method described above. The relative rate was calculated from the integrated form of the differential equation derived from the expressions of 4 and 5 using the method of elimination of time as the independent variable. In a similar manner the catalytic hydrogenation of the *exo-endo* diolefin 1 was carried out.

Stereochemistry and the Mechanism of Catalytic Hydrogenation of Cycloalkenes. V. Isomers of Dimethylcyclopentene[1]

BY SAMUEL SIEGEL AND BASIL DMUCHOVSKY[2]

RECEIVED AUGUST 16, 1963

The stereochemistry of hydrogenation of cycloalkenes upon noble metals provides criteria for identifying the product-controlling surface reactions. To define better the geometries of the several pertinent transition states, 1,2-, 2,3-, 1,3-, and 1,4-dimethylcyclopentene and 2-methyl-1-methylenecyclopentane were hydrogenated on reduced PtO_2 and a supported Pd catalyst. Conformational analysis of the results obtained at high hydrogen pressures on PtO_2 suggests that the geometry of the transition state for the adsorption of the olefin has departed significantly from the geometry of the olefin. However, the previously proposed model for the formation of the "half-hydrogenated state" requires only minor modification to account for the results at low pressures (<1 atm.). Compared to the cyclohexene analog, the relative rate of isomerization (2,3- to 1,2-cycloalkene) to reduction is greater in the five- than in the six-membered cycle. However, the same comparison with respect to the change *exo* to *endo* is smaller for the methylenecyclopentane. Kinetic data support the assumption that over platinum the adsorption of the cycloalkene is neither rate nor product controlling at hydrogen pressures less than one atmosphere.

We have shown previously[3,4] that the mechanism suggested by Horiuti and Polanyi[5] for the surface-catalyzed hydrogenation of olefins can account for the stereochemistry observed in the hydrogenation of disubstituted cycloalkenes on certain platinum and palladium catalysts. An analysis of the relationship between the *cis/trans* ratio of saturated products and the pressure of hydrogen as well as an examination of the extent of isomerization of the initial cycloalkene provide criteria for the recognition of the product-controlling surface reaction. Assuming that this identification has been made correctly, we have sought to define the geometry of these several transition states more precisely by examining the variation of the stereochemistry of hydrogenation as a function of the structure of the cycloalkene. In this paper we consider the isomeric dimethylcyclopentenes. We also have attempted a limited kinetic study of the hydrogenation, in acetic acid, of 1,2-dimethylcyclopentene and 2-methyl-1-methylenecyclopentane over reduced platinum oxide, hoping that the results would assist in defining the mechanism of the reaction.

Experimental

1,2- and 2,3-dimethylcyclopentenes were prepared by the iodine-catalyzed dehydration of 1,2-dimethylcyclopentanol which was obtained conventionally from carefully purified 2-methylcyclopentanone and methylmagnesium iodide.[6] The dried product distilled at 96–98.5° (730 mm.) [1,2-dimethylcyclopentene, lit.[7] b.p. 105.8° (760 mm.); 2,3-dimethylcyclopentene, b.p. 102° (760 mm.)] and the isomers were separated by vapor phase

chromatography (25 ft. of a 0.25 in. o.d. copper tubing packed with a commercial detergent, 40–60 mesh Tide). Analysis on a 25 ft. × 0.25 in. column packed with 60–80 mesh firebrick which had been washed with nitric acid and impregnated with 20% by weight of a 1:1 mixture of silver nitrate in triethylene glycol indicated a purity of 99.9 ± 0.2% for the 1,2-dimethylcyclopentene. In like manner, the 2,3-dimethylcyclopentene was shown to be equally pure. The given assignment of structure is corroborated by the infrared and n.m.r. spectra.

2-Methyl-1-methylenecyclopentane was prepared *via* the Reformatsky reaction from 2-methylcyclopentanone and ethyl bromoacetate.[8] The intermediate unsaturated acid was pyrolyzed at 205–210° in the course of 6 hr. in the manner described by Sauvage, *et al.*[9] Distillation of the dried, crude product through a short Vigreux column yielded material, b.p. 94–95.5° (724 mm.), which when analyzed by gas chromatography on the above-described silver nitrate column indicated the composition: 2-methyl-1-methylene-cyclopentane, 95.5%; 2,3-dimethylcyclopentene, 2.3%; and 1,2-dimethylcyclopentene, 2.2%.

1,3- and 1,4-dimethylcyclopentenes were prepared in a manner analogous to that described for the 1,2- and 2,3-dimethylcyclopentenes, starting from 3-methylcyclopentanone. The distilled product, b.p. 89.5–90° (730 mm.), when analyzed on the silver nitrate column showed two major components, the first fraction 53%, the second 44%, and a third of 3%. Fractionation with the same column provided samples of the two major components with purities estimated as 99.9 ± 0.2%. Nuclear magnetic resonance spectra obtained through the courtesy of the Houston Research Laboratory of the Shell Oil Co., Deer Park, Texas, do not unequivocally distinguish the two structures from one another, although these spectra and the infrared spectra are consistent with either structure. However, since both compounds have essentially the same stereochemistry, the present uncertainty in the assignment of structure need not detract from the conclusions drawn.

Reagents.—The glacial acetic acid used in all hydrogenation experiments was untreated analytical reagent grade acid. The experiments of Newby[10] and Smith[11] showed that further distillation and purification of this solvent had little or no effect on the rate or the stereochemistry of the reaction.

The platinum oxide used was obtained from Engelhard Industries, Inc., Newark, N. J. Palladium on alumina (5%) was purchased from Baker and Co., Inc., Newark, N. J.

(1) (a) This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of said fund. (b) Taken in part from the Doctoral dissertation of Basil Dmuchovsky, University of Arkansas, Jan., 1962. (c) Presented at the 142nd National Meeting of the American Chemical Society, New York, N. Y., Sept. 14, 1962.

