

carbonate, and the solid was filtered and washed with a little water and recrystallized from aqueous ethanol, yielding 4,4-dibromocontinine (1 g.) as needles, m.p. 124° (lit.⁷ m.p. 125°), $\nu_{\max}^{\text{CHCl}_3}$ 1715 cm^{-1} (five-membered lactam).

Continine (5-Oxonicotine) (IV, R = H). 4,4-Dibromocontinine (280 mg.) in glacial acetic acid (10 ml.) was stirred for 18 hr. at room temperature with zinc dust (1 g.). Water (10 ml.) was added and the reaction mixture was rendered alkaline (potassium carbonate) and extracted with chloroform, yielding a clear oil (134 mg.) which was distilled at 130–140° (0.8 mm.) (air-bath temperature).

Nicotine-5,5-d₂. Continine (28 mg.) in anhydrous ether (15 ml.) was reduced with lithium aluminum deuteride (45 mg.). Excess reagent was destroyed with water, the inorganic suspension was removed by filtration, and the residual product (24 mg.) was distilled, b.p. 60–65° (0.8 mm.) (air-bath temperature). Mass spectrometry indicated the presence of 97% *d₂* species.

Continine-4,4-d₂. Continine (55 mg.) was heated under reflux for 12 days with deuterium oxide (2 ml.) containing anhydrous potassium carbonate (60 mg.).⁹ The reaction mixture was cooled and lyophilized, and the dry residue was leached with chloroform. Removal of the solvent afforded continine-4,4-*d₂* (40 mg.), shown by mass spectrometry to contain 92% *d₂* and 8% *d₁* species.

Nicotine-4,4-d₂. Lithium aluminum hydride reduction of continine-4,4-*d₂* (35 mg.) in dry ether (10 ml.) and processing as described for the preparation of nicotine-5,5-*d₂* yielded nicotine-4,4-*d₂* of 92% *d₂* and 8% *d₁* composition (mass spectrometry).

Nicotine-N-d₃. Nornicotine (65 mg.) in methanol (0.1 ml.) was treated with trideuteriomethyl iodide (0.025 ml. 92% *d₃* species) in methanol (0.025 ml.)¹² and the reaction mixture was allowed to stand at

room temperature for 4 days. Ether (1.5 ml.) was added, the reaction mixture was shaken well, and the ether layer was removed. Repetition of this process with ether (1.5 ml.), combination of the ether extracts, and removal of the solvent afforded an oil (25 mg.). Nicotine-N-*d₃* was isolated by preparative vapor phase chromatography¹⁶ and was shown by mass spectrometry to contain 92% *d₃* species.

Nornicotine-2-d₁. Catalytic deuteration of myosmine¹⁴ (95 mg.) over 10% palladium on carbon (50 mg.) in anhydrous ethyl acetate (15 ml.) during 7 hr. and preparative vapor phase chromatography¹⁶ of the product yielded nornicotine-2-*d₁* of 65% *d₁* and 35% *d₀* composition.

Nicotine-2-d₁. Nornicotine-2-*d₁* (70 mg.) was heated under reflux during 5 hr. with 80% formic acid (0.1 ml.) containing 30% formaldehyde (0.2 ml.). The crude reaction mixture was basified (sodium hydroxide), extracted with ether, and nicotine-2-*d₁* was isolated by preparative vapor phase chromatography.¹⁶ Mass spectrometry showed the product to consist of 65% *d₁* and 35% *d₀* species.

Nornicotine-N-d₁ and Anabasine-N-d₁. These compounds were prepared by shaking the amine (20 mg.) with deuterium oxide (0.1 ml.) and then determining the mass spectrum.^{8,12b} The following deuterium incorporations were obtained: nornicotine-N-*d₁*, 90% *d₁* and 10% *d₀*; anabasine-N-*d₁*, 90% *d₁* and 10% *d₀*.

Anabasine-2-d₁. Anabasene dipicrate was prepared according to Späth¹³ and had m.p. 170–172° (lit.¹³ m.p. 173–174°). Anabasene was recovered from its dipicrate as previously described¹³ and distilled, b.p. (0.8 mm.) (air-bath temperature). The product (120 mg.) was immediately dissolved in anhydrous ethyl acetate (20 ml.) and stirred for 20 hr. with 5% palladium on carbon in an atmosphere of deuterium. Anabasine-2-*d₁* was isolated by preparative vapor phase chromatography¹⁶ and shown by mass spectrometry to contain 70% *d₁* and 30% *d₀* species.

Strain Effects. II. Diimide Reductions of Olefins

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Relative rates of diimide reductions of nearly 40 cyclic, exocyclic, and acyclic alkenes have been determined at 80°. The relative reactivities which are found to vary over a range of 38,000 have been qualitatively calculated. The agreement found between the calculated and observed values (generally within a factor of 2) suggests that the major factors that contribute to the observed reactivity differences are torsional strain,

bond angle bending strain, and α -alkyl substituent effects. Some possibly significant conclusions regarding structure vs. reactivity and stereoselectivity of diimide reductions of alkenes are discussed in the light of the available data.

The influence of structure on the reactivities of alkenes toward various types of addition reactions has been investigated in some detail within the past 20

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years.²⁻⁴ These reactions expectedly have been found to exhibit reactivities that are more or less sensitive to the alkene structure. The reactivity trends generally have been interpreted qualitatively; however, those observed for additions to the common- and medium-sized *cis*-cycloalkenes do not appear to be understood very well.

An adequate understanding of relative reactivities of additions to a wide range of cyclic, exocyclic, and acyclic olefins is not likely to result from the consideration of a single effect. The general problems involved in dealing with relative reactivities have been discussed thoroughly.⁵ The various factors that are most likely to contribute to differences in relative reactivities of olefin reactions with a single reagent are given in eq. 1, where the E_σ^* , E_ψ^* , E_ϕ^* , E_ω^* , and E_N^* terms are

$$-RT \ln(k/k_0) = \Delta\Delta G^* = \Delta\Delta E_\sigma^* + \Delta\Delta E_\psi^* + \Delta\Delta E_\phi^* + \Delta\Delta E_\omega^* + \Delta\Delta E_N^* - RT \ln(\Pi Q^*) \quad (1)$$

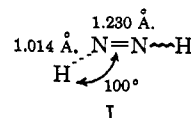
potential energy contributions of polar, resonance, torsional strain, bond angle bending strain, and non-bonded (including transannular) interaction effects, respectively; and $(\Pi Q^*) = q^*q_0/qq_0^*$, an entropy contribution term, where q_0 and q are partition functions for the reference substrate and the substrate being compared, respectively. Zero-point energy contributions are not included in eq. 1 as they might be expected to nearly cancel in their relative comparisons. For many reactions all the terms on the right-hand side of eq. 1 may be expected to contribute significantly to the observed values of k/k_0 .⁵ For such instances, the task of correctly evaluating the various terms on the right-hand side of eq. 1 becomes immensely difficult. However, in some instances, depending upon the nature of the reaction, justification may be given for taking one or more of these terms as approaching zero, thereby reducing the number of variables that contribute to the relative reactivity differences and making the system more amenable to analysis.

In this paper we will discuss relative reactivity trends of diimide reductions of *cis*-cyclic, exocyclic, and acyclic olefins. We will attempt to estimate relative reactivities for a range of alkene structures by considering the terms on the right-hand side of eq. 1. Ultimately it is hoped that a qualitative understanding of the major factors that contribute to the observed reactivity differences will be realized and that a general approach will be defined that may be useful for the

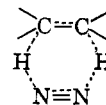
prediction and interpretation of reactivities of other types of olefin addition reactions.

1. Diimide and Its Reduction of Alkenes

Diimide is thought to exist predominantly in the *cis* configuration in the solid state at liquid nitrogen temperature.⁶ In the liquid and gaseous states, diimide reacts to give hydrazine and nitrogen and decomposes to give nitrogen and hydrogen, both processes being sufficiently rapid so as to preclude its isolation. Although the most stable configuration of diimide in the liquid or gaseous states is not known, the infrared spectrum of gaseous diimide is consistent⁶ with structure I computed semiempirically by Wheland and Chen.⁷



Diimide may be formed conveniently by the oxidation of hydrazine,⁸ by the thermal decompositions of potassium azodiformate,^{8,9} *p*-toluenesulfonylhydrazine,¹⁰ and anthracene-9,10-biimine,¹¹ and by the base-catalyzed decompositions of chloramine¹² and hydroxylamine-O-sulfonic acid.¹³ In the presence of olefinic hydrocarbons, the metastable diimide so formed is found to transfer a pair of hydrogens to carbon-carbon double bonds in a very highly stereospecific *cis* manner.^{8b,11,14} The rates of diimide reductions of *trans*-*p*-dimethylamino-, *p*-methoxy-, *p*-chloro-, *p*-nitro-, and *o*-chlorocinnamic acids relative to *trans*-cinnamic acid are found to be essentially unity,¹⁵ and the reductions of symmetrical multiple bonds (e.g., C=C and N=N) proceed readily, whereas more polar functions (e.g., C≡N, C=N, S=O, and C=O) are less reactive toward reduction.¹⁶ These observations regarding the stereochemistry and reactivities of diimide reductions of olefins has led to the general view that the diimide reductions proceed by a synchronous *cis* addition of neutral hydrogen to the olefinic center leading to a transition of negligible ionic character.



