[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF IOWA, IOWA CITY, IOWA]

Influence of Hydrogen Crowding on the Rates of Reactions. The Addition of *cis* Reagents to the Dimethanonaphthalene Ring System[1]

BY J. K. STILLE AND D. R. WITHERELL

The rates of hydroboration, epoxidation, and hydrogenation of the *endo-exo* (**2**), *exo-endo* (**3**), and *endo-endo* (**4**) isomers of 1,2,3,4,4a,5,8,8a-octahydro-1,4,5,8-dimethanonaphthalene have been measured. In general, these rates decrease, in the order **2** > **3** > **4**, as might be predicted by a consideration of the increasing amount of H,H-crowding in the transition states.

Introduction

It has been observed that opposed methylene hydrogens in certain *exo-exo-*, *endo-endo-*, and *endo-exo*-octahydrodimethanonaphthalene systems give rise to anomalously high C—H stretching frequencies in the infrared spectra.[2,3] The displaced C—H stretching appears to be associated with C—H groups where large H,H interference between opposed methylene groups exists. It has also been observed that steric crowding of hydrogens apparently causes an anomalously high =C—H out of plane deformation frequency in compounds in which the hydrogen atoms attached to olefin carbons are opposed by the methylene hydrogens. Unhindered =C—H out of plane deformation frequencies, for example in **2** and **6** (Fig. 1), are 678 and 695 cm.$^{-1}$, respectively, while those for the hindered structures **3** (717 cm.$^{-1}$) and **4** (740 cm.$^{-1}$) are higher.[4] Compound **1**,[5] which contains both hindered and unhindered vinylic hydrogens, shows both maxima at 679 (bond a) and 713 cm.$^{-1}$ (bond b).

These observations suggest that the addition of certain *cis* reagents (which would not cause skeletal rearrangement) to the double bonds in olefins containing the *exo-endo* and *endo-endo* skeletal structures would take place at different rates. For example, the catalytic reduction of olefin **2** results in the saturated hydrocarbon **7**, but the reduction of the double bond does not increase the H,H interference between adjacent methylene groups. However, catalytic reduction of compound **3** to the same hydrocarbon increases the H,H interference since two new methylene groups are formed to oppose the methylene group already present, and the rate of reduction of **3** would be expected to be somewhat slower than that of **2**.

A study of the rate of addition of certain reagents to compounds **1**, **2**, **3**, **4**, and **5** was chosen as a method for the measurement of the differences in H,H crowding in compounds having *exo-endo* and *endo-endo* skeletal structures. The reagents employed were those which would add exclusively *cis* to the double bond without rearrangement of the skeletal structure. The catalytic hydrogenation, epoxidation, and hydroboration reactions are known to proceed by a *cis* addition to a double bond and methods for accurately following their rates are relatively simple.

Discussion

In order to carry out the rate studies, it was absolutely necessary to have pure olefins. Olefin **3** was prepared in a pure form through its silver nitrate complex using a method described for the purification of **1**.[5] Compounds **2**, **4**, and **5** were prepared in a pure form, by repeated distillation in the case of **2**, and repeated recrystallization and sublimation in the case of **4** and **5**. Olefins **4** and **5** had previously been reported as liquids[6,7] but were found to be solids when obtained in a pure form. All the olefins were found to be 100% pure by vapor fractometry. Catalytic reduction of each of these olefins produced saturated hydrocarbons, each showing a single peak in the gas chromatograph.

Under mild conditions, *cis* addition of hydrogen to an olefin on the surface of a catalyst takes place during a single period of adsorption, and rearrangement does not normally take place. The catalytic reduction of the five olefins gave saturated products which all are known. It was therefore assumed that further proof of nonrearrangement was unnecessary.

