Substituent Effects in Heterogeneous Catalysis

VIII. Reactions of 2-Methyl- and 2-Ethylcyclohexanone with Deuterium Catalyzed by Platinum Metals

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2-Methyl and 2-ethyl derivatives of cyclohexanone were allowed to react with deuterium in t-BuOD using platinum group metals as catalysts. The product alcohols and the remaining ketone were examined by mass spectrometry. Over Ru, Os, and Ir, the simple addition of two deuterium atoms to the carbonyl linkage was predominant, accompanied by little isotopic exchange. Over Pt, however, isotopic exchange was significant and over Rh and Pd quite extensive. The samples obtained over Rh and Pd were further analyzed by NMR spectroscopy to determine the loci of the incorporated deuterium atoms. Deuterium exchange over Pd was almost entirely confined to the C(2) and C(6) positions, while that over Rh was smeared beyond these positions. These results can be accounted for by assuming the intermediacy of π-absorbed π-oxaallylic species on Pd and of $\alpha\beta$-diadsorbed species on Rh.

NOMENCLATURE

Reactants and Products

2-MCH	2-methylcyclohexanone
cis-2-MCHol	*cis*-2-methylcyclohexanol
trans-2-MCHol	*trans*-2-methylcyclohexanol
2-ECH	2-ethylcyclohexanone
cis-2-ECHol	*cis*-2-ethylcyclohexanol
trans-2-ECHol	*trans*-2-ethylcyclohexanol
2-RCH	2-alkylcyclohexanone
cis-2-RCHol	*cis*-2-alkylcyclohexanol
trans-2-RCHol	*trans*-2-alkylcyclohexanol

The last three abbreviations are used when either a methyl or an ethyl derivative or both are referred to.

Reaction Intermediates on Rh

c-C_π, c-C_{oa}, c-C_{ia}^{je}, c-B_i^j	Small letter c refers to reaction pathways leading to *cis*-2-RCHol. Capital letters C and B stand for chair and boat conformations, respectively. Superscripts and subscripts indicate the nature and position of the adsorption bond π (π-adsorption), o (oxygen), a (axial), e (equatorial); i and j indicate the carbon position.
t-C_π, t-C_{oe}, t-C_{ia}^{je}, t-B_i^j	*trans*-course counterpart to the corresponding *cis*-course intermediate

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Others

t-BuOD	*tert*-butanol-O-d_1
LIS	lanthanide-induced shift
H(ia), H(ie)	the a (axial) or e (equatorial) hydrogen attached to the ith carbon atom
D_{ia}, D_{ie}	average number of deuterium atoms incorporated into the position indicated by the subscript
D_m	mean number of the incorporated deuterium atoms per molecule

INTRODUCTION

In metal-catalyzed hydrogenation of alicyclic ketones, not only the carbonyl group but also the α carbons may participate in adsorption (*1, 2*). This is especially true with Rh and Pd catalysis (*3, 4*). For unsymmetrical ketones such as 2-MCH, it may well be asked: (i) which of the two α carbons, C(2) or C(6), has a greater preference for participating in adsorption and (ii) which hydrogen at C(6), the axial or equatorial, is preferentially abstracted to form an adsorption bond. These questions could be solved by deuteration of 2-MCH and subsequent location of the deuterium atoms incorporated into the product alcohols and the remaining ketone. Such a tracer study has already been made in our laboratories (*5*). The deuterium distribution patterns for Rh were quite different from those for Pd. This suggests different exchange mechanisms for these catalysts. However, we had to refrain from going into details of these mechanisms owing to rather poor deuterium incorporation. It is hoped that deuterium incorporation would be enhanced by compensating somehow for the isotopic dilution of gas-phase deuterium caused by exchange.

The present work furthers the previous one with emphasis on the mechanistic studies of Rh- and Pd-catalyzed exchange. The isotopic dilution was minimized by choosing t-BuOD as the solvent instead of the cyclohexane used previously. 2-ECH was also used as a reaction substrate for a comparison with 2-MCH.

EXPERIMENTAL

The experimental procedures for ketone deuteration were similar to those detailed in the previous paper of this series (*5*). Only their outline is given herein with some modifications employed this time.

