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Stereochemistry and the Mechanism of Hydrogenation of Cycloölefins on a Platinum Catalyst[1,2]

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Using PtO_2 as a catalyst, the ratio of *cis*/*trans*-1,2-dimethylcyclohexanes obtained from the hydrogenation of 1,2-dimethylcyclohexene (I), 2,3-dimethylcyclohexene (II) and 2-methylmethylenecyclohexane (III) is a function of the pressure of hydrogen. This ratio increases with increasing pressure (0.25–500 atm.) for I but decreases when II or III is the substrate. Isomers of the initial substrate are detected when the reduction of II and III are interrupted, but not when I is used. Small amounts of *o*-xylene are formed in the lower range of pressure (0.25–1.0 atm.). In competitive experiments, the order of selectivity is III, II, I. The results are interpreted in terms of the Horiuti–Polanyi mechanism with the rate-limiting reaction a function of the pressure of hydrogen: at moderate pressures, the *formation* of the "half-hydrogenated state"; at high pressure, the adsorption of the olefin.

Previous work in this Laboratory[3,4] on the stereochemistry of the hydrogenation over platinum oxide of disubstituted benzenes and their related tetrahydro derivatives indicated that the transition state which determines the configuration of the products has a geometry which resembles the reactants. Thus, from an examination of molecular models of the reactants and the application of conformational arguments as well as the "steric interaction" concept of Linstead,[5] it is possible to account for the main saturated stereo-isomer.[6] It was not possible to decide from the data available, however, whether the geometry-controlling step was the adsorption of the olefin or its conversion to a partially reduced intermediate.

A few experiments had indicated that the stereochemistry of hydrogenation on a platinum catalyst was a function of the pressure of hydrogen.[3] This suggested that the ratios of stereoisomers which are formed result from a competition between two or more reaction paths which differ in their dependency upon the pressure of hydrogen. Gas–liquid partition chromatography has provided the tool for a careful examination of the latter variable and the mechanistic consequences of these stereochemical studies will be presented in this and subsequent papers. Pertinent references to the literature on the catalytic hydrogenation of olefins may be found in several recent reviews.[7–10]

Experimental

Materials.—The substrates 1,2-dimethylcyclohexene, 2,3-dimethylcyclohexene and 2-methyl-1-methylenecyclohexane are known compounds.[3] 1,2-Dimethylcyclohexene and 2,3-dimethylcyclohexene were prepared by the dehydration of 1,2-dimethylcyclohexanol.[11] 2-Methylmethylenecyclohexane was obtained by the pyrolysis of the unsaturated acid produced *via* the Reformatsky reaction of 2-methylcyclohexanone and ethyl bromoacetate.[12]

The infrared spectra of the three olefins exhibited the proper patterns[13,14] and showed each olefin to be free from contamination by the other two isomers. The spectra (see ref. 2b) in combination with the gas chromatographic analysis was taken as proof of structure and purity which was better than 99%.

The glacial acetic acid used was purified by the usual method.[15] Absolute ethyl alcohol was obtained from Commercial Solvents Corp. The powdered platinic oxide used was taken from a 10-g. sample purchased from the American Platinum Works, Newark, N. J.

Hydrogenation Apparatus.—Three types of hydrogenation apparatus were used, depending on the pressure of hydrogen desired. For high pressures (40–500 atm.) a rocker type high pressure bomb (American Instrument Co., Inc.) was employed. For intermediate pressures (2–4 atm.) a Parr low pressure hydrogenation apparatus (Parr Instrument Co., model A, No. 112) was used. For low pressures (0.25–1 atm.) a semi-micro constant pressure hydrogenation apparatus was constructed similar to one previously described.[16]

Hydrogenation Procedures.—In using the high pressure apparatus, the substrate was weighed directly into the glass liner, and the solvent was added. The catalyst was weighed on a paper boat and carefully transferred to the above mixture in such a manner that it did not disperse but settled to the bottom. After introducing the hydrogen, a period of from 5 to 10 minutes was allowed for the temperature of the reaction mixture, glass liner and bomb to equilibrate. Calculations indicated that before shaking less than 1% of the substrate would have time to diffuse to the catalyst.

For experiments using the Parr shaker the reaction mixture was compounded as described above. A 30-ml. pear-shaped flask was used as the reaction vessel and before shaking was begun the flask was evacuated and filled with hydrogen at least 3 times to eliminate air. The presence of air was ignored in the high pressure apparatus.

With the semi-micro constant pressure apparatus the catalyst and solvent were placed in the reaction flask (50 ml.) which was then evacuated and filled with hydrogen at least 5 times to eliminate air. The catalyst was then reduced and allowed to settle 10–15 minutes. The substrate was injected from a 0.25-cc. hypodermic syringe through a serum cap into the reaction mixture and the reaction was started by shaking the reaction vessel. To ensure against leakage, the serum cap was isolated from the reaction vessel proper by a stopcock, through which the syringe needle could pass when the tap was open. The cap and stopcock were attached to

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[2] (a) Presented in part before the division of Organic Chemistry at the 135th National Meeting of the American Chemical Society, Boston, Mass., April, 1959. (b) Taken in part from the Doctoral Dissertation of G. V. Smith, University of Arkansas, September, 1959.

