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# Deuteration of 4-t-Butyl-1-cyclohexenyl Methyl Ether Catalyzed by Platinum Metals: Evidence for Staggered $\alpha\beta$-Diadsorbed Intermediates

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Deuteration of 4-t-butyl-1-cyclohexenyl methyl ether was carried out at 80°C in cyclohexane under pressure. Over Ru, Rh, and Pd, the reaction products consisted almost entirely of the *cis* and *trans* mixtures of the corresponding saturated ethers (*cis*- and *trans*-4-t-butyl-1-cyclohexyl methyl ether), whereas over Os, Ir, and Pt, hydrogenolysis to t-butylcyclohexane was not negligible. The isomeric mixtures were separated and analyzed for isotopic distributions by mass spectrometry (MS) and for deuterium positions within each molecule by NMR spectroscopy. With most catalysts, the MS-determined isotopic distribution pattern for the *cis* ether was quite different from that of the *trans* ether. Also the NMR-based deuterium distributions were markedly different between these isomers. These dissimilarities can be best explained by assuming a few staggered $\alpha\beta$-diadsorbed species as intermediates in enol ether hydrogenation.

## INTRODUCTION

It is generally accepted that metal-catalyzed olefin hydrogenation and related reactions proceed by the Horiuti–Polanyi mechanism (*1*), the first step of which represents nondissociative adsorption of the olefin on the catalyst surface. Three different structures have been proposed for this intermediate; $\pi$-bonded species (*2–4*), eclipsed $\alpha\beta$-diadsorbed species (*1, 5*), and staggered $\alpha\beta$-diadsorbed species (*6–9*). To test the former two proposals, a number of reactions of cyclic hydrocarbons with deuterium were conducted and the initial isotopic exchange on both faces of the compounds was closely examined. Recently Burwell's rollover mechanism based on the eclipsed $\alpha\beta$-diadsorption seems to have found more support than Rooney's olefin/$\pi$-allyl interconversion mechanism based on the $\pi$-adsorption (*10, 11*), although there is another view that the $\alpha\beta$-diadsorbed species is not significantly different from the $\pi$-bonded species (*12, 13*). The third proposal, staggered $\alpha\beta$-diadsorption, thus far has received little attention. As far as we know, it is only in our previous work (*8*) that the third proposal has been employed to explain organic substance–deuterium exchange data. In this report we present further kinetic evidence for staggered $\alpha\beta$-diadsorption.

The initial purpose of the present work was to elucidate the mechanism of enol ether hydrogenation in connection with ketone hydrogenation. One might suspect that in ketone hydrogenation the enol tautomer also plays a significant role. Although we (*8, 14*) previously ruled out such an enol role based on deuterium tracer studies, the argument over Rh and Pd catalysts has been questioned by Siegel (*8*). Since 4-t-butyl-l-cyclohexenyl methyl ether (I) is regarded as the methyl-substituted enol form of 4-t-butylcyclohexanone, we felt that studying the reaction of I with deuterium would help solve the problem.

Hydrogenation of enol ethers has already been studied by Acke and Anteunis (*15*) on Pt, and more recently by Nishimura *et al.* (*16*) on six platinum metals. No deuterium tracer studies, however, preceded ours carried out in 1974. The data on Pt in this

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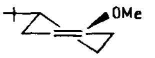
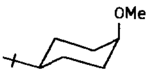
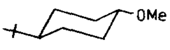


**I**

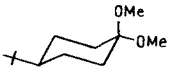


*cis*-**II**

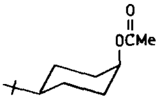


*trans*-**II**

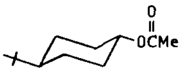
**III**



**IV**



*cis*-**V**



*trans*-**V**

tracer study have already been outlined in a short note (*17*). Herein we cite these data again in order to make a comparison with those on other platinum-group metals.

## EXPERIMENTAL

*Materials*. The reactant **I** was prepared using 4-t-butylcyclohexanone as the starting material, according to a method analogous to that employed by Nishimura *et al.* (*16*) for synthesis of 4-methyl-1-cyclohexenyl ethyl ether. The **I** obtained after distillation under reduced pressure (92 ± 3°C, 13 mm Hg) contained a small amount (2.4 mol%) of 4-t-butylcyclohexanone dimethyl acetal (**IV**), but was used without further purification.

The metal-black catalysts were prepared by the method described previously (*14*). Before use, each catalyst was refluxed for 1–2 hr with $D_2O$, filtered off, and dried under reduced pressure. This $D_2O$ treatment was given to eliminate ordinary adsorbed water and thus to minimize isotopic dilution of the surface deuterium pool during reaction.

Deuterium, 99.9% in stated isotopic purity, was purchased from Showa Denko Company, Tokyo, and used as received. Other chemicals were also commercially obtained and used as received.

