phenyl)phosphinous Chloride (2b), and 1,6-Diphosphatriptycene (10). A mixture of 68.2 g (2.2 g-atoms) of elemental phosphorus, 588 g (4 mol) of *o*-dichlorobenzene, 7 g (0.043 mol) of anhydrous ferric chloride, and 1.3 g (0.0068 mol) of titanium tetrachloride was heated for 4 hr at 325°C (see general remarks) in a sealed tube. After cooling the reaction product was filtered through a coarse fritted glass filter funnel. The crystalline 1,6-diphosphatriptycene (**10**, 45 g) was washed with methanol and recrystallized from tetrachloroethylene. It melted at 313–315°C; ir spectrum (KBr) bands at 3050, 1431, 1258, 1230, 1160, 1102, 1085, 1050, 940, 745 and 725 cm^{-1}.

The filtrate was distilled in vacuo, yielding 50 g of phosphorus trichloride, 116 g of *o*-chlorophenylphosphonous dichloride (**2a**), and 64 g of di(*o*-chlorophenyl)phosphinous chloride (**2b**).

1,6-Diphosphatriptycene Dioxide (12). In a three-neck 500-ml flask, fitted with a stirrer, condenser, and dropping funnel, a clear, hot solution of 12 g of 1,6-diphosphatriptycene (**10**) in 250 ml of tetrachloroethylene was placed. Then 28 ml of a 25% peracetic acid solution in ethyl acetate was added slowly at about 90°C. The reaction was exothermic and the temperature rose to about 120°C while a white, crystalline precipitate separated. Stirring was continued with gentle heating for another 1 hr. After cooling to room temperature the crystalline material was filtered off and recrystallized from 1-propanol: mp 488–490°C; ir spectrum (in chloroform) bands at 3020, 2375, 1450 m, 1240, and 1120 cm^{-1}.

Anal. Calcd for $C_{18}H_{12}P_2O_2$: C, 67.08; H, 3.72; P, 19.25. Found: C, 67.35; H, 3.73; P, 19.18.

1,6-Diphosphatriptycene Disulfide (13). To a solution of 2.9 g of 1,6-diphosphatriptycene in 70 ml of carbon disulfide was added a slurry of 0.64 g of sulfur in 50 ml of carbon disulfide. The mixture was refluxed for 4 hr. After standing overnight at room temperature the reaction mixture was filtered and the filtrate evaporated to dryness at reduced pressure. The crude material (4.2 g) melts at 400–402°C and was recrystallized from 300 ml of hot ethyl acetate: melting point of recrystallized product 396–399°C; ir spectrum (in chloroform) bands at 3010, 2375, 1450, 1268, 1235, 1110, and 1055 cm^{-1}.

Anal. Calcd for $C_{18}H_{12}P_2S_2$: C, 61.02; H, 3.38; P, 17.51; S, 18.07. Found: C, 61.30; H, 3.45; P, 17.30; S, 17.79.

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Registry No.—**1a,** 644-97-3; **1b,** 1079-66-9; **2a,** 1004-78-0; **2b,** 32186-89-3; **5b,** 13685-23-9; **6a,** 1005-32-9; **6b,** 1019-71-2; **7b,** 36024-98-5; **8a,** 56783-19-8; **8b,** 56783-20-1; **10,** 31634-70-5; **12,** 31634-72-7; **13,** 56783-21-2; phosphorus, 7723-14-0; chlorobenzene, 108-90-7; *o*-dichlorobenzene, 95-50-1.

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(7) See also K. G. Weinberg, U.S. Patent 3,557,204 (1971) (assigned to Union Carbide Corp.).
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Comparative Stereochemistry of Catalytic and Diimide Reductions of Alkenes[1ab]

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The stereochemistry of the reduction of alkenes by diimide is compared with the stereochemistry of catalytic hydrogenation. Within selected groups of alkenes, mainly alkylidenecycloalkanes, the relation between the structure of the alkene and the ratio of saturated stereoisomers formed with diimide parallels that obtained on a platinum catalyst at high hydrogen pressures. This kind of correlation is not general; however, the comparisons afford a qualitative estimate of the importance and manner in which intramolecular, nonbonded interactions affect the stereochemistry of these reductions and help reveal the occurrence of exceptional catalytic mechanisms. The cis and trans 1-alkyl-4-*tert*-butylcyclohexanes which were obtained are separable by GLC (300 ft capillary coated with Apiezon L); the more stable trans isomer precedes the cis if the 1-alkyl group is methyl or ethyl but the elution order is reversed if the substituent is 2-propyl or *tert*-butyl.

