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Platinum and Palladium Catalyzed Hydrogenation, Racemization, Exchange and Double Bond Migration in Substituted Cyclohexenes

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Key methyl-substituted cyclohexenes were partially hydrogenated with deuterium, i.e., deuteriumated, and examined for exchange and double bond migration. In (+)-1-*p*-methene and (+)-4-methylcyclohexene double bond migration was assayed by decrease in optical rotation of recovered olefins. Over palladium double bond migration and exchange are extensive. Over platinum, however, virtually no double bond migration occurs in the cyclohexene ring even though as much as 60% of the recovered molecules have been on the surface and 25% of them have exchanged at least one H for D.

INTRODUCTION

Although the classical mechanism (*1–3*) of hydrogenation explains a large body of experimental data, it fails to readily accommodate certain irregular stereochemical results. Attempts to account for these and other anomalies have resulted in the postulation of a number of surface species (*4*). It was the purpose of this present study to investigate in considerable detail one aspect of one of these stereochemical anomalies.

The metal-catalyzed addition of hydrogen or deuterium to 1,2-dimethylcyclohexene produces a mixture of *cis*- and *trans*-1,2-dimethylcyclohexane. The platinum catalyzed reaction produces mainly the *cis* isomer (*3*) and the palladium catalyzed reaction produces mainly the *trans* isomer (*5*, *6*). The classical mechanism predicts formation of only the *cis* isomer providing isomerization to 2,3-dimethylcyclohexene does not occur. Over palladium extensive isomerization occurs (*5*) but over platinum isomerization is difficult to detect (*3*). To account for the formation of this *trans* product over platinum and its relevance to other facts, certain new surface intermediates were postulated (*7*). Recently the elusive isomerization has been detected in small amounts (*8*) and it has been argued that the classical mechanism is indeed the main reaction path over platinum (*7*). The rationale for very little 2,3-dimethylcyclohexene appearing in the reaction mixtures are (a) the 2,3-isomer excludes the 1,2-isomer from the surface (*3*) and, therefore, preferentially reacts and (b) most of the reaction occurs in pores from which the 2,3-isomer has low probability of escaping without undergoing reduction (*8–10*). Because of these two possibilities this system offers few practical experimental approaches to the question of the extent of occurrence of the classical mechanism. To remove the problems one must use either molecules whose isomers have identical reactivities or catalysts with large pores. We have chosen the former approach.

One isomeric pair which will have iden-

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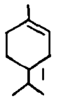
tical reactivities on symmetrical surfaces is (+)- and (−)-*p*-menthene, I and II.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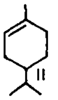
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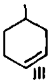
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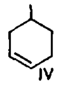
IV

If double bond migration does occur during reduction over platinum then II and I should desorb from the surface during hydrogenation of I, i.e., racemization will occur. Desorption and readsorption of II in pores could prevent detection of racemization; however, such an occurrence can be revealed by examining exchange in I. Another such pair of isomers is (+)- and (−)-4-methylcyclohexene, III and IV. A potential advantage of this pair is their lack of substitution close to the double bond. They partially avoid the possibility that subtle and unknown steric factors may play more than casual roles in directing surface reactions.

EXPERIMENTAL AND RESULTS

With the exception of spectropolarimetry all experimental and analytical procedures have been previously reported (*2*, *3*, *5*). Rotations of (+)-1-*p*-menthene reaction mixtures were measured on a Cary Model 60 spectropolarimeter. In a typical experiment 0.1335 g of (+)-1-*p*-menthene were mixed with 19.2498 g of spectrograde cyclohexane. The measured rotation of the mixture was 0.0973 ± 0.0002° at 28.0°C and 4000 Å. Approximately 5 ml of the mixture was deuterated over 0.0059 g of 5% Pd/C at 22.5°C and 753.5 mm Hg. The reaction was interrupted after consumption of 2.2 ml of D_2 and filtered. Gas–liquid-chromatographic analysis (20 ft × ¼ in. 30% Carbowax 20M on Chromosorb-P, nonacid washed, 150°C, 30 lb/in.^{2} inlet pressure, 42 ml/min exit flow rate at room temperature) revealed 83.3% 1-*p*-methene, 10.5% *trans*-1-methyl-4-isopropylcyclohexane, 4.8% *cis*-1-methyl-4-isopropylcyclohexane and 1.4% of one other substance, presumably 4-methyl-1-isopropyl-1-cyclohexene (*6*). Rotation of the filtered reaction mixture was 0.0441 ± 0.0002° in the same thermostated polarimeter tube (1 = 0.1 dm) as used for the starting mixture. Spectropolarimeter settings were slit, 0.1 mm; range, 0.2° full scale; and the wavelength was fixed at 4000 ± 8.3 Å. The fraction rotation remaining was 0.441/0.0937 or 0.454; i.e., with 83.3% 1-*p*-menthene remaining only 45.4% of the original optical rotation remains. Tables 1 and 2 list data for this and other experiments. The ratio of *trans*/*cis* products was constant at 1.03 ± 0.05 for the platinum catalyst and 2.82 ± 0.36 for palladium.