*Deuteration*. A weighed sample of **I** (5 g, 0.030 mol) dissolved in 20 ml of cyclohexane was placed in a 100-ml autoclave with a magnetically driven stirring device, together with some 20 or 30 mg of a catalyst. Deuterium was introduced into the autoclave to a pressure of about 20 kg/cm$^2$ after several flushings. The autoclave was then immersed in a water bath thermostated at 80°C and allowed to stand until thermal equilibrium was established. The deuterium pressure was adjusted to 22 kg/cm$^2$, and deuteration was started by starting the stirring. The pressure drop due to the reaction was 4 kg/cm$^2$ at most. Other reaction conditions are listed in Table 1. After reaction the reaction mixture was separated by a Shimadzu GC-1C gas chromatograph with a PEG 20M column (140°C). The main reaction products, *cis*- and *trans*-4-t-butylcyclohexyl methyl ether (*cis*- and *trans*-**II**), and a major byproduct, t-butylcyclohexane (**III**), were analyzed for isotopic distribution by NMR and mass spectrometry.

*II to V conversion for NMR–LSR Studies*. Deuteriums incorporated into *cis*- and *trans*-**II** were located by employing the $^1$H NMR–LSR (lanthanide shift reagent) technique (*18*). In the beginning, attempts were made to apply this technique directly to *cis*- and *trans*-**II** samples, but no well-resolved NMR spectra could be obtained. In a further effort at deuterium location we converted *cis*- and *trans*-**II** to the corresponding acetates (*cis*- and *trans*-**V**) by a modification of the method applied to a

TABLE 1

Deuteration of **I**: Reaction Conditions and Selectivities

| Expt | Catalyst | | Temp (°C) | $P_{D_2}$[a] (atm) | Time (min) | $X$[b] (%) | $S_c$[c] (%) | $S_h$[d] (%) |
|---|---|---|---|---|---|---|---|---|
| | Metal | mg | | | | | | |
| 1 | Ru | 20 | 80 | 22–18 | 10 | 100 | 40 | 0.5 |
| 2 | Rh | 20 | 80 | 22–18 | 10 | 100 | 68 | 0.1 |
| 3 | Pd | 20 | 80 | 22–18 | 15 | 100 | 89 | 0.1 |
| 4 | Os | 20 | 80 | 22 | 60 | 12 | 45 | 3.6 |
| 5 | Os | 31 | 80 | 22–19 | 190 | 58 | 41 | 2.1 |
| 6 | Ir | 20 | 80 | 22–18 | 85 | 98 | 50 | 7.2 |
| 7 | Pt | 20 | 80 | 22–18 | 8 | 100 | 74 | 16.4 |

[a] Pressure of $D_2$.

[b] Conversion = 100 ([*cis*-II] + [*trans*-II] + [III])/([I] + [*cis*-II] + [*trans*-II] + [III]).

[c] Stereoselectivity to *cis* = 100[*cis*-II]/([*cis*-II] + [*trans*-II]).

[d] Extent of hydrogenolysis = 100[III]/([*cis*-II] + [*trans*-II] + [III]).

steroid methyl ether by Narayanan and Iyer (*19*). The conversion product, *cis*- and *trans*-V, gave well-resolved NMR spectra by aid of LSR, thus permitting one to estimate the axial and equatorial deuterium contents at each carbon position. In order to ensure that these estimations well represent those for the original *cis*- and *trans*-**II** samples we conducted the following subsidiary experiments.

Prior to the chemical conversion, the *cis*- and *trans*-**II** samples obtained on the different catalysts were all subjected to ordinary NMR spectrometry, and it was confirmed that no deuteriums are contained in the methoxyl group which is eliminated by subsequent chemical conversion. That the chemical conversion leaves intact the deuteriums incorporated into the cyclohexane ring was ascertained by comparing the mass spectral data taken before and after chemical conversion. These data will be shown in the Results section.

The typical procedure for the **II** to **V** conversion was as follows. Boron trifluoride etherate (1 ml) was added dropwise to a solution of *cis*- or *trans*-**II** (400 μl) in acetic anhydride (10 ml) cooled to −20°C. The mixture was allowed to stand at this temperature for 2 hr, after which ice-cold water (10 ml) was added all at once, and then potassium carbonate to a pH of 7. The neutral solution was extracted with diethyl ether. The extract was dried over sodium sulfate and subjected to preparative gas chromatography using a PEG 20M column. The yields of *cis*- and *trans*-**V** collected were about 40 and 20%, respectively.

*Mass spectrometry.* Mass spectra were run with a Hitachi RMS-4 instrument at a low electron accelerating voltage of 8 V to minimize fragmentation. Except for *cis*- and *trans*-**V**, the isotopic distributions of various deuteromolecules were determined from the parent ion ($P^+$) peaks after corrections for naturally occurring $^{13}C$ and $^{18}O$. In the case of *cis*- and *trans*-**V**, the $P^+$ peak was so low that we chose for isotopic analysis the $(P-15)^+$ peak, which is presumably formed by the loss of the acetoxyl methyl. In estimating isotopic distribution, the assumption was made that during fragmentation no deuterium scrambling occurs.