The reactions of norbornene (**8**) under various epoxidizing conditions have appeared to yield a single product. Additional evidence has shown, however, that the product of epoxidation is actually a mixture containing 95% *exo-* and 6% *endo*-2,3-epoxynorbornene.[8] Within the limits of experimental error in our rate studies, the epoxidation of norbornene is stereospecific and occurs without rearrangement. The epoxides of olefins **2**, **3**,[4] and **4** (Fig. 2) were prepared by treating the olefins with perbenzoic acid in chloroform or carbon tetrachloride. After suitable purification, all the epoxides gave correct carbon–hydrogen analysis. Olefin **2** gave the epoxide **9** which, when reduced with hydrogen over a Raney nickel catalyst, gave the *exo*-alcohol **10**[4] whose structure has been established.[9] Oxidation of the alcohol with potassium permanganate produced the α-diacid **2a**[4] of known configuration.[10]

Epoxide **11**, obtained by the epoxidation of **3**, was reduced to the alcohol **12** with hydrogen and Raney nickel. Oxidation of **12** with potassium permanganate gave the known β-diacid **3a**.[10] Apparently no appreciable rearrangement of the skeletal structure occurs during the epoxidation of these olefins.

Hydroboration–oxidation of olefins **2** and **3** gave alcohols **10** and **12**, respectively. The melting point of each of these alcohols with authentic samples of each

(2) D. Kivelson, S. Winstein, P. Bruck, and R. L. Hansen, *J. Am. Chem. Soc.*, **83**, 2938 (1961).
(3) L. de Vries and P. R. Ryason, *J. Org. Chem.*, **26**, 621 (1961).
(4) J. K. Stille, P. R. Kasper, and D. R. Witherell, *ibid.*, **28**, 682 (1963).
(5) J. K. Stille and D. A. Frey, *J. Am. Chem. Soc.*, **81**, 4273 (1959).
(6) P. Bruck, D. Thompson, and S. Winstein, *Chem. Ind.* (London), 405 (1960).
(7) S. B. Soloway, A. M. Damiana, J. W. Sims, H. Bluestone, and R. E. Lidov, *J. Am. Chem. Soc.*, **82**, 5377 (1960).
(8) H. Kwart and T. Takeshita, *J. Org. Chem.*, **28**, 670 (1963).
(9) L. de Vries and S. Winstein, *J. Am. Chem. Soc.*, **82**, 5363 (1960).
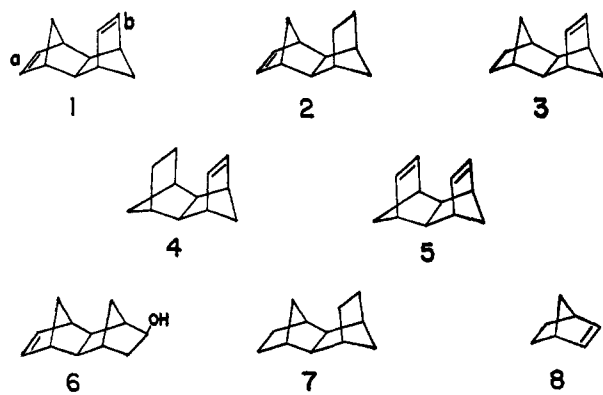(10) S. B. Soloway, *ibid.*, **74**, 1027 (1952).

Figure 1.

Figure 2.

Figure 3.

was undepressed and the infrared spectrum of each alcohol with that of an authentic sample was superimposable. Hydroboration–oxidation of **4** has been reported to give the *endo-endo*-alcohol **14** and hydroboration–oxidation of **5** has been reported to give the monoalcohol **16**.[6]

In the addition of a *cis* reagent to the monoolefins **2, 3,** and **4,** the rate of addition would be expected to follow the order **2 > 3 > 4** since, in the transition state, the olefin hydrogens on **3** and **4** would be approaching the methano and ethano bridge hydrogens (**3b** and **4b**, respectively, Fig. 3) in going from an sp² to an sp³ hybrid. H,H crowding would result, increasing the activation energy for the reaction. In olefin **2,** this type of crowding already exists but is not increased as a result of the reaction (**2b**). This increase in H,H crowding could be expected to be the main factor which determines the relative rates of addition in the dimethanonaphthalene ring system.