[3] S. Siegel and M. Dunkel, "Advances in Catalysis," Vol. IX, Academic Press, Inc., New York, N. Y., 1956, p. 15.

[4] S. Siegel and G. S. McCaleb, THIS JOURNAL, **81**, 3655 (1959).

[5] R. P. Linstead, W. E. Doering, S. B. Davis, P. Levine and R. R. Whetstone, *ibid.*, **64**, 1985 (1942).

[6] This view has recently been repeated after a consideration of the stereochemistry of hydrogenation of α-pinene derivatives; G. W. Eigenmann and R. T. Arnold, *ibid.*, **81**, 3440 (1959).

[7] G. C. Bond, *Quart. Revs.* (*London*), **8**, 279 (1954).

[8] B. M. W. Trapnell, *ibid.*, **8**, 404 (1954).

[9] R. L. Burwell, Jr., *Chem. Revs.*, **57**, 895 (1957).

[10] T. I. Taylor in "Catalysis," Vol. 5, edited by P. H. Emmett, Reinhold Publishing Corp., New York, N. Y., 1957, Chap. 5.

[11] F. K. Signaigo and P. L. Cramer, THIS JOURNAL, **55**, 3326 (1933).

[12] J. W. Baker and J. B. Holdsworth, *J. Chem. Soc.*, 728 (1945).

[13] R. N. Jones and C. Sandorfy, "Techniques of Organic Chemistry," Vol. IX (A. Weisberger, Editor), Interscience Publishers, Inc., New York, N. Y., 1956, pp. 247–563.

[14] S. Pinchas, J. Shabtai and E. Gil-Av, *Anal. Chem.*, **30**, 1863 (1958).

[15] W. C. Eichelberger and V. K. LaMer, THIS JOURNAL, **55**, 3633 (1933).

[16] T. Freund and H. M. Hulbert, *J. Phys. Chem.*, **61**, 909 (1957).

the flask proper by a ball joint. An inner tube attached to the neck of the reaction flask by a ring seal prevented contact between the reaction mixture and either the stopcock or the joint and excluded the mixture from the side tube connection to the hydrogen source.[17]

Analytical Procedures.—Immediately following each hydrogenation the reaction mixture was filtered. Two different methods were employed in isolating the hydrogenation products from the filtrate. No difference in results could be distinguished between the two methods. In the first 10% of the experiments the above filtrate was extracted with carbon disulfide, concentrated and analyzed by gas chromatography.[4] In the remainder of the experiments (except when ethanol was the solvent) the filtrate was collected in a small-neck 50-ml. volumetric flask and 8 *N* sodium hydroxide was added in portions while the mixture was cooled with tap water. In the final addition the total volume of liquid was adjusted to an amount which filled the flask to approximately half way up the neck. The hydrocarbon layer which separated to the top was easily sampled and analyzed by gas chromatography. When ethanol was the solvent, a saturated solution of sodium bicarbonate was used to salt out the hydrocarbon layer. These procedures did not induce a fractionation of the mixture.

A 25′ × 1/4″ copper tube packed with 40–60 mesh dried Tide was operated at 90°. The isomeric olefins and saturated products, as well as *o*-xylene, gave separate symmetrical peaks.

The weight per cent. of each component was determined from the areas under the curves drawn by the recording potentiometer. The areas were obtained by multiplying the peak height times the width at half the peak height. The validity of this method was demonstrated by analyzing a weighed standard mixture of hydrocarbons used in this research. The analysis was within the experimental error of weighing the hydrocarbons and agreed with reported results.[18] Except where noted in Tables I, II, III and IV, the data are the average value of three successive analyses.

TABLE I

HYDROGENATION OF 1,2-DIMETHYLCYCLOHEXENE ON PtO_2 AT 25°, ACETIC ACID SOLVENT

Pressure, atm.	Reduced,[a] %	% *cis* of saturates[b]	Pressure, atm.	Reduced,[a] %	% *cis* of saturates[b]
0.25	45	80.8[c]	40	100	88.9
0.50	78	81.1[d]	150	100	93.4[e]
1.0	100	81.8	300	97	95.5[e]
2.0	100	83.1	500	99	95.4[e]
4.0	100	83.3			

[a] The recovered olefin is the 1,2-isomer. [b] Analysis reproducible to better than ±0.5. [c] *o*-Xylene present, 1.2 ± 0.2%. [d] *o*-Xylene present, 0.8 ± 0.1%. [e] Single analysis.