*NMR spectrometry.* The NMR spectrometer used was a Varian HA-100D instrument. First-order NMR spectra were obtained for both *cis*- and *trans*-**V** dissolved in $CCl_4$ containing a LSR. The LSR used was $Eu(fod)_3$ for *cis*-**V** and $Pr(fod)_3$ for *trans*-**V**. Proton assignments were based on the chemical shifts, integrals, multiplicity, and spin decoupling. The stereochemical isotopic distributions were estimated from the integral curves of the shifted NMR spectra using the acetoxyl protons as the "intramolecular standard."

## RESULTS

*Reaction products.* The main reaction was the reduction of **I** to *cis*- and *trans*-**II** accompanied more or less by hydrogenolysis to **III**. Small amounts of 4-t-butylcyclohexanone and 4-t-butylcyclohexanol (combined yield ≤0.7 mol%) were also detected, but they may have come from the **IV** contained in **I** as an impurity. Table 1 includes the data on conversion ($X$), the stereoselectivity for *cis*-**II** ($S_c$), and the extent of hydrogenolysis ($S_h$). In agreement with the experiments reported by Nishimura *et al.* (Table 1 of Ref. (*16*), hydrogenolysis is more significant on the heavy triad (Os, Ir, Pt) than on the light one (Ru, Rh, Pd).

*Mass data.* The isotopic distributions of *cis*- and *trans*-**II** are given in Table 2 together with the data for the mean number of deuterium atoms incorporated per product molecule ($D_m$). The listed $d_i$ values were reproducible to approximately ±0.2% when $d_i < 10\%$ and to a factor of 1.02 when $d_i > 10\%$. Of particular interest is the significant difference in distribution pattern between *cis*- and *trans*-**II**, except for the case of Pd and Pt.

Before examining Table 2 in more detail it is pertinent to consider the correlation of

TABLE 2

Isotopic Analysis of Reaction Products from **I** Deuteration

| Expt | Catalyst | Isomer | Percentage of each isotopic species | | | | | | | | | $D_m$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | $d_0$ | $d_1$ | $d_2$ | $d_3$ | $d_4$ | $d_5$ | $d_6$ | $d_7$ | $d_8$ | |
| **II** (4-t-butylcyclohexyl methyl ether) | | | | | | | | | | | | |
| 1 | Ru | *cis* | 4.2 | 19.2 | 34.8[a] | 22.5 | 11.4 | 5.2 | 2.6 | 0.2 | 0 | 2.45 |
| | | *trans* | 3.7 | 18.2 | 39.3[a] | 23.5 | 9.9 | 4.1 | 1.2 | 0.2 | 0 | 2.36 |
| 2 | Rh | *cis* | 10.9 | 24.3 | 25.8[a] | 19.7 | 11.3 | 5.5 | 2.1 | 0.5 | 0 | 2.23 |
| | | *trans* | 9.7 | 22.9 | 28.4[a] | 20.7 | 10.8 | 5.2 | 1.8 | 0.5 | 0 | 2.25 |
| 3 | Pd | *cis* | 11.8 | 21.7 | 25.1 | 21.0 | 13.8 | 5.9 | 0.7 | 0.2 | 0 | 2.24 |
| | | *trans* | 8.9 | 20.2 | 25.9 | 22.0 | 15.0 | 6.9 | 0.8 | 0.2 | 0 | 2.39 |
| 4 | Os | *cis* | 1.8 | 9.1 | 65.1[a] | 19.5[a] | 3.5[a] | 1.0 | 0.2 | 0 | 0 | 2.18 |
| | | *trans* | 2.7 | 8.9 | 76.7[a] | 10.3[a] | 1.1[a] | 0.3 | 0 | 0 | 0 | 1.99 |
| 5 | Os | *cis* | 0.6 | 7.0 | 69.6[a] | 18.1[a] | 3.8[a] | 0.9 | 0.2 | 0 | 0 | 2.21 |
| | | *trans* | 1.4 | 8.2 | 77.5[a] | 11.4[a] | 1.3[a] | 0.3 | 0 | 0 | 0 | 2.04 |
| 6 | Ir | *cis* | 1.1 | 10.0[a] | 55.9[a] | 24.9 | 6.1 | 1.6 | 0.4 | 0 | 0 | 2.31 |
| | | *trans* | 1.8 | 6.9[a] | 63.1[a] | 22.7 | 4.4 | 0.9 | 0.2 | 0 | 0 | 2.25 |
| 7 | Pt | *cis* | 6.4 | 25.3 | 29.6 | 21.9 | 12.3 | 4.4 | 0 | 0 | 0 | 2.21 |
| | | *trans* | 8.5 | 23.5 | 30.3 | 21.7 | 11.8 | 4.2 | 0 | 0 | 0 | 2.17 |
| **III** (t-butylcyclohexane) | | | | | | | | | | | | |
| 5 | Os | | 1.6 | 1.2 | 5.5 | 34.1 | 28.6 | 15.9 | 8.9 | 3.0 | 1.2 | 3.93 |
| 6 | Ir | | 1.0 | 1.8 | 9.7 | 38.6 | 31.1 | 12.8 | 3.9 | 1.0 | 0.3 | 3.58 |
| 7 | Pt | | 4.0 | 11.7 | 22.1 | 26.8 | 20.0 | 11.3 | 4.0 | 0.2 | 0 | 2.98 |
| **V** (4-t-butylcyclohexyl acetate converted from **II**) | | | | | | | | | | | | |
| 2 | Rh | *cis* | 10.2 | 21.1 | 25.3 | 20.3 | 12.8 | 6.8 | 2.7 | 0.7 | 0 | 2.39 |
| | | *trans* | 9.5 | 21.0 | 27.2 | 21.1 | 11.9 | 6.2 | 2.4 | 0.8 | 0 | 2.37 |