(2) K. Ziegler, H. G. Gellert, H. Martin, K. Nagel, and J. Schneider, *Ann.*, **589**, 99 (1954); K. Ziegler and H. Froitzheim-Kuhlhorn, *ibid.*, 157 (1954).

(3) H. C. Brown and A. W. Moerikofer, *J. Am. Chem. Soc.*, **83**, 3417 (1961); **85**, 2063 (1963) (Professor Brown has informed us that the second-order rate constants for cycloheptene and cyclooctene in Table III are in error and should read 72×10^4 l. mole⁻¹ sec.⁻¹ and 266×10^4 l. mole⁻¹ sec.⁻¹, respectively. The relative reactivity entries for these alkenes in Table III should be changed accordingly); H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962.

(4) A. P. Krapcho and M. E. Nadel, *J. Am. Chem. Soc.*, **86**, 1096 (1964); M. A. Muhs and F. T. Weiss, *ibid.*, **84**, 4697 (1962); D. Swern, *ibid.*, **69**, 1962 (1947); W. E. Doering and W. A. Henderson, Jr., *ibid.*, **80**, 5274 (1958); P. E. Paterson and G. Allen, *J. Org. Chem.*, **27**, 1505 (1962); S. V. Anantkrishnan and R. Venkataraman, *Chem. Rev.*, **33**, 27 (1943).

(5) R. W. Taft, Jr., "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 13; J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1963.

(6) (a) E. J. Blau, B. F. Hochheimer, and H. J. Unger, *J. Chem. Phys.*, **34**, 1060 (1961); E. J. Blau and B. F. Hochheimer, *ibid.*, **41**, 1174 (1964); (b) Dr. Blau has informed us (private communication) that there does not appear to be anything in his spectral data that would specifically include or exclude the presence of the unsymmetrical form of diimide (NNH₂).

(7) G. W. Wheland and P. S. K. Chen, *J. Chem. Phys.*, **24**, 67 (1956). (8) (a) E. J. Corey, W. L. Mock, and D. J. Pasto, *Tetrahedron Letters*, 347 (1961); (b) R. Müller and W. Thier, *ibid.*, 353 (1961).

(9) R. S. Dewey and E. E. van Tamelen, *J. Am. Chem. Soc.*, **83**, 3729 (1961).

(10) E. E. van Tamelen, R. S. Dewey, and R. J. Timmons, *ibid.*, **83**, 3725 (1961).

(11) E. J. Corey and W. L. Mock, *ibid.*, **84**, 685 (1962).

(12) E. Schmitz and R. Ohme, *Angew. Chem.*, **73**, 807 (1961).

(13) R. Appel and W. Büchner, *ibid.*, **73**, 807 (1961).

(14) E. J. Corey, D. J. Pasto, and W. L. Mock, *J. Am. Chem. Soc.*, **83**, 2957 (1961).

(15) S. Hünig and R. Müller, *Angew. Chem. Intern. Ed. Engl.*, **1**, 213 (1962); *Angew. Chem.*, **74**, 215 (1962).

(16) E. E. van Tamelen, R. S. Dewey, M. F. Lease, and W. H. Pirkle, *J. Am. Chem. Soc.*, **83**, 4302 (1961); E. E. van Tamelen, M. Davis, and M. F. Deem, *Chem. Commun. (London)*, 71 (1965).

The possibility that the unsymmetrical isomer of diimide, $N^+H_2=N^-$, participates at least to some degree in reductions of alkenes^{9,14} cannot be excluded rigorously at this time.^{6b} Preliminary results¹⁷ on the relative reactivities of alkene reductions by diimide generated by the thermal decomposition of anthracene-9,10-biimine¹¹ are not found to differ significantly from those obtained by diimide generated by the thermal decomposition of *p*-toluenesulfonylhydrazine (work reported here).^{10,18} As the former decomposition probably leads initially to diimide of the *cis* configuration, these results suggest either that the reactive form of diimide formed by decomposition of *p*-toluenesulfonylhydrazine (α - and β -elimination) ultimately also is of the *cis* configuration or that both decompositions lead to the same rapidly equilibrating mixture of isomeric forms of diimide.

It is considered in the present work that the form of diimide that is effective toward the reduction of alkenes bears the symmetrical *cis* configuration and that the unsymmetrical form, if present at all, is of no kinetic significance to relative rates of reduction.

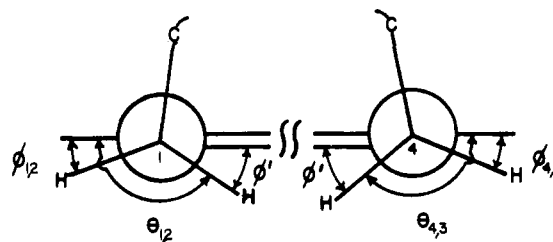
2. Structures and Partial Conformations of Alkenes

(a) *Cyclic and Bicyclic Alkenes.* The C—C=C bond angles (ω) and H—C—C—H torsional angles (φ and θ) that define the partial conformations of the bicyclic and cyclic alkenes we have investigated have been discussed in considerable detail along with supporting experimental data in the first paper of this series.^{19,20} These parameters, which are adopted also for the present study, are given in Table III. We should point out that, with the exception of cyclohexene, *cis*-cyclododecene, and *cis*-cyclododecene, the adopted partial conformations II^{19,20} exhibit a plane of symmetry perpendicular to and bisecting the carbon-carbon double bond axis, and require that torsional angles $\varphi_{1,2} = \varphi_{4,3} = \varphi$. For these cycloalkenes, unsymmetrical partial conformations where $\varphi_{1,2} = \varphi_{4,3}$, as in cyclohexene, also would be consonant with the experimental data,^{19,20} but they would appear to lead to highly unfavorable conformations as may be seen readily from Dreiding models.²¹ More detailed information on the conformations of the *cis*-cycloalkenes than the partial conformations (II) discussed here is not thought to be necessary (see section 3).

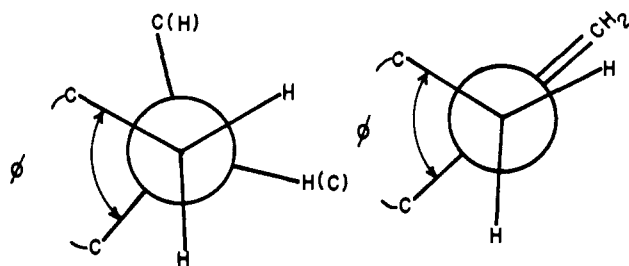
(b) *Acyclic and Exocyclic Alkenes.* Propene²² and isobutene²³ are known to exist in minimum energy conformations in which the allylic hydrogens eclipse the carbon-carbon double bond ($\varphi = 60^\circ$). 1-Butene, 1-hexene, and 3-methyl-1-butene appear to exist in solution in similar equilibrium conformations ($\varphi \cong 60^\circ$) with no appreciable energy difference

between allylic alkyl and hydrogen eclipsing of the carbon-carbon double bonds.^{24,25} This conclusion is substantiated further by the effectively equal heats of hydrogenation of propene, 1-butene, isopropylethene, and *t*-butylethene.²⁶ Consequently, for monoalkylated, 1,1-dialkylated, and *trans*-1,2-dialkylated alkenes investigated in this work, φ is taken to equal 60° with no distinction between the type of groups (*i.e.*, C—H or C—C) that bear this dihedral angle. We assume also that for these alkenes the C=C—C bond angles (ω) are unstrained and equal to 122° .¹⁹

Acyclic *cis*-1,2-dialkylated alkenes such as *cis*-2-butene and *cis*-4-methyl-2-butene are more highly strained than the unstrained *trans* isomers by about 1.0 kcal./mole.²⁷ For *cis*-2-butene with $\omega = 122^\circ$ and $\varphi = 60^\circ$ (see II) and using other standard parameters and Hendrickson's²⁸ nonbonded interaction function, the interpenetration of the opposed hydrogens leads to a repulsion of about 3 kcal./mole. This repulsive interaction becomes negligible when the torsional angles φ decrease to about 40° as in cyclohexene (unsymmetrical conformation II), but the torsional strain increases from zero to about 1.0 kcal./mole. The strain energy of *cis*-2-butene may be accounted for also through a minimized com-



II



III

IV

combination of angle bending strain, torsional strain, and nonbonded strain by increasing ω from the unstrained¹⁹ value of about 122° and decreasing φ

(17) E. W. Garbisch, Jr., and D. B. Patterson, unpublished results.

(18) S. Hünig and R. Müller, *Angew. Chem. Intern. Ed. Engl.*, **2**, 214 (1963); *Angew. Chem.*, **75**, 298 (1963).

(19) Paper I: E. W. Garbisch, Jr., *J. Am. Chem. Soc.*, **87**, 505 (1965).

(20) E. W. Garbisch, Jr., *ibid.*, **86**, 5561 (1964).

(21) It has been pointed out earlier¹⁹ that because the torsional angles adopted for the cycloalkenes were derived from n.m.r. and e.s.r. spectral data, information relating to the conformational homogeneity of the molecules cannot be ascertained with certainty.

(22) D. R. Lide and E. E. Mann, *J. Chem. Phys.*, **27**, 868 (1957); D. R. Herschback and L. C. Krisher, *ibid.*, **28**, 728 (1958).

(23) V. W. Laurie, *ibid.*, **34**, 1516 (1961).

(24) A. A. Bothner-By and C. Naar-Colin, *J. Am. Chem. Soc.*, **83**, 231 (1961); A. A. Bothner-By, C. Naar-Colin, and H. Gunther, *ibid.*, **84**, 2748 (1962).