The mechanism for the transfer of hydrogen from diimide (diimine or diazene)[2] to a carbon–carbon double bond is believed to consist of a single elementary process, the two hydrogen atoms being transferred simultaneously from nitrogen to carbon.[3] The apparent simplicity of the reaction commends it as a reference for the study of the stereochemistry of other cis addition reactions, and indeed van Tamelen and Timmons have compared the proportions of geometrical isomers obtained on the reduction of several olefins by diimide with the proportions obtained from catalytic hydrogenation, but the treatment was cursory.[4] In this paper we extend this comparison to learn how it may assist the disentanglement of the complex mechanisms of catalytic hydrogenation.

Substituted cyclo- or semicyclic alkenes, which yield a pair of geometrical isomers via cis addition to the opposite faces of the double bond, are suitable objects of this study. The ratio of isomers (cis/trans), which is obtained from a particular alkene upon reduction with diimide, is a measure of the difference in conformational energy of the diastereomeric transition states of the product controlling reaction, one leading to the cis isomer, the other to the trans. Because diimide is a small molecule, nonbonding interactions between it and the alkene at the transition state are likely to be small and virtually the same for both approaches.[3] Apparently, there are a few exceptions to this expectation.[4,5]

If other reducing agents are used, the ratio may be different because in comparison to the transition state for reduction by diimide, (1) the reaction centers have a completely

Table I
Comparative Stereochemistry of the Reduction of Exocyclic Alkenes (% Cis)

Alkene	(No.)	Catalytic[a] Low pressure[b]	Catalytic[a] High pressure[c]	Diimide
4-*tert*-Butylmethylenecyclohexane	(1)	87[d]	61[d]	49 (49)[e]
4-*tert*-Butylethylidenecyclohexane	(2)	32	17	46
4-*tert*-Butylisopropylidenecyclohexane	(3)	21	11	30
2-Methylmethylenecyclohexane	(4)	70[d]	67[d]	61 (61)[e]
β-Pinene	(5)	85[f]	90[f]	96[e]
2-Methylcyclopentylidenecyclopentane	(6)		21[g]	24[g]

[a] Catalyst is PtO_2 in acetic acid. Temperature ca. 27°. [b] 0.25–1 atm. [c] 80–100 atm. [d] Reference 1a. [e] Reference 4; temperature of reduction was 55°. [f] J. Sellick, M. S. Thesis, University of Arkansas, 1965. [g] Reference 6.

different arrangement, (2) the geometry of the reaction centers is similar (e.g., coplanar) but the degree of advancement through the product controlling step is different, i.e., the transition state may be relatively more product- (or reactant-) like, and (3) the preferred geometry of the reaction centers is similar but the effective size of the reagent introduces a steric effect which favors the formation of one of the stereoisomers.

If the application of these principles of comparative stereochemistry to the mechanisms of catalytic hydrogenation is to be fruitful, one needs an adequate description of the transition state of the reference reaction, some notion of the elementary processes which occur in catalytic hydrogenation, and the knowledge of the circumstances under which a particular process is likely to be product controlling. This is the order in which our subject will be discussed.

