g. (1.0 mmole) of α-methyl-3,4-dipropionoxycinnamic acid in 15 ml. of thionyl chloride was allowed to reflux on the steam-bath for 2 hr. The excess thionyl chloride was removed by evaporation, and 5 ml. of benzene was added. The benzene was removed by evaporation. The benzene addition and removal was twice repeated. The resulting acid chloride was dissolved in 10 ml. of chloroform.

A solution of 0.426 g. (1.0 mmole) of penta-*O*-acetyl-neo-inosamine-2 hydrochloride (XIV) and 0.202 g. (2.0 mmoles, 0.28 ml.) of triethylamine in 20 ml. of chloroform was magnetically stirred with the acid chloride solution for 2 hr. The chloroform solution was washed with water, dried over magnesium sulfate, and evaporated to give a gum which was dissolved in 15 ml. of ethanol. The ethanol solution was concentrated at atmospheric pressure to 5-ml. volume and diluted with 5 ml. of water. This precipitated a gum which crystallized on scratching to give 0.517 g. (76% yield) of cream-colored crystals, m.p. 157–160° after two recrystallizations from dilute alcohol. The material had λ_{max}^{MeOH} 209 (ϵ 20,600) and 260 mμ (ϵ 18,700); λ_{max}^{HCl} 209 (ϵ 21,100) and 260 mμ (ϵ 19,300); λ_{max}^{NaOH} 252 (ϵ 12,900) and 316 mμ (ϵ 7,130); λ_{max}^{KBr} 2.96, 5.69, 5.98, 6.10, 6.56(shoulder), 6.63, and 8.13 μ.

Anal. Calcd. for $C_{32}H_{39}NO_{15}$: C, 56.71; H, 5.80; N, 2.07. Found: C, 56.83; H, 5.60; N, 2.16.

In a second experiment this product was obtained in 69% yield.

2-Deoxy-2-(3,4-dihydroxy-α-methylcinnamido)-neo-inositol (XVI).—A solution of 0.465 g. (0.69 mmole) of 1,3,4,5,6-penta-*O*-acetyl-2-deoxy-2-(α-methyl-3,4-propionoxycinnamido)-neo-inositol (XV) and 0.146 g. (1.45 mmoles, 0.20 ml.) of triethylamine in 25 ml. of anhydrous methanol was allowed to reflux for 2 hr. The solution was acidified with glacial acetic acid and evaporated. The amber residual sirup was treated with 1.5 ml. of glacial acetic acid and allowed to stand at room temperature for 10 min. during which time crystals separated. The mixture was diluted with 5 ml. of acetone and filtered to give 0.175 g. (71% yield) of white crystals, m.p. 248–252° dec. This material was recrystallized from water to give buff-colored crystals, m.p. 256–259° dec. A mixture of this material with the $C_{16}H_{21}NO_8$ degradation product (m.p. 253–258° dec.) of the antibiotic hygromycin melted at 253–259° dec. Furthermore, the infrared spectra of the two samples were identical, and the ultraviolet spectra of the degradation product and the synthetic material were essentially the same.

Anal. Calcd. for $C_{16}H_{21}NO_8$: C, 54.08; H, 5.96; N, 3.94. Found: C, 53.71; H, 6.01; N, 4.06.

Paper Chromatography.—Circular paper chromatograms were run in the apparatus described by Kawerau.[34] The apparatus (26-cm. diameter) was purchased from the Shandon Scientific Co., London, Eng., and modified in the manner described by Kissman and Weiss.[35] The paper used was a special Whatman #1 filter paper (KCT-26) which had been slotted for the Kawerau apparatus. Solvents were mixed just before use, and the paper was not equilibrated with the solvent mixture. The inosamine derivatives were detected with the silver nitrate–sodium hydroxide reagent described by Trevelyan, *et al.*,[36] as modified by Anet and Reynolds,[37] and the chromatograms were fixed by spraying with thiosulfate.[33]

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[34] E. Kawerau, *Chromatographic Methods*, **1,** No. 2, 7 (1956) [published by H. Reeve Angel and Co., 52 Duane Street, New York 7, N. Y.].

[35] H. M. Kissman and M. J. Weiss, *J. Am. Chem. Soc.*, **80,** 5559 (1958).

[36] W. E. Trevelyan, D. P. Proctor and J. S. Harrison, *Nature*, **166**, 444 (1950).