There is yet another steric factor to consider in assessing the rates of addition. H,H crowding already exists in **2** and this crowding may produce a distorted geometry (**2c**) in the molecule which helps to protect the *exo* face of the double bond, thus slowing the rate of addition of a *cis* reagent from the *exo* side. This effect would be expected to be much smaller, however, than transition state crowding, and may be ignored in most cases in predicting the order of rate of addition. A certain amount of skeletal twisting can also occur in both **4** and **13** such that the nonbonded hydrogen interactions are reduced by moving the hydrogens out of an eclipsed position.

On the basis of strain alone, norbornene (**8**) would be expected to react with *cis* reagents at a slower rate than the dimethanonaphthalenes. The norbornene carbocyclic skeleton is relieved in converting the double bond to a single bond. It would be expected that olefins **2, 3,** and **4** would have some additional ring strain other than that present in the simple norbornene system since these olefins have an extra fused ring attached. Relief of ring strain in these olefins could be expected to result in faster rates of epoxidation, for example, than does norbornene (**8**). This argument is basically the same as that advanced by Brown and Moerikofer[11] to explain why cyclopentene and cycloheptene react much faster with disiamylborane than does cyclohexene.

Rates of Hydroboration.—The order of rate of addition of disiamylborane to olefins **2, 3,** and **4** was found
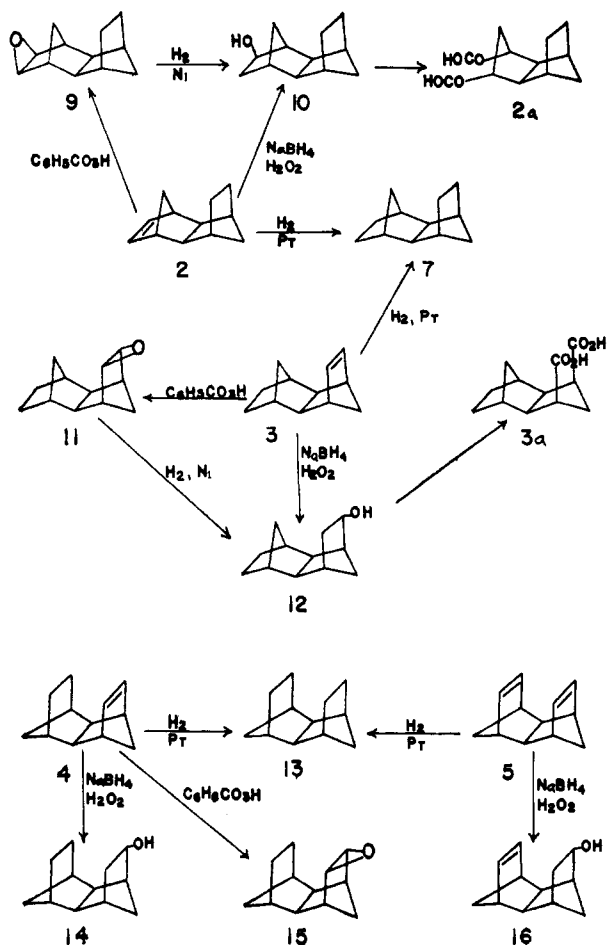
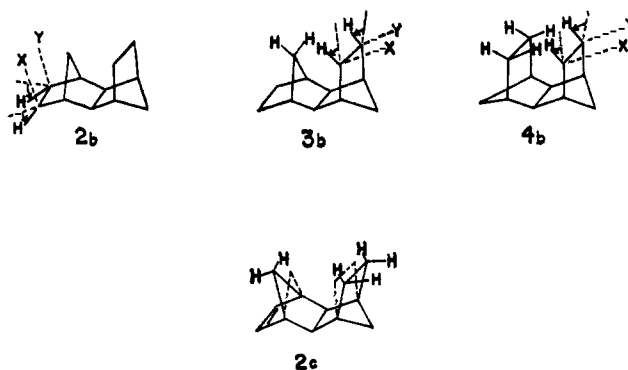(11) H. C. Brown and A. W. Moerikofer, *J. Am. Chem. Soc.*, **83**, 3417 (1961).