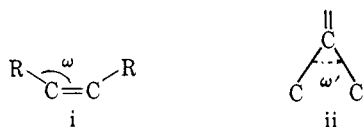
(25) It should be noted that the long-range and vicinal allylic-vinyl proton spin couplings for propene, 1-butene, 1-hexene, and 2-methyl-1-butene²⁴ agree in magnitudes and in signs with those predicted on the basis of equal populations of each allylic substituent in the carbon-carbon double bond eclipsed conformation.²⁰

(26) From the work of Kistiakowsky and co-workers; see R. B. Williams, *J. Am. Chem. Soc.*, **64**, 1395 (1942).

(27) C. T. Mortimer, "Reaction Heats and Bond Strengths," Pergamon Press, New York, N. Y., 1962.

(28) J. B. Hendrickson, *J. Am. Chem. Soc.*, **83**, 4537 (1961).

from 60°. Consequently, angles ω and φ will not be assigned to the RC=CR (i) groupings, and it will be sufficient for our purposes to simply assign a strain energy (E_φ) of 1.0 kcal./mole for each such grouping where R is a methyl or an ethyl group (see section 7).



Angles ω' (ii) are assumed to be unstrained (*i.e.*, 116°) for the six- through eight-membered ring methylenecycloalkanes. These ring systems should accommodate a single angle of this magnitude without significantly altering the strain energy content from that of the corresponding saturated hydrocarbon.²⁹ Angle ω' for 2-methylenebicyclo[2.2.1]heptane should not differ significantly from ω adopted for bicyclo[2.2.1]heptane³¹ (Table III). Because angle bending strain associated with all of the internal angles of methylenecyclopentane are likely to change upon reduction to methylcyclopentane, the angle bending strain difference between the two molecules as estimated by Pitzer and Donath³² is employed for estimating $\Delta\Delta E_{\omega^*}$ (see later).

To select the preferred conformations of the methylenecycloalkanes, the following procedure is used. The minimum energy conformations of the cycloalkanes^{28, 30, 32} are considered and the methylene groupings associated with the largest sum of torsional strain (E_φ) and nonbonded hydrogen repulsion (E_N) are replaced by the $>C=CH_2$ group. This follows, since torsional potentials for ethane and propene²² bear parallel relationships to angles φ in III and IV, but the torsional barrier is slightly lower (by a factor of 0.69) for the latter. Consequently, minimum total torsional strains of the methylenecycloalkanes result by placing the $>C=CH_2$ group at the methylene groupings of the cycloalkanes that are associated with maximum torsional strains. If serious nonbonded repulsions exist between the methylene hydrogens in the cycloalkanes, it is clear that removal of such interactions may dictate the positioning of the $>C=CH_2$ group. Torsional angles φ (see III and IV employed are given in Table III).

3. Structure of the Activated Complex

An adequate conception of the structure of the activated complex for the diimide reductions is as important for estimating relative reactivities as a good estimation of the important structural parameters for the starting alkenes. We presume that the transition states for these reductions probably occur fairly early along the reaction coordinates and that the π -bond orders of the olefinic double bonds in the activated complexes are still large. Rotations about these

(29) Cycloheptane and cyclooctane have internal C-C-C angles that probably are somewhat larger^{29, 30} than the unstrained angle¹⁹ of about 112° and should accommodate a single angle of 116° without appreciable torsional angle changes and with negligible angle bending strain.

(30) J. B. Hendrickson, *J. Am. Chem. Soc.*, **86**, 4854 (1964).

(31) Because of the rigidity of the norbornane structure, C=C=C and C-C-C angles are not expected to vary appreciably.¹⁹

(32) K. S. Pitzer and W. E. Donath, *J. Am. Chem. Soc.*, **81**, 3213 (1959).

bonds then would not be expected to contribute significantly to minimizing the strains associated with these structures (in ethene, 0.2, 0.8, and 1.8 kcal./mole are required to twist 5, 10, and 15°, respectively, about the double bond³³). We picture V as a possibly applicable structure for the activated complex. Other likely structures would be those with angle α being greater or less than 180°. First-order principles do not lead to a revelation as to the electronically most favorable angle α ; however, repulsive electron correlations between nonbonded orbitals and electronic kinetic energies (principle of minimum bending of molecular orbitals³⁴) might be expected to be at a minimum for the collinear overlap of "reaction" orbitals as shown.

Angles ω^* (C=C-C) and ω'^* (C-C-C) that are taken to apply to the activated complex structures (V) are estimated from eq. 2 where angles ω and ω' have been defined previously; $\Delta\omega$ and $\Delta\omega'$ are the differences between angles ω and ω' of the alkenes and the respective angles in the saturated hydrocarbons, and χ^* is defined as the percentage progression along the reaction coordinate³⁵ at which the transition state is found. It is assumed that these bond angles change in a linear fashion from alkene to alkane as a function of χ and that other bond angles do not change significantly from those in the parent alkenes. The C-C-C angles of the acyclic alkanes, cyclohexanes, and bicyclo[2.2.2]octane are taken as 112°—the average bond angles observed for the *n*-alkanes³⁶ and cyclohexane.³⁷ Angles of 105 and 104° are adopted for cyclopentane³⁸ and the appropriate C-C-C angle of bicyclo[2.2.1]heptane,³⁹ respectively, and angles of 116° are considered qualitatively applicable to cycloheptane and the medium-sized cycloalkanes.⁴⁰

$$\begin{aligned}\omega^* &= \omega - \chi^* (\Delta\omega) \\ \omega'^* &= \omega' - \chi^* (\Delta\omega')\end{aligned}\quad (2)$$

As a consequence of the expected restricted rotation about the partial carbon-carbon double bond of V, it seems reasonable to assume for the *cis*-cycloalkenes that there will be no significant ring conformational change between the starting and transition states. For these alkenes, torsional angles φ are taken to change

(33) $E = 1.8 \times 10^{-12}$ erg radian⁻² (Δ)² where Δ is the dihedral angle of the CH₂ groups in ethylene about the carbon axis: F. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 183.

(34) H. Eyring, G. H. Stewart, and R. P. Smith, *Proc. Natl. Acad. Sci. U. S.*, **44**, 259 (1958).

(35) The reaction coordinate may be defined in terms of the σ -bond order between the carbon and bonding hydrogen; however, this function alone will not describe the structures of the reacting molecules, and the coordinate can be viewed as well simply as being an indication of the fractional progress of conversion of alkene to alkane taken from zero to unity.

(36) R. A. Bonham, L. S. Bartell, and D. A. Kohl, *J. Am. Chem. Soc.*, **81**, 4765 (1959).

(37) M. Davis and O. Hassel, *Acta Chem. Scand.*, **17**, 1181 (1963); R. A. Wohl, *Chimia*, **18**, 219 (1964). The authors are indebted to Professor E. L. Eliel for bringing these works to our attention.

(38) J. B. Hendrickson, *J. Am. Chem. Soc.*, **85**, 4059 (1963).

(39) H. Krieger, *Suomen Kemistilehti*, **31**, 348 (1959); C. F. Wilcox, Jr., *J. Am. Chem. Soc.*, **82**, 414 (1960).

(40) The C-C-C angles in cycloheptane and the medium-sized cycloalkanes either have been estimated by machine computations or determined by X-ray diffraction to be considerably larger than 109.5°: see J. Dunitz and R. F. Bryan, *Helv. Chim. Acta.*, **43**, 3 (1960); E. Huber and J. D. Dunitz, *ibid.*, **760** (1960); J. D. Dunitz and H. M. M. Shearer, *Proc. Chem. Soc.*, 348 (1958); V. Prelog, *J. Pure Appl. Chem.*, **6**, 545 (1963); ref. 28 and 30.

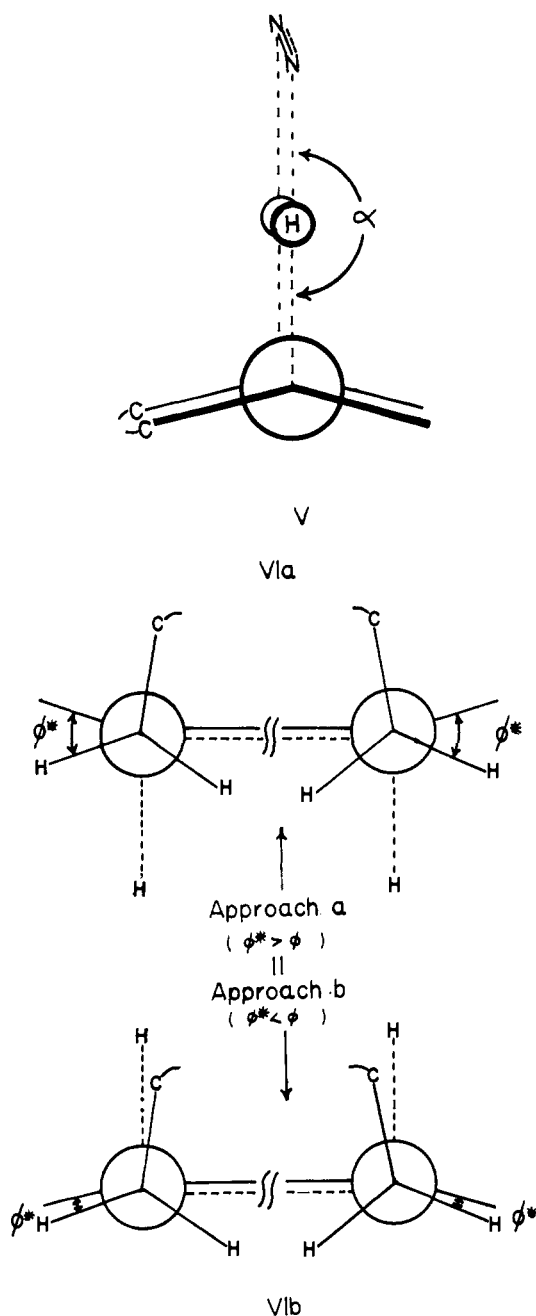
linearly by $\pm 60^\circ$ as a function of χ .³⁵ Angles φ^* , then, are given by eq. 3a. As seen in VIa and VIb, two activated complex structures must be considered for the cycloalkenes having symmetrical partial conformations II, one arising from an approach with diimide (approach a) that leads to $\varphi^* > \varphi$ (VIa) and a second arising from an opposite approach (approach b) that leads to $\varphi^* < \varphi$ (VIb). For the other cycloalkenes, a- and b-approaches lead to identical transition-state structures that contain two unique angles φ^* .