[37] E. F. L. J. Anet and T. M. Reynolds, *ibid.*, **174**, 930 (1954).

[38] S. J. Angyal, D. J. McHugh and P. T. Gilham, *J. Chem. Soc.*, 1432 (1957).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ARKANSAS, FAYETTEVILLE, ARK.]

Stereochemistry and the Mechanism of Hydrogenation of Cyclo-alkenes.[1] IV. 4-*tert*-Butyl-1-methylcyclohexene and 4-*tert*-Butyl-1-methylenecyclohexane on Platinum Oxide and a Palladium Catalyst[2]

BY SAMUEL SIEGEL AND BASIL DMUCHOVSKY[3]

RECEIVED OCTOBER 25, 1961

The ratio of the saturated stereoisomers obtained upon the hydrogenation of 4-*tert*-butyl-1-methylcyclohexene (I) and 4-*tert*-butyl-1-methylenecyclohexane (II) on reduced PtO_2 is a function of the pressure of hydrogen. The *tert*-butyl group magnifies the steric effects over those previously observed. A simple mathematical analysis of the previously proposed mechanistic scheme is shown to be consistent with the stereochemical information. The characteristics of the reaction in the presence of a palladium catalyst are also accounted for with the assumption that the rate-limiting surface reaction occurs at a later stage than that which pertains on platinum.

Previous stereochemical studies of the hydrogenation of 1,2-dimethylcyclohexene and several of its isomers on platinum[4] and palladium[1] catalysts had suggested that the distribution of the saturated stereoisomers, as well as the isomeric cycloalkenes formed concurrently, may serve to identify the product and/or rate-controlling surface reaction and also to define the geometry of the pertinent transition states. Arguments based upon conformational theory were employed and the treatment of mechanism was qualitative. In the present work, 4-*tert*-butyl-1-methylcyclohexene and 4-*tert*-butyl-1-methylenecyclohexane have been hydrogenated in the liquid phase (acetic acid solvent) and in contact with reduced PtO_2. The bulk of the *tert*-butyl group restricts the conformations of the six-membered cycle to which it is attached to those in which this group is equatorial or quasi equatorial[5]; consequently, conformational effects and analysis are simplified, and the resulting stereochemistry is more readily identified with a simple, mathematical treatment of the proposed mechanistic scheme.

Experimental

Preparation of 4-*tert*-Butyl-1-methylenecyclohexane.—4-*tert*-Butyl-1-methylenecyclohexane was prepared by the pyrolysis of the unsaturated acid obtained *via* the Reformatsky reaction of 4-*tert*-butylcyclohexanone and ethyl bromoacetate.[6,7] The crude olefin, b.p. 185–187° (730 mm.)

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[1] For the previous paper in this series, see S. Siegel and G. V. Smith, *J. Am. Chem. Soc.*, **82**, 6087 (1960).

[2] The support by a grant (NSF-G-9920) from the National Science Foundation is gratefully acknowledged. A grant from the Monsanto Chemical Co. provided a fellowship (B. D.) and additional valued assistance.

[3] Taken in part from the M.S. thesis of B. D., January, 1960.

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

[5] S. Winstein and N. S. Holness, *ibid.*, **77**, 5562 (1955).

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[7] B. Cross and G. H. Whitham, *ibid.*, 3892 (1960).

TABLE I

HYDROGENATION OF 4-*tert*-BUTYL-1-METHYLCYCLOHEXENE ON PLATINIC OXIDE

Pressure of hydrogen, atm.	% *cis* Isomer	% Reaction
0.25	35	47
0.53	35	38
1	36[a]	48
1	36	43
2	39	100
3	40	100
4	39	100
55	47	100
300	47	97

[a] Average of two analyses.

TABLE II

HYDROGENATION OF 4-*tert*-BUTYLMETHYLENECYCLOHEXANE ON PLATINIC OXIDE

Pressure of hydrogen, atm.	% *cis* Isomer	% Reaction
0.25	87	100
0.53	86	49
1	83[a]	55
1	84	57
2	79	100
3	76	100
4	75	100
62	62	100
300	61	100

[a] Endocyclic isomer was 0.1% of starting material; product contained 1.9% of this isomer.

TABLE III

HYDROGENATION ON CATALYSIS SUPPORTED ON ALUMINA

Catalyst	Substrate	Pressure of hydrogen, atm.	% *cis* Isomer	% Reaction
5% Pt	*exo*	1	70[a]	55
5% Pt	*exo*	3	68	91
5% Pt	*exo*	62	53	100
5% Pd	*exo*	1	33[b]	65
5% Pd	*endo*	1	34[b]	56

[a] 4.0% of the product is the endocyclic olefin. [b] All the olefin remaining is endocyclic.