TABLE II

HYDROGENATION OF 2,3-DIMETHYLCYCLOHEXENE ON PtO_2 AT 25°, ACETIC ACID SOLVENT

Pressure, atm.	Reduced, %	% *cis* of saturates	Pressure, atm.	Reduced, %	% *cis* of saturates
0.25	53.6	81.1[a]	2.0	100	71.9
0.50	100	76.8	4.0	100	70.6
1.0	20.8	77.6[b]	40	100	68.8
1.0	48.9	78.7[c]	150	100	71.1[e]
1.0	76.6	75.0[d]	500	100	69.7[e]
1.0	100	76.6			

Complete analysis of products in mole per cent.: [a] *trans* 10.1, *cis* 43.5, 2,3- 44.3, 1,2- 1.5, and *o*-xylene 0.7; [b] *trans* 4.7, *cis* 16.1, 2,3- 78.4, 1,2- 0.8, and *o*-xylene 0.0; [c] *trans* 10.4, *cis* 38.5, 2,3- 49.1- 1,2- 1.6, and *o*-xylene 0.4; [d] *trans* 19.1, *cis* 57.5, 2,3- 21.4, 1,2- 1.5, and *o*-xylene 0.3; [e] single analysis.

TABLE III

HYDROGENATION OF 2-METHYLMETHYLENECYCLOHEXANE ON PtO_2 AT 25°, ACETIC ACID SOLVENT

Pressure, atm.	Reduced, %	% *cis* of saturates	Pressure, atm.	Reduced, %	% *cis* of saturates
0.25	60.2	70.1[a]	4.0	95.7	68.7[c]
0.50	100	70.3	40	100	67.0
1.0	100	70.2	150	100	68.7[d]
1.0	80.1	69.4[b]	500	100	67.3[d]

Complete analysis of product in mole per cent.: [a] *trans* 18.0, *cis* 42.2, 2,3- 1.3, *exo* 38.5; [b] *trans* 24.6, *cis* 55.5, 1,2- 0.4, *exo* 19.9; [c] *trans* 65.8, *cis* 29.9, 1,2- 0.3, exo 3.9; [d] single analysis.

TABLE IV

COMPETITIVE HYDROGENATIONS ON PtO_2, SOLVENT ACETIC ACID (1 ATM.)

Compn. of substrate	Reduction, %	Composition of product, %					
		trans	*cis*	*exo*	2,3-	1,2-	*o*-Xylene
1,2- 54.7% 1,2- 45.3%	28.7	6.5	22.2	0.0	16.8	54.4	0.0
Same	57.5	12.0	45.0	0.0	0.0	42.6	0.5
2,3- 50.6% *Exo*- 49.4%	51.2	15.2	36.0	2.2	46.6	0.0	0.0

For experiments in which the reaction was interrupted before the reduction was completed, the composition of the hydrocarbon mixture is shown by recording in a footnote to the table the mole percentage of each unsaturated compound (unless only the starting olefin is present) in addition to the percentage of the saturated hydrocarbons which is the *cis* isomer.

In the preliminary experiments performed in the constant pressure apparatus, an unknown poison, possibly stopcock grease, affected the rates but apparently not the stereochemistry of the reaction. After the design of the reaction flask was changed to exclude grease, the rates were reproducible and reaction proceeded to completion.

If hydrogen is not introduced, the reactants are recovered unchanged.

Rate Measurements.—The rates of reduction of the olefins could be followed conveniently in the low pressure (0.25–1.0 atm.) apparatus and the rates were generally reproducible, with the exceptions noted above. With a 15% variation in the amount of catalyst (0.0200 g.–0.0230 g.) the rates were proportional to the weight. Further, the rate was a function of the substrate although essentially independent of its concentration. Under these conditions, therefore, it is probable that neither the dissolution of hydrogen nor the bulk phase diffusion of the olefin to the catalyst is rate limiting. Although a more detailed study will be required to satisfactorily establish the kinetic parameters, the preliminary results which are given in Fig. 4 are useful in showing some of the regularities as well as the complexities of the reaction.

Results

cis-1,2-Dimethylcyclohexane is the predominant saturated product formed when 1,2- or 2,3-dimethylcyclohexene or the exocyclic isomer is hydrogenated in contact with reduced platinum oxide in the range of pressure of hydrogen examined (0.25–500 atm.). The ratio of *cis* to *trans* isomers is not only a function of the pressure (Fig. 1), but also of the structure of the initial olefin. Thus, while the ratio increases with increasing pressure when the 1,2-isomer is the substrate, it *decreases* when either of the other two olefins is used, the effect of pressure being more noticeable with 2,3-dimethylcyclohexene than with 2-methylmethylenecyclohexane.