to be **2 > 3 > 4.** This is the order expected based on the increase of hydrogen crowding in the transition state. The absolute rates of hydroboration of these olefins compare quite favorably with that of cyclohexene.[11]

Rates of Epoxidation.—The epoxidation of olefins **2, 3, 4,** and **8** gave anomalous results in that olefins **2** and **3** appear to be in the wrong order based on H,H crowding. This may be rationalized by an inspection of the geometry attending the product epoxide (Fig. 4). The two hydrogens (H₂) are not only moving toward the hydrogen (H₁) on the methano bridge (away from the attacking species), but are also being spread to accommodate the strain in bonding in the three-membered ring. Since the oxirane ring has a tendency
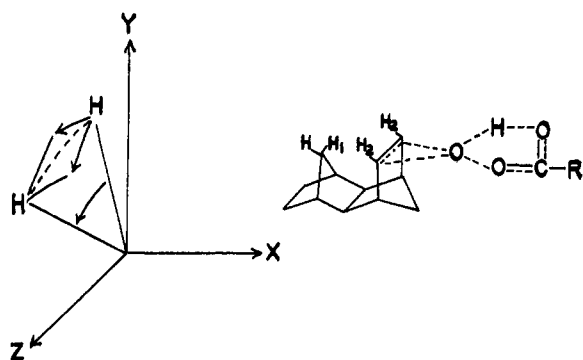
Figure 4.

toward sp² character in its bonds rather than sp³, the two hydrogens (H₂) are not only moving in the (−) X direction, but also in the (+) and (−) Z direction so that they are no closer to (H₁) during or at the end of the reaction than they were originally. From models of olefin **3**, the bond distance between the olefinic hydrogen atoms and the hydrogen on the methano bridge was found to be 2.0 Å. From a model of the epoxide **11**, the distance between these same hydrogen atoms was found to be 1.87 Å. Thus H,H crowding has increased very little. In such cases where H,H crowding in the transition state has little effect, the importance of the warped geometry of **2** (**2c**) could become an important factor in determining relative rates. The approach of the bulky peracid molecule from the *exo* face of **2** may be hindered to the extent that this has the effect of decreasing the rate of reaction **2** to a rate slower than that of **3**.

Rates of Hydrogenation.—The relative rates of addition of hydrogen to olefins **2**, **3**, and **4** fall in the order which might be expected from a consideration of H,H

Figure 5.

reagents approach norbornene from the *exo* side, platinum will coordinate from the *endo* side.[12]

A study was made of the catalytic reduction of the *exo-endo* diolefin **1** (Fig. 5) in order to determine the ratio of K_1/K_2, the ratio K_3/K_4 having already been determined (see Table III). Although a mathematical expression may be written to describe this system, the data obtained do not fit the equation. If it may be assumed that olefin **3** is being formed 1.8 times faster and is being reduced 1.8 times slower than olefin **2**, a buildup of **3** after the addition of 1 mole of hydrogen to the diolefin **1** would be expected. Actually, the buildup of **3** should be approximately 3.2 times that of **2**. This is not the case. The assumption that $K_1 = K_4$ and $K_2 = K_3$ is evidently incorrect. This is possibly true because the rate of complex formation of the olefins on the catalyst surface enters into the reaction so that the complex rate of **1** with respect to either bond a or bond b cannot be compared to the complex rate of **2** or **3**.

TABLE I
RATES OF HYDROBORATION WITH DISIAMYLBORANE

Olefin	Temp. °C.	Relative rate	K, l./mole sec.
2	0	1.83 ± 0.09	2.83 ± 0.12 × 10⁻⁵
	2.4	2.06 ± .11	. . .
3	0	1.45 ± .07	1.88 ± 0.09 × 10⁻⁵
	2.4	1.60 ± .08	. . .
Cyclohexene	0	1.01 ± .05	1.30 × 10⁻⁵ᵃ
	2.4		. . .
4	0	1.0	1.29 ± 0.06 × 10⁻⁵
	2.4	1.0	. . .

ᵃ See ref. 11.