(2) NSF Cooperative Fellow, 1960–1961.

(3) S. Siegel and G. V. Smith, *J. Am. Chem. Soc.*, **82**, 6082 (1960).

(4) S. Siegel and G. V. Smith, *ibid.*, **82**, 6087 (1960).

(5) J. Horiuti and M. Polanyi, *Trans. Faraday Soc.*, **30**, 1164 (1934).

(6) F. K. Signaigo and P. L. Cramer, *J. Am. Chem. Soc.*, **55**, 3326 (1933).

(7) A.P.I. Research Project 44, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons," Carnegie Press, Pittsburgh, Pa., 1953, p. 47.

(8) J. W. Baker and J. B. Holdsworth, *J. Chem. Soc.*, 728 (1945).

(9) J. F. Sauvage, R. H. Baker, and A. S. Hussey, *J. Am. Chem. Soc.*, **82**, 6090 (1960).

(10) W. E. Newby, Ph.D. Dissertation, Northwestern University, Aug., 1950.

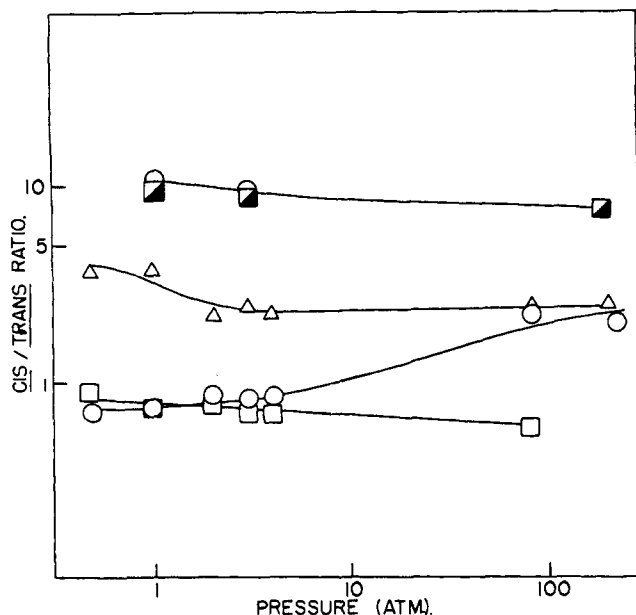(11) G. V. Smith, Ph.D. Dissertation, University of Arkansas, Sept., 1959.

Fig. 1.—Variation of the *cis/trans* ratio as a function of pressure in the reduction, over PtO₂, of 1,2- (O), 2,3- (□), 1,3- (◑), and 2,4-dimethylcyclopentene (◪) and 2-methyl-1-methylene-cyclopentane (△).

Apparatus.—A constant pressure system for reductions at about one atmosphere, a Parr shaker for two to four atmospheres, and a high pressure rocker type bomb were used in this work and have been described previously.[3] The kinetic studies employed only the constant pressure system.

Analytical Procedure.—All hydrogenations were carried out in 5.0 ± 0.1 ml. of glacial acetic acid containing a known amount of catalyst. At the conclusion of a reaction the mixture was filtered through medium fluted filter paper into a thin-necked 50-ml. volumetric flask. Sodium hydroxide (6–8 N) was then added to the filtrate, with cooling by running tap water, until the liquid level reached the 50-ml. mark. The flask was then swirled at an angle to permit the bubbles of hydrocarbon to rise, thus forming an immiscible upper layer. Samples, from 0.5 to 10 μl., could then be withdrawn by syringe or capillary and injected into the v.p.c. column.

Compositions were determined by using areas obtained by integration or by triangulation. The accuracy attained by both methods for complete separations was better than 1%.

On the silicone column (6 ft. × 0.25 in. o.d., silicone on 60–80 mesh firebrick) *trans*-1,2-dimethylcyclopentane preceded the *cis* isomer with relative retention times of 1.5 to 1. On silver nitrate the relative retention times were 3.0, 2.2, 2.0, 1.5, and 1.0 for 2-methyl-1-methylenecyclopentane, 2,3-dimethylcyclopentene, 1,2-dimethylcyclopentene, *cis*-1,2-dimethylcyclopentane, and *trans*-1,2-dimethylcyclopentane, complete separations being achieved. In the 1,3-series the olefins were separated, but the saturated isomers were incapable of resolution with this column but were analyzed on a 500-ft. capillary, coated with squalane, through the courtesy of the Shell Oil Co.

Reaction Vessels.—For low pressure work the type of flask described previously[3] was used for early experiments. For later experiments, the volume of the flask was increased to 125 ml. to increase the surface to volume ratio, and the socket joint holding the injection port was modified by the elimination of the stop-cock. This last change reduced the possibility of introducing stopcock grease when the alkene is added.

Kinetic Procedure and Analysis.—The experiments employed the usual 5 ml. of glacial acetic acid, 0.10 to 0.20 ml. of substrate, and between 0.16 to 45 mg. of platinum oxide. The catalyst was reduced for a minimum of 30 min. after which the olefin was introduced through a pressure-tight serum cap (changed every four runs) and allowed to come to thermal equilibrium.