[a] Notice the significant difference between isomers.

isotopic distribution pattern with the mechanism of hydrogenation and exchange. The simple addition of two deuterium atoms to the double bond of **I** will lead exclusively to *cis*- and *trans*-**II**-$d_2$. If deuterium addition is preceded by isotopic exchange at the C(2) and C(6) positions (subsequently abbreviated to C(2, 6) in view of the equivalence of the two positions on **II**), then isotopic species **II**-$d_2$ to **II**-$d_5$ will be formed. Owing to the isotopic dilution of the surface deuterium pool caused by exchange, species $d_0$ and $d_1$ may also be produced. If deuterium addition and exchange at C(2, 6) are restricted to either axial or equatorial, then deuterium incorporation to **II** will be limited to $d_0$–$d_3$.

With these considerations in mind, let us inspect Table 2 once again. Obviously, all the metals more or less cause isotopic exchange, producing **II**-$d_3$ and more highly deuterated species. However, little or no $d_6$–$d_8$ species are seen. Thus, it seems very likely that on all the metals isotopic exchange is mostly limited to the C(2, 6) positions, and deuterium smear beyond these positions is almost negligible. In the case of Os and Ir, $d_4$ and $d_5$ are much smaller than $d_2$ and $d_3$, thus suggesting that either axial or equatorial hydrogens at C(2, 6) are selectively exchanged.

Table 2 also lists the observed isotopic distributions for **III** and **V**. Here we compare the isotopic distribution patterns on Rh between *cis*-**II** and *cis*-**V** and also between *trans*-**II** and *trans*-**V**. In both pairs little difference is seen, thus confirming that the conversion of **II** to **V** has left intact the deuterium atoms already incorporated into the cyclohexane ring of **II**. On this basis we can view the NMR-determined deuterium distributions of V as representing those of **II**.

*NMR data.* On the cyclohexane ring of *cis*- and *trans*-**II** there are six different kinds of hydrogens, distinguished by the carbon position and C–H bond direction (axial or equatorial). The extents of deuterium substitution for these hydrogens are listed in Table 3. As was anticipated from the mass spectral data, deuterium incorporation is largely or entirely limited to the C(1) and C(2, 6) positions for all the catalysts. Also in accord with the expectation from the mass spectral data, deuterium incorporation at C(2, 6) observed on Os and Ir is either axial or equatorial selective: $D_{2,6a} \gg D_{2,6e}$ for *cis*-**II** and $D_{2,6a} \ll D_{2,6e}$ for *trans*-**II**. This tendency is also seen for Ru and Rh, although it is less remarkable in these cases.

There are small discrepancies between the mass spectral data of Table 2 and the NMR data of Table 3. For instance, on Ru, a small but significant amount of $d_6$ was found by mass spectrometry for *trans*-**II**, suggesting deuterium smear beyond the C(2, 6) position. However, no deuteriums were detected at C(3, 5) and C(4) by NMR. Discrepancies of this sort are due to a lower sensitivity and accuracy of NMR detection compared with those of mass spectrometry. The numerical data of Table 3 are considered to be accurate within 0.05 or 0.1.

## DISCUSSION

### *Introductory Remarks*

Here we explain the observed deuterium incorporation patterns at the C(2, 6) positions of *cis*- and *trans*-**II** by invoking the concept of staggered $\alpha\beta$-diadsorption. A closer look at Tables 2 and 3 reveals the following characteristic features concerning the isotopic distributions:

(i) In general, the isotopic distributions of *cis*-**II** is more spread out, with a lower maximum peak at $d_2$, compared with *trans*-**II**.