(approximately 95% exocyclic isomer), was purified by gas–liquid chromatography yielding a product which by g.l.c. analysis is 99.9% a single component, $n^{25}D$ 1.4604. Consistent with the assigned structure is the infrared spectrum with bands at 885,[8,9] 1653,[9] 1778[10] and 3060[10] cm.$^{-1}$.

Anal. Calcd. for $C_{11}H_{20}$: C, 86.78; H, 13.22. Found: C, 86.84; H, 13.16.

Preparation of 1-Methyl-4-*tert*-butylcyclohexene.—This cycloalkene was prepared from carefully purified 4-*tert*-butylcyclohexanone *via* the iodine-catalyzed dehydration of 1-methyl-4-*tert*-butylcyclohexanol. It was purified by gas chromatography; $n^{25}D$ 1.4585, reported[11] $n^{20}D$ 1.4599. Analysis *via* g.l.p.c. indicated a purity of 99 mole per cent. The infrared spectrum showed bands at 800,[9,10] 823,[9,10] 1051[8] and 1680[9] cm.$^{-1}$.

Catalysts.—The platinum oxide was obtained from J. Bishop and Co. Platinum Works, and the catalysts, supported on alumina, 5% palladium or platinum, were purchased from Baker and Co., Inc., Newark, N. J.

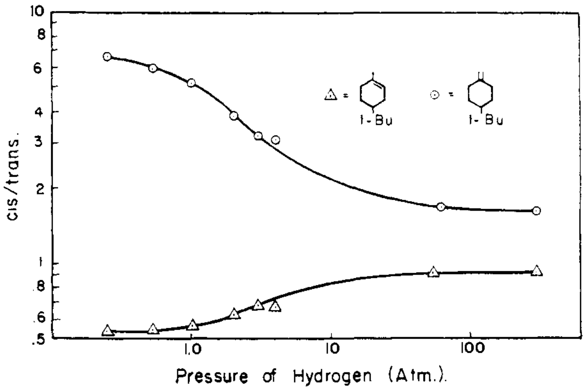

Fig. 1.—Hydrogenation of 4-*tert*-butyl-1-methylcyclohexene and 4-*tert*-butyl-1-methylenecyclohexene on PtO_2.

Procedures.—The hydrogenation of the olefins was performed as described previously.[4] The amounts of solvent (5.0 ml. of glacial acetic acid), substrate (0.2 ml.), and catalyst (0.02 g.) were the same for each experiment.

Analysis of the mixtures (in triplicate for each mixture except where noted) was accomplished by gas–liquid chromatography using the Aerograph Gas Chromatographic Instrument, model A-90-C, obtained from Wilkens Instrument and Research, Inc., Berkeley, Calif. The column consisted of 18 m. of 6-mm. o.d. copper tubing filled with "Craig polyester succinate on Chromosorb," also obtained from the Wilkens firm.

At 103–105°, and a flow rate of 50 cc. per minute (helium), the following retention times were recorded: 4-*tert*-butyl-1-methylenecyclohexane, 51 min.; 4-*tert*-butyl-1-methylcyclohexene, 59 min.; *cis*-4-*tert*-butyl-1-methylcyclohexane, 36 min.; *trans*-4-*tert*-butyl-1-methylcyclohexane, 31 min.; and *p*-*tert*-butyltoluene, 70 min. The peaks were symmetrical and well separated.

Results

In agreement with our previous studies, the ratio of saturated stereoisomers obtained upon the hydrogenation of 4-*tert*-butyl-1-methylcyclohexene (I) (Table I) and 4-*tert*-butyl-1-methylenecyclohexane (II) (Table II) on reduced PtO_2 is a function of the pressure of hydrogen (Fig. 1). The *tert*-butyl group has indeed magnified the steric effects, particularly in the reduction of the exocyclic double bond. Again a small amount of the more stable endocyclic isomer is formed at a relatively low pressure of hydrogen and, in so far as it is reduced, tends to decrease the *cis*/*trans* ratio obtained from II. The reduction of the endocyclic double bond in I yields somewhat more of the *trans* than the *cis* isomer.[4,11]

Isomerization of the alkene occurs to a greater extent on a platinum–alumina catalyst than on PtO_2, although not to the degree found with palladium (Table III). Apparently either the alumina modifies the chemical properties of the platinum, or the physical structure of the support affects the balance among the competitive reactions through diffusional effects.[12]

The explanation advanced previously seems to account for these results also. Thus, the ratio of isomers produced on reduced PtO_2 in the low pressure range is governed by the energetics of the transition states leading to the "half-hydrogenated" state (C, D) of Horiuti and Polanyi,[13] while

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(8) S. Pinchas, J. Shabtai and E. Gil-av, *Anal. Chem.*, **30**, 1863 (1958).