For each experiment a zero-order (with respect to substrate) rate was computed from the slope of a plot of the volume of hydrogen absorbed *vs.* time and expressed in the units moles atm.⁻¹ sec.⁻¹ for the weight of catalyst employed. The effect of the pressure of hydrogen upon the rate was established by independent experiments in which the pressure differed, as well as by
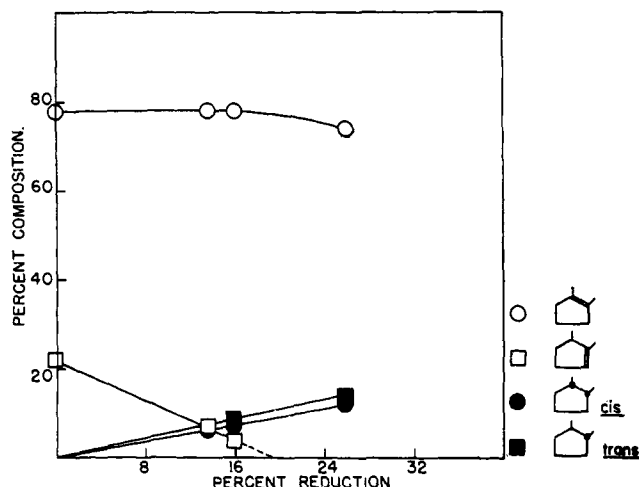

Fig. 2.—Competitive reduction of 1,2- (O) and 2,3-dimethyl-cyclopentene (□) over PtO₂ (1 atm.): *cis-* (●) and *trans-* (■) 1,2-dimethylcyclopentanes.
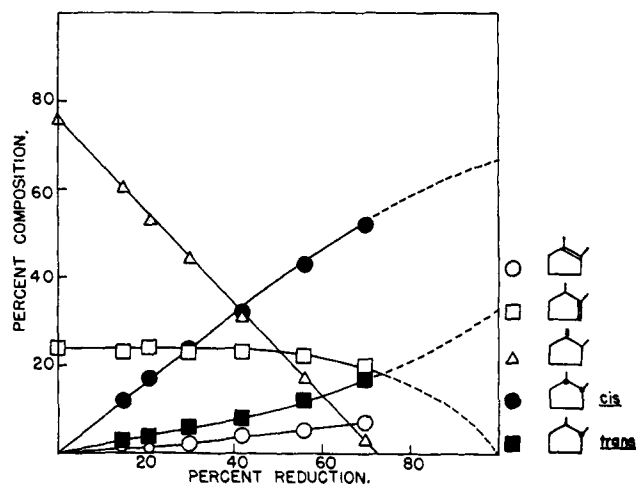

Fig. 3.—Competitive reduction of 2-methyl-1-methylene-cyclopentane (△) and 2,3-dimethylcyclopentene (□) over PtO₂ (1 atm.); *cis-* (●) and *trans-* (■) 1,2-dimethylcyclopentanes, 1,2-dimethylcyclopentene (O).

interrupting a particular experiment to change the pressure to a new value for the remainder of the run.

Results

Studies on Reduced Platinum Oxide.—The stereochemistry of the hydrogenation of the isomeric dimethylcyclopentenes reproduces several features of the hydrogenation of the dimethylcyclohexenes reported previously.[3,4] The ratio of *cis/trans*-dimethylcyclopentanes obtained from a given alkene is a function of the pressure of hydrogen. The magnitude and the direction of the change is a function of the structure of the unsaturated substrate (Fig. 1). Over reduced platinum oxide, the fraction of *cis* product obtained from 1,2-dimethylcyclopentene increases with increasing pressure, and in the low pressure range, the ratio is the same as that obtained from 2,3-dimethylcyclopentene. Also, in competitive experiments, the 2,3-isomer is selectively reduced (Fig. 2 and 3). The identical relationships hold for 1,2- and 2,3-dimethylcyclohexene.[3]

The relationship between the pressure of hydrogen and the fraction of the *cis* product obtained from 2-methyl-1-methylenecyclopentane is also similar to the cyclohexane analog, the *cis/trans* ratio decreasing with increasing pressure. The same relationship is obtained
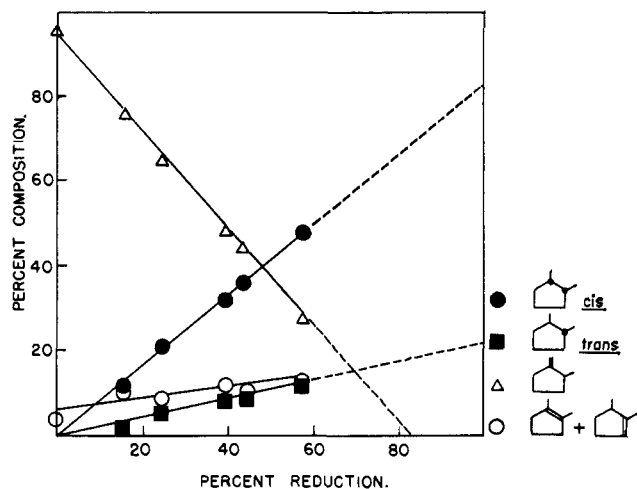
Fig. 4.—Reduction of 2-methyl-1-methylenecyclopentane (△) on PtO_2 (1 atm.): cis- (●) and trans- (■) 1,2-dimethylcyclopentanes, and mixture of 1,2- and 2,3-dimethylcyclopentenes (○).

from the other dimethylcyclopentenes studied, although the effect is small. In a previous paper, we reported examples showing analogous but much magnified stereochemical effects, e.g., the hydrogenation of 4-t-butyl-1-methylcyclohexene and 4-t-butyl-1-methylenecyclohexane.[12]

The competition between the several alkenes for the surface is also illustrated in Fig. 3, and evidently the alkene with the exocyclic double bond reacts preferentially to the endocyclic. Some isomerization of 2-methyl-1-methylenecyclopentane is observed, both 1,2- and 2,3-dimethylcyclopentenes being formed along with the saturated products (Fig. 4). The amount so produced is small as with the cyclohexene analog. However, relative to the rate of hydrogen addition the amount of isomerization of the 2,3- to the 1,2-dimethylcyclopentene is much greater than observed previously with 2,3-dimethylcyclohexene (Table I).