Materials. Commercial 2-MCH was purified as described previously. 2-ECH was synthesized and generously donated by Mr. T. Chihara in our laboratory. The synthetic procedure consisted of hydrogenation of 2-acetylphenol over Ni (*6*) to 2-ECHol, followed by chromic acid oxidation (*7*). Repeated distillations under reduced pressure gave 2-ECH as a colorless liquid, and no impurity peaks were detected by gas chromatography. Other chemicals were all commercially available and used as received. The procedures for catalyst preparation have been described previously (*8*).

Apparatus. The all-glass reaction vessel used for both deuteration and exchange reactions has been described previously (*8*). The instruments used for product separation and analyses were a Shimadzu GC-1C gas chromatograph, a Hitachi RMS-4 mass spectrometer, and a Varian HA-100D NMR spectrometer.

Kinetic procedures. Deuterations of 2-MCH and 2-ECH were all conducted at 30°C and atmospheric pressure using t-BuOD as the solvent. Other experimental conditions are listed in Table 1. After reaction, the reaction mixture was shaken first with twice its volume of saturated Na_2SO_4 (to convert the OD group of the product alcohols to OH) and then with ether to extract the ketone and alcohols. The ether extract was separated into components by preparative gas chromatography. Each gas chromatographic peak was collected and subjected to mass and NMR spectrometry for isotopic distributions.

Analytical procedures. The mass spectrometer was operated at a low electron-

TABLE 1

Reaction Conditions and Stereoselectivities (30°C)

Expt.	Catalyst		Time	Conv.[a]	cis[b]
	Metal	mg	(min)	(%)	(%)
	2-MCH				
1	Ru	60	87	72.8	56.4
2	Rh	60	85	69.5	55.6
3	Pd	200	190	41.1	73.4
4	Os	50	47	71.4	71.1
5	Ir	120	44	70.3	60.4
6	Pt	100	324	70.7	49.5
	2-ECH				
7	Rh	60	105	70.7	53.0
8	Pd	250	330	51.5	68.2

[a] Conversion = $100([cis\text{-}2\text{-RCHol}] + [trans\text{-}2\text{-RCHol}])/([2\text{-RCH}] + [cis\text{-}2\text{-RCHol}] + [trans\text{-}2\text{-RCHol}])$.

[b] Percentage is = $100[cis\text{-}2\text{-RCHol}]/([cis\text{-}2\text{-RCHol}] + [trans\text{-}2\text{-RCHol}])$.

accelerating voltage of 8 V to minimize fragmentation. The isotopic distributions of the ketones and alcohols were all determined from the parent ion peaks P^+ after suitable corrections for naturally occurring ^{13}C and ^{18}O. The P^+ intensity was sufficiently high even for cis- and trans-2-RCHol to allow quantitative analyses to be made (5).

The axial and equatorial deuterium contents at each carbon position were estimated from LIS spectra in NMR for the ketones and alcohols. The estimation was made by comparing the integration of the axial or equatorial proton at a certain carbon position with that of a reference proton. The LIS reagents and internal reference protons chosen for 2-MCH, cis-, and trans-2-MCHol have already been described (5). For the ethyl derivatives these were

2-ECH	Yb(fod)₃	H(3a)
	Pr(fod)₃	H(3a)
cis-2-ECHol	Eu(fod)₃	H(3e) + H(4e) + H(4a) (partly resolved)
trans-2-ECHol	Pr(fod)₃	H(3a).

The choice of these protons on the sample molecule itself as reference is based on the tacit assumption that they are not contaminated by deuterium. It will be shown later in this paper that this assumption is, if not correct, a good approximation.

Signal assignments for the ethyl derivatives (2-ECH, cis-, and trans-2-ECHol) will be given elsewhere. However, it seems worth noting that in the case of trans-2-ECHol, one proton at the C(7) position (H(7α)) appeared as a triplet and the other (H(7β)) as a doublet upon irradiation of the C(8)-methyl protons.
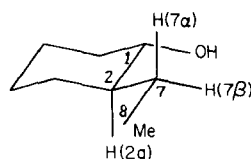
(Possible orientation of the alkyl side chain of trans-2-ECHol upon coordination to the LIS reagent.)