(ii) The four quantities concerning the deuterium content at C(2, 6) fall in the sequence,

$$D^{t}_{2,6e} > D^{c}_{2,6a} > D^{c}_{2,6e} > D^{t}_{2,6a}. \qquad (1)$$

TABLE 3

Stereochemical Deuterium Distributions within Each Molecule in Product **II**

| Expt | Catalyst | II | Average number of deuterium atoms[a] | | | | | | | $D_m$ |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | $D_{1a}$ | $D_{1e}$ | $D_{2,6a}$ | $D_{2,6e}$ | $D_{3,5a}$ | $D_{3,5e}$ | $D_{4a}$ | |
| 1 | Ru | *cis* | | 0.72 | 0.90 | 0.50 | 0 | 0.22 | 0 | 2.34 |
| | | *trans* | 0.74 | | 0.28 | 1.17 | 0 | 0 | 0 | 2.19 |
| 2 | Rh | *cis* | | 0.49 | 0.77 | 0.62 | 0 | 0.22 | 0 | 2.10 |
| | | *trans* | 0.52 | | 0.54 | 1.07 | 0 | 0.08 | 0 | 2.21 |
| 3 | Pd | *cis* | | 0.52 | 0.93 | 0.92 | 0 | 0 | 0 | 2.37 |
| | | *trans* | 0.48 | | 0.81 | 1.10 | 0 | 0 | 0 | 2.39 |
| 4 | Os | *cis* | | 1.0 | — | — | — | — | — | — |
| | | *trans* | 1.0 | | 0 | 1.01 | 0 | 0 | 0 | 2.01 |
| 5 | Os | *cis* | | 0.89 | 0.88 | 0.21 | 0 | 0.07 | 0 | 2.05 |
| | | *trans* | 1.0 | | 0.09 | 1.08 | 0 | 0 | 0 | 2.17 |
| 6 | Ir | *cis* | | 0.88 | 0.89 | 0.33 | 0 | 0.19 | 0 | 2.29 |
| | | *trans* | 0.90 | | 0.22 | 1.14 | 0 | 0 | 0 | 2.26 |
| 7 | Pt[b] | *cis* | | 0.55 | 0.82 | 0.81 | 0 | 0 | 0 | 2.18 |
| | | *trans* | 0.53 | | 0.79 | 0.99 | 0 | 0 | 0 | 2.31 |

[a] $D$ represents the number of deuterium atoms specified by the subscript: here the figure designates the carbon position and a and e stand for axial and equatorial, respectively.

[b] The data are slightly different from and more precise than those given in Ref. (*17*).

Herein superscripts *c* and *t* refer to *cis* and *trans,* respectively. These characteristic features are quite clear for four metals (Ru, Rh, Os, and Ir) but are rather blurred on Pd and Pt. Characteristic feature (i) suggests that the hydrogenation path leading to *cis*-**II** causes more deuterium exchange compared with the *trans* counterpart. Characteristic feature (ii) suggests that it is in the *trans* course that the axial and equatorial hydrogens at C(2, 6) are quite different from each other in their tendency to exchange. The reaction scheme we propose in Fig. 1 is completely compatible with these suggestions.

### *Hydrogenation Mechanism and Exchange Modes*

In the hydrogenation scheme of Fig. 1, the thick arrows indicate the reaction pathway of simple hydrogen addition to yield *cis*- and *trans*-**II.** Unless otherwise stated, the steps indicated by dashed arrows are disregarded. This means that among five half-hydrogenated intermediates (HI), the role of those having a C(2)–metal bond is discounted, thus leaving only *c*-$\mathrm{HI_{1e}}$ and *t*-$\mathrm{HI_{1a}}$ as the important species. Singling out these two might be rationalized in terms of the attractive interaction of the oxygen lone pair with the catalyst surface or in terms of the electron-releasing effect of the methoxy group (*20*).

Now let us examine the simple addition pathway in some detail. The first step represents the $\pi$-adsorption of **I** in two distinct forms, *c*- and *t*-$\mathrm{I}_\pi$, depending upon which face of the six-membered ring is directed toward the catalyst surface. The *c*-$\mathrm{I}_\pi$ is then transformed into staggered diadsorbed spe-