Stereochemistry of Reductions by Diimide. In their detailed analysis of the structural factors which govern the relative reactivity of olefins toward diimide, Garbisch et al. assumed a structure for the activated complex in which the "reaction orbitals" are coplanar.[3] The π-bond order of the olefinic double bond was assumed to be large so that rotation about this bond was not expected to be significant. Accordingly, for the cis cycloalkenes no appreciable ring conformation change between the starting and transition states was expected. Similar considerations lead them to conclude that, in general, changes in nonbonded repulsive energies could be neglected. They predicted that the reduction of bicyclo[2.2.1]heptene, cyclopentene, and cycloheptene through cyclononene should be stereoselective. In these compounds, differences in the torsional energy of the diastereomeric transition states arise from the opposite approaches to the double bond. The stereoselectivity observed in the reduction of 4-*tert*-butyl-1-methylcyclohexene, however, was not anticipated. This failure was attributed to the approximate manner in which the torsional potential for the activated complex was treated. It was noted that of the alternative approaches of diimide to the double bond (Figure 1) approach a, leading to the trans isomer, causes the dihedral angle $\Phi_{1,6}$ to increase and $\Phi_{2,3}$ to decrease whereas in the b approach the change is reversed. The a approach is favored because eclipsing a C–H bond with C–R results in a larger torsional strain than eclipsing C–H bonds. These effects might also be called changes in nonbonded interactions due to changes in conformation, and although small enough to be neglected in the calculations of the relative reactivities of alkenes whose structure differs markedly, they are significant factors in the determination of the stereochemistry of a particular alkene.

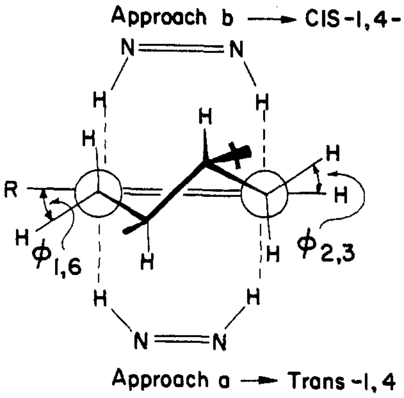


Figure 1. Model of the transition state for the transfer of hydrogen from diimide to an alkene according to Garbisch et al., ref 3.

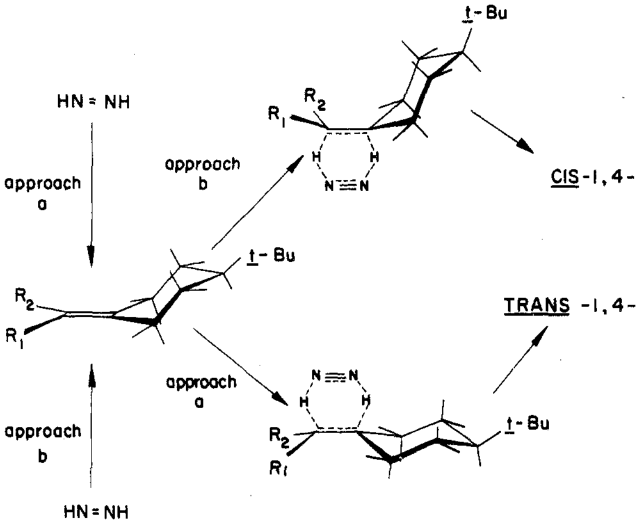


Figure 2. Change in geometry of an alkene from the ground to the diastereomeric transition states in its acceptance of hydrogen from diimide.

Results and Discussion of Diimide Reductions. The reduction of a series of exocyclic alkenes, 4-*tert*-butylmethylenecyclohexane (**1**), 4-*tert*-butylethylidenecyclohexane (**2**), and 4-*tert*-butylisopropylidenecyclohexane (**3**) yield increasingly larger proportions of the trans isomer (Table I). The result is in accord with the model of the transition state (Figure 2) which, according to Garbisch et al., occurs at about one-third of the "distance" along the reaction coordinate (χ) of this elementary step.[3] Apparently, the change in conformation of the alkene has introduced repulsive interactions between the vinyl substituents and the axial hydrogens at C-3 and C-5. If the conformation of the alkene did not change, all three compounds should yield the same cis/trans ratio with possibly some preference for the cis isomer if the diimide molecule exerted a steric effect. A small steric contribution may account for the excess cis isomer from 2-methylmethylenecyclohexane (**4**) and a larger contribution for β-pinene (**5**). Compounds obtained by replacing the methylene groups of either **4** or **5** by isopropylidene groups should give proportionally greater amounts of the trans isomer. Accordingly, we were not surprised to find that 2-methylcyclopentylidenecyclopentane (**6**) gives 76% *trans*-2-methyl-1-cyclopentylcyclopentane.[6,7]