TABLE II
EPOXIDATION RATE DATA AT 25°

Olefin	K, l./mole sec.	Rate ratio	E^*, kcal./mole	ΔS^*, e.u.
3	0.0297 ± 0.0009	4.14 ± 0.12	11.42 ± 0.19	−20.26 ± 0.07
2	.01555 ± .0003	2.15 ± .04	11.65 ± .29	−21.56 ± .11
8	.01150 ± .0003	1.60 ± .03	11.24 ± .28	−22.15 ± .11
4	.00718 ± .0002	1.0	11.72 ± .21	−23.08 ± .08

crowding in the transition state. However, the results must be taken with some reservation. The rates may be a reflection of the ability of the olefin in question to sit down on the catalyst surface rather than the rate of addition of hydrogen. The addition of hydrogen to **2** might be expected to be twice as fast as the addition to **3** since hydrogen can add from either the *exo* or *endo* face of **2**. Statistically, it would be reasonable to expect a double rate factor. This is not unreasonable from a chemical point of view, since, although many
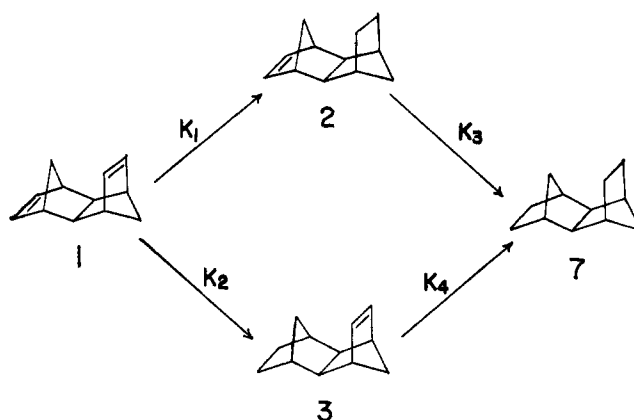
TABLE III
RELATIVE RATES OF CATALYTIC REDUCTION

Olefin	Rel. rate of reduction
2	3.37 ± 0.26
3	1.85 ± .14
5	1.32 ± .10ᵃ
4	1.0

ᵃ The relative rate of catalytic reduction of olefin **5** reflects the reduction of the first double bond as compared with the reduction of the second. Reduction of one double bond on **5** results in olefin **4** whose relative rate of catalytic reduction is 1.0.

It is evident, however, that in the addition of hydrogen to bond a of **1**, neither the H,H crowding nor the warped geometry which protects the *exo* face can influence the addition of hydrogen. In olefin **2**, H,H crowding is not present, but the *exo* face is more protected by the warped geometry. Therefore, K_2 should be greater than K_3, and K_1 and K_4 should be about equal. The buildup of **3** should be accentuated and somewhat greater than 3.2 which is the case. The ratio of **3** to **2** was found experimentally to be 7.5, indicating that K_2 equals about twice K_3. The effect of a warped geometry protecting the *exo* face from the bulky catalyst surface is about as important as H,H crowding in the transition state.

(12) See, for example, N. C. Baenziger, J. R. Doyle, G. F. Richards, and C. L. Carpenter in "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 131.

The differences in the rates of addition of any one of these reagents to **2, 3,** and **4** are indeed small. This could reflect the reactant-like geometry of the transition state. It is also possible that the hydrogen distances in the monoolefins and the saturated products are not as small as shown by the models and that a decrease of nonbonded interactions can be made at little expense by slight bond angle distortions throughout these systems. These results do indicate, however, that there is a measurable amount of H,H crowding.

Experimental

Purification of 1,2,3,4,4a,5,8,8a-Octahydro-1,4,5,8-*exo-endo*-dimethanonaphthalene (3).—To 63.0 g. (0.393 mole) of olefin **3,** prepared as described,[10] was added slowly 39 ml. of a saturated solution of silver nitrate with stirring. The mixture, which immediately set up into a hard gel, was recrystallized from absolute ethanol to give 100 g. (77%) of a colorless crystalline complex. *Anal.* Calcd. for $C_{12}H_{16}AgNO_3$: C, 43.60; H, 4.89. Found: C, 43.24; H, 4.91.