In the lower pressure range (0.25–1.0 atm.) isomers of the initial substrates are detected when the hydrogenation of the 2,3- and *exo*-olefins are interrupted but not when 1,2-dimethylcyclohexene is used. A small amount of *o*-xylene is found, also in experiments with the 1.2- and 2,3- but not the *exo* isomer.

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[17] D. F. DeTar, THIS JOURNAL, **78**, 3911 (1956).

[18] J. F. Haskin, G. W. Warren, L. J. Priestley, Jr., and V. A. Yarborough, *Anal. Chem.*, **30**, 217 (1958).

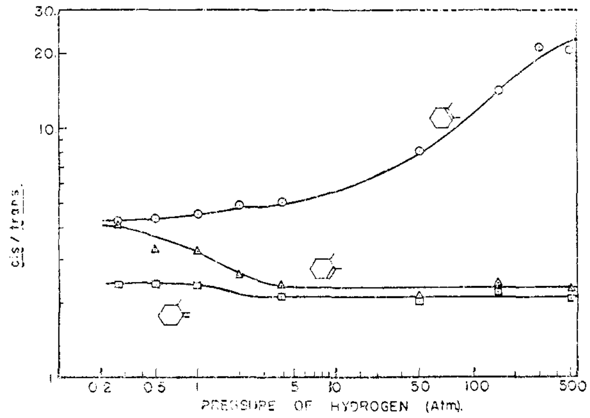

Fig. 1.—The pressure dependence of the *cis* to *trans* ratio of the isomeric 1,2-dimethylcyclohexanes obtained in the hydrogenation over PtO$_2$ of (⊙) 1,2-dimethylcyclohexene, (△) 2,3-dimethylcyclohexene and (□) 2-methyl-1-methylenecyclohexane.

The hydrogenation of 2,3-dimethylcyclohexene was examined in detail (Table II and Fig, 2). As hydrogen is consumed, the concentrations of 1,2-dimethylcyclohexene and *o*-xylene increase until approximately 60% of the hydrogen calculated for complete reduction has been absorbed. Thereafter, the concentration of each unsaturated compound present decreases and in view of the data recorded in Table IV, the concentration of the 2,3-olefin must drop below that of the 1,2- isomer before reduction is complete.

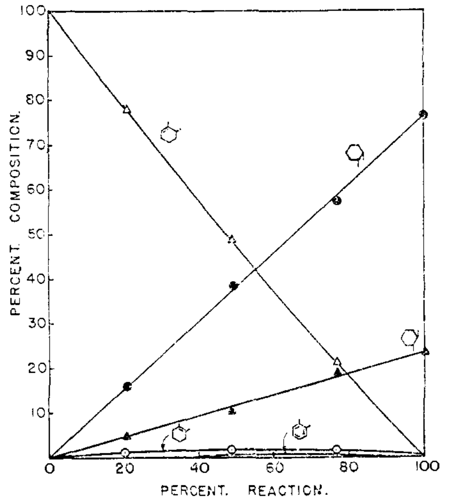

Fig. 2.—The products formed in the hydrogenation of (△) 2,3-dimethylcyclohexene over PtO$_2$ at 1.0 atm. (25°): (⊙) 1,2-dimethylcyclohexene, (●) *cis* 1,2-dimethylcyclohexane, (▲) *trans* 1,2-methylcyclohexane and (●) *o*-xylene.

The isomeric olefins react at different rates as shown in Fig. 3; and the individual rates approximately double when the pressure of hydrogen is increased from 0.5 to 1.0 atmosphere, the reactions being approximately zero order with respect to the substrate. The reaction rates decrease in the order *exo*- 2,3- > 1,2-. Apparently when the isomerization of the initial olefin is observed, only the less reactive isomers are formed in observable amounts (see above).

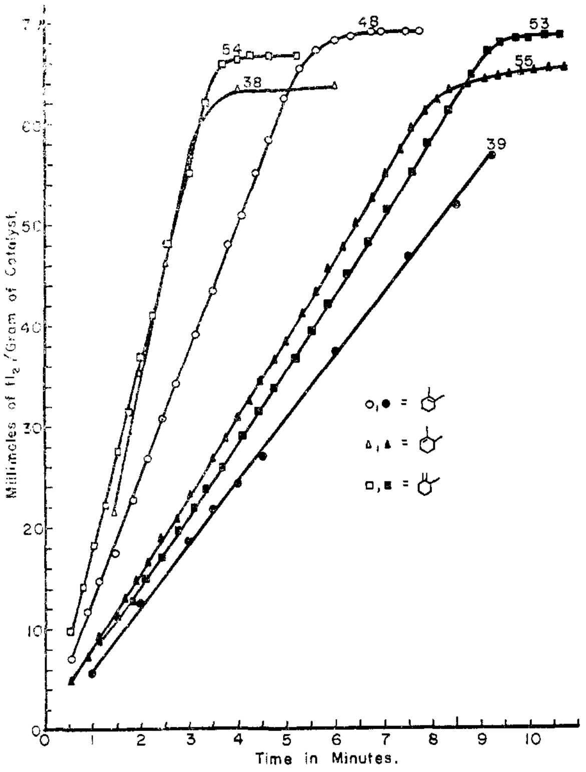

Fig. 3.—Rate of hydrogenation of (O, ●) 1,2-dimethylcyclohexene, (△, ▲) 2,3-dimethylcyclohexene and (□, ■) 2-methyl-1-methylenecyclohexane on PtO$_2$: 1.0 atm. (O, □, △), 0.5 atm. (●, ■, ▲).