Similarly, conformational effects are noted in compounds with endocyclic double bonds (Table II). In both 2,3-dimethylcyclopentene (**7**) and 2,3-dimethylcyclohexene

Table II
Comparative Stereochemistry of the Reduction of Endocyclic Alkenes (% Cis)

		Catalytic[a]		
Alkene	(No.)	Low pressure[b]	High pressure[c]	Diimide
2,3-Dimethylcyclopentene	(7)	48[d]	37[d]	31
2,3-Dimethylcyclohexene	(8)	81[d]	70[d]	29 (24)[e]
1,4-Dimethylcyclohexene	(9)	55[d]	65[d]	45
1-methyl-4-*tert*-butylcyclohexene	(10)	35[d]	47[d]	30[f]
1,4-Di-*tert*-butylcyclohexene	(11)[g]	90 (Rh)	88 (Rh)	38
4-Methyl-1-*tert*-butylcyclohexene	(12)			49[f]
2,4-Di-*tert*-butylcyclohexene	(13)	45 (Rh)[g]		48[f]

[a] Catalyst is PtO_2 with the exception of **11** and **13**, for which 5% Rh/Al_2O_3 (Rh) was used. Temperature ca. 27°. [b] 0.25–1 atm. [c] 80–100 atm. [d] Reference 1a. [e] Reference 4. [f] Reference 3. [g] Reference 21.

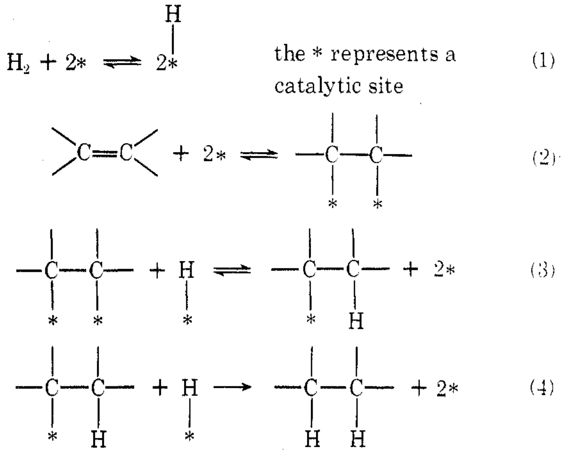
(**8**), the predominance of the trans isomer corresponds to a preferred approach of diimide to the double bond which permits the methyl groups to move away from one another. Garbisch's explanation for the stereoselective reduction of 4-*tert*-butyl-1-methylcyclohexene (**10**)[3] can be applied unaltered to the reduction of 1,4-di-*tert*-butylcyclohexene (**11**); however, the stereoselectivity of 1,4-dimethylcyclohexene (**9**) and 4-methyl-1-*tert*-butylcyclohexene (**12**)[3] is virtually nil. In Garbisch's model for the reduction of **10**, the *tert*-butyl group is restricted to a pseudoequatorial position; a methyl group would not be as restricted because the difference in energy of a pseudoequatorial–pseudoaxial methyl group is certain to be much less, less than the 1.6 kcal/mol difference between axial and equatorial methylcyclohexane.[8] Accordingly, a lower stereoselectivity is to be expected for compounds **9** and **12** relative to **10** and **11**. We have nothing to add to the previous speculations concerning the low stereoselectivity in the reduction of **13**.[3]