To 100.0 g. (0.303 mole) of the complex was added 400 ml. of ammonium hydroxide and the solution was heated to reflux temperature for 3 hr. After cooling to room temperature and extracting with ether, the combined ether extracts were washed with water and dried. The ether was removed under reduced pressure to yield 45.0 g. (71%) of a colorless oil, b.p. 86° (6 mm.), $n^{22.5}D$ 1.5245, reported[10] $n^{27}D$ 1.5197. Vapor fractometry revealed a pure product. The infrared spectrum showed absorption maxima at 2940 (C—H str.), 3050 (=C—H str.), and 717 cm.$^{-1}$ (=C—H def.).

1,4,4a,5,6,7,8,8a-Octahydro-1,4,5,8-*endo-endo*-dimethano-naphthalene[6] (4).—The olefin prepared as described[6] was found to be 80% pure by vapor fractometry. The oil was subjected to a careful vacuum distillation on a spinning band column. Fractions of 0.5 ml. were collected until the distillate began to solidify in the receiver. The pot residue was then recrystallized from methanol and further purified by sublimation to give a white solid, m.p. 64–65°. Vapor fractometry revealed a pure product. The infrared spectrum showed absorption maxima at 3060 (=C—H str.), 2940 (C—H str.), 775, and 740 cm.$^{-1}$. *Anal.* Calcd. for $C_{12}H_{16}$: C, 89.94; H, 10.06. Found: C, 90.01; H, 9.95.

1,4,4a,5,8,8a-Hexahydro-1,4,5,8-*endo-endo*-dimethanonaph-thalene[6,7] (5).—The diolefin prepared as described was subjected to a careful distillation and a fraction, b.p. 97–105° (17 mm.), was collected. The oil, which partially solidified in the receiver, was recrystallized from absolute methanol. The white solid was further purified by sublimation at 60° (0.1 mm.). The diolefin was found to be unstable to air and sunlight. Freshly sublimed compound had a sealed capillary melting point near 132° which was difficult to determine accurately because of the waxy nature of the product. Vapor fractometry revealed a product greater than 98% pure. The infrared spectrum showed absorption maxima at 3060 (=C—H str.), 2950 (C—H str.), 2875, 1735, 743, and 713 cm.$^{-1}$ (=C—H def.). *Anal.* Calcd. for $C_{12}H_{14}$: C, 91.08; H, 8.92. Found: C, 90.82; H, 8.85.

2,3-Epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4,5,8-*endo-endo*-di-methanonaphthalene (15).—To 3.0 g. (0.019 mole) of **4** dissolved in 50 ml. of carbon tetrachloride was added 150 ml. of a cold carbon tetrachloride solution containing approximately 5.0 g. of perbenzoic acid. After standing at 0° for 5 days, the solution was washed several times with 100-ml. portions of 6 *N* sodium hydroxide followed by water. The solution was dried and the solvent was removed under reduced pressure to leave 2.5 g. (76%) of a white solid, m.p. 111–112° after sublimation at 65° (0.5 mm.). The infrared spectrum showed absorption maxima at 2960, 1000, 980, 843, and 795 cm.$^{-1}$. *Anal.* Calcd. for $C_{12}H_{16}O$: C, 81.77; H, 9.17. Found: C, 81.84; H, 9.16.

Hydroboration of 1,2,3,4,4a,5,8,8a-Octahydro-1,4,5,8-*endo-exo*-dimethanonaphthalene (2).—To a solution of 5.17 g. (0.036 mole) of boron trifluoride etherate and 0.7 g. (0.019 mole) of sodium borohydride in 75 ml. of tetrahydrofuran was added 10.8 g. (0.067 mole) of **2** dissolved in 75 ml. of tetrahydrofuran. The reaction mixture was allowed to stand overnight. To the solution was added 6.3 ml. of 3 *N* sodium hydroxide and 6.3 ml. of 30% hydrogen peroxide. The entire contents of the flask were poured

into 500 ml. of water and extracted three times with 100-ml. portions of ether. After washing the combined ether extracts with water, the solution was dried and the ether was removed under reduced pressure to leave a white solid. The solid was recrystallized from hexane to yield 3.0 g. (25%) of **10**, m.p. 118–120°, reported[9] 123–124°. The melting point of a mixture of the alcohol with an authentic sample was undepressed, and the infrared spectra of the two were superimposable. *Anal.* Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.48; H, 10.12.