(9) H. W. Thompson and D. H. Whiffen, *J. Chem. Soc.*, 1412 (1948).

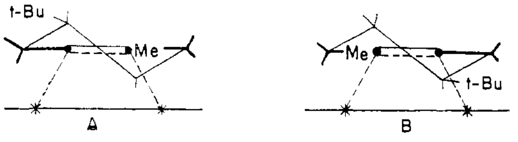
(10) R. N. Jones and C. Sandorfy, "Techniques of Organic Chemistry," Vol. IX, A. Weissberger, Editor, Interscience Publishers, Inc., New York, N. Y., 1956, pp. 247-263.

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

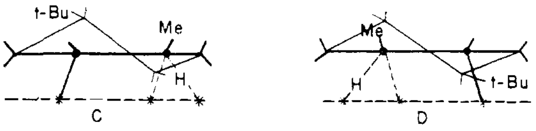
(12) A. Wheeler, "Advances in Catalysis," Vol. III, Academic Press, Inc., New York, N. Y., 1951, pp. 317-322.

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

the ratio obtained at high pressure is determined by the energetics of the transition states leading to the adsorbed olefin (A, B). (Only the most stable conformations of these states are represented.)



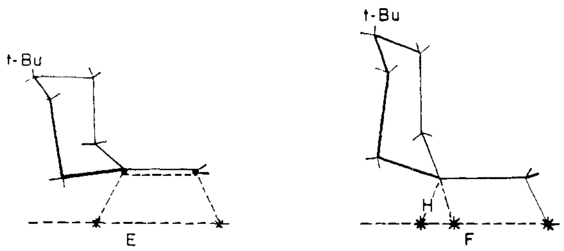
Adsorption of 1-Methyl-4-t-Butylcyclohexene



Formation of "Half-hydrogenated" state from A and B

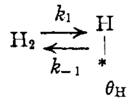
One should note that the geometry of the former transition states (C, D) is taken to be, approximately, the geometry of the saturated cycle having its bonds to the surface eclipsed while the transition state (A, B) for the adsorption of the olefin has a geometry resembling the olefin with the π orbital of the double bond directed toward the surface.[4]

Steric considerations suggest that the difference in energy of the transition states which lead to the *cis* or *trans* diadsorbed alkanes upon the adsorption of the cyclo-alkenes is less than the difference in energy for the transition states which yield the respective "half-hydrogenated states,"[4] and although we are not able to account, from our model, for the dominance of the *trans* isomer which is obtained in the hydrogenation of 4-*tert*-butyl-1-methylcyclohexene on PtO_2,[14] the ratio changes in the predicted way when the pressure of hydrogen is increased. The *chosen* model for adsorption accounts for the closer approach to unity of the ratio of stereoisomers obtained at *high pressure* from 4-*tert*-butyl-1-methylcyclohexene than from 4-*tert*-butyl-1-methylenecyclohexane for in the former the π-orbital of the double bond is equally approachable from either side of the molecule, whereas in the latter, the cycle, which is frozen in the chair conformation by the *tert*-butyl group, provides greater hindrance from the one direction which yields the *trans* isomer than the other which yields the *cis*. The same limiting ratio of isomers is obtained at high pressure in the hydrogenation of 2-methyl-1-methylenecyclohexane and, presumably, for the same reason.

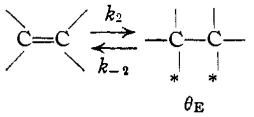


Adsorption of 4-t-Butyl-1-methylenecyclohexane (E) and the formation of "half-hydrogenated" state from E.

