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Details of the Alkene Hydrogenation Mechanism Obtained by the Hydrogenation of Selectively Deuterated Substrates[1]

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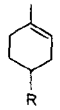
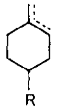
The deuterated alkenes, 7,7,7,-d_3-1-methycyclohexene and 2,6,6,-d_3-1-methylcyclohexene, were hydrogenated to 25% completion over Pt/C, Rh/C, and Pd/C, and the deuterium compositions of recovered olefin and product alkanes determined. From these data it has been determined that while exocyclic adsorbed species are present on the catalyst they are minor components of the reaction mixture and are detected only by exchange reactions. Endocyclic adsorbed entities are present to a much larger extent on the catalyst surface and product formation occurs through their saturation.

Classic studies of the mechanism of catalytic hydrogenation of alkenes have made extensive use of product stereochemistry variations occurring with changes in reaction conditions (*2*), rates of H_2 uptake, extent of double-bond isomerization (*3, 4*), and D incorporation and exchange (*4, 5*). All of these factors were involved in a recent evaluation of the mechanistic differences associated with the use of the different noble metal catalysts in the hydrogenation of olefins (*6*). It was concluded from these data that Rh, like Pt, promoted this reaction by way of the classic Horiuti–Polanyi mechanism (*7*) but with Pd a π-allyl adsorption of the olefin is involved.



1a; R = t-Bu
b : R = H

2a: R = t-Bu
b : R = H



3a: R = t-Bu
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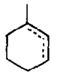

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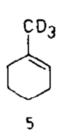

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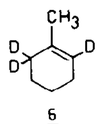

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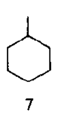

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Product stereochemistry data obtained on hydrogenation of 4-*tert*-butyl methylcyclohexene (**1a**) over Pd showed that the π-allyl species involved in this reaction was the 6,1,2-moiety (**2a**) and not the 7,1,2-species (**3a**). However, deuteration of methylcyclohexene (**1b**) over Pd gave extensive amounts of a d_5 product which mass spectral fragmentation data (*8*) indicated contained a —CD_3 entity. These two results seemed incompatible since the exo π-allyl, **3**, would be required to obtain the —CD_3 species but the product stereochemistry data indicated that **2** was the primary π-allyl present. The 1,2,3-π-allyl species, **4**, is evidently not involved in this reaction.

It was apparent that a more detailed investigation of this exchange reaction was warranted. To accomplish this the *hydrogenations* of the selectively *deuterated* olefins, 7,7,7-trideuteromethylcyclohexene (**5**), and 1,6,6-trideuteromethylcyclohexene (**6**) were run and the extent of H/D exchange determined for both the saturated product, methylcyclohexane (**7**), and recovered starting material after the hydrogenation had run to 25% completion. While the primary reason for this study was to resolve the apparent dichotomy in the Pd-catalyzed reaction, the hydrogenations of **5** and **6** were also run over Pt and Rh catalysts to see what additional information

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could be obtained concerning these catalysts as well. The catalysts used were the same commercial 5% Pt/C, 5% Rh/C, and 5% Pd/C catalysts used in the previous work (*6*). The reactions were also run in both an inert solvent, heptane, and in ethanol to determine the extent to which exchange on the OH group of ethanol was involved in the overall process.

EXPERIMENTAL METHODS

All hydrogenations were carried out in a sloping manifold hydrogenation apparatus (9) using 10 ml of solvent, 25 mg of catalyst, and 0.25 ml of olefin following the procedure described previously (6). After 25% of the theoretical amount of hydrogen was absorbed the reaction was stopped, an aliquot extracted and centrifuged and the supernatant subjected GC/MS analysis using a Hewlett–Packard HP 5985 GC/mass spectrometer. The deuterium distribution was corrected for natural isotopic abundance using standard procedures (*10*). With methyl cyclohexane no M-1 peak was present in the mass spectrum of the fully protiated standard so the normal correction procedure was used for the saturated products from all runs. With methylcyclohexenes, however, the M-1 peak was about 20% of the molecular run peak and, thus, could not be properly ignored. Since M-1 corrections are not applicable with polydeuterated species (*10*) the determination of the exact D compositions for these alkenes was not possible. Since these data were to be used for the comparison of compounds having rather broadly different D compositions it was felt that approximate values calculated using standard M-1 and M+1 corrections (*10*) would suffice in the present instance. These corrected data are listed in Tables 2–7. Duplicate hydrogenation runs and mass spectral analyses showed that the results obtained were reproducible to within ±1%.