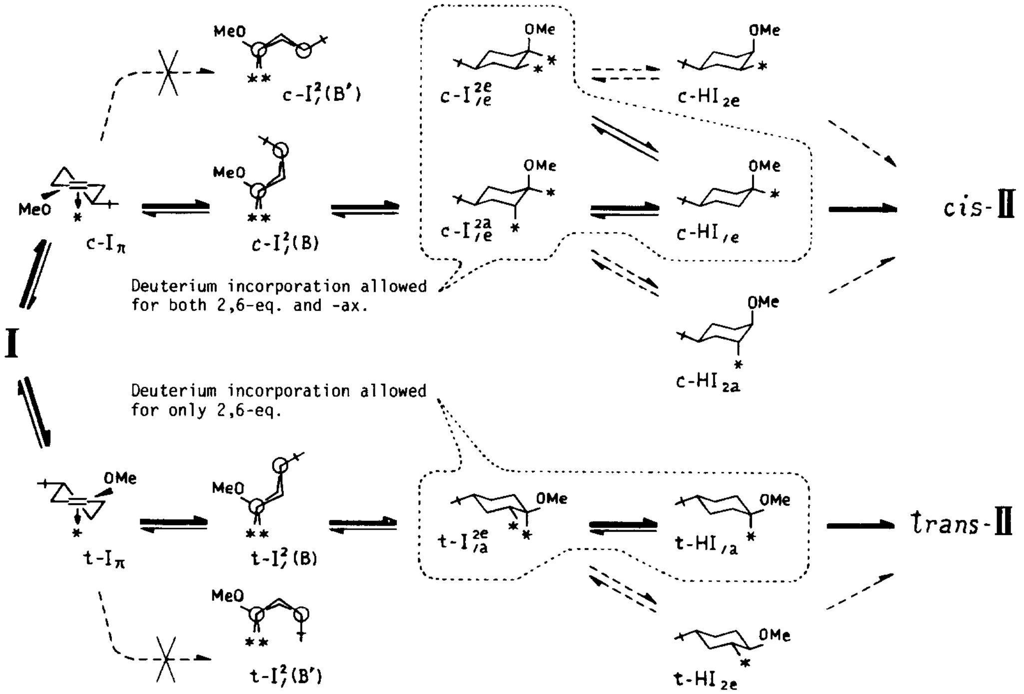


FIG. 1. Main reaction scheme for **I** hydrogenation. The labeling of intermediates: Prefixes *c*- and *t*- indicate those intermediates that are led to *cis*- and *trans*-**II**, respectively; HI represents those intermediates that are half-hydrogenated by taking up one hydrogen atom; (B) and (B′) indicate that the intermediate is in the boat form; the subscript and the superscript specify the adsorption bonds, with a and e standing for axial and equatorial, respectively; asterisk * represents the adsorption site. Once reduced to a half-hydrogenated state HI, the substrate molecule has a symmetrical plane and therefore the adsorption bond 2 (subscript 2 and superscript 2) should also be read as the adsorption bond 6.

cies $c\text{-I}^{2a}_{1e}$, possibly via eclipsed diadsorbed species $c\text{-I}_1{}^2(\text{B})$. We disregard an alternative eclipsed conformation $c\text{-I}_1{}^2(\text{B}')$ on account of repulsive interaction of the boat-axial hydrogens at C(4) and C(5) with the catalyst surface. Stepwise addition of two hydrogen atoms to $c\text{-I}^{2a}_{1e}$ forms final product *cis*-**II** via $c\text{-HI}_{1e}$. Similarly, $t\text{-I}_\pi$ is led to *trans*-**II** by transformation into staggered diadsorbed $t\text{-I}^{2e}_{1a}$, followed by stepwise hydrogen uptake.

In the case of deuteration these simple addition pathways produce only *cis*- and *trans*-**II**-$d_2$. The observed extensive isotopic distributions beyond $d_2$ are explained by assuming alternation between mono- and diadsorbed intermediates, as shown by the dotted-line enclosures in Fig. 1. It is of particular importance that both axial and equatorial hydrogens at C(2, 6) are exchangeable in the *cis*-course alternation, but only the equatorial hydrogens are exchangeable in the *trans*-course alternation. On $t\text{-HI}_{1a}$ the axial hydrogens are not exchangeable because they point away from the catalyst. It is this difference in exchangeability between $c\text{-HI}_{1e}$ and $t\text{-HI}_{1a}$ that brings about characteristic features (i) and (ii).

### *Semiquantitative Interpretation of the Exchange Data*

We shall now derive sequence (1) theoretically based on the mechanism of Fig. 1. We also deal with the $D_1$ value in connection with the four $D_{2,6}$ values. Let us start out with defining three reaction rates $R_H$, $R_A$, and $R_I$. The $R_H$ is the rate for **I** hydrogenation to *cis*- or *trans*-**II** due to simple hydrogen addition. As our discussion is restricted to a semiquantitative level, we regard the rate of *cis*-**II** formation as identical with the rate of *trans*-**II** formation. The $R_A$ represents the rate of the three alternation steps within the dotted-line enclosures. For the sake of simplicity we take the rates of these steps as identical. The $R_I$ is the rate of interconversion of $c\text{-HI}_{1e}$ to $t\text{-HI}_{1a}$ or its reverse through starting substrate **I**.

In the deuteration of **I**, the extent and pattern of deuterium incorporation into C(2, 6) must vary depending upon the relative rates $R_A/R_H$ and $R_I/R_H$. Let us consider this correlation in reference to Table 4 and on the assumption of *cis*-addition of adsorbed deuterium atoms from the catalyst side. Under condition 1 where the simple addition mechanism prevails, only two deuterium atoms should be found per product molecule; one at C(1) and the other at C(2, 6a) for *cis*-**II**, and one at C(1) and the other at C(2, 6e) for *trans*-**II**. Under condition 2 where alternation predominates, the axial and equatorial bonds at C(2, 6) are equally well deuterated in *cis*-**II** while only the equatorial bonds at C(2, 6) are deuter-