Effect upon the Rate of Reaction with Diimide of Substituting a Methyl Group for a Vinyl Hydrogen Atom. The relative rates of reduction by diimide at 80° of methylenecyclohexane (**14**) and the 4-*tert*-butylalkylidenecyclohexanes (**1**, **2**, and **3**) are (3.3), 3.4, 0.59, and 0.21, respectively, the scale being normalized to cyclohexene by assuming that the relative rate constant for **14** is the value previously reported.[3] To compare the effect of substituting a methyl group for a vinyl hydrogen in this series with previous work, the relative rates are corrected to the rate of attack at the favored face of the double bond; the corrected values are 3.5, 0.64, and 0.29, respectively, for **1**, **2**, and **3**. Substituting one vinyl hydrogen of **1** by a methyl group reduces the rate by a factor of 0.19 (compare with 0.14 ± 0.03 reported)[3] and the second substitution reduces the rate by only 0.45. In both instances the substitution has introduced a strain which is associated with cis-dialkyl substituents and this counters the expected stabilizing hyperconjugative interaction of the methyl and vinyl groups.[9] The only part of the observed relative reactivity in this series which can be attributed to changes in conformation is the change in stereospecificity with the change in vinyl substituents.

Conformational changes between the ground and transition state appear to affect the relative reactivity of certain groups of alkenes. For example, Garbisch et al. found that 1-substituted cyclohexenes are about 50% more reactive than the corresponding 4,4-dimethylcyclohexene whether the substituent is methyl, *tert*-butyl, or phenyl and they suggested that it is due, in part, to a hindered approach of diimide past the axial C-4 methyl group. We suggest, however, that the changes in geometry on proceeding through the transition state engender a repulsive interaction between the emerging axial hydrogen at C-2 and an axial methyl group at C-4, the effect being independent of the 1 substituent. The relative rate of about 1.5 at 80° corresponds to a $\Delta\Delta G^\ddagger$ of 0.3 kcal/mol, which is approximately one-third of the value of a single butanelike gauche interaction, one-third being the fraction of change effected on attaining the transition state.[3]

The above discussion illustrates the rationale employed to account for the stereochemistry of diimide reductions. Catalytic hydrogenations are more complex reactions but a similar analysis should apply to a series of compounds if the product-controlling step is the same for each compound. The correspondence with the ratio of isomers obtained from diimide will be the greater, the closer the transition states in the reaction series resemble the transition states of the reference reaction.

Comparison of the Stereochemistry of Catalytic Hydrogenation with Reductions by Diimide. The mechanism of the addition of hydrogen to alkenes catalyzed by various group 8 elements, in the form of films or small crystallites supported upon finely divided inert solids, is generally thought to proceed via the Horiuti–Polanyi mechanism, which is represented conventionally as follows.[10]



$$H_2 + 2* \rightleftharpoons 2\overset{H}{\overset{|}{*}} \quad (1)$$

$$>C{=}C< + 2* \rightleftharpoons -\underset{*}{\underset{|}{C}}-\underset{*}{\underset{|}{C}}- \quad (2)$$

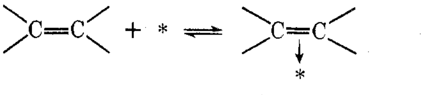
$$-\underset{*}{\underset{|}{C}}-\underset{*}{\underset{|}{C}}- + \underset{*}{\underset{|}{H}} \rightleftharpoons -\underset{*}{\underset{|}{C}}-\underset{H}{\underset{|}{C}}- + 2* \quad (3)$$

$$-\underset{*}{\underset{|}{C}}-\underset{H}{\underset{|}{C}}- + \underset{*}{\underset{|}{H}} \longrightarrow -\underset{H}{\underset{|}{C}}-\underset{H}{\underset{|}{C}}- + 2* \quad (4)$$

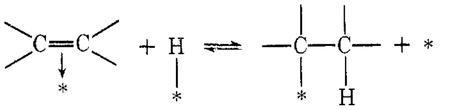
The stereoselectivity (cis/trans ratio) found in the reduction of a compound such as 4-*tert*-butylmethylenecyclohexane (**1**) should depend, therefore, on which of the reactions (2, 3, or 4) is product controlling.[1a,13] For example, **1** is hydrogenated over reduced platinum oxide, one of the more stereoselective catalysts, to give a ratio of cis/trans products which changes with increasing pressure from 6.7 at 0.25 atm to 1.6 at 100 atm. The possibility that reaction 4 is product controlling can be excluded because isomerization of **1** to 4-*tert*-butyl-1-methylcyclohexene (**10**), the more stable and less reactive alkene, is not observed. The results can be understood if one assumes that increasing the pressure has changed the product controlling reaction from (3) the formation of the "half hydrogenated" state to (2) the formation of the (α,β-diadsorbed) alkane. Similar results are obtained with various other cyclic and semicyclic alkenes.