Materials. The catalysts used were aged 5% metal on carbon obtained from Engelhard Industries. These were the same catalysts used in the previous deuteration reactions (*6*). The hydrogen used was passed through a Deoxo unit, a drying tower, and a filter before use. The iodomethane-d_3 (99.5% atom %D) and D_2O (99% atom %D) were obtained from MSD Isotopes. The ethanol used was absolute and distilled from sodium before use. The heptane was reagent grade and distilled from Raney nickel before use.

7,7,7-d_3-1-Methyl-1-cyclohexene (**5**) was prepared by modification of existing procedures (*11, 12*). To a three-neck 250-ml round-bottom flask equipped with a pressure-equalizing dropping funnel, condenser, and stirring bar, all of which were dried in an oven, were added 2.2 g (0.09 g-atom) of magnesium. The apparatus was flamed out with a burner while a stream of dry N_2 flowed through it. After cooling in a stream of dry N_2, 30 ml of anhydrous ether were added to the flask. To the dropping funnel was added a solution of 12.5 g (0.086 mol) of iodomethane-d_3 in 50 ml of anhydrous ether. With the flask under a dry-nitrogen atmosphere and under mild reflux with constant sitrring, the iodomethane-d_3/ether solution was added dropwise. After the addition was complete the reaction mixture was refluxed another 30 min and a solution of 8.4 g (0.086 mol) of distilled cyclohexanone in 50 ml of anhydrous ether was added dropwise over 1.5 h under N_2 under reflux with stirring. When this addition was complete the reaction mixture was refluxed for 30 min and then cooled to room temperature. At that time 50 ml of a saturated aqueous solution fo NH_4Cl was then added dropwise with stirring to the reaction mixture to hydrolyze it. After this, the organic layer was removed, washed twice with saturated aqueous $NaHSO_3$ and three times with water, and then dried over anhydrous $MgSO_4$. After filtration the ether was removed to give 7,7,7-d_3-1-methyl-1-cyclhexanol in 82.4% yield. This alcohol was dehydrated by heating in the presence of a trace amount of I_2 (0.1% by weight of alcohol) in a distilling apparatus with the product being collected at about 110°C. This distillate was taken up in pentane, dried over anhydrous $MgSO_4$, filtered, and then passed through a neutral alumina column to remove any residual iodine. Distillation first removed the pentane and then gave 2.09 g of 7,7,7-d_3-1-methyl-1-cyclohexene (31%) (bp 108–110°C). NMR analysis showed the absence of protium on the methyl group and gas chromatography established that the product was at least 98% pure. The deuterium distribution in **5** corrected as described above is given in Table 1.

The preparation of 2,6,6-d_3-1-methyl-1-cyclohexene (**6**) followed the same procedure but using iodomethane and 2,2,6,6-d_4-cyclohexanone (*13*) as reagents. The product, **6**, was obtained in 42.5% yield. NMR analysis showed the olefin to be almost completely deuterated at the 6 position but with some hydrogen present at the 2 position. GC analysis showed the product to be at least 93% pure. The deuterium distribution in **6** corrected as described above is given in Table 1.

RESULTS AND DISCUSSION

The deuterated 1-methylcyclohexenes, **5** and **6**, were prepared by a classic Grignard procedure (*11, 12*) using appropriately deuterated reagents; iodomethane-d_3 for the preparation of **5** and 2,2,6,6-d_4-cyclohexanone (13) for the synthesis of **6**. The deuterium distributions in these olefins are listed in Table 1. These olefins were *hydrogenated* over the same 5% metal on carbon catalysts used in our previous methylcyclohexene deuteration studies (*6*) in order to make comparison of the data obtained in these two series of reactions more direct.