TABLE 4

Stereochemical Deuterium Distributions within Molecule **II** Expected from the Mechanism of Fig. 1

| Condition | | | Deuterium distribution[a] | | | | |
|---|---|---|---|---|---|---|---|
| | $R_A/R_H$ | $R_I/R_H$ | $D_1$ | $D^c_{2,6a}$ | $D^c_{2,6e}$ | $D^t_{2,6a}$ | $D^t_{2,6e}$ |
| 1 | $\approx 0$ | $\approx 0$ | $X$ | $X$ | 0 | 0 | $X$ |
| 2 | $\gg 1$ | $\approx 0$ | $X$ | $2X$ | $2X$ | 0 | $2X$ |
| 3 | $\gg 1$ | $\gg 1$ | $X$ | $2X$ | $2X$ | $2X$ | $2X$ |
| 4[b] | $\approx 1$ | $\approx 0$ | $X$ | $X + x$ | $2x$ | 0 | $X + x$ |
| 5[c] | $\approx 1$ | $\approx 1$ | $X$ | $X + x - \epsilon_1$ | $2x + \epsilon_2$ | $\epsilon_3$ | $X + x - \epsilon_4$ |

[a] $X$ is the deuterium-atomic fraction of the surface pool of the adsorbed mixture of hydrogen and deuterium.

[b] $X > x > 0$.

[c] Led to the observed sequence (1) when $\epsilon \lesssim x$.

ated in *trans*-**II**. Under condition 3, hydrogenation is overwhelmed not only by alternation but also by interconversion. Rapid interconversion serves to equalize deuterium distributions for *cis*- and *trans*-**II**, thus leading to the same value for the four $D_{2,6}$ quantities and $2D_1$. It is to be noted that conditions 1 to 3 are all at an extreme in the sense that one or two of the three rates overwhelm the rest. Since none of these extremes can account for the observed sequence (1), let us turn to intermediate conditions.

Condition 4 lies between conditions 1 and 2 in the magnitude of $R_A/R_H$. Therefore, each of the four $D_{2,6}$ values under condition 4 is also expected to lie between the corresponding values under conditions 1 and 2. This requirement alone unambiguously leads to $D^t_{2,6a} = 0$ under condition 4. In order to speculate upon the other three $D_{2,6}$ quantities, let us assume that they are given by the $x$-functions listed in Table 4. These intuitively chosen $x$-functions not only meet the above intermediate requirement but also correctly predict the limiting values under conditions 1 and 2 at $x = 0$ and $= X$, respectively. It is thus expected that the $x$-functions approximately, if not precisely, represent the $D_{2,6}$ values under condition 4. The sequence of $D_{2,6}$ values derived from the $x$-functions is

$$D^t_{2,6e} = D^c_{2,6a} > D^c_{2,6e} > D^t_{2,6a} = 0. \quad (2)$$

Now let us proceed to condition 5 where interconversion is also comparable to hydrogenation. A consequence of interconversion is the virtual deuterium exchange between $c$-$\mathrm{HI}_{1e}$ and $t$-$\mathrm{HI}_{1a}$, in more specific terms, between the 2,6-axial on $c$-$\mathrm{HI}_{1e}$ and that on $t$-$\mathrm{HI}_{1a}$ and also between the 2,6-equatorial on $c$-$\mathrm{HI}_{1e}$ and that on $t$-$\mathrm{HI}_{1a}$. Illustrating these two virtual exchange routes on sequence (2), we have

$$\begin{tikzcd}[column sep=small] D^t_{2,6e} \arrow[rrrr, bend right, "\text{e–e exchange}"'] & = & D^c_{2,6a} \arrow[rrrr, bend left, "\text{a–a exchange}"] & > & D^c_{2,6e} & > & D^t_{2,6a} & = 0. \end{tikzcd} \quad (3)$$

Here the arrows indicate the direction of net deuterium flow which is anticipated when the opposing rates of the interconversion between $c$-$\mathrm{HI}_{1e}$ and $t$-$\mathrm{HI}_{1a}$ are almost equal. The extent of the next deuterium flow in the a–a exchange is probably greater than that in the e–e exchange, since the relation $D^c_{2,6a} - D^t_{2,6a} > D^t_{2,6e} - D^c_{2,6e}$ holds at least in the initial stage. Then, the virtual deuterium exchange due to interconversion decreases $D^c_{2,6a}$ more than $D^t_{2,6e}$, thus changing sequence (2) to sequence (1).

The assumed interconversion between $c$-$\mathrm{HI}_{1e}$ and $t$-$\mathrm{HI}_{1a}$ finds support in our preliminary experiments conducted using Ru, Rh, Pd, and Pt catalysts. Before completion of **I** deuteration, we took the reaction mixture. Mass spectrometry confirmed a small but significant amount of deuterium incorporation into **I** for all the catalysts.