Optical rotations of (+)-4-methylcyclohexene and its reaction products were

TABLE 1
CHANGE IN OPTICAL ROTATION OF (+)-1-*p*-MENTHENE DURING HYDROGENATION ON 5% Pd/C CATALYST

p-Menthene (%)	Saturate (%)	Other[a] (%)	α_m/α_o[b]
99.97 ± 0.01	0.03 ± 0.01	0.00 ± 0.01	1.000
90.2 ± 1[c]	8.0 ± 1	1.8 ± 1	0.566
83.3	15.3	1.4	0.454
35.8	57.7	6.5	0.0370
10.4	86.3	3.3	0.0286
0.00	100.0	0.0	0.000

[a] Probably (+)-4-methyl-1-isopropyl cyclohexene (*6*); optical purity was not assessed but α_m/α_o is high for 86.3% reduction.

[b] Ratio of rotation of reaction mixture after reaction to rotation before, i.e., fraction of starting rotation remaining.

[c] Average deviations of analyses were no worse than this; low precision is due to small amounts of solute, 0.4 mole %, in cyclohexane solvent.

TABLE 2

Change in Optical Rotation of (+)-1-*p*-Menthene Reaction Mixtures During Hydrogenation on 5% Pt/C Catalyst[a]

p-Menthene (%)	Saturate (%)	α_m/α_o
99.97 ± 0.01	0.03 ± 0.01	1.000
71.6 ± 1	28.4 ± 1	0.698
61.0	39.0	0.632
36.7	63.3	0.361
36.4	63.6	0.342
0.0	100.0	0.000

[a] All headings and numbers mean same as in Table 1.

measured in a 0.995 mm path length one-piece glass cell with a Bendix-NPL automatic polarimeter series 1100 using a mercury green filter (5461 Å) and are shown in Table 3.

Olefin exchange experiments were carried out less carefully than those for optical rotation. Approximately 1 ml of pure 1-*p*-menthene was deuteriumated over 5% Pt/C to a mixture of 34% saturate and 66% 1-*p*-menthene. Isolation of 1-*p*-menthene by glc and analysis by mass spectrometry revealed the distribution of deuterated species shown in Table 5. Other olefins were similarly exchanged for comparison. Data for (+)-4-methylcyclohexene in Tables 3 and 4 were obtained over a different batch of 5% Pt/C at a later date than other experiments. Data for palladium are shown in Table 6.

Catalysts were donated by Engelhard Industries and (+)-1-*p*-menthene was prepared by partial hydrogenation of *d*-limonene followed by fractional distillation. The dimethylcyclohexenes were prepared as previously described (*3*), the racemic monomethylcyclohexenes were purchased from Aldrich Chemical Co. and further purified by fractionation and preparative glc. The cyclohexene was purified similarly. (+)-4-Methylcyclohexene was prepared from (+)-3-methylcyclohexanone by hydroboration to the alcohol, conversion to the acetate and pyrolysis at 470°. Preparative glc on a dibutyltetrachlorophthalate column yielded 99.9% pure III $[+154.2]_{5\cdot6}^{26°}$. Deuterium (99.5%) was obtained from General Dynamics and used without further purification.