$$\varphi^* \cong \varphi \pm (60)(\chi^*) \quad \text{cis-cycloalkenes} \quad (3a)$$

$$\varphi^* \cong \varphi \cong 60^\circ \quad \text{mono-, 1,1-di-, and} \\ \text{trans-1,2-dialkylated} \\ \text{alkenes} \quad (3b)$$

$$\varphi^* \cong \varphi \quad \text{exocyclic alkenes} \quad (3c)$$

For the mono-, 1,1-di-, and *trans*-1,2-dialkylated acyclic alkenes, it is assumed (eq. 3b) that $\varphi^* = \varphi =$



60° (see section 7). Angles φ for the exocyclic alkenes are those found at the same carbon sites in the minimum energy conformations of the parent unsubstituted cycloalkanes and are not expected to change appreciably (eq. 3c) for moderate values of χ where transannular interactions with the incipient methyl group are of little consequence. Changes in the angles φ' (II) as a function of χ are not discussed, since these angles will not apply to the approximate calculations (see section 7).

4. Steric and Entropy Contributions

The steric factors (nonbonded repulsions) involved for addition of hydrogen to carbon-carbon multiple bonds are likely to be small. If the collinear activated complex V is indeed the electronically most favored one, steric effects there will be negligible except for extreme cases.⁴¹ Also, as there are expected to be no significant conformational changes between the alkenes and the activated complex structures, it seems reasonable to take ΔE_N^* , the difference between nonbonded repulsive energies in the starting alkene and in V, as closely approximating zero.

For reactions bearing nonpolar activated complex structures and involved in minimal steric interactions that would lead to differences in relative molecular rotational and vibrational degrees of freedom between starting and activated complex structures, ΔS^* should be close to zero.³ In this event, πQ^* (eq. 1) will be close to unity.⁵ According to our conception of the structures of the activated complexes and of the olefin structures, and from the trends so far reported for diimide reductions (see earlier), adoption of the above condition would seem justified.

5. Polar and Resonance Contributions

It is likely that both polar and resonance effects are important in contributing to the reactivities of diimide reductions of alkenes. The effects of polar substituents in the nonpolar activated complex structures for these reactions will be minimized for alkyl substituents. However, specific alkyl group interactions which are known to affect the ground-state energies of olefins will be important. These interactions are not commonly understood in terms of any single theoretical consideration.⁴² We will consider arbitrarily that olefin stabilization effects of alkyl groups originate from resonance or hyperconjugative interactions (E_ν); however, for our purposes we could equally consider that these effects are dominated by polar-type contributions.⁴²

Heats of hydrogenations of olefins exhibit a fairly uniform trend in olefin stabilization per alkyl substituent if adjustments are made for the destabilization arising from *cis*-dialkyl substituents.^{27,43} The trends recently reported⁴³ for the isomeric hexenes are considered typical, and the average of the difference in heats of hydrogenation (in the liquid state) between 1-hexene and *trans*-2-hexene, *trans*-3-hexene, and *trans*-4-methyl-2-pentene (-3.23 kcal./mole) is taken as the olefinic stabilization energy per alkyl group in the absence of other complicating effects. It will be as-

(41) E. E. van Tamelen and R. J. Timmons, *J. Am. Chem. Soc.*, **84**, 1067 (1962).

(42) M. J. S. Dewar, "Hyperconjugation," The Ronald Press Co., New York, N. Y., 1962.

(43) H. F. Bartolo and F. D. Rossini, *J. Phys. Chem.*, **64**, 1685 (1960).

sumed for the estimations of values of $\Delta\Delta E_{\psi}^*$ that this stabilization energy will decrease numerically from -3.23 kcal./mole/alkyl substituent to zero in an approximately linear manner as a function of χ . The same approach is applied for a phenyl substituent, although a stabilization energy of -4.6 kcal./mole is used.⁴⁴

6. Bond Angle Bending Strain Contributions

Bond angle bending strains in the alkenes (E_{ω}) and transition state structures (E_{ω}^*) are estimated from eq. 4 where the factor of 17.5 cal./mole is equal to one-half the bending force constant, k (8×10^{-12} erg radian⁻²), which is taken to be the same for the in-plane bending of the C=C-C, C-C-C, and C-C-C angles^{32,45}; ω (or ω') has been discussed in section 2; ω^* (or ω'^*) is given by eq. 2; ω_e (or ω'_e) is 122° (or 116°) and is taken as the C=C-C (or C-C-C) equilibrium bond angle in an unstrained acyclic system (see section 2)¹⁹; and $\omega_e^* = 122^\circ - 10\chi$ (or $\omega'_e^* = 116^\circ - 4\chi$) and represents the ideal unstrained bond angle in the activated complex arising from reduction of an unstrained acyclic alkene.

$$\begin{aligned} E_{\omega} &= 17.5(\omega_e - \omega)^2 \\ E_{\omega}^* &= 17.5(\omega_e^* - \omega^*)^2 \end{aligned} \quad (4)$$

7. Torsional Strain Contributions

Relative torsional potentials for alkylated olefins (E_{φ}) and the corresponding alkanes (E_{φ_s}) are given by eq. 5a and 5b, respectively, where $K = 1.0$ kcal./mole and $K_s = 1.4$ kcal./mole; angles φ are those given in II

$$E_{\varphi} = a + K(1 + \cos 3\varphi) \quad (5a)$$

$$E_{\varphi_s} = K_s(1 + \cos 3\varphi_s) \quad (5b)$$

and IV, and φ_s are those angles in the corresponding saturated hydrocarbon; a is a constant which defines the potential curve for propene relative to that for ethane and will be zero if at $\varphi = \varphi_s = 60^\circ$, $E_{\varphi} = E_{\varphi_s}$.

The origins of rotation barriers, even in the simplest molecules, remain to be understood.⁴⁶ Recent attempts to understand the origin of barriers to internal rotation in ethane and similar-type molecules have concentrated on the hypothesis that the barriers may be accounted for solely in terms of proton-proton repulsions modified by electron shieldings.⁴⁷ Extension of this hypothesis to the more complex alkenes does not appear straightforward, especially in view of the recent discovery by Sastry and Curl⁴⁸ that N-methylmethylimine ($\text{CH}_3\text{N}=\text{CH}_2$) has a torsional barrier almost

(44) J. E. Bloor and S. Gartside, *Nature*, **184**, 1313 (1959); difference of heats of hydrogenation in the gas phase between ethene and the olefinic bond of styrene.

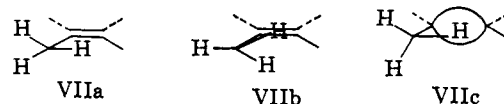
(45) C. W. Beckett, N. K. Freeman, and K. S. Pitzer, *J. Am. Chem. Soc.*, **70**, 4227 (1948); F. H. Westheimer, "Steric Effects in Organic Chemistry," M. S. Newman, Ed., John Wiley and Sons, Inc., New York, N. Y., 1956, Chapter 12.

(46) E. B. Wilson, Jr., *Advan. Chem. Phys.*, **2**, 367 (1959); E. B. Wilson, Jr., *Tetrahedron*, **17**, 191 (1962); D. J. Millen, "Progress in Stereochemistry," Vol. III, P. B. D. de la Mare and W. Klyne, Ed., Butterworths, Washington, D. C., 1962, Chapter 4.

(47) R. G. Parr, *J. Chem. Phys.*, **40**, 3726 (1964); M. Karplus and R. G. Parr, *ibid.*, **38**, 1547 (1963); see also K. Ruedenberg, *ibid.*, **41**, 588 (1964); B. Kirtman, *ibid.*, **41**, 3262 (1964); R. E. Wyatt and R. G. Parr, *ibid.*, **41**, 3262 (1964).