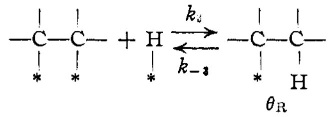
The preceding argument may be formalized through a steady-state treatment of the Horiuti–Polanyi mechanism, which may be represented as



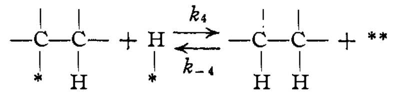
$$\mathrm{H_2} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \begin{array}{c}\mathrm{H}\\ |\\ *\\ \theta_{\mathrm{H}}\end{array} \tag{1}$$



$$\begin{array}{c}\diagdown \quad \diagup \\ \mathrm{C{=}C} \\ \diagup \quad \diagdown\end{array} \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} \begin{array}{c} |\quad\; | \\ -\mathrm{C}-\mathrm{C}- \\ |\quad\; | \\ *\quad\; * \\ \theta_{\mathrm{E}}\end{array} \tag{2}$$



$$\begin{array}{c} |\quad\; | \\ -\mathrm{C}-\mathrm{C}- \\ |\quad\; | \\ *\quad\; * \end{array} + \begin{array}{c}\mathrm{H}\\ |\\ *\end{array} \underset{k_{-3}}{\overset{k_3}{\rightleftarrows}} \begin{array}{c} |\quad\; | \\ -\mathrm{C}-\mathrm{C}- \\ |\quad\; | \\ *\quad\; \mathrm{H} \\ \theta_{\mathrm{R}}\end{array} \tag{3}$$



$$\begin{array}{c} |\quad\; | \\ -\mathrm{C}-\mathrm{C}- \\ |\quad\; | \\ *\quad\; \mathrm{H} \end{array} + \begin{array}{c}\mathrm{H}\\ |\\ *\end{array} \underset{k_{-4}}{\overset{k_4}{\rightleftarrows}} \begin{array}{c} |\quad\; | \\ -\mathrm{C}-\mathrm{C}- \\ |\quad\; | \\ \mathrm{H}\quad\; \mathrm{H} \end{array} + ** \tag{4}$$

where θ_{H}, θ_{E}, and θ_{R} represent the fraction of the accessible surface which is covered by hydrogen, alkene (diadsorbed alkane) and "half-hydrogenated state," respectively. A superscript, *t*, ($\theta_{\mathrm{E}}{}^{\mathrm{t}}$, $\theta_{\mathrm{R}}{}^{\mathrm{t}}$, $k_2{}^{\mathrm{t}}$, etc.) will refer to the adsorbed species, which by further abstraction of hydrogen from the surface would lead to the *trans*-1,4-dialkylcyclohexane, and the superscript c to the related *cis* forming species.

Because the suggested pathways leading to the respective *cis* and *trans* isomers separate at the act of adsorption, the rate of formation of each isomer can be written independently of the other as

$$\mathrm{d}[cis]/\mathrm{d}t = k_4{}^{\mathrm{c}}\theta_{\mathrm{R}}{}^{\mathrm{c}}\theta_{\mathrm{H}} \tag{5}$$

$$\mathrm{d}\theta_{\mathrm{E}}{}^{\mathrm{c}}/\mathrm{d}t = k_2{}^{\mathrm{c}}\,[\mathrm{E}] - k_{-2}{}^{\mathrm{c}}\,\theta_{\mathrm{E}}{}^{\mathrm{c}} - k_3{}^{\mathrm{c}}\theta_{\mathrm{E}}{}^{\mathrm{c}}\,\theta_{\mathrm{H}} + k_{-3}{}^{\mathrm{c}}\,\theta_{\mathrm{R}}{}^{\mathrm{c}} = 0 \tag{6}$$

$$\mathrm{d}\theta_{\mathrm{R}}{}^{\mathrm{c}}/\mathrm{d}t = k_3{}^{\mathrm{c}}\theta_{\mathrm{E}}{}^{\mathrm{c}}\theta_{\mathrm{H}} - k_{-3}{}^{\mathrm{c}}\theta_{\mathrm{R}}{}^{\mathrm{c}} - k_4{}^{\mathrm{c}}\theta_{\mathrm{R}}{}^{\mathrm{c}}\theta_{\mathrm{H}} = 0 \tag{7}$$