Discussion

The two questions most important to establishing the extent of participation of the classical mechanism in the hydrogenation of 1,2-dimethylcyclohexene [and 1,2-dimethylcyclopentene (*11*) and 9,10-octalin (*2*, *12*)] are (a) does platinum catalyze double bond migration in substituted cycloalkenes to the extent required to account for the incursion of the *trans* products, and (b) if (a) occurs then is some process such as diffusion control in pores (*8*) or incomplete desorption (*12*) preventing observation of large quantities of isomerized olefin in the bulk liquid phase? The answer to

TABLE 3

Deuteriumations[a] of (+)-4-Methylcyclohexene[b] on 5% Pt/C. Experimental Conditions and Product Compositions

Expt no.	Cat. wt (g)	Temp (°C)	Sat (%)	Product composition (% each component) 4-Methyl-cyclohexene	3-Methyl-cyclohexene	1-Methyl-cyclohexene	Decrease[c] in rot. (%)
136	0.0200	27.0	57[d]	—	—	—	—
148	0.0200	25.5	32.90	65.80	1.06	0.24	4.52

[a] All experiments were run at 1 atm pressure.

[b] Amount of 4-methylcyclohexene is 0.7 ml.

[c] Percentage difference between rotation of starting and recovered 4-methylcyclohexenes.

[d] Estimated from glc collection peaks.

TABLE 4
DEUTERIUMATIONS OF (+)-4-METHYLCYCLOHEXENE, PERCENTAGE DEUTERIUM DISTRIBUTIONS IN ISOLATED REACTION PRODUCTS

	Expt 136				Expt 148			
	4-Methyl	3-Methyl	1-Methyl	Sat	4-Methyl	3-Methyl	1-Methyl[a]	Sat
d_0	67.6	31.2	26.6	17.7	74.9	35.2	35.7	19.7
d_1	24.9	35.7	29.5	36.0	20.1	35.5	32.0	39.3
d_2	5.86	20.1	25.1	30.1	4.13	19.6	23.2	31.2
d_3	1.26	8.23	10.7	11.2	0.65	6.70	6.04	7.44
d_4	0.32	3.72	6.39	3.39	0.03	2.34	2.36	1.69
d_5	0.00	0.76	1.21	1.09	0.01	0.51	0.50	0.45
d_6	0.00	0.30	0.46	0.38	0.00	0.20	0.22	0.14
d_7	0.00	0.00	0.00	0.15	0.00	0.00	0.00	0.06
d_8	0.00	0.00	0.00	0.06	0.00	0.00	0.00	0.04
d_9	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00
d_{av}	0.417	1.210	1.462	1.528	0.311	1.079	1.097	1.346

[a] Corrected for 0.24% starting material.

both must be yes if the classical mechanism is the only path.

Double Bond Migration

When double bond migration occurs during reduction, the newly formed isomer may not be detected if it reduces faster than its progenitor (*3*). This problem is overcome by the use of an enantiomeric pair; both isomers will exhibit identical reactivities toward a symmetrical surface. Racemization of (+)-1-*p*-methene can occur by migration of the double bond to the opposite side of the methyl group. As shown in Tables 1 and 2, racemization is extensive over palladium but doubtful over platinum. Comparisons of the exchange patterns in Table 5 reveal that *p*-menthene exchange over platinum is as slow as both 1,2-dimethylcyclohexene and 2,3-dimethylcyclohexene and slower than the less substituted cyclohexenes. In contrast, over palladium *p*-menthene behaves like the less substituted olefins (compare Tables 4, 5 and 6), i.e., it exchanges and desorbs readily. This catalyst-specific change in behavior is not intuitively obvious and demonstrates the caution which must be exercised in extrapolating information from one catalyst–substrate system to another. Clearly, since (+)-1-*p*-menthene does not desorb appreciably from Pt it is a poor choice for examining double bond migration on that catalyst.