TABLE 1

Deuterium Composition of the Methylcyclohexenes **5** and **6**

	d_0	d_1	d_2	d_3	d_{ave}
5	1	1	3	96	2.9
6	1	8	36	55	2.5

TABLE 2

Deuterium Distributions Obtained on Hydrogenation of **5** over Pt/C

	Heptane			Ethanol		
	1b[a]	**7**		**1b**[a]	**7**	
		M[b]	M-15[c]		M[b]	M-15[c]
d_0	2	4	78	2	4	91
d_1	0	7	18	0	7	7
d_2	4	20	3	3	22	1
d_3	93	58	1	95	63	1
d_4	1	10			3	
d_5		1				
d_{ave}	2.9	2.6	0.2	2.9	2.5	0.1

[a] m/z = 96 (d_0) through 100 (d_4).
[b] m/z = 98 (d_0) through 103 (d_5).
[c] m/z = 83 (d_0) through 86 (d_3).

The deuterium distributions of the recovered olefin and methyl cyclohexane products obtained on hydrogenation of **5** and **6** over 5% Pt/C in both heptane and ethanol are listed in Tables 2 and 3. Since the primary fragmentation of methylcyclohexane (**7**) has been shown to be the direct loss of the methyl group (8) data from the M-15 region of the mass spectrum of **7** is also

TABLE 3

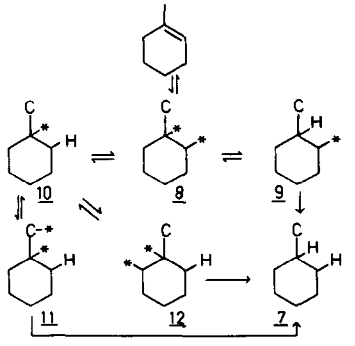
Deuterium Distributions Obtained on Hydrogenations of **6** over Pt/C

	Heptane			Ethanol		
	1b[a]	**7**		**1b**[a]	**7**	
		M[b]	M-15[c]		M[b]	M-15[c]
d_0	1	2	4	1	1	3
d_1	6	7	10	9	8	11
d_2	34	29	28	39	29	29
d_3	57	45	43	51	48	45
d_4	1	16	15		13	13
d_5		1	1		1	
d_{ave}	2.4	2.7	2.6	2.4	2.7	2.5

[a] m/z = 96 (d_0) through 100 (d_4).
[b] m/z = 98 (d_0) through 103 (d_5).
[c] m/z = 83 (d_0) through 87 (d_4).

included in these tables to show the deuterium distribution in the cyclohexane portion of the product. Analysis of these data is best accomplished by consideration of the Horiuti–Polanyi mechanism (*7*) as applied to 1-methylcyclohexene shown in Scheme 1.

The data in Tables 2 and 3 show that the olefins recovered from the hydrogenation reactions over Pt have essentially the same deuterium composition as the starting materials **5** and **6** (Table 1). These results confirm earlier conclusions that over Pt there is little, if any, reversal of the olefin adsorption step in the Horiuti–Polanyi mechanism (*6*). With the methylcyclohexane formed on hydrogenation of **5** over Pt in heptane (Table 2) there is a considerable decrease in the d_3 component and an increase in the d_4, d_2, and d_1 species. The M-15 data show that while the d_0 component predominates there is a substantial amount of a d_1 species present. These results indicate that **11** (Scheme 1) must be involved to remove D from the methyl group and, further, that this D is then incorporated into the surface H/D pool and then reincorporated into a ring position on saturation via species **8**, **9**, **10**, and/or **12**. In ethanol there is also a decrease in the d_3 component but this is accompanied only by an increase in the d_1 and d_2 species. The M-15 region is almost all d_0, so the D removed from the methyl group via **11** apparently becomes lost to further reaction by exchange with the ethanol —OH group (*5b*). This assumption was not verifiable, however, because the relatively large amount of ethanol present as the solvent precluded an accurate determination of any deuterated species which might be present.



Scheme 1

The methylcyclohexane formed on the hydrogenation of **6** over Pt in both heptane and ethanol shows a decrease in d_2 and d_3 along with an increase in the d_4 component. These data indicate that an equilibrium between **8**, **9**, **10**, and **12** is occurring but since there is no difference between the ethanol and heptane solution results there is, apparently, little exchange with the ethanol in this reaction. The marked similarity between the methylcyclohexane and the M-15 data show that transfer of D from the ring to the methyl group via **11** does not take place to any appreciable extent.