TABLE I

TYPICAL COMPOSITION OF PRODUCTS (MOLE PER CENT) IN HYDROGENATIONS OVER PtO_2 AT ONE ATMOSPHERE

Compd.[a]	Redn.	exo-	2,3-	1,2-	cis	trans
2,3-DMCP[b]	35	..	54	11	17	18
2,3-DMCP	41	..	47	12	17	23
2-MMCP[c]	25	66	5	4	21	4
2-MMCP[c]	44	44	5	6	36	8
2,3-DMCH[d]	49	..	49	1.6	39	10

[a] 2,3-Dimethylcyclopentene (2,3-DMCP), 2-methyl-1-methylenecyclopentane (2-MMCP), 2,3-dimethylcyclohexene (2,3-DMCH). [b] Pressure, 0.5 atm. [c] Starting material: 2-MMCP, 95.5%; 2,3-DMCP, 2.3%; and 1,2-DMCP, 2.2%. [d] Reference 3, Table II.

Some pains were taken to obtain kinetic data for the reduction of 1,2-dimethylcyclopentene and 2-methyl-1-methylenecyclopentane on reduced platinum oxide. Because the reaction is heterogeneous, transport processes may be either rate limiting or modify the rate relationships so as to obscure the kinetics of the surface reaction which we hoped to observe.[13]

When large amounts of catalyst are employed, the rate of reduction of 1,2-dimethylcyclopentene reaches a value which is a measure of the rate of transfer of hydro-

(12) S. Siegel and B. Dmuchovsky, J. Am. Chem. Soc., **84**, 3132 (1962).
(13) (a) A. Wheeler, "Advances in Catalysis," Vol. III, Academic Press, Inc., New York, N. Y., 1951; (b) R. Ciola and R. L. Burwell. Jr., J. Phys. Chem., **65**, 1158 (1961).

TABLE II

THE MOLE PER CENT OF THE cis ISOMER IN THE SATURATED PRODUCT AS A FUNCTION OF THE PRESSURE OF HYDROGEN, PtO_2, AT 25°

Press., atm.	1,2-DMCP[a]	2,3-DMCP	2-MMCP[b]	1,3-DMCP	1,4-DMCP
0.5	42	48	79	..	..
1.0	43	44	81	92	91
2.0	47	44	69	..	..
3.0	45	41	71	91	91
4.0	46	41	69	..	..
81	69	..	70	..	..
200–300	67[c]	37[d]	72[e]	..	88[e]

[a] DMCP is dimethylcyclopentene. [b] 2-Methyl-1-methylenecyclopentane. [c] 230 atm. [d] 290 atm. [e] 210 atm.

gen from the gas to the liquid phase.[14] However, the rate is proportional to the weight of catalyst for amounts less than about 3 mg. per 5 ml. of solution in the reaction vessel employed. The stereochemistry is constant (43 ± 1% cis) with the exception of an experiment in which only 0.16 mg. of catalyst was used (53% cis) and another with 0.3 mg. which was also abnormally slow (5% in 5 hr., 68% cis); see Fig. 5.

The catalyst changed in activity rather abuptly after the first series of experiments which were completed during a 2-month period, and the later results are seen to fall below the curve of the earlier work (Fig. 5). Nonetheless, the relative rates of reaction of the isomeric olefins appear reasonably consistent within a given period and the stereochemistry is not sensitive to this particular change. Others have reported similar difficulty with platinum oxide and it does not seem to be an ideal material for quantitative work.[15]

TABLE III

SAMPLE KINETIC RESULTS ON PLATINUM OXIDE AT 25°

Cat. wt., mg.	P, atm.	Rate × 10⁵, moles min.⁻¹	k × 10⁴ [a]
	1,2-Dimethylcyclopentene		
1.03	0.98	3.15	5.20[b]
1.19	.49	1.80	5.13
1.67	.49	2.79	5.67
1.67	.97	4.92	5.28
	2-Methyl-1-methylenecyclopentane		
1.71	0.98	8.20	8.12[c]
2.17	.48	4.30	6.80
2.17	.97	8.90	7.02

[a] Units of k are moles atm.⁻¹ g.⁻¹ (catalyst) sec.⁻¹. [b] The average value of k for the 1,2-isomer in seven experiments, where the rate is proportional to the weight of catalyst, was 5.0 ± 0.3 × 10⁻⁴ in the first series. After the catalyst became less active, five experiments yielded a value of 3.2 ± 0.3 × 10⁻⁴. [c] The average of seven experiments with the exo isomer, using the same catalyst and interspersed in time with the runs above, b, gave a value of 7.4 ± 1.1 × 10⁻⁴. The less active catalyst gave a value of 5.5 × 10⁻⁴ in one experiment at 26°.

The rate of reaction of 1,2-dimethylcyclopentene deviated from a strictly zero-order dependence upon the substrate concentration when small amounts of catalyst were used. The data fitted an equation of the form

$$1/b \ln C_0/C + (C_0 - C) = kwtPV^{-1} \quad (A)$$

where C_0 and C are the concentrations of substrate at times t_0 and t, b is the equilibrium constant for the adsorption of the olefin, w is the weight of catalyst, V

(14) H. C. Yao and P. H. Emmett, J. Am. Chem. Soc., **81**, 4125 (1959).
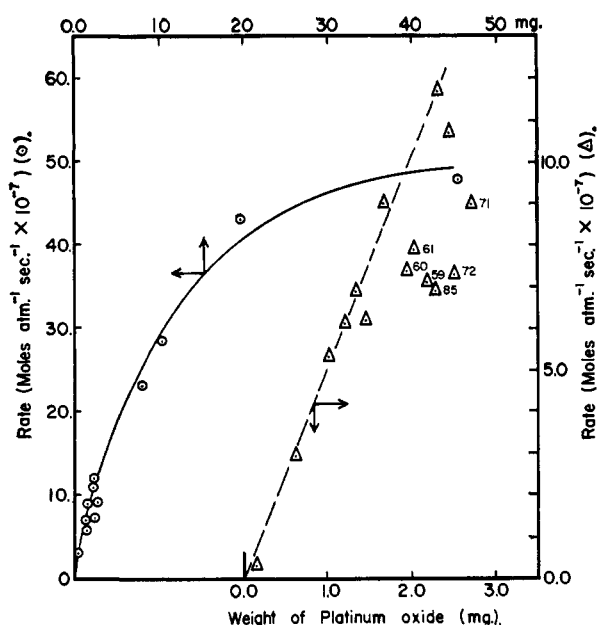(15) G. V. Smith and R. L. Burwell, Jr., ibid., **84**, 925 (1962).