TABLE 5
EXCHANGE ON 5% Pt/C

	Cyclohexene	1-Methylcyclohexene	*p*-Menthene	2,3-Dimethylcyclohexene	1,2-Dimethylcyclohexene
d_0	85.4	88.1	94.5	94.5	96.0
d_1	11.3	9.99	3.4	4.1	2.23
d_2	2.30	1.27	0.75	0.66	0.91
d_3	0.60	0.40	0.47	0.37	0.41
d_4	0.20	0.14	0.19	0.13	0.23
d_5	0.02	0.07	0.00	0.12	0.08
d_6	0.00	0.00	0.00	0.03	0.05
d_7	0.00	0.00	0.00	0.00	0.03
d_{av}	0.186	0.148	0.071	0.078	0.070
% Sat	34	34	34	34	31

TABLE 6
EXCHANGE ON 5% Pd/C

	4-Methyl-cyclohexene	1-Methyl-cyclohexene	*p*-Menthene	2,3-Dimethyl-cyclohexene	1,2-Dimethyl-cyclohexene
d_0	53.5	57.0	57.2	72.7	78.7
d_1	26.3	27.3	24.8	15.4	12.1
d_2	19.6	11.3	12.5	7.66	5.78
d_3	0.50	3.40	4.50	2.9	2.26
d_4	0.00	0.80	0.94	0.95	0.64
d_5	0.00	0.20	0.12	0.29	0.23
d_6	0.00	0.05	0.00	0.10	0.11
d_7	0.00	0.00	0.00	0.06	0.00
d_{av}	0.670	0.646	0.677	0.456	0.350
% Sat	35	33	34	34	31

Cyclohexene and the methylcyclohexenes desorb from Pt about three times faster than the disubstituted cyclohexenes and, therefore, should furnish good opportunities for observation of double bond migration. Consequently, (+)-4-methylcyclohexene was deuteriumated over Pt to nearly the same percentage reduction as compounds in Table 5. There is a 4.52% decrease in rotation of (+)-4-methylcyclohexene and 60.3% of the 4-methylcyclohexene molecules have been on the surface. This latter value comes from the fact that 25.1% 4-methylcyclohexene is exchanged (Table 4, Expt 148) and 35.2% of desorbed 3-methylcyclohexene contains no deuterium even though all such molecules have been on the surface (it is an isomerized olefin).

From this information and the data in Table 3 it is possible to calculate the relative percentages of all species including desorbed and starting (+)-4-methylcyclohexene (Fig. 1). For comparison consider the methylcyclohexane which samples the surface H/D ratio as it is formed. Since its average deuterium content is 1.346 (it would be 2.00 if only D were on the surface), about 32.7% hydrogen is on the surface. The 32.7% surface H indicated by the saturate and the 35.2% surface H indicated by the isomerized olefin are in close agreement and preclude extensive incursion of processes other than the classical mechanism. Since isomerized olefins and recovered 4-methylcyclohexene contain about 7%, i.e., [(35.2 − 32.7)/35.2]100, more hydrogen than the surface, processes not incorporating deuterium, e.g., [1–3]-sigmatropic shifts or [1–3]-stepwise shifts, could be occurring to the extent of only about 0.2%, i.e., (0.07) (1.49 + 1.06) = 0.18. In 1-methylcyclohexene d_0 is slightly larger than d_0 in 3-methylcyclohexene (even though d_{av} is larger) because the double bond has shifted twice. The slightly smaller amount of 3-methylcyclohexene compared to (−)-4-methylcyclohexene could, among other possibilities, be due to a faster rate of reduction of 3-methylcyclohexene or due to a stereo-directing of double bond migration by the methyl group. In any case it seems clear that over Pt little isomerization–desorption occurs in methyl-substituted cyclohexenes in stark contrast to the rapid isomerization–desorption occurring in (+)-apopinene over Pt (*13*).

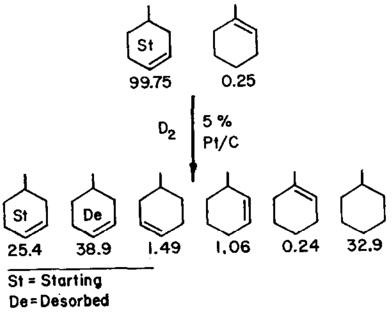

FIG. 1. Percentage composition of reaction mixture from deuteriumation of (+)-4-methylcyclohexene over Pt/C.