Table 3 shows that, although the observed sequence (1) is common to all the metals, it is most distinct for Os with the largest value of difference $D^t_{2,6e} - D^t_{2,6a}$, and becomes blurred gradually in the sequence Os > Ir > Ru > Rh > Pd > Pt. This is explicable in terms of relative rates $R_A/R_H$ and $R_I/R_H$; the decreasing sequence reflects a gradual approach from condition 5 to condition 3. According to this view, Pd and Pt, in which the four $D_{2,6}$ values are only slightly different from one another, are thought to lie very close to condition 3. The close similarity in the four $D_{2,6}$ values on Pd and Pt may also be brought about by the additional mechanism shown in Fig. 2. In this mechanism there are two $\pi$-adsorbed allylic species, $c$- and $t$-$\mathbf{I}_{\pi\pi}$, which are presumably stabilized with the aid of the oxygen lone pair. If the rate of interconversion between $c$- and $t$-$\mathbf{I}_{\pi\pi}$ is rapid compared with $R_H$, then the four $D_{2,6}$ values should become very similar to one another, as was actually observed for Pd and Pt. The assumption of the rapid $c$-$\mathbf{I}_{\pi\pi} \rightleftharpoons t$-$\mathbf{I}_{\pi\pi}$ interconversion is consistent with the finding that on Pd and Pt little or no deuterium enters into the $C_{3,5}$ positions despite the extensive deuterium exchange at $C_{2,6}$.

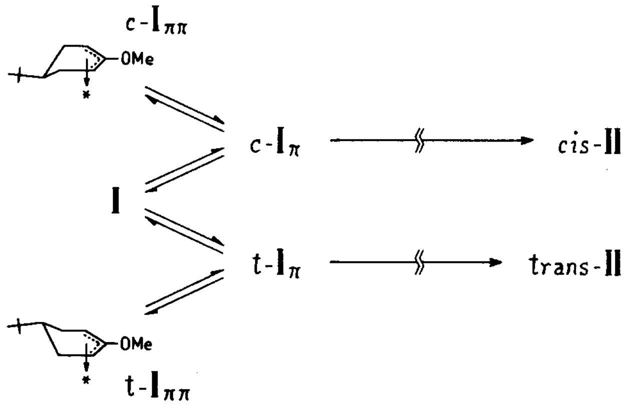


FIG. 2. Additional exchange path through $\pi$-allylic species assumed for Pd and Pt.

## *Stereoselectivity and Hydrogenolysis*

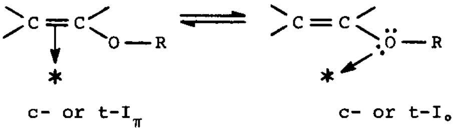
In the context of the proposed hydrogenation scheme, it may be possible to explain qualitatively the observed stereoselectivity data (Table 1) and the deuterium distribution for II (Table 2), but we shall not attempt to do so now.

## CONCLUSION

The observed isotopic distributions of *cis*- and *trans*-II produced by the reaction of I with deuterium can best be explained by assuming the intermediacy of staggered $\alpha\beta$-diadsorbed species. The staggered diadsorption requires the chair-form conformation. In six-membered rings the chair conformer is usually much more stable than the boat conformer. The difference in conformation energy amounts to as much as 6.9 kcal (*21*) for cyclohexane, and could even be greater upon introduction of certain substituents. This makes it doubtful that the eclipsed $\alpha\beta$-diadsorption is always more stable than the corresponding staggered adsorption, even if the former is energetically favored in adsorption bonding itself.

## APPENDIX

A referee suggested an alternative interpretation of the observed isotopic exchange at the C(2, 6) positions of *cis*- and *trans*-II by assuming the following alternation process:



Herein $I_0$ represents an intermediate possessing an oxygen–metal $\sigma$-adsorption bond. He states that "conversion of $I_\pi$ to $I_0$ furnishes a route for the exchange of both hydrogens at C(6) without the desorption of the vinyl ether because rotation about the vinyl carbon to oxygen bond should be relatively free." We admit that this exchange mechanism is not deniable. The observed dissimilarity in deuterium distribution pattern at C(2, 6) between *cis*- and *trans*-II, however, does not seem explicable based on this mechanism because of the structural similarity between *c*- and *t*-$I_\pi$ and also between *c*- and *t*-$I_0$.

Another referee put up another mechanistic candidate to explain the observed isotopic exchange at C(2, 6). The proposal may be represented by the scheme:

$$I\left\{\begin{array}{l} \rightleftharpoons \text{c-HI}_{1e} \longrightarrow \text{cis-II} \\ \rightleftharpoons \text{t-HI}_{1a} \longrightarrow \text{trans-II} \end{array}\right.$$

In this scheme, eclipsed diadsorption is assumed, and *t*-$HI_{1a}$ has a somewhat greater tendency to revert to I. Therefore, *c*-$HI_{1e}$ would find more D at C(2, 6e) than would *t*-$HI_{1a}$ at C(2, 6a), thus leading to the results of Table 3. Although this mechanism is also undeniable, it is not clear why $t$-$HI_{1a}$ should have a greater tendency to revert. In contrast, our mechanism enjoys a clear depiction (the dotted-line enclosures in Fig. 1) which illustrates the cause of the difference in deuterium incorporation between *cis*- and *trans*-**II**.

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