$$-\overset{|}{\underset{*}{C}}-\overset{|}{\underset{H}{C}}- \ +\ H\ \overset{\longrightarrow}{\underset{\longleftarrow}{}}\ -\overset{|}{\underset{H}{C}}-\overset{|}{\underset{H}{C}}- \ +\ 2^* \qquad (4)$$

The influence of pressure is most simply explained as an indication of a change in the product-limiting surface reaction from reaction 3, the formation of the "half-hydrogenated state" at low pressure to reaction 2, and the adsorption of the alkene which is product limiting at high hydrogen pressures.

Fig. 6.—The reduction of 2-methyl-1-methylenecyclopentane ($\triangle$) on 5% palladium on charcoal (1 atm.): cis ($\bullet$) and trans ($\blacksquare$) 1,2-dimethylcyclopentanes and mixture of 1,2- and 2,3-dimethylcyclopentene (O).

The reversal of steps 3 and 2 may lead to an alkene isomeric with the original substrate. Increasing the pressure of hydrogen increases the rate at which the half-hydrogenated state is further reduced (reaction 4) and, consequently, diminishes the fraction which can return to alkene. Clearly, the rate of reaction 3 is thereby also increased, but not so much as reaction 4, the rate of the latter being of higher order in the surface concentration of hydrogen. Stereochemistry reveals this relationship when the original alkene and the possible isomerized products yield different ratios of the saturated geometrical isomers. For example, 1,2-dimethylcyclopentene should yield only cis-1,2-dimethylcyclopentane via the one-sided addition of hydrogen, whereas the same mechanism of addition will yield both cis and trans isomers from 2,3-dimethylcyclopentene, an obvious isomerization product of the 1,2-isomer. In the low pressure region (Fig. 1), one must assume that essentially all of the 1,2-derivative has isomerized before it is reduced. The proposition that 2,3-dimethylcyclopentene is an intermediate in the hydrogenation of 1,2-dimethylcyclopentene cannot be dismissed on the grounds that it was not detected in reaction mixtures of the latter because in competitive experiments the 2,3-isomer is selectively reduced (Fig. 2 and 3).

The over-all stereochemistry is thus consistent with the Horiuti–Polanyi mechanism of hydrogenation, which depicts the transformation as a series of interrelated simple reactions which occur on the surface of the catalyst.

Kinetic Studies.—The kinetic data do not unambiguously identify the rate-limiting reaction. If a reaction on the catalyst surface were rate limiting, the

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Fig. 5.—Rate of reduction of 1,2-dimethylcyclopentene as a function of the weight of catalyst (mg.). The numbered $\triangle$'s refer to a later group of experiments with less active catalyst; see Table III.
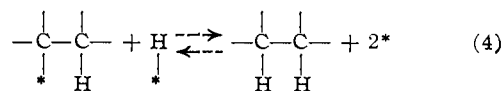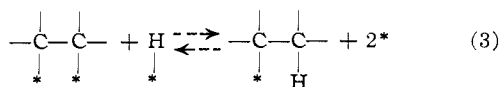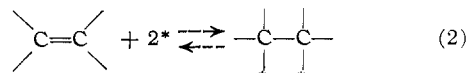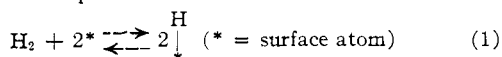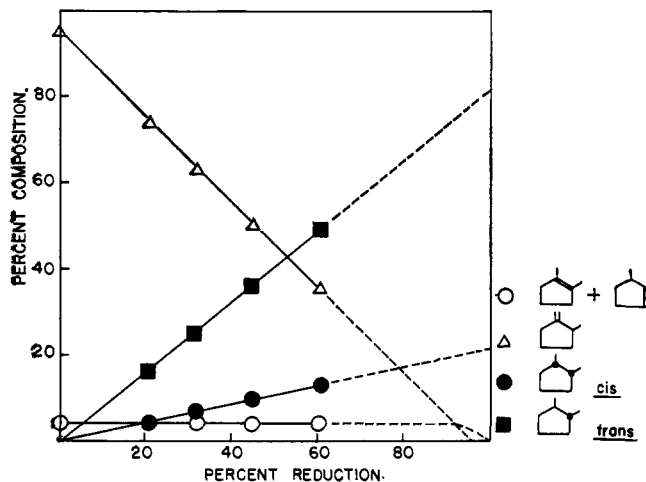
the volume of solution, P the pressure of hydrogen, and k the specific rate constant.[16] Values of 1×10^2 l. mole^{-1} for b and 3.95×10^{-4} mole atm.$^{-1}$ g.$^{-1}$ sec.$^{-1}$ for k reproduce well the data in expt. 71 to 97% of complete reaction. However when b is this order of magnitude, more precise data than are at hand are required to establish with confidence the kinetic significance of such a result.

Studies on Palladium.—Only the 2-methyl-1-methylenecyclopentane was studied on a palladium catalyst. The ratio of cis/trans isomers is much less than unity, as was expected, the more stable saturated stereoisomer predominating in the product (Fig. 6). However, the amount of endocyclic olefin formed (less than 1%) in competition with the reduction of the exocyclic isomer was much less than in the cyclohexene analogs previously studied. The latter was almost completely isomerized by the time one-third of the calculated amount of hydrogen had been adsorbed.