(48) K. V. L. N. Sastry and R. F. Curl, Jr., *ibid.*, **41**, 77 (1954); J. T. Yardly, J. Hinze, and R. F. Curl, Jr., *ibid.*, **41**, 2562 (1964).

identical with that of propene and an eclipsed allylic hydrogen double bond minimum energy conformation as found in all the simple alkenes so far investigated.²²⁻²⁴ Exchange interactions would not be expected to contribute greatly to the torsional potentials for σ - π representations of alkenes, since the σ -electron and σ - π exchange interactions in the minimum (VIIa) and maximum (VIIb) energy conformations are expected to be comparable.⁴⁹



Pauling has suggested⁵⁰ a "bent-bond" structure for olefins (VIIc) which derives from mixing d- and f-character in the carbon orbitals forming the carbon-carbon double bond. This "bent-bond" description of carbon-carbon double bonds accounts⁵⁰ qualitatively for the deviation from trigonal angles observed in alkenes and for the rotation barrier observed in propene. When visualizing the alkene as an ethane-like molecule, it predicts the observed minimum energy conformations for alkylated ethenes.²²⁻²⁴ This description of the bonding in alkenes leads to the attractive prediction that propene ($\varphi = 60^\circ$), and similar alkenes where there is no constraint on rotation about C(sp²)-C(sp³) bonds, may be converted to propane ($\varphi_s = 60^\circ$) with $(\partial E_{\varphi}/\partial \chi)_{\varphi=60^\circ} = a$ where a is given in eq. 5a. It would be difficult to arrive at the same prediction for the σ - π formalization of alkenes where terms involving angles φ' (see II) and dihedral angles between allylic orbitals and the rehybridizing p-orbitals might be expected to appear in an appropriate potential function.

For estimations of E_{φ}^* , we assume that an approximate transition-state potential function can be formulated in terms of angles φ , K (eq. 5), K_s (eq. 5), and χ ; and that $a = 0$, $(\partial E_{\varphi}/\partial \chi)_{\varphi=60^\circ} = 0$, and that K changes linearly to K_s as a function of χ . These assumptions are incorporated in eq. 6 which is used to estimate values of E_{φ}^* (where $K^* = K + \chi^*(K_s - K)$). For the methylated cycloalkenes and methylenecycloalkanes, we do not employ $K_s (= 1.7)$ for propane as might

$$E_{\varphi}^* = K^*(1 + \cos 3\varphi^*) \quad (6)$$

seem appropriate, since the slightly larger K_s for propane as compared with that for ethane is due presumably to nonbonded repulsive interactions which are not likely to become important in activated complex structures where bond angles are not very much different from those in the alkenes.

It is recalled from section 2b that the origin of the strain energies associated with *cis*-1,2-dialkylated alkenes could not be defined easily and that the experimental values of about 1.0 kcal./mole were assigned to E_{φ} . Referring to the proposed structure of the activated complexes (V), it appears likely that $E^*_{\text{strain}} \geq E_{\text{strain}}$ for these cases, since $\omega_e^* < \omega_e$ and it would be difficult to minimize the various strain contributions (E_{N}^* , E_{φ}^* , and E_{ω}^*) to a total value below that of the starting alkene; however, the starting alkene and ac-

(49) M. Karplus, *ibid.*, **33**, 316 (1960).

(50) L. Pauling, "Theoretical Organic Chemistry" (Kekulé Symposium), Butterworths, Washington, D. C., 1959, p. 1 ff; L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960, p. 136 ff.

Table I. Summary of Relative Rate Cross Checks and Influence of Per Cent Reaction on Relative Rates of Diimide Reductions of Alkenes at 80°

Alkene ^a		k_A/k_B (direct)	k_B/k_6^b (direct)	k_A/k_6^b (direct)	K_A/K_6^b (indirect) ^c	Alkene		% reacted		k_C/k_D
A	B					C	D	C	D	
Cyclo-C ₅	1- <i>n</i> -C ₆	0.730	20.2	15.5	14.7			24.5	1.1	25.8
						31.3	1.3	26.7		
Bicyclo- [2.2.2]-C ₃	Cyclo-C ₅	1.83	15.5	31	28.4			57.8	2.6	33.2
						59.1	3.8	30.4		
Cyclo-C ₃	Cyclo-C ₇	1.41	12.1	17.0	17.1			28.8	15.1	2.03
Cyclo-C ₅	Cyclo-C ₇	1.24	12.1	15.5	15.0			47.7	27.1	2.06
Cyclo-C ₉	Cyclo-C ₈	0.415	17.0	5.7	7.1	Cyclo-C ₁₀		28.0	31.7	0.852
Cyclo-C ₁₂	Cyclo-C ₁₀	0.757	0.90	0.642	0.68			88.2	90.5	0.923
								35.6	30.2	1.25
								54.2	47.8	1.23
								34.6	12.4	3.22
								43.7	17.1	3.09
								72.5	31.0	3.50

^a Cycloalkenes have *cis* configuration. ^b k_6 is for cyclohexene. ^c $(k_A/k_B)(k_B/k_6)$.

tivated complex strains may not be appreciably divergent. It is assumed for these *cis*-alkenes that $\Delta E^*_{\text{strain}} \cong 0$ ($E_\phi^* \cong E_\phi$), and it should be remembered that this assumption may lead to maximum values of estimated relative reactivities.

8. Results and Discussion

Competitive reductions of the alkenes by diimide were accomplished by thermostating at 80° solutions of *p*-toluenesulfonylhydrazine (*ca.* 0.1 g.), triethylamine (*ca.* 0.1 g.), two alkenes (*ca.* 0.02 g. each), and 1.0 ml. of diglyme in sealed tubes for periods of about 15 hr. The triethylamine was found to be required in order to eliminate acid-catalyzed equilibrations of a number of alkenes by *p*-toluenesulfinic acid, a product arising from the decomposition of the sulfonylhydrazine. A thorough study of the competitive reductions of 1-methylcyclohexene *vs.* 1-methyl-4-*t*-butylcyclohexene showed that the efficiency of the reduction (total moles of alkene reduced per moles of *p*-toluenesulfonylhydrazine) was somewhat greater (*ca.* 0.3) in the presence of triethylamine than in its absence (*ca.* 0.2) or in the presence of *p*-toluenesulfinic acid (*ca.* 0.2 g.). However, relative rates had an average deviation of less than 3%. We cannot say much at this time about the reason for the efficiency differences, although base-catalyzed and thermal decompositions of the *p*-toluenesulfonylhydrazine may proceed differently or protonated diimide may be ineffective as a reducing agent. Triethylamine also catalyzes the decomposition of *p*-toluenesulfonylhydrazine as evidenced by the <16 hr. normally required for its complete decomposition in the presence of triethylamine under the reaction conditions employed, as opposed to *ca.* 90–150 hr. required in its absence or in the presence of *p*-toluenesulfinic acid.

Relative rates were calculated using eq. 7, where $[A_n]_i$ and $[A_n]_f$ represent the initial and final concentrations of alkene A_n . The values of the terms of the right-hand side of eq. 7 were obtained by gas chromatographic analysis after appropriate manipulation of the reduction mixtures (see Experimental). Gas chromatographic

$$k_1/k_2 = (\log [A_1]_i - \log [A_1]_f) / (\log [A_2]_i - \log [A_2]_f) \quad (7)$$

Table II. Results from Competitive Diimide Reductions of Substituted Cyclohexenes at 80°

No.	A	B	k_A/k_B
1			1.05 ± 0.02
2			1.82 ± 0.03
3			1.02 ± 0.03
4			1.01 ± 0.03
5			1.09 ± 0.06
6			1.11 ± 0.06
7			1.23 ± 0.03
8			
	Boat (100%)	Chair (100%)	16 ^a
	Boat (5%) + chair (95%)	Chair (100%)	1.8 ^a

^a Estimated using $\varphi_{\text{chair}} = 40, 40^\circ$, $\varphi_{\text{boat}} = 15, 15^\circ$, $\omega_{\text{boat}-(\text{chair})} = 120^\circ$, and $\chi = 0.34$ (see later and Table III).

peak areas, determined by planimeter integration, were taken to be proportional to molar concentrations. Calibrations showed that in only a few instances were small corrections (<10%) required. The consistency of k_1/k_2 values as determined by direct and indirect competitions and the relatively insensitive dependence of values of k_1/k_2 in the percentage reduction are illustrated in Table I and serve to validate the method of

Table III. Calculated and Experimental Rates of Diimide Reductions of Alkenes Relative to Cyclohexene at 80°C^a