Rearranging 7 yields

$$\theta_{\mathrm{E}}{}^{\mathrm{c}} = (k_{-3}{}^{\mathrm{c}} + k_4{}^{\mathrm{c}}\theta_{\mathrm{H}})\theta_{\mathrm{R}}{}^{\mathrm{c}}/k_3{}^{\mathrm{c}}\theta_{\mathrm{H}} \tag{8}$$

which is substituted into 6 to obtain, after rearrangement of terms

$$\theta_{\mathrm{R}}{}^{\mathrm{c}} = \frac{k_2{}^{\mathrm{c}}k_3{}^{\mathrm{c}}[\mathrm{E}]\theta_{\mathrm{H}}}{\left(\dfrac{k_{-2}{}^{\mathrm{c}}k_{-3}{}^{\mathrm{c}}}{k_4{}^{\mathrm{c}}} + k_{-2}{}^{\mathrm{c}}\theta_{\mathrm{H}} + k_3{}^{\mathrm{c}}\theta_{\mathrm{H}}{}^2\right)k_4{}^{\mathrm{c}}} \tag{9}$$

and

$$\frac{\mathrm{d}\,[cis]}{\mathrm{d}t} = \frac{k_2{}^{\mathrm{c}}k_3{}^{\mathrm{c}}[\mathrm{E}]\theta_{\mathrm{H}}{}^2}{\dfrac{k_{-2}{}^{\mathrm{c}}k_{-3}{}^{\mathrm{c}}}{k_4{}^{\mathrm{c}}} + k_{-2}{}^{\mathrm{c}}\theta_{\mathrm{H}} + k_3{}^{\mathrm{c}}\theta_{\mathrm{H}}{}^2} \tag{10}$$

An equation, identical in form, is obtained for the rate of formation of the *trans* isomer.

The assumption that the rate-limiting surface reaction is the formation of the "half-hydrogenated" state (reaction 3) provides the condition that $k_{-3}{}^{\mathrm{c}}/k_4{}^{\mathrm{c}} << 1$ and, consequently, leads to the approximate expression

$$\frac{\mathrm{d}\,[cis]}{\mathrm{d}t} = \frac{k_2{}^{\mathrm{c}}k_3{}^{\mathrm{c}}[\mathrm{E}]\theta_{\mathrm{H}}}{k_{-2}{}^{\mathrm{c}} + k_3{}^{\mathrm{c}}\,\theta_{\mathrm{H}}} \tag{11}$$

and similarly for the rate of formation of the *trans* isomer. The ratio of isomers is expressed as

$$\frac{[cis]}{[trans]} = \frac{k_2{}^{\mathrm{c}}k_3{}^{\mathrm{c}}(k_{-2}{}^{\mathrm{t}} + k_3{}^{\mathrm{t}}\theta_{\mathrm{H}})}{k_2{}^{\mathrm{t}}k_3{}^{\mathrm{t}}(k_{-2}{}^{\mathrm{c}} + k_3{}^{\mathrm{c}}\theta_{\mathrm{H}})} \tag{12}$$

If $k_{-2} > k_3\theta_{\mathrm{H}}$, *e.g.*, the pressure of hydrogen is sufficiently low, then the equation reduces to 13

$$\frac{[cis]}{[trans]} = \frac{k_2{}^{\mathrm{c}}k_3{}^{\mathrm{c}}k_{-2}{}^{\mathrm{t}}}{k_{-2}{}^{\mathrm{c}}k_3{}^{\mathrm{t}}k_2{}^{\mathrm{t}}} = \frac{k_3{}^{\mathrm{c}}}{k_3{}^{\mathrm{t}}} \times \frac{K^{\mathrm{c}}}{K^{\mathrm{t}}} \tag{13}$$

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(14) See, however, ref. (11).

where K^c and K^t are the equilibrium constants for the adsorption of the alkene to form, respectively, the *cis* or *trans* diadsorbed alkane. Under these conditions, the ratio of the isomeric alkanes is determined by the ratio of the rate constants for the formation of the respective "half-hydrogenated states" from the alkene.

At high pressures of hydrogen, it is probable that $k_3\theta_H > k_{-2}$ and accordingly the *cis* to *trans* ratio, would approach k_2^c/k_2^t, the ratio of the rate constants for the two modes of adsorption of the alkene.

The manner in which θ_H will change with the external pressure of hydrogen will depend upon both the rate of the surface reactions involving hydrogen and the rate of transport of the hydrogen to the surface. If the former are relatively slow, θ_H will vary approximately as the square root of the pressure of hydrogen at low relative pressures of hydrogen.

When palladium catalysts are employed, the isomerization of the alkene is extensive, and the more stable saturated isomer (1,4-*trans*) is obtained in the larger amount. These results are also in harmony with those previously recorded, and we choose to interpret them in the same way:[1] namely, that on palladium, the rate-controlling surface reaction is the reduction of the "half-hydrogenated state," the previous steps being rapid and reversible by comparison.