If an approximately equal molar mixture of two of the olefins is allowed to react until between 30–50% of the theoretical amount of hydrogen has been taken up, the apparent relative rates of disappearance of the isomeric olefins (*exo*- > 2,3- > 1,2-) is far greater than would be predicted from the rates observed for the olefins separately under otherwise comparable conditions. This kind of selectivity is not uncommon and is characteristic of a heterogeneous reaction in which the substrates compete for a limited surface upon which the chemical reaction occurs.[19] The result is consistent, also, with the apparent zero-order dependence of the rate upon the concentration of the olefin.

Discussion of Results

The reaction of hydrogen and simple olefins has been studied in considerable detail by numerous investigators, mainly by physical-chemical techniques, and several different mechanisms have been proposed to account for the results.[7–10] One of the most satisfactory theories was suggested by Horiuti and Polanyi[20] and is represented as

$$H_2 + ** \underset{r_{-1}}{\overset{r_1}{\rightleftarrows}} 2\,\underset{*}{\overset{H}{|}} \quad (* = \text{catalyst}) \qquad (1)$$

$$\rangle C{=}C\langle + ** \underset{r_{-2}}{\overset{r_2}{\rightleftarrows}} \rangle\underset{*}{C}-\underset{*}{C}\langle \qquad (2)$$

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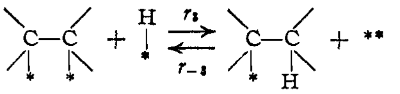
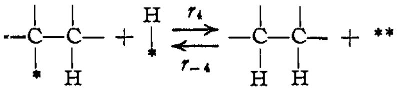
[19] B. B. Corson in "Catalysis," Vol. 3, Edited by P. H. Emmett, Reinhold Publishing Corp., New York, N. Y. (1955), p. 79–93.

[20] I. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, **30**, 1164 (1934).



$$\underset{*\quad *}{>\text{C}-\text{C}<} + \underset{*}{\overset{\text{H}}{|}} \underset{r_{-3}}{\overset{r_3}{\rightleftarrows}} \underset{*\quad \text{H}}{>\text{C}-\text{C}<} + ** \qquad (3)$$



$$-\underset{*}{\overset{|}{\text{C}}}-\underset{\text{H}}{\overset{|}{\text{C}}}- + \underset{*}{\overset{\text{H}}{|}} \underset{r_{-4}}{\overset{r_4}{\rightleftarrows}} -\underset{\text{H}}{\overset{|}{\text{C}}}-\underset{\text{H}}{\overset{|}{\text{C}}}- + ** \qquad (4)$$

The mechanism readily accounts for most of the important facts concerning the hydrogenation of olefins: the occurrence of isomerization of an olefin by an apparent intramolecular shift of hydrogen atoms, the dominant stereochemistry of addition (both atoms of hydrogen add from the same side of the molecule), the occurrence of exchange of deuterium for hydrogen simultaneously with the reduction by deuterium, and the formation of molecules of deuterated saturated hydrocarbons with more than the two atoms of deuterium per molecule expected, as well as species with none or only one.[10]

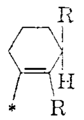
The mechanism is supported, also, by the infrared spectral studies of Eischens and Plisken[21] who have identified the molecular species resulting from the adsorption of olefins upon materials such as nickel supported on alumina or silica with the intermediates posulated by Horiuti and Polanyi.[16]

Our data are accommodated by a mechanism of the above form, and will consequently be discussed within the framework of this theory. The relationship between the structure of the reactants investigated and the configuration of the principal intermediates which lead to the observed products is shown in Fig. 4. Other intermediates might be represented, but for the present discussion these will be neglected.

This reaction scheme offers a simple explanation for the change in the stereochemistry of hydrogenation of 1,2-dimethylcyclohexene as a function of the pressure of hydrogen. The reaction path leading to the *trans* stereoisomer branches from the path yielding exclusively the *cis* isomer at the "half hydrogenated" intermediate (b).

The relative rates of reaction along these branches are clearly a function of the pressure of hydrogen, higher pressures favoring the path yielding only the *cis* isomer. As diagramed, 2,3-dimethylcyclohexene is a required intermediate in order that any of the *trans* isomer be formed. And although the latter olefin is not detected during the reduction of 1,2-dimethylcyclohexene, this is to be expected in view of the observed selectivity in the reduction of mixtures of these two isomers.