Discussion

These data demonstrate the stepwise nature of the addition of hydrogen to the alkene and that the relative rates of the successive and parallel reactions which occur are influenced by changing the pressure of hydrogen and presumably its concentration on the surface of the catalyst.

As we have shown previously, the Horiuti–Polanyi mechanism is of the proper form to account for such results and is represented as

$$H_2 + 2^* \ \overset{\longrightarrow}{\underset{\longleftarrow}{}}\ 2\overset{H}{\underset{*}{|}} \quad (^* = \text{surface atom}) \qquad (1)$$

$$\overset{\diagdown}{\diagup}C{=}C\overset{\diagup}{\diagdown} \ +\ 2^* \ \overset{\longrightarrow}{\underset{\longleftarrow}{}}\ -\overset{|}{\underset{*}{C}}-\overset{|}{\underset{*}{C}}- \qquad (2)$$

$$-\overset{|}{\underset{*}{C}}-\overset{|}{\underset{*}{C}}- \ +\ H\ \overset{\longrightarrow}{\underset{\longleftarrow}{}}\ -\overset{|}{\underset{*}{C}}-\overset{|}{\underset{H}{C}}- \ +\ 2^* \qquad (3)$$

(16) F. L. Morritz, E. Lieber, and R. B. Bernstein, J. Am. Chem. Soc., **75**, 3116 (1953).

Figure 7.

over-all rate must be proportional to the weight of the catalyst. However, the converse is not true because the reaction might be limited by the rate at which one component, in this instance hydrogen, diffuses into the pores of the catalyst[13] where the reaction mainly occurs. The zero-order dependence of the rate upon the concentration of alkene would follow as would the proportionality between the rate and the pressure of hydrogen.

That the rate of transfer of hydrogen to the catalyst surface dominates the kinetics, unless the activity of the catalyst is reduced, is also suggested by the stereochemistry. The ratio of cis/trans dimethylcyclopentanes obtained from the 1,2-alkene is independent of the weight of the catalyst unless very small amounts are used and the resulting rates are erratic and slow. Probably in these instances the catalyst is partially poisoned and this less reactive material permits the concentration of hydrogen within the pores to attain a higher value and a larger proportion of the cis isomer is formed.

The deviation of the rate of reduction of 1,2-dimethylcyclopentene from zero order with respect to the substrate may indicate that this olefin is weakly adsorbed, but the surface kinetics are masked by the above effect of diffusion, for it would tend to increase the apparent value of b in equation A over the value which would pertain if diffusion were not important. Of the several isomers studied, this compound must have the smallest value for its adsorption constant. The fact that one isomeric cycloalkene can prevent another from reacting indicates that the surface is saturated with the adsorbed hydrocarbon species. The ease of displacement falls in the order 1,2-, 2,3-, exo.

Clearly, the rate- or product-controlling surface reaction on this platinum catalyst at the lower hydrogen pressures (0.3–1.0 atm.) cannot be the rate of adsorption of the cycloalkene on the surface. But whether reaction 3 or 4 has this role is not distinguished by these kinetic data.

The Geometry of the Transition State for Adsorption.—Although the general pattern of results support our previous conclusions regarding the mechanism of the reaction, the new information provides further insight into the geometry of the pertinent transition states. Perhaps the most significant feature is that the 2,3-dimethylcyclopentene yields proportionally more of the trans saturated isomer at all pressures relative to 2,3-dimethylcyclohexene which yields principally the cis isomer. However, the variation in this ratio with the pressure of hydrogen is about the same for both cycloalkenes. This suggests that a structural factor is operating in 2,3-dimethylcyclopentene which is minimized in the substituted cyclohexene, and we identify it with the increase in vicinal methyl interactions which accompany the changing geometry of the
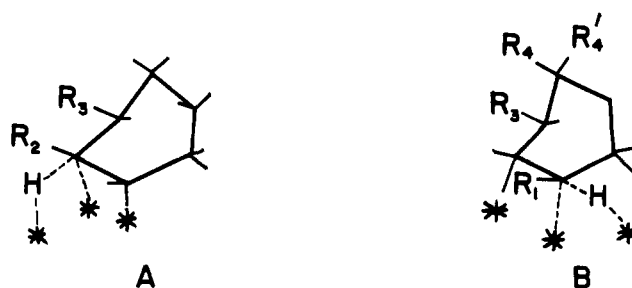

Figure 8.

organic moiety as it progresses along the reaction path leading to cis-1,2-dimethylcyclopentane. Because the cis/trans ratio is less than unity at high pressures, we conclude that the spatial disposition of the transition state for the adsorption of the olefin has departed significantly from the most stable conformation of the cycloalkene.

The effect which we attribute to the interactions between vicinal methyl groups disappears when the substituents are not on adjacent carbon atoms. Thus, both 1,3- and 1,4-dimethylcyclopentene yield mainly the cis-1,3-dimethylcyclopentane (92% at 1 atm., 88% at 200 atm.) and the result obtained at high hydrogen pressure is taken as a measure of the interaction between the surface and the distal methyl group attached to the cycle, relatively uncomplicated by intracyclic effects, during the adsorption process. The analogous dimethylcyclohexenes (1,3- and 2,4-) yield a smaller cis/trans ratio; presumably the interactions between the methyl group and the surface can be minimized by the flexing of the cycle.