The data found on hydrogenation of **5** (Table 2) and **6** (Table 3) over Pt appear to be contradictory. With **5** in heptane exchange occurs on the methyl group, with a transfer of D from the methyl group to the ring. The reverse transfer of D from the ring to the methyl group is not observed on hydrogenation of **6**. Thus, it would appear from these results that **11** is involved in the hydrogenation of **5** but not in the hydrogenation of **6**. Yet, one cannot modify a reaction mechanism to that extent by changing the positions of the D atoms present on the starting olefins. One must keep in mind, however, that all three D on **5** are available for exchange by the rotation of the exocyclic single bond in **10**. With **6**, though, the only D which can be exchanged during a single adsorption is one of the D on C_6. Thus, with **5** the D_*/H_* ratio is higher than it is with **6**, so transfer processes occurring through **10** $\rightleftharpoons$ **11** are more likely to be observed. With **6** such transfer process can occur but they are more likely to involve H_* and, thus, would not be readily observable.

The data from the hydrogenations of **5** and **6** over Rh (Tables 4 and 5) show some similarity with the Pt-catalyzed data but there are some differences, as well. In the

TABLE 4

Deuterium Distributions Obtained on Hydrogenations of **5** over Rh/C

	Heptane			Ethanol		
	1b[a]	**7**		**1b**[a]	**7**	
		M[b]	M-15[c]		M[b]	M-15[c]
d_0	2	6	47	2	5	42
d_1	0	13	34	1	13	38
d_2	6	19	13	12	20	14
d_3	90	34	4	82	33	4
d_4	2	19	1	3	20	1
d_5		8			7	
d_6		2			2	
d_{ave}	2.9	2.8	0.7	2.8	2.7	0.8

[a] m/z = 96 (d_0) through 100 (d_4).
[b] m/z = 98 (d_0) through 104 (d_6).
[c] m/z = 83 (d_0) through 87 (d_4).

hydrogenation of **6** in both heptane and ethanol and the hydrogenation of **5** in heptane the recovered olefins have essentially the same deuterium distribution as the starting materials. In the hydrogenation of **5** in ethanol, however, there is a decrease in the d_3 component and an increase in the d_2 of the recovered olefin. It appears, then, that exchange with the ethanol (*5b*) and reversal of the olefin adsorption is taking place in this latter instance. Again, the observation that this exchange with ethanol takes place only with **5** and not **6** is in accord with the conclusions arrived at above; with **5** the D_*/H_* ratio is larger than it is with **6**; therefore exchange can more readily take place.

In the methylcyclohexane (**7**) formed on hydrogenation of **5** over Rh in both ethanol and heptane there is a considerable loss of the d_3 entity and a marked increase in the d_4, d_5, and even some d_6 species. The M-15 region shows that the cyclohexane ring has rather large amounts of d_1 and d_2 species so transfer of D from the methyl group to the ring has taken place. An increase in d_4 is also observed in the **7** obtained on hydrogenation of **6**. These results and those mentioned above are illustrative of the previously reported (*6*) mechanistic differences between Pt and Rh in olefin hydrogenations; with Rh there is somewhat more reversal of the olefin adsorption step and considerably more equilibration of the adsorbed species than is the case with a Pt catalyst.

As mentioned previously (*6*) the product stereochemistry obtained on hydrogenation of 1,4-disubstituted cyclohexenes over Pd is best accounted for by involving as an intermediate in the process the 6,1,2-π-allyl species, **2**. The 7,1,2-π-allyl entity, **3**, would give a different product stereochemistry than what is observed (*6*). Yet, the extensive D exchange on the methyl group observed on deuteration of methylcyclohexene over Pd requires that **3** be involved in the reaction. The 1,2,3-π-allyl species, **4**, is apparently not involved in this reaction (*6*). Data obtained on hydrogenation of **5** and **6** over Pd in both heptane and ethanol are listed in Tables 6 and 7. The olefin recovered from the hydrogenation of **5** shows a considerable reordering of the deuterium as expected from previous results (6). In the saturated product there is a marked decrease in the d_3 entity and a

TABLE 5

Deuterium Distributions Obtained on Hydrogenations of **6** over Rh/C[a]

	Heptane			Ethanol		
	1b[b]	**7**		**1b**[b]	**7**	
		M[c]	M-15[d]		M[c]	M-15[d]
d_0	2	2	4	1	2	4
d_1	7	10	15	9	10	12
d_2	34	32	32	32	29	29
d_3	54	43	39	57	41	42
d_4	2	11	9	1	17	13
d_5		1	1		3	1
d_{ave}	2.4	2.5	2.3	2.4	2.7	2.5

[a] After hydrogenation to 50% completion.
[b] m/z = 96 (d_0) through 100 (d_4).
[c] m/z = 98 (d_0) through 103 (d_5).
[d] m/z = 83 (d_0) through 88 (d_5).