Alkene ^b	Alkene						*						$\Delta\Sigma E^*$	$\Delta\Delta\Sigma E^*$	k_{rel}^{calcd} ^d	k_{rel}^{obsd} ^e
	φ (θ)	ω^c	E_φ	E_ω^c	E_ψ	ΣE	φ^*	ω^{*c}	E_φ^*	E_ω^{*c}	E_ψ^*	ΣE^*				
Cyclo-C ₆	40, 40 (80, 80)	120	1.00	0.14	-6.46	-5.32	20, 60	117.3	1.70	0.06	-4.26	-2.50	2.82	0.00	1.00	1.00
Bicyclo[2.2.1]-C ₇ ^f	20, 20 (140, 140)	107	3.00	7.88	-6.46	4.42	(a) 40, 40 (b) 0, 0	106 106	1.13 4.54	5.57 5.57	-4.26 -4.26	2.44 5.85	-1.98 1.43	-4.80 -1.39	4.5 × 10 ²	4.5 × 10 ²
Bicyclo[2.2.2]-C ₈	0, 0 (120, 120)	115	4.00	1.71	-6.46	-0.75	20, 20	114	3.41	0.74	-4.26	-0.11	0.64	-2.18	22	29 ^g
Cyclo-C ₆ (C _a)	40, 40 (80, 80)	111.5	1.00	3.86	-6.46	-1.60	(a) 60, 60 (b) 20, 20	109.3 109.3	0.0 3.41	3.02 3.02	-4.26 -4.26	-1.24 2.17	0.36 3.77	-2.46 0.95	16	15.5
1-Methylcyclo-C ₆ (C _a) ^h	40, 40 (80, 80)	111.5	1.00	3.86	-9.69	-4.83	(a) 60, 60 (b) 20, 20	109.3 109.3	0.0 3.41	3.02 3.02	-6.39 -6.39	-3.37 .13	1.46 4.94	-1.36 2.12	3.4	1.63
1-Methylcyclo-C ₆	40, 40 (80, 80)	120	1.00	0.14	-9.69	-8.55	20, 60	117.3	1.70	0.06	-6.39	-4.63	3.92	1.10	0.21 (0.15) ^p	0.109
1,2-Dimethylcyclo-C ₆ ⁱ	40, 40 (80, 80)	120	2.00 ⁿ	0.14	-12.92	-10.78	20, 60	117.3	2.70 ⁿ	0.06	-8.52	-5.76	5.02	2.20	0.043 (0.018) ^p	0.012
1-Phenylcyclo-C ₆ ⁱ	40, 40 (80, 80)	120	1.00	0.14	-11.06	-9.92	20, 60	117.3	1.70	0.06	-7.30	-5.54	4.38	1.56	0.11	0.13
Cyclo-C ₇	15, 15 (135, 135)	122	3.41	0.00	-6.46	-3.05	(a) 35, 35 (b) 5, 5	120 120	1.68 4.47	0.07 0.07	-4.26 -4.26	-2.51 0.29	0.54 3.34	-2.28 0.52	13	12.1
1-Methylcyclo-C ₇	15, 15 (135, 135)	122	3.41	0.00	-9.69	-6.28	(a) 35, 35 (b) 5, 5	120 120	1.68 4.47	0.07 0.07	-6.39 -6.39	-4.64 -1.85	1.64 4.43	-1.18 1.61	2.7	2.45
Cyclo-C ₈	25, 25 (145, 145)	122	2.51	0.00	-6.46	-3.95	(a) 45, 45 (b) 5, 5	120 120	0.66 4.47	0.07 0.07	-4.26 -4.26	-3.53 0.28	0.42 4.23	-2.40 1.41	15	17.0
1-Methylcyclo-C ₈	25, 25 (145, 145)	122	2.51	0.00	-9.69	-7.18	(a) 45, 45 (b) 5, 5	120 120	0.66 4.47	0.07 0.07	-6.39 -6.39	-5.66 -1.85	1.52 5.33	-1.30 2.51	3.1	2.50
Cyclo-C ₉	35, 35 (155, 155)	122	1.48	0.00	-6.46	-4.98	(a) 55, 55 (b) 15, 15	120 120	0.08 3.88	0.07 0.07	-4.26 -4.26	-4.11 -0.31	0.87 4.67	-1.95 1.85	7.9	5.70
Cyclo-C ₁₀	60, 0 (180, 120)	122	2.00	0.00	-6.46	-4.46	20, 40	120	2.27	0.07	-4.26	-1.92	2.54	-0.28	1.5	0.85
Cyclo-C ₁₂	60, 0 (180, 120)	122	2.00	0.00	-6.46	-4.46	20, 40	120	2.27	0.07	-4.26	-1.92	2.54	-0.28	1.5	0.64
Methylenecyclohexane	60, 60	116	0.00	0.00	-6.46	-6.46	60, 60	114.6	0.00	0.00	-4.26	-4.26	2.20	-0.62	2.4	3.27
Methylenecyclopentane (C ₂) ^j	15, 15	<i>k</i>	3.41	0.90 ^k	-6.46	-2.15	15, 15	<i>k</i>	3.88	0.60	-4.26	0.22	2.37	-0.45	1.9	4.0
2-Methylenenorbornane ^j	40, 0	107	2.50	1.42	-6.46	-2.54	40, 0	106	2.84	1.29	-4.26	-0.13	2.41	-0.41	1.8	3.6
Methylenecycloheptane ^{j, l}	97, 75 ^l	116	1.65	0.00	-6.46	-4.81	97, 75	116	1.87	0.03	-4.26	-2.36	2.45	-0.37	1.7	3.6
Methylenecyclooctane ^{j, m}	43, 105 ^m	116	2.08	0.00	-6.46	-4.38	43, 105	116	2.36	0.03	-4.26	-1.87	2.51	-0.31	1.6	2.4
1-Pentene	60	122	0.00	0.00	-3.23	-3.23	60	118.6	0.00	0.00	-2.13	-2.13	1.10	-1.72	12	20.2
<i>trans</i> -2-Pentene	60, 60	122	0.00	0.00	-6.46	-6.46	60, 60	118.6	0.00	0.00	-4.26	-4.26	2.20	-0.62	2.4	2.59
<i>cis</i> -2-Pentene	<i>n</i>	<i>n</i>	1.00 ⁿ	<i>n</i>	-6.46	-5.46	<i>n</i>	<i>n</i>	1.00 ⁿ	<i>n</i>	-4.26	-3.26	2.20	-0.62	2.4	2.65
2-Methyl-1-pentene	60, 60	122	0.00	0.00	-6.46	-6.46	60, 60	118.6	0.00	0.00	-4.26	-4.26	2.20	-0.62	2.4	2.04
2-Methyl-2-butene	<i>n</i>	<i>n</i>	1.00 ⁿ	<i>n</i>	-9.69	-8.69	<i>n</i>	<i>n</i>	1.00 ⁿ	<i>n</i>	-6.39	-5.39	3.30	0.48	0.50	0.28
2,3-Dimethyl-2-butene ^o	<i>n</i>	<i>n</i>	2.00 ⁿ	<i>n</i>	-12.92	-10.92	<i>n</i>	<i>n</i>	2.00 ⁿ	<i>n</i>	-8.52	-6.52	4.40	1.58	0.11	0.50

^a All potential energy terms are given in kcal./mole. ^b Competitive reductions are with cyclohexene unless stated otherwise. The cycloalkanes are of the *cis* configuration. ^c Or angles ω' . ^d Given by $(k_a + k_b)/2k_{6a}$, where k_a and k_b refer to the rate constants of approaches a and b (see VI and VIII) and k_{6a} is equal to k_{6b} for cyclohexene. In those instances where $k_a = k_b$, only one entry is made for the E^* -terms and is equal to $1/2(E_a^* + E_b^*)$. ^e The values given are thought to be reliable to $\pm 5\%$. ^f Competition with cyclopentene. ^g Average results from competition with cyclohexene and cyclopentene. ^h Competition with 2-methyl-1-pentene. ⁱ Competition with 1-methylcyclohexene. ^j Competition with methylenecyclohexane. ^k See section 2b. The angle bending strain associated with methylenecyclopentane³² is presumed to decrease to that associated with methylcyclopentane³² as a linear function of χ . ^l Taken from structure V for cycloheptane in ref. 28. ^m Taken from structure BC for cyclooctane in ref. 30. ⁿ See last paragraph of section 7. ^o Competition with 1,2-dimethylcyclohexene. ^p See second last paragraph of section 8.

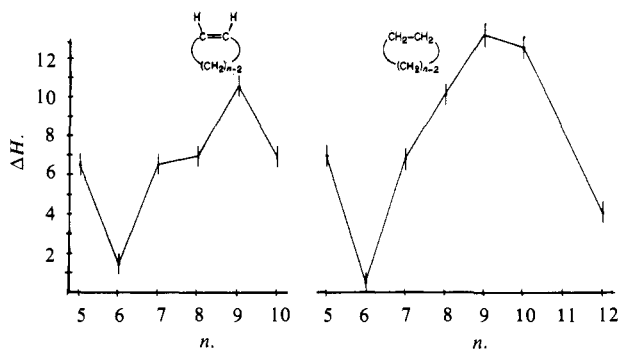


Figure 1. Strain energies (ΔH) of cycloalkanes (right) in kcal./mole determined from heats of combustion.⁶⁴ Strain energies of cycloalkenes (left) estimated using the equation $\Delta H = \Delta\Delta H_h + \Delta H_s$, where ΔH is the difference between the cycloalkene strain energy and that of cyclohexene (taken as 1.0–2.0 kcal./mole and based upon heats of hydrogenation of cyclohexene and *trans*-2-butene²⁷ and a probable small positive torsional strain of ca. 0.5 kcal./mole associated with cyclohexane³⁷), $\Delta\Delta H_h$ is the difference in solution heats of hydrogenation between the cycloalkene and cyclohexene at 25°, and ΔH_s is the difference between the total strain energy of the cycloalkane and that of cyclohexane as determined from heats of combustion data in the gas phase at 25°.²⁷

analysis and the assumptions inherent in eq. 7 that the reaction is first order with respect to alkene.