This indicates that upon coordination of trans-2-ECHol to the LIS reagent the internal rotation about the C(2)–C(7) axis is restricted, with a preferred conformation in which the C(7)–H(7α) bond is parallel or antiparallel to the C(2)–H(2a) bond. Also for 2-ECH and cis-2-ECHol, the C(8)-methyl proton decoupled signals of H(7α) and H(7β) were different from each other, although not well defined. Presumably, 2-ECH and cis-2-ECHol are coordinated to the LIS reagent in the conformation in which the C(7)–H(7α) bond is a little tilted—the dihedral angle H(7α)–C(7)–C(2)–H(2a) is neither 180 nor 0°.

RESULTS

Mass Spectrometry

The results are summarized in Table 2. Let us first examine the data on 2-MCH deuteration, experiments 1 through 6. Three characteristic features are noteworthy. (i) With respect to 2-MCH, the extent of deuterium exchange (D_m) is in the order, Pd > Rh ≫ Pt ≫ Ru ≈ Ir ≈ Os. (ii) With respect to 2-MCHol, deuterium distribution

TABLE 2

Isotopic Analysis of the Residual Ketone and Product Alcohols

Expt.	Isomer	Cat.	Percentage of each isotopic species									D_m
			d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	d_8	
			2-MCH									
1		Ru	95.3	4.7	0	0	0	0	0	0	0	0.05
2		Rh	27.7	27.2	21.2	10.0	5.8	3.7	2.3	1.4	0.7	1.71
3		Pd	2.4	17.9	41.8	33.8	3.7	0.4	0	0	0	2.20
4		Os	99.3	0.6	0.1	0	0	0	0	0	0	0.01
5		Ir	97.3	2.0	0.5	0.2	0	0	0	0	0	0.04
6		Pt	81.5	8.9	2.9	1.6	2.9	1.0	0.6	0.4	0.2	0.44
			2-ECH									
7		Rh	30.5	25.5	21.7	10.4	6.2	3.5	1.4	0.5	0.2	1.56
8		Pd	1.5	12.7	38.6	40.0	6.5	0.7	0	0	0	2.39
			2-MCHol[a]									
1	cis	Ru	3.1	93.2	2.8	0.5	0.2	0.1	0	0	0	1.02
	trans		4.8	91.5	2.9	0.5	0.2	0.1	0	0	0	1.00
2	cis	Rh	17.7	45.4	16.3	9.7	4.5	2.8	1.8	1.1	0.7	1.63
	trans		16.8	47.0	16.1	9.6	4.4	2.7	1.6	1.0	0.6	1.61
3	cis	Pd	8.6	25.6	34.4	23.4	7.2	0.8	0.1	0	0	1.98
	trans		9.3	26.4	34.2	22.4	6.8	0.8	0.1	0	0	1.94
4	cis	Os	4.5	92.7	2.6	0.1	0.1	0	0	0	0	0.99
	trans		4.6	93.0	2.1	0.2	0.1	0	0	0	0	0.98
5	cis	Ir	7.3	89.6	2.8	0.2	0.1	0	0	0	0	0.96
	trans		6.7	90.9	2.1	0.3	0.1	0	0	0	0	0.96
6	cis	Pt	8.5	81.6	8.0	1.0	0.4	0.2	0.2	0.1	0	1.05
	trans		7.5	84.5	6.6	0.8	0.3	0.2	0.1	0	0	1.03
			2-ECHol[a]									
7	cis	Rh	19.2	45.9	15.4	10.0	4.5	2.7	1.5	0.7	0.3	1.54
	trans		17.7	44.4	17.9	10.2	4.8	2.6	1.4	0.7	0.3	1.58
8	cis	Pd	8.7	22.3	31.8	25.9	9.7	1.3	0.3	0.1	0	2.11
	trans		10.1	22.1	30.5	25.0	10.1	1.8	0.3	0.1	0	2.10

[a] Hydroxyl deuterium was replaced by hydroxyl hydrogen before mass spectrometric analysis.

patterns are essentially identical for cis and trans isomers on all the catalysts. (iii) The amounts of highly deuterated species (d_4–d_8 for 2-MCH and d_5–d_8 for 2-MCHol) are greater for Rh than for Pd although Rh is smaller in D_m. These features have already been met in the previous study (5) conducted in cyclohexane solvent. Since t-BuOD was used as solvent in the present study, it is very likely that characteristic features (i)–(iii) are little affected by solvent and reflect the properties of the catalyst itself. Experiments 7 and 8 show that characteristic features (ii) and (iii) hold also for 2-ECH deuteration.