An alternate postulate would, however, equally well explain the results. Burwell has suggested that the *trans* isomer might result from a surface reaction involving an intermediate such as IV which represents a dissociatively adsorbed olefin.[22] Formation of this intermediate from adsorbed 1,2-dimethylcyclohexene (a) followed by its reduction could yield both *cis* and *trans* isomers. And as the pressure of hydrogen is increased, the reduction of (a) would be speeded relative to its dehydrogenation to IV as in the first reaction scheme.



IV

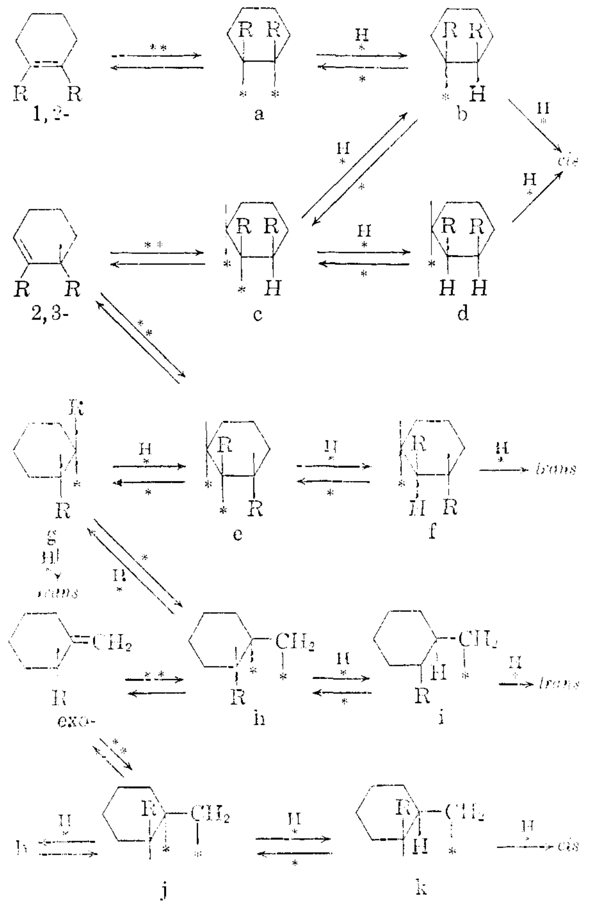


Fig. 4

The influence of pressure on the *cis*/*trans* ratio obtained from 2,3-dimethylcyclohexene is also readily accommodated by the reaction scheme in Fig. 4. The data suggest the following relationships. If the pressure of hydrogen is less than 1 atmosphere, the rate-controlling surface reaction is the formation of the "half-hydrogenated" intermediates b, d, f and g (reaction 3) which mainly are converted to the saturated product, but a small fraction of these intermediates revert to diadsorbed species such as a, c and e and the desorbed olefins 2,3- and 1,2-dimethylcyclohexene.[23] As the pressure of hydrogen is increased, the elementary reactions requiring hydrogen are accelerated and the reverse reactions which require vacant surface sites for hydrogen (and carbon) are slowed. Consequently, the rate-controlling step shifts toward the adsorption of the olefin (reaction 2).

The change in the rate-controlling reaction coincides with a change in the ratio of stereoisomers. Neither rate-controlling reaction can be identified with the last step in the mechanism (4), the forma-

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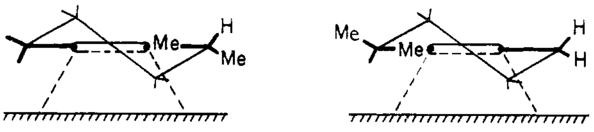
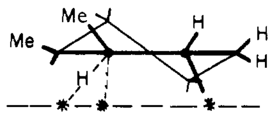
[21] R. P. Eischens and W. A. Plisken, "Advances in Catalysis," Vol. X, Academic Press, Inc., New York, N. Y., 1958, p. 1.

[22] R. L. Burwell, Jr., B. K. S. Shim and H. C. Rowlinson, This Journal, **79**, 5142 (1957).

[23] Compare G. C. Bond and J. Turkevich, *Trans. Faraday Soc.*, **49**, 281 (1953).



A. Adsorption of 2,3-Dimethylcyclohexene



B. Formation of "Half-hydrogenated" State

Fig. 5.

tion of saturated products from the half-hydrogenated states. For if this were the case, the rate of isomerization of the 2,3- to the 1,2-olefin would be much faster than hydrogenation; yet, the observed ratio of 2,3- to 1,2-dimethylcyclohexene remains far from the equilibrium value (85% 1,2-)[24] throughout the major part of the reduction of the former. Also, the principal saturated product would be expected to be the *trans* rather than the *cis* isomer, a conclusion which follows directly from a conformational analyses of the intermediates b, d, f and g, and the assumption that their conversion to saturated products either have comparable rate constants or the constants are grouped d, f > b, g.[24]

It is difficult to see how the postulate of an intermediate such as IV would fit into an explanation for the pressure dependence of the *cis/trans* ratio obtained from 2,3-dimethylcyclohexene; consequently, we prefer the unified mechanistic scheme of Fig. 4 to explain the stereochemistry of hydrogenation of the isomeric olefins examined in this study.