Since it was convenient experimentally to determine rates of reduction relative to cyclohexene with the exception of a few of the very reactive or unreactive alkenes and the methylenecycloalkenes, it is desirable to show that cyclohexene is not an abnormal selection insofar as it is not conformationally deformed from the chair form to a significant extent. To this end we have competitively reduced a series of 1-substituted cyclohexenes and 1-substituted 4-*t*-butylcyclohexenes (and several disubstituted cyclohexenes). It may be deduced from sections 2–7 that the boat or an appreciably distorted chair version of cyclohexene may be expected to be significantly more reactive (by about an order of magnitude) than the chair form. This predicted increased reactivity derives primarily from a high torsional strain ($\varphi \sim 15^\circ$) associated with the partial conformation II of the boat form. This torsional strain is expected to be relieved in the transition state (approach a), whereas that for the chair conformation is expected to be increased. If a significant population of cyclohexene molecules exist in the boat or a distorted chair conformation, this population would be expected to be reduced to some extent for the 4-*t*-butyl derivative owing to the greater torsional and repulsive strains expected upon substitution of a *t*-butyl group for a hydrogen at C-4 in a deformed cyclohexene ring as opposed to an ideal ring in the chair conformation. Consequently, k_{4-H}/k_{4-t-Bu} would be expected to be greater than unity. Table II gives the results of the competitive diimide reductions mentioned above. Included in the table are estimated (see Table III) k_A/k_B values assuming that 100 and 5%, respectively, of A exists in the boat conformation and B is conformationally homogeneous in the chair form. For all purposes, k_A/k_B values are effectively unity for no. 1 and 3–7. The somewhat lower reactivity of *cis*-3,5-*di-t*-butylcyclohexene relative to cyclohexene probably is significant, but this may be a special case and will be discussed with others like it later.

These results are interpreted to indicate that cyclohexenes A and B react essentially in the ideal chair conformations and that any structural changes that occur for cyclohexenes A in the activated complexes relative to the starting states occur identically for cyclohexenes B. A little later we will discuss the stereochemistry of reductions of cyclohexenes B (no. 3–7).

We find that a value of 0.34 for χ leads to the best agreement between the calculated (k_{rel}^{calcd}) and observed (k_{rel}^{obsd}) rates relative to cyclohexene of diimide reductions of the alkenes investigated. Referring to sections 1–7, values for relative rates have been calculated and compared with the experimentally determined values. The results are summarized in Table III. The relative rates are seen to cover a range of 38,000 [$k_{rel}(\text{bicyclo}[2.2.1]\text{heptene})/k_{rel}(1,2\text{-dimethylcyclohexene})$] and the agreement between the observed and calculated values is seen to be quite close—generally within a factor of two. This agreement is very good in view of the rudimentary approach used and would suggest that the major contributing factors, E_ψ , E_ω , and E_ϕ , that appear to influence the reactivities of diimide reductions of alkenes have been characterized and evaluated approximately.

We might discuss now several general trends observed for the reactivities of diimide reductions of alkenes and consider also some possibly significant conclusions regarding structure vs. reactivity and stereoselectivity that can be derived from the data available.

One significant trend observed for the diimide reductions is the comparable relative reactivities of 2-methyl-1-pentene, 2-methylenebicyclo[2.2.1]heptane, and the five- through eight-membered ring methylenecycloalkanes. The calculated and observed relative reactivities agree very well. This insensitivity of reactivity to structure for the diimide reduction is in marked contrast to the pronounced reactivity differences observed for the sodium borohydride reductions of cyclic ketones.^{51b} Cyclohexanone is found to be over several orders of magnitude more reactive than the acyclic and medium-sized cyclic ketones toward sodium borohydride reduction.^{51b} Rationalizations^{51–54} of these and other reactivity trends of the cycloalkanones have been based on the high energy content of cyclohexanone which arises either from presumably unfavorable α , α' -diequatorial carbon–hydrogen bond interactions with the carbonyl function^{51,53} which are not borne out experimentally⁵² or from the absence of a stabilizing effect which is suggested to be associated peculiarly with the α -carbon–hydrogen bonds of ketones.⁵² These effects, which are thought to lead to the increased reactivity of cyclohexanone relative particularly to the acyclic ketones, would be expected to operate also in methylenecyclohexane and thereby lead to an increased reactivity of this alkene relative to comparatively substituted acyclic alkenes. This expectation which is

(51) (a) H. C. Brown, J. H. Brewster, and H. Shechter, *J. Am. Chem. Soc.*, **76**, 407 (1954); (b) H. C. Brown and K. Ichikawa, *Tetrahedron*, **1**, 221 (1957).

(52) W. D. Cotterill and M. J. T. Robinson, *Tetrahedron Letters*, 1833 (1963).

(53) N. L. Allinger, *J. Am. Chem. Soc.*, **81**, 5727 (1959); N. L. Allinger, J. Allinger, and M. A. DaRooge, *ibid.*, **86**, 4061 (1964).

(54) See E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp. 240, 245, and 267; J. Sicher, ref. 46, pp. 227–229.

neither observed nor predicted as a result of our calculations (see above) suggests that the origins of the reactivity trends of the cycloalkanone reactions⁵¹⁻⁵⁴ should be reconsidered.

The reactivity trend observed for the cycloalkenes as a function of ring size and structure is seen to be closely estimated. Figure 1 shows the strain energies of the common- and medium-sized *cis*-cycloalkenes and cycloalkanes. It is instructive to note that the relative reactivities of diimide reductions and of other olefin *cis*-addition reactions^{2,3} (see Figure 2) do not parallel either the relative ground-state strain energies of the cycloalkanes or the relative differences between product and reactant strain energies. The high reactivities observed for bicyclo[2.2.1]heptene, bicyclo[2.2.2]octene, and cyclopentene originate primarily from a compilation of angle bending and torsional strains in the partial structures II of these alkenes, which are relieved as the reactions proceed to the transition states. This is in contrast to cyclohexene, which acquires an increase in torsional strain during the rate-controlling addition process. Consequently, cyclohexene is somewhat less reactive than the unstrained disubstituted acyclic alkenes where a minimum combination of strains is maintained during the course of reaction. The variable reactivities of cycloheptene and the medium-sized cycloalkenes appear to originate primarily from changes in torsional strains associated with partial structures II.

The agreement between the calculated and observed properties as a function of ring size (and structure) found here and in a divergent reaction system¹⁹ using identical structural parameters^{19,20} for the alkenes offers rather compelling empirical evidence that the partial conformations (II) adopted for the cycloalkenes are qualitatively correct and should be applicable for appreciating reactivity trends for other olefin addition reactions.

The relative reactivities of diethylaluminum hydride² and hexachlorocyclopentadiene² additions to the cycloalkenes at 78° (see Figure 2) show trends comparable to those recorded for the diimide reductions, and as a consequence the alkene activated complex structures for these reactions may be comparable. The disiamylborane reactions with several of the cycloalkenes³ at 0° exhibits a greater degree of selectivity than is observed for the diimide reductions (see Figure 2). Cycloheptene and cyclooctene are considerably more reactive than cyclopentene toward disiamylborane, whereas the reactivities are comparable for the diimide reductions. The low temperature used for the disiamylborane additions may account in part for the large selectivity differences; however, this factor alone will not account for the greater reactivities of cycloheptene and cyclooctene relative to cyclopentene. It appears likely that a somewhat greater value of χ than used for the diimide reactions may be required to explain the relative reactivity trends observed. For example, taking $\chi = 0.50$ the rates of disiamylborane additions to cyclopentene, cycloheptene, cyclooctene, and *trans*-2-pentene relative to cyclohexene at 0° are calculated to be 175, 625, 400, and 11, respectively. These values are to be compared with the observed³ relative rates of 108, 550, 2000, and 23, respectively. The calculated and experimental values agree reasonably well and the

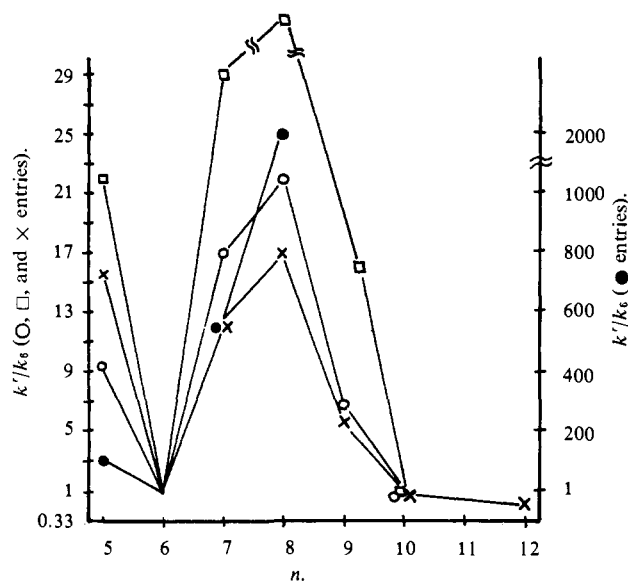


Figure 2. Relative rates (k_n/k_6) of diethylaluminum hydride addition at 78° (O),² hexachlorocyclopentadiene addition at 78° (□),² disiamylborane addition at 0° (●),³ and diimide reduction (X; this work) at 80° of *cis*-cycloalkenes as a function of ring size, n .

higher reactivities of cycloheptene and cyclooctene relative to cyclopentene are predicted. Calculated relative rates of disiamylborane additions to monoalkenes and 1,1-dialkylated alkenes are in poor agreement with experimental values; however, this is not unexpected as polar (ΔE_p) and steric (ΔE_N) contributions are known to be important for these reactions.³

The effect of n -alkyl substituents on the relative rates of diimide reductions of alkenes is shown collectively in Table IV. For the cyclic or acyclic alkenes, substitution of a methyl, ethyl, or n -propyl group for a vinyl hydrogen leads to a reduced reactivity with diimide by a factor of about 7.7 ± 2 at 80°. This agrees rather closely with the calculated rate reduction factor of 5 that arises from the E_ψ term of eq. 1 (see also section 5). Noteworthy also is that substitution of a vinylalkyl substituent *cis* or *trans* to an originally substituted alkyl group leads approximately to the same observed rate reduction factor (see also Table III; $k_{rel}(cis-2-pentene) = k_{rel}(trans-2-pentene)$). The assumption that $\Delta E_{strain}^* = 0$ (section 7) for the *cis*-dialkylated acyclic and cyclic alkenes, therefore, is substantiated. In contrast, however, reactions of disiamylborane with *cis*-dialkylated olefins are faster than with the *trans* isomers by factors ranging from 2.5 to 9.5.³ Brown and Moerikofer have interpreted this trend as compatible with the higher strain energies known to be associated with *cis*- relative to the *trans*-alkenes, but do not suggest a process by which these strains are relieved during progression to the transition states. As it is not readily visualized how $\Delta\Delta E_N^*$ (eq. 1) would be significantly different for the isomeric alkenes, possibly χ is sufficiently greater for this reaction than for the diimide reaction, as suggested earlier, and rotations about the partial carbon-carbon double bonds of the *cis* isomers may be significant in the activated complex structures.