The Geometry of the Transition State Yielding the "Half-hydrogenated State."—We have shown that on reduced platinum oxide in the low pressure region the product-limiting surface reaction is the formation of the "half-hydrogenated state."[3,12] The geometry of the corresponding transition state is assumed to approximate the geometry of a cis-1,2-diadsorbed cycloalkane having the bonds to the cycle eclipsed. This geometrical requirement would be met best by the C_s (envelope) configuration of the five-membered cycle as shown in Fig. 7, the groups attached to carbon atoms 1 and 2 being eclipsed and carbon atom 4 being the flap of the cycle.[17]

To minimize interactions with the surface, a group at C-3(R_3) should be trans to the surface bond at C-2 and this can account for the large cis/trans ratio at low pressures for 1,3-dimethylcyclopentene.

To account for the cis/trans ratio of about unity obtained from 2,3-dimethylcyclopentene, one must assume that the interaction between the eclipsed methyl groups at C_2–C_3 is comparable with the interaction between a methyl group and an adjacent bond to the surface. As noted above, the cyclohexene analog can minimize such eclipsing effects because of the greater flexibility of the larger cycle. Whether the most stable conformation for cyclopentane substituted at C-4 should have the substituent cis or trans to the surface bond is not obvious. However, one is able to obtain a consistent predictive pattern if one makes the assumption that the cycle and its substituents will tend

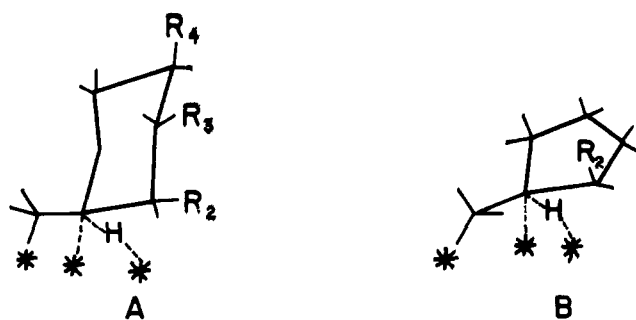(17) F. V. Brutcher, T. Roberts, S. J. Barr, and N. Pearson, J. Am. Chem. Soc., **81**, 4915 (1959).

Figure 9.

Figure 10.

to be arranged so as to give the maximum extension of the molecule in a direction perpendicular to the surface providing that the cost in energy which might result from enforcing less favorable internal group interactions (intracyclic or conformational effects) is less than about 2–5 kcal. per mole. With this assumption, one can bypass the question of whether the flap of the five-membered cycle is directed toward or away from the surface. Applied to the reduction of disubstituted cyclohexenes, it provides a rationalization for the assumption that the transition state for the addition of the first hydrogen atom to the cycle can be described as in Fig. 8, in which the cycle is shown in the boat form rather than in a distorted chair.

This model is similar to the one suggested by Sauvage, Baker, and Hussey to account for the stereochemistry of hydrogenation of cycloalkenes having an endocyclic double bond.[9] However, their model referred to the adsorptive process for the alkene, rather than the formation of the "half-hydrogenated state."

The justification for the assumption that the mass of the adsorbed species, such as the "half-hydrogenated states," be disposed so as to maximize its extension outward from the catalyst surface, even at the expense of enforcing an unfavorable intracyclic conformation, may be found in the probable situation that under the reaction conditions the active surface is saturated with the adsorbed hydrocarbon species and the attainment of this maximum surface concentration entails crowding the organic groups and thereby affects the conformations of the adsorbed cycle.

Turning to the exocyclic alkenes, the present postulate yields the same model as that used previously to account for the stereochemistry of hydrogenation of 2-, 3-, or 4-alkyl-1-methylenecyclohexanes. It is illustrated in Fig. 9A. Likewise, the result predicted for 2-methyl-1-methylenecyclopentane is mainly cis, for with only one atom of the cycle bonded to the surface, the neighboring groups can be rotated out of the eclipsed positions via the envelope conformation which has the bond to the surface equatorial[18] (Fig. 9).

Alkene Isomerization, Stereochemistry on a Palladium Catalyst.—On palladium the predominant saturated isomer produced from 2-methyl-1-methylenecyclopentane is the more stable one, trans-dimethylcyclopentane. This is consistent with the previous postulate that reaction 4 is product controlling on this catalyst. However, little of the isomeric olefins is formed concurrently with the reduction.

In contrast, 2-methyl-1-methylenecyclohexane is completely isomerized by the time about one-third of
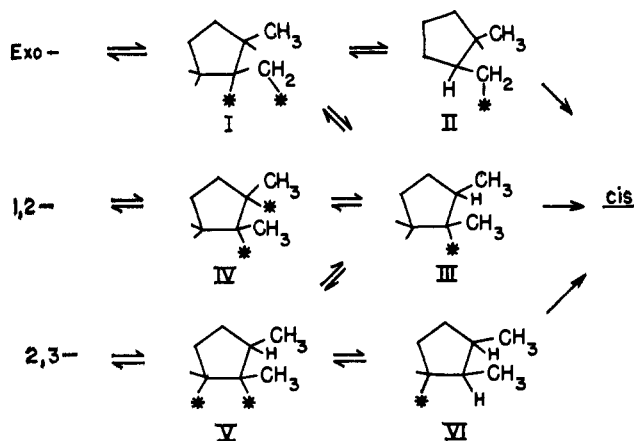
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the theoretical amount of hydrogen has been consumed.[4] Thus relative to its rate of reduction, the shift of the double bond from an exo to an endo position is slower in the five- than in the six-membered cycle. Apparently some of the intermediate stages of reaction are not so readily reversed in the reduction of methylenecyclopentane as in methylenecyclohexane; e.g., II → I in Fig. 10.

Although little isomerization of 2,3- to 1,2-dimethylcyclohexene accompanies the reduction of the former on platinum oxide, a considerable amount of 1,2-dimethylcyclopentene is found when 2,3-dimethylcyclopentene is partially reduced under the same conditions (Table I). Apparently the shift of a double bond within the ring is faster in the five-membered cycle. This probably reflects the greater constraints upon the motion of the parts and appendages of the smaller cycle which, in comparison with the analogous cyclohexene derivatives, reduces the barriers to isomerization by raising the minima in the potential surface (the olefins and adsorbed species IV and V) more than the energy of the saddle points (transition states).