This condition also follows from the preceding analysis in that if reaction 4 is the rate-limiting surface reaction, $k_{-3}^c/k_4^c > 1$, and if in addition $k_3^c \leqq k_{-2}^c$, then the first term in the denominator will be dominant (note $\theta_H \leqq 1$). Equation 10 reduces to

$$\frac{d\,[cis]}{dt} = \frac{k_2^c k_3^c k_4^c [E]\theta_H^2}{k_{-2}^c k_{-3}^c} = k_4^c K_{2,3}^c [E]\theta_H^2 \qquad (14)$$

where $K_{2,3}$ represents the equilibrium constant relating the alkene to the half-hydrogenated state. Likewise

$$d[trans]/dt = k_4^t K_{2,3}^t [E]\theta_H^2 \qquad (15)$$

and the ratio

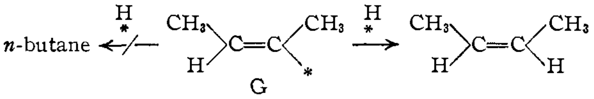
$$\frac{[cis]}{[trans]} = \frac{k_4^c}{k_4^t} \times \frac{K_{2,3}^c}{K_{2,3}^t} \qquad (16)$$

The significance of this expression is that the ratio of saturated stereoisomers is a function of the distribution of half-hydrogenated states ($K_{2,3}^c$, $K_{2,3}^t$) and the rates at which these react with hydrogen (k_4^c, k_4^t). It appears likely that the most stable "half-hydrogenated" states whether "*cis*" or "*trans*" will be bonded to the surface *via* equally substituted carbon atoms, primary where possible, but otherwise secondary, and the rate constants for the further reduction of these several intermediates (k_4^c, k_4^t) should depend primarily on the immediate environment of the surface-bonded carbon atom.

Clearly the reaction of these cycloalkenes on the palladium catalysts fits a mechanism in which reaction 4 is rate controlling, for not only does the *cis/trans* ratio approach the expected equilibrium distribution of the saturated isomers, but equilibrium among the isomeric alkenes is also realized.

Sauvage, Baker and Hussey[15] suggest that data such as described here and for the reduction of cycloalkenes on a palladium catalyst are best explained in terms of the properties of a postulated "stereochemically symmetrical intermediate." This is a hypothetical surface complex which by further reaction with hydrogen can yield both *cis* and *trans* saturated disubstituted cyclo-alkanes.[16] Structurally, it corresponds to a dissociatively adsorbed alkene. The principal basis for advancing this proposal is the observation that upon hydrogenation over PtO_2, 36% of the *cis* product is obtained from 4-methyl-1-isopropylidenecyclohexane (III) while 1-isopropyl-4-methylcyclohexene (IV) yields 58%, and it is presumed that the latter is the most likely and indeed only observed isomerization product. In our view, an important isomerization product should be *trans*-1-isopropenyl-4-methylcyclohexane (V) which should yield almost exclusively the *trans* isomer, and thus account for the difference in stereochemical reduction of III and IV. This would require that the preferred configuration for the adsorption of III would lead, by further addition of hydrogen, to the *trans* isomer in contrast to the result predicted and found with 2-, 3- and 4-alkyl-1-methylenecycloalkanes. The failure to observe V when reduced platinum oxide is the catalyst is to be expected on the basis of the considerable selectivity this catalyst displays for the reduction of alkenes which differ in the degree of substitution at the double bond. It is observed in the reduction of III and IV on a palladium catalyst where the olefins are equilibrated before half the initial charge has been reduced.[16]

Apparently the most likely product of the reduction of the "stereochemically symmetrical intermediate" is an alkene. Hamilton and Burwell[17] have shown that the hydrogenation of 2-butyne over a palladium catalyst yields only *cis*-2-butene so long as the alkyne is in excess.



G

In this instance, the probable intermediate G cannot be converted to a saturated hydrocarbon without the intervention of the desorbed alkene. And, consequently, structures such as these cannot be significant intermediates in the hydrogenation of alkenes.