It should be noted that 2-RCH can accommodate only three deuterium atoms at C(2) and C(6), and therefore the formation of d_4 and more highly exchanged species is indicative of deuterium smear beyond these positions. In the case of cis- and trans-RCHol, the formation of d_5 and higher species proves deuterium smear. Inspection of Table 2 with this in mind shows that deuterium smear is most pronounced on Rh followed by Pt. Interestingly, deuterium smear for Pd is rather small in view of the dearth of the high d_i species ($i \geq 4$ for 2-MCH and $i \geq 5$ for 2-RCHol) although D_m is greatest for Pd.

NMR Spectrometry

Table 3 lists the stereochemical deuterium distributions for 2-RCH and 2-RCHol samples, i.e., the axial and equatorial deuterium contents at various carbon positions worked out based on NMR data. The last two columns compare the D_m values estimated from the NMR data with those from the mass spectrometric data (Table 2). The agreement is satisfactory or fairly good except for 2-ECH in experiment 7, thus providing evidence for what we have assumed in the Experimental section for estimations of deuterium content from NMR data. The exceptional disagreement is probably due to the contamination of the particular sample with unidentified impurities accidentally introduced during the separation procedure after reduction.

In Table 3 no data for cis-2-MCHol (experiments 2 and 3) are given because of poor separation of the LIS spectra. Noteworthy with the deuterium incorporation pattern in the C(2) and C(6) positions is a substantial difference between Rh and Pd ($D_{6a} > D_{2a} \approx D_{6e}$ on Rh and $D_{2a} > D_{6a} \approx D_{6e}$ on Pd) no matter which sample (2-RCH, cis-, or trans-2-RCHol) is looked at. In terms of substituent effect it might be said that on Rh the alkyl substituent hinders the exchange of the hydrogen (H(2a)) ipso to the substituent, but rather accelerates it on

Pd. This contrast is a reinforcement to the previous observation (5) in 2-MCH deuteration in a different solvent (cyclohexane). Deuterium smear beyond the C(2) and C(6) positions is significant only for Rh. Although the previous work failed in pinpointing the smeared deuterium atoms, it is now clear that they are concentrated at C(5e) and C(7). In experiment 7, a close inspection of the LIS spectra of the two hydrogens at C(7) on 2-ECH and cis-2-ECHol has disclosed that one hydrogen is preferentially replaced by deuterium. This suggests that in the course of 2-ECH deuteration (or hydrogenation) on Rh, the ethyl side chain is conformationally fixed with one H(7) pointing to the catalyst.

DISCUSSION

Catalysts Other Than Rh and Pd

The paucity of deuterium exchange on Ru, Os, and Ir indicates that 2-RCH hydrogenation catalyzed by these metals proceeds almost entirely through the simple addition of two hydrogen atoms to the carbonyl bond. The simple addition mechanism is also dominant on Pt, which, however, must be accompanied by some mechanistic complication, judged from the observed moderate exchange.

Deuterium Exchange on Pd

The observed deuterium exchange ac-

TABLE 3

Stereochemical Distributions of the Deuterium Atoms Incorporated into Ketones and Alcohols

| Expt.	Cat.	Sample	D_{1a}	D_{2a}	D_{6a}	D_{6e}	D_{3e}	D_{5e}	D_7	Others	D_m NMR	D_m MS
2	Rh	2-MCH	—	0.15	0.50	0.17	0.05	0.35	0.32	0	1.54	1.71
		trans-2-MCHol	0.64	0.08	0.32	0.11	0	0.19	0.11	0	1.45	1.61
3	Pd	2-MCH	—	0.81	0.56	0.60	0	0	0	0	1.97	2.20
		trans-2-MCHol	0.44	0.71	0.40	0.35	0	0	0	0	1.90	1.94
7	Rh	2-ECH	—	0.26	0.38	0.17	0	0.17	0.14	0	1.12	1.56
		cis-2-ECHol	0.73	0.14	0.26	0.14	0	0.07	0.14	0	1.48	1.54
		trans-2-ECHol	0.74	0.16	0.32	0.16	0	0.08	0	0	1.46	1.58
8	Pd	2-ECH	—	0.83	0.71	0.74	0	0	0	0	2.28	2.39
		cis-2-ECHol	0.60	0.64	0.47	0.44	0	0	0	0	2.15	2.11
		trans-2-ECHol	0.48	0.71	0.41	0.38	0	0	0	0	1.98	2.10
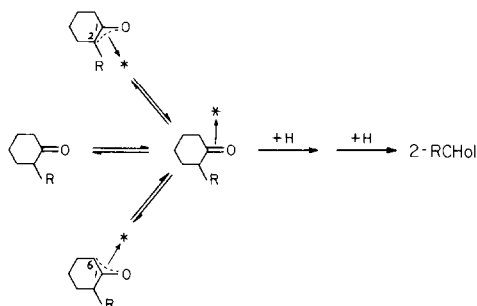
FIG. 1. Reaction scheme for 2-RCH hydrogenation over Pd.