The rotational barriers within cyclopentane and cyclohexane are influenced by similar restrictions being lower in the five-membered cycle.[18]

π-Complexes as Reaction Intermediates in the Hydrogenation of Alkenes.—Recently it has been suggested that when hydrocarbons are adsorbed on metallic surfaces, π-complexes are formed.[19] Such complexes had been previously discussed with respect to the reactions of hydrocarbons with deuterium on chromium oxide gel.[20] One type is held to be analogous to the Pt–ethylene grouping as in $K(C_2H_4)PtCl_3$[21] and another the allyl–metal structure as in π-butenylcobalttricarbonyl.[22,23] Olefins can form the first type of complex by association with a surface atom; the second involves, in addition, the dissociation of a hydrogen atom.

Clearly the kinetic form of a mechanism in which an associatively formed π-complex is rapidly and reversibly converted to a 1,2-diadsorbed alkane is indistinguishable from the Horiuti–Polanyi formulation and

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obviously one can retain the latter's mechanistic simplicity if the π-complex structure is substituted for the 1,2-diadsorbed alkane. However, our present stereochemical information does not demand such a distinction.

Our studies suggest that the stereochemistry which is observed at high hydrogen pressures is governed by a reaction which precedes the formation of the "half-hydrogenated" state. The organic moiety of the transition state for this reaction has a geometry similar to the reactants; however, the hybridization of the unsaturated carbon atoms has progressed from sp² to sp³ to the extent that eclipsing effects between groups attached at C-2 and C-3, as in 2,3-dimethylcyclopentene, are observable. These geometrical requirements are met either by our formulation of the Horiuti–Polanyi mechanism or the π-complex concept. The groups attached to the π-bonded carbon atoms of the complex are apparently not in a plane which includes the latter.

π-Allyl complexes may be involved in the isomerization of alkenes as suggested by Smith and Burwell,[15] but our stereochemical data are adequately described without this additional postulate.

Aromatic Substitution. XXI.[1a] Friedel–Crafts Acetylation of Benzene, Alkylbenzenes, and Halobenzenes with Acetyl Halides and Acetic Anhydride

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The Friedel–Crafts acetylation of benzene, alkylbenzenes, and halobenzenes has been investigated with acetyl halides (fluoride, chloride, and bromide) and acetic anhydride in the presence of a variety of Lewis and Brønsted acid catalysts. Relative reactivities compared with benzene and isomer distributions of homogeneous reactions in nitromethane solution were determined by a gas–liquid chromatographic analytical technique. Certain aspects of the mechanism and the nature of the acetylating agents are discussed on the basis of the experimental data, including n.m.r. investigations.

Introduction

The Friedel–Crafts acylation of aromatics with acid anhydrides and acyl halides in the presence of acidic halide catalysts has been the subject of a great many investigations during the 86 years since the discovery of the reaction. Extensive reviews have critically discussed the reaction mechanism, and we will therefore confine our discussion to work directly related to our own investigations.

Earlier investigations of the Friedel–Crafts acetylation reaction of aromatics have reported only small substrate reactivity differences between benzene and toluene. Ogata and Oda[2] have observed a relative rate $k_{\text{toluene}}:k_{\text{benzene}}$ of 8.35 and McDuffie and Dougherty[3] that of 13.3 in a competitive reaction using acetyl chloride and aluminum chloride in an excess of the hydrocarbons at 10°. McDuffie and Dougherty also have reported relatively low substrate selectivity for the acetylation of m-xylene and mesitylene.

Table I

Relative Rates of Acetylation of Benzene and Methylbenzenes (McDuffie and Dougherty[3])

	$k_{\text{Ar}}:k_{\text{benzene}}$
Benzene	1.0
Toluene	13
m-Xylene	100
Mesitylene	27

These investigations, however, were carried out under heterogeneous reaction conditions and no homogeneous kinetic work was available until the investigations of Brown and his co-workers.

Relative rates and isomer distributions of the aluminum chloride-catalyzed acetylation of benzene and alkylbenzenes with acetyl chloride in ethylene dichloride solution at 25° were investigated by Brown, Marino, and Stock.[4,5] Their data are summarized in Table II.

Table II

Aluminum Chloride-Catalyzed Acetylation of Benzene and Alkylbenzenes with Acetyl Chloride in Ethylene Dichloride Solution at 25° (Brown and Co-workers[4,5])

Aromatic hydrocarbon	$k_{\text{Ar}}:k_{\text{benzene}}$	Alkylacetophenone, % ortho	meta	para
Benzene	1.0			
Toluene	128	1.2	1.2	97.6
Ethylbenzene	129	0.3	2.7	97.0
Isopropylbenzene	128		3.0	97
t-Butylbenzene	114		3.8	96.2

As seen from the investigations of Brown and his co-workers, toluene, ethylbenzene, isopropylbenzene, and t-butylbenzene all react with practically the same velocity, although the reactions were shown to be first order in aromatic substrates. The observed isomer distributions were also very similar. In the acetylation system investigated, using ethylene dichloride solvent (which has very poor solvent properties for aluminum halides, but dissolves to a certain degree the CH₃COCl–AlCl₃ complex in the form of the donor–acceptor complex and not as the oxocarbonium salt), the acylations show both high substrate and positional selectivity.

The essential absence of o-isomers was attributed to the bulkiness of the acetylating agent: namely, the acetyl chloride–aluminum chloride complex.[4] Similar explanations had been advanced previously to account for the general absence of o-substitution in Friedel–Crafts acylation of alkylbenzenes.

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