Hydroboration of 1,2,3,4,4a,5,8,8a-Octahydro-1,4,5,8-*exo-endo*-dimethanonaphthalene (3).—Hydroboration of **3** was carried out exactly as described for olefin **2.** From 7.37 g. (0.047 mole) of **3,** 0.48 g. (0.013 mole) of sodium borohydride, and 3.53 g. (0.025 mole) of boron trifluoride etherate was obtained 2.0 g. (24%) of **12.** Purification of the alcohol was accomplished by sublimation at 90° (1.0 mm.), m.p. 99–100°, reported[4] 99.5–100°. The melting point of a mixture of alcohol **12** and an authentic sample was undepressed and the infrared spectra of the two were superimposable. *Anal.* Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.83; H, 10.18.

Procedure for the Competitive and Absolute Rates of Hydroboration.—Into a 125-ml. serum bottle was placed approximately 0.7 g. (weighed accurately) of each of any two of olefins **2, 3, 4,** or **17** (cyclohexene) dissolved in 15 ml. of tetrahydrofuran freshly distilled from lithium aluminum hydride. Approximately 0.4 g. of the *exo-endo* saturated hydrocarbon **7** (internal standard) was weighed accurately and added to the bottle. The bottle was flushed with dry nitrogen and sealed with a rubber serum cap. After cooling to the required temperature in a constant temperature bath, a 5-ml. sample of a standard disiamylborane solution[13] was added by syringe. The amount of disiamylborane added was insufficient to hydroborate completely one of the two olefins present. After standing at the required temperature for 38 hr., the concentrations of unreacted olefins were determined by gas chromatography. The relative rates of hydroboration were then calculated using an equation described by Brown.[13] Since the absolute rate of hydroboration of cyclohexene is known at 0°, the absolute rates at 0° for olefins **2, 3,** and **4** were easily calculated.

Procedure for Absolute Rates of Epoxidation.—The rates of epoxidation of olefins **2, 3, 4,** and **8** (norbornene) at several different temperatures were determined. Samples were withdrawn from the reaction mixture by pipet and the rate of disappearance of perbenzoic acid was measured by iodometric titration of the iodine liberated from potassium iodide by the perbenzoic acid which remained after a known period of time. The iodine was titrated with standard thiosulfate solution from a microburet. From these data, the second-order rate constant was calculated for each sample, using the standard second-order rate formula. The rates of epoxidation for each olefin was measured at four different temperatures. A plot of the Arrhenius equation (rate dependence on temperature) gave a straight line for each olefin. Energies and entropies of activation (E^* and ΔS^*) were calculated from the slope of the line and the rate constants at 25°.

Procedure for Catalytic Hydrogenation Rate Study.—A sample composed of approximately 150 mg. (weighed accurately) of each of any two of the monoolefins **2, 3,** or **4** was hydrogenated in an apparatus suitable for measuring the quantitative absorption of hydrogen.[14] At various intervals during the reduction, samples were withdrawn and the exact composition of the reaction mixture was determined by gas chromatography. Relative rates of reduction were determined using the following equation derived from the rate expressions of each olefin

$$\frac{\log C_B/C_{B^0}}{\log C_A/C_{A^0}} = K = \text{rel. rate of catalytic reduction}$$

where C_A and C_B are the concentrations of olefins A and B at any time and C_{A^0} and C_{B^0} are the concentrations of olefins A and B at time T = zero.

The relative rate of hydrogenation of the first and second double bond on the *endo-endo* diolefin **5** was determined from the experimental data obtained from the catalytic reduction of **5** using the

(13) H. C. Brown and A. W. Moerikofer, *J. Am. Chem. Soc.*, **85**, 2063 (1963).

(14) R. L. Shriner and W. T. Smith, Jr., "The Examination of New Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1956, p. 126.

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]

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.