companying 2-RCH deuteration over Pd is characterized by considerable deuterium incorporation into C(2) and C(6) and little deuterium smear beyond these positions. In order to explain this characteristic feature, we have previously (5) proposed an exchange mechanism (Fig. 1) where deuterium exchange is brought about by two preequilibrium steps involving three π-adsorbed species: one step between 2-RCH and OC(1)C(2)-π-oxaallyl, and the other between 2-RCH and OC(1)C(6)-π-oxaallyl.

Deuterium Exchange on Rh

Since deuterium smear beyond the C(2) and C(6) positions is quite extensive on Rh, it is highly unlikely that the adsorbed π-oxaallylic species play a dominant role as in the case of Pd. Rather, deuterium exchange on Rh is considered to proceed via adsorption-bond migration due to interconversion of monoadsorbed and $\alpha\beta$-diadsorbed species. The term "$\alpha\beta$ process" has been coined to identify this interconversion process (9).

In the case of a six-membered ring, the $\alpha\beta$-diadsorbed species could be either in the chair conformation with staggered adsorption bonds or in the boat conformation with eclipsed adsorption bonds. Inspection of a molecular model shows that the results $D_{5e} > D_{5a} = 0$ and $D_{6a} > D_{6e}$ (Table 3) are hardly explicable in terms of the staggered intermediates. The usually accepted eclipsed intermediate (10) seems to play a dominant role also in this case.

The mechanism shown in Fig. 2 is based on the $\alpha\beta$ process involving the eclipsed $\alpha\beta$-diadsorbed intermediates, and regarded as a stereochemically elaborated version of the mechanism we have previously (5) proposed for 2-MCH deuteration and exchange over Rh. Before explaining the observed stereochemical deuterium distributions based on this mechanism, it is necessary to examine the proposed reaction pathway. The hydrogenation starts out with π adsorption of 2-RCH. Two distinct π-adsorbed species, c-C_π and t-C_π, are formed, depending upon which face of the six-membered ring is pointed to the catalyst surface. The c-C_π and t-C_π are eventually hydrogenated to *cis*- and *trans*-2-RCHol, respectively, through a series of elementary steps.

In the *trans* course, t-C_π is first converted to the diadsorbed species t-C_{oe}^{1a}, followed by hydrogen (or deuterium) uptake to form a monoadsorbed species, either t-C_{oe} or t-C_{1a}. Since t-C_{1a} ought to undergo serious steric hindrance due to the close proximity of H(3a) and H(5a) to the catalyst surface, the path through t-C_{oe} is probably predominant. In the case of deuteration, the t-C_{oe} path introduces deuterium atoms only to the C(1) and O positions. Alternation between t-C_{1a} and t-B_1^6 is highly unlikely to occur because t-B_1^6 suffers from a great van der Waals strain due to steric crowding of the flagpole alkyl. Thus, little or no deuterium exchange is expected in the *trans* course.