This result can be deduced from the principle which has been employed successfully to rationalize the stereochemistry of displacement,[18] addition[19] and elimination[20] reactions in homogeneous systems. Fundamentally, a reaction proceeds most rapidly *via* the transition state which conserves the overlap of the molecular orbitals involved in the concerted bond breaking and forming processes. Thus, nucleophilic displacements on a carbon atom occur with inversion of configuration. And both the addition of electrophiles to a double bond and the elimination of α,β-substituents to form a double bond[21]

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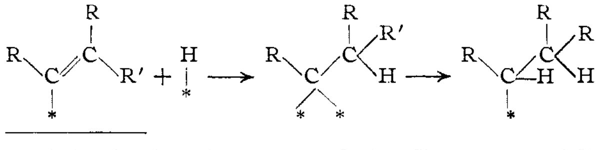
occur *via* transition states whose probable geometry conforms to the above principle.

The surface reactions in which carbon to hydrogen bonds are formed appear to be analogous to the electrophilic displacement reactions on carbon atoms which take place with retention of configuration.[22-24] In this transition state, the molecular orbital joining the carbon atom to the surface is divided so as to overlap both a surface orbital and the hydrogen atom being removed from the surface.

Of the possible one-step transformation products of the "stereochemically symmetrical intermediate" which would not yield an alkene directly but would be a reasonable step along the path toward saturation, the following appears to us to be most likely[25]



Because the π-orbital in H is directed parallel to the surface, it is not properly oriented to rehybridize in a manner which will both overlap with a hydrogen atom leaving the surface and the second indicated surface orbital without a *prior* destruction of the π-bond.

This reaction path would, therefore, be expected to have a higher energy barrier than one yielding the alkene directly.

In conclusion, the data and arguments presented here are consistent with the Horiuti–Polanyi mechanism for the hydrogenation of unsaturated hydrocarbons on an active surface.[26] Our study shows how the stereochemistry of the reaction may be employed to define the rate-limiting surface reaction as well as to describe the geometry of the pertinent transition states.

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The Stereochemistry of the Hydrogenation of the Isomeric Xylenes and *p*-*tert*-Butyltoluene over a Platinum Catalyst[1,2,3]

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The ratio of *cis* and *trans* disubstituted cyclohexanes which is obtained from the hydrogenation of the isomeric xylenes and *p*-*tert*-butyltoluene, dissolved in acetic acid and in contact with reduced platinum oxide, is a function of the structure of the substrate and the pressure of hydrogen. The proportion of the *cis* isomer increases with an increase in the pressure of hydrogen for pressures over two atmospheres. At lower pressures the ratio changes in a manner characteristic of the individual aromatic hydrocarbon. A comparison of these data with the stereochemistry of the hydrogenation of the related cycloalkenes suggests that the latter are intermediates in the reduction of the aromatic cycle.

Introduction

The stereochemistry of the hydrogenation of an aromatic compound, diphenic acid, was the subject of a series of papers presented almost twenty years ago by Linstead and his students.[4] Their results suggested that when an aromatic cycle was reduced during a single period of adsorption on the catalyst, it gave rise to stereoisomers in a proportion determined by steric interaction between the substituents on the cycle and the catalyst. They recognized that some aromatic compounds produced intermediate reduction products which were released from the surface, *e.g.*, cyclohexanone from the reduction of phenol.[5,6] We have sought to provide detailed stereochemical information with simple disubstituted benzenes and related cyclohexenes to examine the extent to which the stereochemistry of the latter, which are possible intermediates, might account for the results.[7,8] Work which we reported earlier was subject to more limited analytical techniques than are now available but indicated the major stereochemical trends.[7]

Experimental

Materials.—The *o*- and *m*-xylenes were the Research-Grade obtained from the Phillips Petroleum Co. and were stated to be at least 99.8% pure. *p*-Xylene was purified by repeated crystallization, the material used having the properties, m.p. 12.3–12.6°, n^{25}D 1.4936, lit.[9] m.p. 13.2°, n^{25}D 1.4932. *p*-*tert*-Butyltoluene was carefully fractionated on a column rated at 90 theoretical plates. A center cut, b.p. 191–192°, which was free of impurities by g.l.c. analysis, was used.

Apparatus and Procedures.—Three types of hydrogenation apparatus were used, depending on the pressure of the hydrogen; at high pressures (40–300 atm.), a rocker-type high pressure bomb (American Instrument Co., Inc.); for intermediate pressures (2–4 atm.), a Parr low pressure hydrogenation apparatus (Parr Instrument Co., model A, no. 112); and at low pressures (0.25–1 atm.), a semi-micro constant pressure hydrogenation apparatus.[10]

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