The geometry of the transition state for reaction 2 is likely to be closely related to the geometry of the transition state for the reduction of an olefin with diimide.[1a,13b] In both reactions, the carbon atoms of the double bond become attached to a pair of atoms located to one side of the molecule, and if the transition state is to conserve the combined symmetry of the reactants, the new bonds will be formed in an eclipsed conformation. The transition states of these two reactions are unlikely to lie at the same degree of advancement along the reaction coordinate (defined as χ)[3] but the similarity in the required geometry of the reaction centers in the transition states should affect similar changes in the conformational energy associated with the rest of the olefin structure. Consequently the differences in the ratio of saturated epimers which are produced from these two reactions will reflect differences in χ as well as differences in nonbonded interactions between reagent and unsaturated substrate, the classical steric effect. The degree of advancement, χ, should be greater for reaction 2 than for the transfer of hydrogen from diimide because the enthalpy of adsorption of an alkene on the catalyst is certain to be less than the heat of reduction by diimide; accordingly, the change in intramolecular compressions also will be greater. On the other hand, the catalyst would be expected to exhibit the larger "classical steric effect" which affects the cis/trans ratio in the opposite sense.

As a variation of the above mechanism, the adsorbed alkene might be represented as a π complex.[1b,12,13b,14] The transition state for reaction 2′ could have the geometry described above to the transition state of reaction 2 because the geometry of the alkene in the π complex corresponds to that of an intermediate stage in the conversion of the alkene to the eclipsed conformation of the α,β-diadsorbed alkane postulated by Burwell.[12] The interactions enumerated for the transition state of reactions 2 or 2′ will be intensified in the transition state for 3 or 3′ because, in the later, the alkene is more tightly bound to the catalyst. The π-complex model is appropriate for hydrogenations catalyzed by soluble complexes of transition elements in which both hydrogen and alkene are associated with a single metal atom prior to the transfer of hydrogen to the alkene carbon atom and may be the better description for the surface catalyzed reaction too.[15–18]



(2′)



(3′)

Results and Discussion of Stereochemistry of Catalytic Hydrogenations Relative to Reduction by Diimide. If reaction 2 (or 2′) is product controlling as it appears to be for 1 and 10 over reduced platinum oxide at high hydrogen pressure,[13b] then the ratio of stereoisomers obtained under these conditions should parallel the ratio obtained with diimide. The data in columns 2 and 3 (Table I) shows the anticipated parallelism, and with one exception, 5, the differences in the ratios are those to be expected if the platinum catalyst exerts a greater steric effect than diimide, the cis isomer being favored.

The data in column 1 also parallel that in column 3 but the difference is somewhat greater than in the preceding comparison. The model for the transition state for reaction 3 (or 3′) conforms to these results; however, the conclusion that the product-controlling reaction is the same for this series (low hydrogen pressure on platinum) must be accepted with caution.

Isomerization may occur undetected (except by tracer experiments) if the isomeric product is hydrogenated more rapidly than its precursor, a situation common among highly alkylated ethylenes, particularly if the pressure of hydrogen is low.[11,12]

The data in Table II are not so easily rationalized. In each instance, diimide yields less of the cis isomer than does catalytic hydrogenation on platinum. However, there is no obvious parallelism for the data in the several columns. This implies that the structures of the transition states are not generally related, perhaps because the catalyst causes the alkene to adopt a conformation which is quite different from that attained in the transition state for reductions by diimide or because the mechanism is not constant within the series.[1a,19]