Now let us follow the *cis* course leading to *cis*-2-RCHol. Each of the first three steps up to c-C_{oa} or c-C_{1e} are analogous to the *trans*-course counterpart except that no serious steric hindrance to adsorption is expected for c-C_{1e}, unlike t-C_{1a}. We assume that the path through c-C_{1e} is favored over that through c-C_{oa}. The c-C_{1e} is either directly hydrogenated to the *cis* alcohol or undergoes hydrogen abstraction to give diadsorbed species c-B_1^2 or c-B_1^6. When 2-RCH is deuterated, alternation between c-C_{1e} and these diadsorbed species contributes to deuterium exchange at the C(2) and
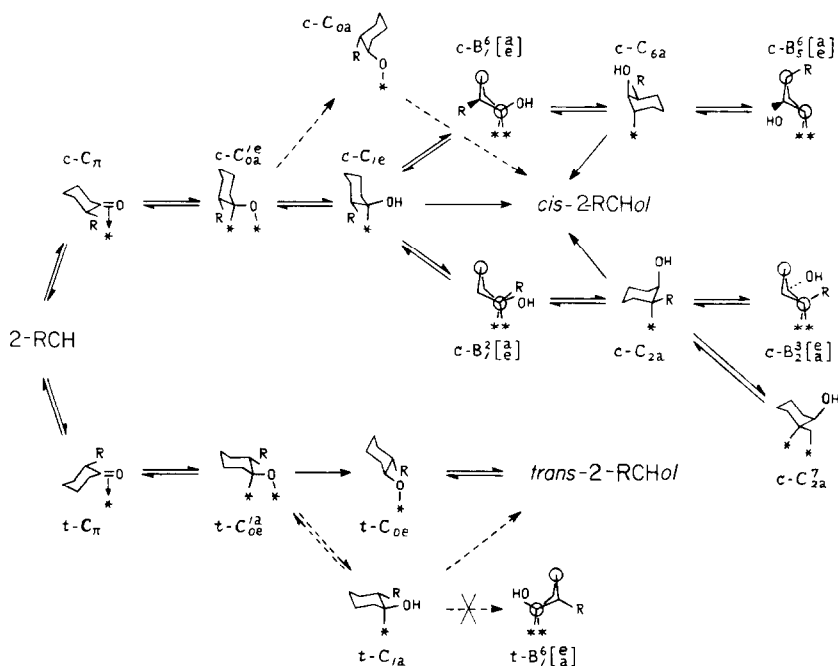
$c\text{-}C_{oa}$ $c\text{-}B_7^6[\frac{a}{e}]$ $c\text{-}C_{6a}$ $c\text{-}B_5^6[\frac{a}{e}]$

$c\text{-}C_\pi$ $c\text{-}C_{oa}^{/e}$ $c\text{-}C_{/e}$ $cis\text{-}2\text{-}RCHol$

2-RCH

$c\text{-}B_1^2[\frac{a}{e}]$ $c\text{-}C_{2a}$ $c\text{-}B_2^3[\frac{e}{a}]$

$c\text{-}C_{2a}^7$

$t\text{-}C_\pi$ $t\text{-}C_{oe}^{/a}$ $t\text{-}C_{oe}$ $trans\text{-}2\text{-}RCHol$

$t\text{-}C_{/a}$ $t\text{-}B_7^6[\frac{e}{a}]$

FIG. 2. Reaction scheme for 2-RCH hydrogenation over Rh. Symbols enclosed by brackets at the right-hand side of intermediates c- and t-B_i^j, etc., indicate which position (axial or equatorial) is occupied by the hydrogen or deuterium atoms picked up by adsorption bond i and j when the intermediate is converted to the alcohol. In $c\text{-}B_1^6[_e^a]$, for instance, the deuterium atoms picked up by the adsorption bonds of the intermediate occupy the C(1)-equatorial and C(6)-axial positions of cis-2-RCHol.

C(6) positions. The $c\text{-}B_1^6$ may also be converted to other diadsorbed species $c\text{-}B_5^6$ through $c\text{-}C_{6a}$. Similarly, $c\text{-}B_1^2$ may become $c\text{-}B_2^3$ or $c\text{-}C_{2a}^7$. The alternation processes involving these species cause deuterium exchange at C(3), C(5), and C(7).

The reaction scheme in Fig. 2 can explain most of the results obtained for Rh. First, let us recall the close similarity between cis- and $trans$-2-RCHol in the isotopic distribution patterns determined by mass spectrometry. If the rate-controlling step is the hydrogen uptake by $t\text{-}C_{oe}^{1a}$ in the $trans$ course and the hydrogen uptake by the monoadsorbed species ($c\text{-}C_{1e}, c\text{-}C_{6a}, c\text{-}C_{2a}$) in the cis course, then these four intermediates must be in preequilibrium with one another. It is by this preequilibrium that a close similarity is brought about between cis- and $trans$-2-RCHol in the isotopic distribution pattern. Second, let us consider the result $D_{5e} > D_{5a} = 0$. Molecular