Examples of double bond migration on

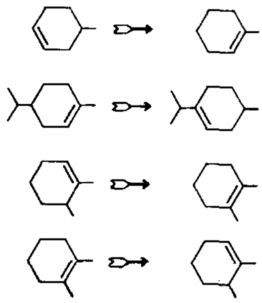

FIG. 2. Double bond migrations observed on palladium but not on platinum.

palladium are legion, but examples on platinum are scarce. In this work we observed on palladium but not on platinum the migrations shown in Fig. 2. The last reaction has been detected on platinum; the 2,3-isomer reaches a concentration of 0.2 mole % at 10% reduction (*8*), in agreement with 4-methylcyclohexene results. Noncyclic systems follow a similar pattern. For example, terminal double bonds undergo extensive migration on palladium (*14*) but only slight migration on platinum (*2*). At slightly elevated temperatures (40°C) the internal double bond in methyl oleate (pure *cis*) undergoes more extensive migration on palladium than on platinum (*15*). On platinum, the double bond is found as many as four positions on either side of its origin; however, only a small percentage of molecules have the double bond moved more than one position. The evidence suggests that platinum can catalyze double bond migration under certain conditions, but the question still remains as to whether or not migration is extensive enough to account for the *trans* products from 1,2-dimethylcyclohexene and 9,10-octalin. Why, for example, is not more of the thermodynamically favored 1,2-dimethylcyclohexene observed during the reduction of the 2,3-isomer? If it forms and desorbs it should be excluded from the surface by the 1,3-isomer (*3*). The same question can be asked of the octalin system in which the 1,9-isomer excludes the 9,10-isomer from the surface (*2*). To account for the products from the tetra-substituted olefins in both systems at least 70% isomerization–desorption must be postulated over platinum.

Most of the evidence in favor of migration on platinum is circumstantial and derived from the stereochemistry (*3, 8, 11*) and deuterium distributions (*2, 10, 12*) in saturated products. On the basis of such compelling data and the simplicity of the classical mechanism it is tempting to try to explain as double bond migration the evidence just presented in the two preceding paragraphs. We suggest, however, that our new data in combination with that presented above are not so readily explained and point to a low probability of double bond migration occurring on platinum. The argument, unfortunately, is based on the lack of appearance of isomerized products in the bulk liquid phase and this depends upon desorption and diffusion out of pores.

The Desorption and/or Pore Diffusion Problems

Examine the hypothesis that on platinum the isomerized–desorbed olefin does not get out of the pore before much of it has become readsorbed and reduced. How much gets out will depend on its concentration and reactivity. High concentration and low reactivity will increase the probability of escape from the pore. If the pore is small the reactivity must be very low or the concentration very high for escape to occur (*9*).

We have tried to eliminate the pore size problem by using catalysts on identical supports. Assuming that 5% Pd/C and 5% Pt/C have the same pore sizes and distributions, then product variations should reflect differences in concentrations and reactivities. If the rate of hydrogenation of 1,2-dimethylcyclohexene were high on platinum then little isomerization–desorption product should escape from the pore. We not only find a slightly higher rate of reduction on palladium but also escaped isomerization–desorption product. Our rate data are crude but confirm our earlier work on the alumina supported metals (*16*). An independent confirmation that diffusion may not be serious comes from a comparison of the percentage *cis*-1,2-dimethylcyclohexane obtained on the different supported metals. On the 5% Pt/alumina 75%

cis is obtained (*3, 16*) but on 5% Pt/C 82% *cis* is obtained. It has been shown that diffusion problems are more serious in charcoal supported platinum than alumina supported platinum (*17*). If diffusion were important and limiting escape from the pores, then the charcoal supported platinum, not the alumina supported platinum should produce the lower percentage *cis*. In addition it should be noted that (+)-apopinene, a molecule of higher mass and therefore lower diffusion rate than the methylcyclohexenes, readily isomerizes, desorbs and reappears in the bulk liquid phase over 5% Pt/C (*13*). Over Pt, therefore, it seems clear that certain structural features (*13, 18*) allow extensive surface gyrations as well as extensive desorption while other structural features, e.g., tetra-substituted alkenes (*2, 3, 5–8, 10–12, 19*) permit extensive surface gyrations but little desorption. The suggestion that desorption need only occur to the extent that the isomerized molecules can flip over and readsorb (*12, 20*) seems to require the postulate of different strengths of physical adsorption on palladium and platinum.

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