Some comparisons seem useful. For example, 2,3-dimethylcyclopentene (**7**) yields with diimide about the same fraction of the cis isomer (31%) as does 2,3-dimethylcyclohexene (**8**). At high pressure on platinum, **8** yields much more of the cis isomer (70%) than does **7** (37%).[20] The explanation for the stereochemistry of the diimide reductions is the same as that for **10**; the repulsive interaction between the adjacent methyl groups is less in the transition state which leads to the trans isomer. The proportion of geometrical isomers obtained upon catalytic hydrogenation of 2,3-dimethylcyclohexene (**8**) is opposite to that given by diimide, i.e., mainly cis, but the proportion of cis isomer obtained from 2,3-dimethylcyclopentene (**7**) differs only slightly. We attribute this difference in behavior of **8** and **7** to the greater flexibility of the six-membered cycle which can *relieve* the methyl group interactions more easily than can the five-membered ring. The driving forces for the above change in stereochemistry are the nonbonded interactions between the olefin and the catalyst, the corresponding interactions with diimide being small.

The strikingly different results given by 1,4-di-*tert*-butylcyclohexene (**11**) when hydrogenated over a rhodium catalyst, ~90% cis, compared with the 38% cis obtained with diimide, indicates important differences in the geometry of the transition states of the product-controlling steps of these reactions. The high proportion of the cis isomer appears inconsistent with the ratio of isomers obtained catalytically from **9** and **10**, albeit on a platinum catalyst, and indicates that it is the mechanism on rhodium which is exceptional. The dissociative mechanism discussed by Smith and Burwell, may permit **11** to isomerize preferentially (steric effect?) to *cis*-3,6-di-*tert*-butylcyclohexene (**14**) which would yield only *cis*-1,4-di-*tert*-butylcyclohexane upon the addition of hydrogen.[21]

Equilibration and Chromatographic Separation of *cis*- and *trans*-1-Alkyl-4-*tert*-butylcyclohexanes. Following known procedures, the 1,4-disubstituted cyclohexanes were characterized as cis or trans by equilibrating a mixture of the epimers obtained by hydrogenating a particular alkylidenecyclohexane over Pt/C. The equilibration was accomplished at 250° by heating the resulting mixture and 5% Pd/C in a sealed tube.[3] From the measured ratio of epimers the difference in free energy, $\Delta G°$, was calculated to be 1.8, 2.1, and 2.3 kcal/mol for the products obtained from **1**, **2**, and **3**, respectively. These results agree satisfactorily with previous estimates of the free energy difference between axial and equatorial methyl, ethyl, and 2-propyl groups.[8]

The GLC analysis of mixtures of these pairs of epimers varies in difficulty in part because the order of elution is apparently a function of the shape or size of the alkyl substituent. The more stable, trans isomer precedes the cis if the 1-alkyl group (1-alkyl-4-*tert*-butylcyclohexane) is methyl or ethyl but the order is reversed if the substituent is 2-propyl or *tert*-butyl. For such hydrocarbons, the order of elution can be expected to follow the order of increasing boiling point. In their critical review of the Auwers–Skita rule, van Bekkum, van Veen, Verkade, and Wepster have noted that, although generally the isomer of lower enthalpy has the lower boiling point, the reverse relationship applies to the epimers of 1,4-diisopropylcyclohexane and 1,4-di-*tert*-butylcyclohexane.[22] We found that of the epimeric pairs encountered the *cis*- and *trans*-1-ethyl-4-*tert*-butyl- and 1,4-di-*tert*-butylcyclohexanes were the most difficult to separate by GLC.[21,23]

Conclusions

Changes in conformation between the ground and transition state affect the relative rates of reduction of alkenes by diimide through changes in repulsive nonbonded interactions. Although the effects are small in comparison to the range of effects caused by other structural factors, they are important in determining the stereospecificity of the reaction.

Comparisons between the stereochemistry of reductions by diimide and hydrogenations conducted on a platinum catalyst at high pressure indicate similarities in their product-controlling transition states. However, complications resulting from competing reactions, or differences in the nature of the product-controlling step as a function of the catalyst or the conditions, probably account for the lack of any general correlation between the stereochemistry of these catalytic hydrogenations and reductions by diimide. Nevertheless, a comparison may furnish an indicator of unusual or exceptional catalytic behavior.