models indicate that alternation $c\text{-}C_{6a} \rightleftharpoons c\text{-}B_5^6$ can bring deuterium to the equatorial but not to the axial position at C(5), in accord with experiment. Third, the result $D_{2a} < D_{6a}$ is understandable if one compares the conformation of $c\text{-}B_1^2$ with that of $c\text{-}B_1^6$. In $c\text{-}B_1^2$ the boat-axial OH at C(1) and the boat-axial alkyl at C(2) are eclipsed by each other, thus causing severe steric crowding. In $c\text{-}B_1^6$ the alkyl is at the bowsprit position with minimal crowding. Therefore, alternation $c\text{-}C_{1e} \rightleftharpoons c\text{-}B_1^6$ is favored over alternation $c\text{-}C_{1e} \rightleftharpoons c\text{-}B_1^2$, thus leading to the result $D_{2a} < D_{6a}$. Finally, let us take a look at the result $D_{6a} > D_{6e}$. Inspection of a molecular model reveals that the favored alternation $c\text{-}C_{1e} \rightleftharpoons c\text{-}B_1^6$ can bring a deuterium to the C(6)-axial but not to the C(6)-equatorial position. The proposed reaction scheme in Fig. 2 thus can account for the preferential deuterium incorporation at the C(6)-axial position, but

fails to explain the smaller but significant deuterium incorporation at the C(6)-equatorial position.

This failure may be due to the oversimplification implicit in the reaction scheme, e.g., neglect (i) of staggered $\alpha\beta$-diadsorbed intermediates; (ii) of the chair conformer of 2-RCH with the alkyl substituents at axial despite its significant population, which amounts to 10.3% for 2-MCH and 14.5% for 2-ECH in conformational equilibrium at 31.9°C (11); (iii) of the eclipsed $\alpha\beta$-diadsorption of Type II compared with Type I (Fig. 3). Item (iii) is made on the supposition that the intermediate type II suffers from steric hindrance to adsorption caused by the boat-axial hydrogens on the δ and ϵ carbons. One might think that the intermediacy of t-C_π is unrealistic because there would be a strong repulsion between the ring and the surface. It should be noted, however, that such ring–surface interaction, even though enormous when the C=O linkage is parallel to the surface, becomes less significant as the angle between the C=O bond and the surface increases. There is good evidence that the C=O linkage of adsorbed ketones is closer to perpendicular rather than parallel to the catalyst plane (12). In such an orientation, t-C_π would be free from any serious ring–surface repulsion.

In our previous study (13) of deuteration of enol ether (4-t-butyl-1-cyclohexenyl methyl ether) catalyzed by platinum group metals, we have provided evidence for the intermediacy of the staggered $\alpha\beta$-diadsorbed species. The question now raised is why the $\alpha\beta$-diadsorbed intermediate is
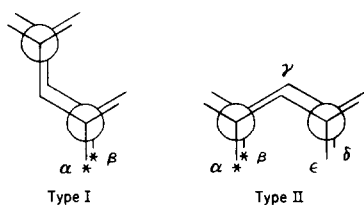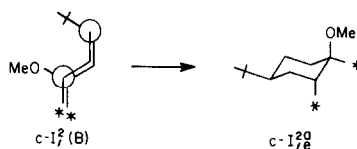

Fig. 4. Possible intermediates in the metal-catalyzed hydrogenation of 4-t-butyl-1-cyclohexenyl methyl ether. Release of steric strain due to the bulky t-butyl by conversion of the eclipsed diadsorbed species to the staggered diadsorbed species.

staggered for enol ether reaction and eclipsed for 2-RCH reaction. There is a conjecture as to the reason for this difference. The eclipsed $\alpha\beta$-diadsorbed species of the enol ether corresponding to c-B_1^2 or c-B_1^6 is given in Fig. 4 as c-$I_1^2(B)$. Since in c-$I_1^2(B)$ the t-butyl occupies the boat-axial position, there ought to be severe repulsive interaction around the bulky group. This repulsion must be relieved upon conversion to c-I_{1e}^{2a}, which is in the chair form with the t-butyl at the equatorial position. In the case of the 2-RCH reaction, c-B_1^6 and c-B_1^2 seem to be free from such strong repulsive interaction.

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Fig. 3. Two types of $\alpha\beta$ diadsorption for the cyclohexane ring in the boat form.

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