepared.

Catalytic hydrogenation. The following general procedure was used. A known amount of substrate and catalyst in solvent was stirred with H_2 at an ordinary temp. The catalyst was removed by the centrifugal method and the mixture was analysed by gas chromatography. At high H_2 pressure, a known amount of substrate, catalyst and EtOH were placed in a 100 ml autoclave and a certain initial pressure of H_2 was set. After stirring for 5 hr the catalyst and the mixture was analysed.

Gas chromatography. Hitachi F-6 and K-53 gas chromatograph equipped with flame ionization detector was used with Infortonics digital integrator. Phenylcyclohexanols were analysed on a 15 m × 0·25 mm Goley column of PEG 4000 at 160°. Others were analysed on a 45 m × 0·25 mm Goley column of PEG 4000; methylcyclohexanols, 100°; 2-ethylcyclohexanols, 120°; 2-isopropyl-, 3,3,5-trimethyl- and t-butylcyclohexanols, 150°; 2-cyclohexylcyclohexanols, 140°.

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