TABLE 6

Deuterium Distributions Obtained on Hydrogenations of **5** over Pd/C

	Heptane			Ethanol		
	1b[a]	**7**		**1b**[a]	**7**	
		M[b]	M-15[c]		M[b]	M-15[c]
d_0	3	3	28	5	2	25
d_1	13	6	33	15	6	30
d_2	27	14	22	29	13	23
d_3	42	28	11	36	26	13
d_4	12	25	5	13	24	6
d_5	2	15	2	2	17	2
d_6	1	6		1	8	1
d_7		2			3	
d_8		1				
d_{ave}	2.5	3.5	1.4	2.4	3.7	1.5

[a] m/z = 96 (d_0) through 102 (d_6).
[b] m/z = 98 (d_0) through 106 (d_8).
[c] m/z = 83 (d_0) through 89 (d_6).

TABLE 7

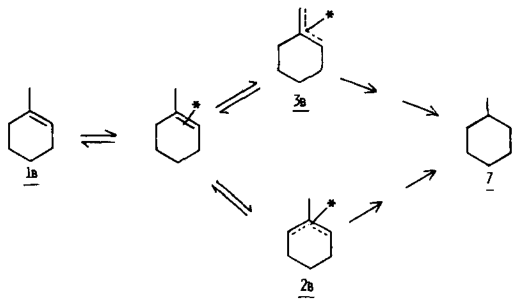
Deuterium Distributions Obtained on Hydrogenations of **6** over Pt/C

	Heptane			Ethanol		
	1b[a]	**7**		**1b**[a]	**7**	
		M[b]	M-15[c]		M[b]	M-15[c]
d_0	2	4	5	2	2	5
d_1	14	9	14	13	9	14
d_2	37	27	31	42	27	29
d_3	37	36	37	34	36	38
d_4	8	19	12	8	19	12
d_5	2	5	2	1	6	2
d_6		1			1	
d_{ave}	2.3	2.8	2.4	2.3	2.8	2.4

[a] m/z = 96 (d_0) through 100 (d_5).
[b] m/z = 98 (d_0) through 104 (d_6).
[c] m/z = 83 (d_0) through 89 (d_6).

corresponding substantial increase in the d_4 and d_5 species. The M-15 data shows that the cyclohexane ring contains considerable amounts of the d_1, d_2, d_3, and d_4 moities indicating that there is extensive transfer of D from the methyl group to the ring as expected from a π-allyl species, such as **3b**. Very similar results are observed with ethanol as the solvent showing that there is little solvent involvement in this Pd-catalyzed hydrogenation.

In the hydrogenation of **6** there are, again, very similar results obtained in both ethanol and heptane. As in the hydrogenation of **5** there is a reordering of the deuterium in the recovered olefin and a loss of d_2 and d_3 and an increase in d_4 and d_5 in the product alkane but the changes are not as great as observed with **5**. The M-15 data show that as observed in the other hydrogenations of **6** there is no transfer of D from the ring to the methyl group. Again, as discussed above, the lower D_*/H_* ratio present in the hydrogenation of **6** is probably responsible for this.



SCHEME 2

These data along with the product stereochemistry mentioned previously can be explained using the mechanism shown in Scheme 2. It is possible that this π-allyl process, or something similar to it, could be involved in both the Pt- and Rh-catalyzed reactions but our previous data (*6*) indicate that, if so, it would have to be so only to a small extent. Exocyclic adsorbed species are present in these reactions but they are minor components of the reaction mixture and are detected only by exchange reactions. Endocyclic adsorbed entities are present to a much larger extent on the catalyst surface and product formation occurs through their saturation.

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