One should note, however, that the product and rate-controlling steps are not necessarily identical and, indeed, the suggested mechanism for the hydrogenation of the 1,2-isomer does not require that these steps be the same. For in the lower pressure range, the rate may be controlled by either the rate of diffusion of hydrogen to the catalyst or by the rate of formation of the "half-hydrogenated state" while the ratio of products is determined by the reactions which the latter undergoes. At sufficiently high pressure only one saturated stereoisomer should result because unless an isomeric olefin (*e.g.*, 2,3-) can be desorbed as an intermediate, only the *cis* saturated product will be produced.

The ratio of saturated stereoisomers obtained from 2-methylmethylenecyclohexane is not so greatly influenced by a change in the pressure of hydrogen as shown by the other olefins. However, it resembles the pattern for the 2,3- rather than the 1,2-dimethylcyclohexene. And we conclude that the change in the ratio of isomers signals the same change in the rate-determining reaction as in the preceding example.

Following the above arguments, a discussion of the geometry of the transition states leading to the formation of adsorbed olefin (1,2-diadsorbed alkane[22]) as well as the transition state for the formation of the "half-hydrogenated state" of Polanyi seems appropriate. The data suggest that subtle though significant differences exist between the geometry of these two "species."

It is reasonable to assume that the olefinic moiety in the transition state for the adsorption of the olefin should have a geometry that resembles the free olefin.[25] The reaction occurs rapidly. Bonding between the olefin and the surface undoubtedly develops so as to maximize the overlap between the π-orbital of the olefin and the metallic orbitals of the surface. The relationships are indicated in Fig. 5A for 2,3-dimethylcyclohexene.

The "transition state" leading from the adsorbed olefin to the "half-hydrogenated state" has a different geometry which is illustrated in Fig. 5B. Here, one bond between the olefin and the catalyst is a σ-bond while the second is split between the catalyst and a hydrogen atom in transition from the surface. This transition state can be identified with the critical complex involved in the exchange reaction between a saturated hydrocarbon and deuterium in which vicinal hydrogen atoms are replaced during a single period of residence of the hydrocarbon on the catalyst's surface. Burwell[22] has shown that this kind of exchange occurs only when the groups attached to the adjacent carbon atoms can attain an eclipsed conformation without an undue expenditure of energy. Therefore, as an approximation, one might assume that the conformation of the hydrocarbon part of this critical complex is the same as the cyclohexane in which a pair of adjacent bonds to the cycle are eclipsed. The most stable geometry for such a cycle appears to be a strained chair conformation,[26,27] which is similar to the conformation of the related cycloolefin. Thus it is that the geometry of the organic moiety of the transition states for either the adsorption of an olefin or the formation of the "half-hydrogenated states" are similar. However, it is evident that this moiety is under greater compressional stresses in the latter than the former state because the distance between the bonding carbon atoms and the surface is shorter. Any stresses so introduced are distributed throughout the molecule.[28] Consequently, no matter how uncertain may be the estimate of the relative energies of the transition states leading to the isomeric products, the steric effects operating in the cycle will be enhanced in the critical complex for the formation of the "half-hydrogenated states" relative to that for the adsorption of the olefin. Thus, as the pressure of hydrogen increases, the ratio of isomers (*cis/trans*) should change in the direction of a diminished selectivity, *e.g.*, toward unity, except for olefins such as 1,2-dimethylcyclohexene which yields the same stereoisomer whichever side it presents to the catalyst.

Apparently, a methyl group on a carbon atom

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[24] S. Siegel and G. V. Smith, THIS JOURNAL, **82**, 6087 (1960).

[25] C. W. Beckett, N. K. Freeman and K. S. Pitzer, *ibid.*, **70**, 4227 (1948).

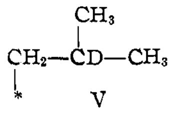
[26] S. G. Angyal and C. G. MacDonald, *J. Chem. Soc.*, 686 (1952).

[27] B. Ottar, *Acta Chem. Scand.*, **1**, 283 (1947).

[28] F. H. Westheimer in "Steric Effects in Organic Chemistry," Chap. 12, Edited by M. S. Newman, John Wiley and Sons, Inc., New York, N. Y., 1956, p. 523.