Nishimura et al. have shown that a supported iridium catalyst is exceptionally stereospecific for the addition of hydrogen to alkenes such as 1,2-dimethylcyclohexene.[24] The catalyst has relatively little tendency to cause alkene isomerization. Accordingly we expect that the use of such catalysts to saturate the alkenes given in Table I and II at any pressure of hydrogen will yield ratios of stereoisomers similar to those obtained with platinum catalysts at high pressures of hydrogen. This conclusion is based upon our belief that the high stereospecificity and low isomerization activity of the iridium catalysts indicate that the adsorption of alkene on these catalysts is virtually irreversible and accordingly product controlling.

Experimental Section

Alkenes. With the exception of 2-methylcyclopentylidenecyclopentane (**6**), whose preparation and properties are described in the following paper,[6] all of the alkenes have been reported previously. As judged by GLC analysis, the samples used were >99% pure. When necessary, the alkenes were purified by preparative chromatography. The assigned structures were consistent with their ir and NMR spectra.[23] β-Pinene was obtained through the generosity of Hercules Inc., Wilmington, Del. Compound **3** was prepared initially by Keulks via the Reformatsky reaction of 4-*tert*-butylcyclohexanone with ethyl α-isobutyrate and zinc.[25] It has been more recently prepared by Corey and Kwiatkowski.[26]

Hydrogenations and Reductions by Diimide. The hydrogenation procedures have been described previously.[1a,13] Except where noted, the diimide reductions, including the competitive reactions, followed the procedure of Garbisch et al., in which benzenesulfonylhydrazide is decomposed at 80° in diglyme containing triethylamine. In the alternative procedure, diimide was generated at 5° by the acid-catalyzed decomposition of potassium azodicarboxylate dissolved in methanol.[5]

Analytical Procedures. Mixtures were analyzed by GLC using either the Perkin-Elmer Model 881 gas chromatograph fitted with a flame ionization detector or an instrument equipped with a Beckman Hydrogen Flame Detector. For most analyses a column 50 ft × 0.125 in., 2% polyethylene glycol 1000 distearate supported on 80/100 mesh Chromosorb W, acid washed, was used. To separate the *cis*- and *trans*-4-*tert*-butyl-1-ethylcyclohexanes the column used was 45 ft × 0.125 in., 2.5% Carbowax 750 on Chromosorb W, acid washed. The separation of the *cis*- and *trans*-1,4-di-*tert*-butyl cyclohexanes required a capillary column, 300 ft × 0.02 in., coated with purified Apiezon L.[21] The analysis of a mixture containing **6** and its reduction products is given in the following paper.[6]

Equilibration Experiments. Following the procedure of Garbisch et al., the 1,4-disubstituted cyclohexanes were characterized as cis or trans by the equilibration of the hydrocarbon mixtures obtained from the complete reduction of 0.15 ml of the olefin (**1**, **2**, and **3**) at 4 atm over 0.02 g of 5% Pt/C in 5 ml of cyclohexane.[3] One milliliter of the resulting mixture was placed with 0.05 g of 5% Pd/C in 8 mm × ca. 15 cm Pyrex tubes which were sealed and heated at 250° in a steel bomb. After 72 hr, the tubes were removed from the bomb, cooled in a Dry Ice–2-propanol bath, and carefully opened. The reaction mixtures were analyzed by GLC.

Registry No.—**1**, 13294-73-0; **2**, 14033-64-8; **3**, 14033-75-1; **4**, 2808-75-5; **5**, 127-91-3; **6**, 56761-48-9; **7**, 16491-15-9; **8**, 1759-64-4; **9**, 2808-79-9; **10**, 3419-74-7; **11**, 5009-02-9; **12**, 3419-69-0; **13**, 3419-75-8.

References and Notes

(1) (a) Preceding paper in this series: S. Siegel, M. Dunkel, G. V. Smith, W. Halpern, and J. Cozort, *J. Org. Chem.*, **31**, 2802 (1966). (b) Financial support by the National Science Foundation is gratefully acknowledged (NSF-GP7466). (c) Undergraduate Research Participant supported by NSF, GE-2935, 1965. (d) Permission to reproduce Figure 1 from ref 3 was given by the copyright holders, the American Chemical Society.

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