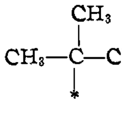
adjacent to the carbon–carbon double bond exerts a steric effect on adsorption to about the same extent whether the double bond is exo- or endocyclic. The ratio of *cis/trans* isomers obtained from each is almost identical at high pressures. The effect is in the nature of a non-bonded interaction between the methyl group attached to the saturated carbon atom and the surface. However, the greater change in *cis/trans* ratio for the 2,3-isomer on going to low pressures suggests that the compressional factors are more pronounced in it than for the *exo* at the "half-hydrogenated state." Perhaps this is related to the greater constraint present in the six-membered cycle when it is adsorbed endocyclic rather than exocyclic. Indeed, in the latter, the cycle is approximately an unstrained chair conformation.

Of the possible transition states which yield the "half-hydrogenated states," those of lowest energy are probably the ones leading to the monoadsorbed hydrocarbon having the least substituted carbon atom. This follows from the experiments of Wilson, Otvos, Stevenson and Wagner[29] who showed that when isobutylene is deuterated, almost no exchange of deuterium for hydrogen is observed in the olefin, although the deuteration and exchange of 1- or 2-butene occurs with comparable rates. They interpreted this to mean that practically all of the "half-hydrogenated state" formed from isobutylene was V rather than VI because the formation of an olefin from VI would of certainty lead to one which contained deuterium. Curiously the same orientation is shown in the addition of boron hydrides to olefins, although in this instance the reaction is effectively irreversible.[30]



$$\underset{\downarrow \atop *}{CH_2}—\overset{CH_3}{\overset{|}{C}}D—CH_3$$

V



$$CH_3—\underset{\downarrow \atop *}{\overset{CH_3}{\overset{|}{C}}}—CH_2D$$

VI

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[29] J. N. Wilson, J. W. Otvos, D. P. Stevenson and C. D. Wagner, *Ind. Eng. Chem.*, **45**, 1480 (1953).

[30] H. C. Brown and B. C. Subba Rao, THIS JOURNAL, **81**, 6423 (1959).

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The Stereochemistry of the Hydrogenation of Cycloölefins on Supported Palladium Catalysts[1,2]

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The sterochemistry of the hydrogenation (1 atm.) of 1,2- (I) and 2,3-dimethylcyclohexene (II) and 2-methylmethylenecyclohexane (III) has been examined using palladium supported on alumina or charcoal as a catalyst and in a solvent (acetic acid or ethanol). The principal saturated product is *trans*-1,2-dimethylcyclohexane (IV), the more stable stereoisomer. Isomerization of the olefin competes with hydrogenation but does not occur in the absence of hydrogen. When the initial reactant is III (Pd-on-carbon), the relative concentrations of I and II remain far from the equilibrium ratio until III disappears. This indicates a competition between I, II and III for the catalytically active surface. Initially, III yields less of IV (61%) than does either I or II (73%). The results are interpreted in terms of the Horiuti–Polanyi mechanism in which the rate-controlling surface reaction is the conversion of the "half-hydrogenated states" to products.

In connection with our studies into the mechanism of the liquid phase hydrogenation of cycloölefins on noble metal catalysts,[4,5] we have noted as have others,[6] that palladium catalysts yield lower percentages of the less stable (*cis*) stereoisomer from 1,2- or 1,4-disubstituted cyclohexenes than does platinum.

Studies of a probably related phenomenon, the variation in the *cis/trans* ratio of olefins formed in the hydrogenation of disubstituted acetylenes as a function of the catalyst, have been numerous,[7,8] although except for relatively recent work[8,9] have suffered from inadequate analytical techniques. Also work on the simultaneous addition and exchange of deuterium with propylene on platinum and nickel catalysts suggests that the hydrogenation of an olefin occurs *via* similar mechanisms[10] on these catalysts although the distinctive features of the several catalytic systems are not sharply delineated.

We have now examined in some detail the behavior of 1,2-dimethylcyclohexene (I), 2,3-dimethylcyclohexene (II) and 2-methylmethylenecyclohexane (III) when treated in the liquid phase with hydrogen at near atmospheric pressures and ambient temperature, in contact with palladium supported upon alumina or charcoal to determine whether the observed stereochemistry would further clarify the mechanism of this reaction.

Experimental

The cyclolefins I, II and III and the solvents were those used in the preceding paper[5] and were at least 99% pure. The palladium catalysts (5% by weight) obtained from Baker and Company, Inc., of Newark, N. J., were supported on alumina, charcoal or calcium carbonate.

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[2] Presented at the Cleveland Meeting of the American Chemical Society, April, 1960.

[3] Taken in part from the doctoral dissertation of Gerard V. Smith, University of Arkansas, June, 1959.

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[6] A. S. Hussey, Department of Chemistry, Northwestern University, private communication.

[7] K. N. Campbell and B. K. Campbell, *Chem. Revs.*, **31**, 77 (1942).

[8] R. L. Burwell, Jr., *ibid.*, **57**, 895 (1957).

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