In section 4 it was presumed that $\Delta\Delta E_N^*$ should be negligible except for extreme cases.⁴¹ The high calculated and observed k_{rel} for bicyclo[2.2.2]octene

Table IV. Effects of *n*-Alkyl Substituents on the Relative Rates of Diimide Reductions of Alkenes at 80°

A															
B															
k_A/k_B	0.11 ^a	0.11	0.11	0.20 ^a	1.6 ^a	0.13 ^a	0.10 ^a	0.16 ^a	0.14 ^a	0.11 ^a	0.17 ^a				

^a Indirect comparison.

would appear to substantiate this assumption, since the approach for reaction is comparable to the *endo* approach for bicyclo[2.2.1]heptene, which is thought to be hindered for most addition-type reactions. Also, 1-methylene-4-*t*-butylcyclohexane has been reported⁴¹ to be reduced to a mixture of equal amounts of *cis*- and *trans*-1-methyl-4-*t*-butylcyclohexanes. Items no. 1–3 in Table V show that an allylic equatorial *t*-butyl group on cyclohexene does not lead to a large reduction in rate relative to cyclohexene and that vinylic *t*-butyl groups in cyclohexene and cyclopentene actually lead to a slight increase in reduction rates relative to the respective 1-methylcycloalkenes.⁵⁵ The observed reduction of 2-bicyclo[2.2.1]heptene-2,3-dicarboxylic acid primarily by *exo* approach with diimide is predicted on the basis of stereotorsional control, since the b-approach (see Table III and structures VIa and VIb) to bicyclo[2.2.1]heptene leads to an increase in E_p^* , whereas, in the a-approach, E_p^* is relieved relative to that in the alkene. This stereotorsional control is predicted to lead to highly stereoselective a-approach for diimide reductions of cyclopentene and cycloheptene through cyclononene. For these alkenes, however, the a-approaches seem to be more hindered than the b-ones, thereby making it difficult to demonstrate unambiguously the origin of the effects that may lead to this expected stereoselectivity.⁵⁶

The diimide reductions of 4-*t*-butyl-1-methylcyclohexene and 4-*t*-butyl-1-phenylcyclohexene (no. 10 and 11 in Table V) are found to be partially stereoselective, approach a being more favored than approach b in VIII (R = CH₃ or C₆H₅). Our calculations do not anticipate this stereoselectivity, possibly because of the very approximate manner of handling the torsional potential, E_p^* (eq. 6), for the activated complex structures (see section 7). It may be recalled that *K* (for propene) was considered to change linearly to *K_s* (for ethane) as a function of χ . This, at best, must be

(55) The equilibrium constant for 1-*t*-butyl-4-methylcyclohexene \rightleftharpoons 4-*t*-butyl-1-methylcyclohexene (base-catalyzed) has a value of 1.48 at 88 \pm 2° (unpublished results of Garbisch) and may indicate for no. 2 of Table V that A is less stable than B by about 0.3 kcal./mole (88°). A greater reactivity (*ca.* 1.5) of A relative to B may be expected then, however, only if the excess strain in A relative to B is somehow relieved during the course of reduction. Alternatively, the increased reactivity of A relative to B may come about, in part, by a retardation of approach b reduction of B which is not observed for A (see later discussion).

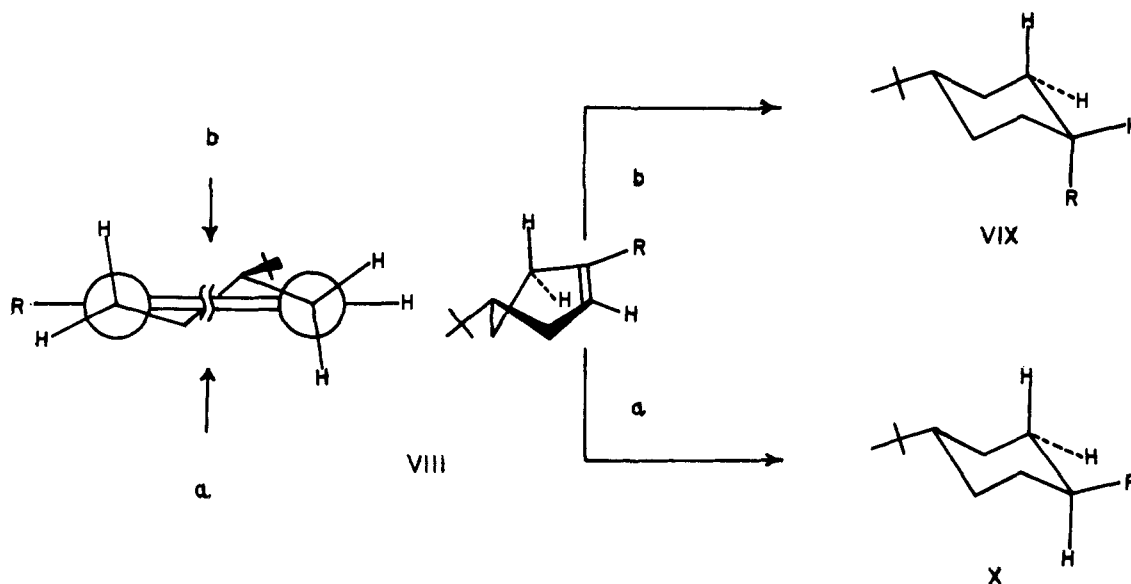
(56) The diimide reduction of camphene proceeds by predominant *exo* approach⁴¹ in opposition to an expected nonstereoselectivity. We have not as yet been able to determine whether or not a comparable stereoselectivity is observed for the diimide reduction of 2-methylenebicyclo[2.2.1]heptane. An interesting example of stereoselectivity has been reported for diimide reductions of several 7-alkoxybicyclo[2.2.1]heptadienes (W. C. Baird, Jr., B. Franzus, and J. H. Surridge, Abstracts, 148th National Meeting of the American Chemical Society, Aug. 31–Sept. 4, 1964, p. 91S).

Table V. Steric Effects and Stereochemistry of Diimide Reductions of Substituted Cycloalkenes at 80°

No.	A	B	k_A/k_B^a	<i>trans/cis</i> product
1			1.8	0.00
2			2.05 \pm 0.03	
3			1.46 \pm 0.01	
4			0.31 \pm 0.02	
5			1.11 \pm 0.06	
6			1.60 \pm 0.07	
7			1.49 \pm 0.06	
8			1.52 \pm 0.02	
9				<0.01
10				2.3
11				3.2
12				1.05
13				1.1

^a Direct competition.

an approximate assumption. As bond angles ω^* and ω'^* are somewhat smaller than those in the alkenes and somewhat larger than those in the products, values for *K* and *K_s* that apply to the activated complexes probably will be slightly different from those adopted—



particularly when $R \neq H$ in VIII. It is likely, therefore, when $R = \text{alkyl}$ (in VIII) and $\varphi_R^* < 60^\circ$ that E_φ^* , as determined by eq. 6, will be underestimated owing to a probably larger torsional strain resulting from eclipsing a C-R bond as opposed to a C-H bond. This consideration, when applied to the cases in point (no. 10 and 11, Table V), leads to a qualitative prediction of the observed stereoselectivities. For example, approach b leads to $\varphi_{R,H}^* \sim 20^\circ$ and $\varphi_{H,H}^* \sim 60^\circ$ and approach a leads to $\varphi_{R,H}^* \sim 60^\circ$ and $\varphi_{H,H}^* \sim 20^\circ$. Since the torsional strain associated with $\varphi_{R,H}^* \sim 20^\circ$ is likely to be greater than that associated with $\varphi_{H,H}^* \sim 20^\circ$, but the strains associated with $\varphi_{R,H}^* \sim 60^\circ$ and $\varphi_{H,H}^* \sim 60^\circ$ are minimum and comparable, $k_a/k_b > 1$. The result that $k_a/k_b \cong 1$ for no. 13 in Table V is not consonant with this rationale, and it can be suggested only that there must be a balance of strains arising from approaches a and b in the 1-butylcyclohexene derivatives.

The above discrepancies do not affect significantly the calculated relative reactivities as given in Table III, although with known values of k_b/k_a for given ring systems corrections can be applied which may improve relative rate estimates by accounting empirically for the inadequacies of the calculations. For example, entry no. 3 in Table II suggests that values of k_a and k_b are the same for 1-methylcyclohexene and 4-*t*-butyl-1-methylcyclohexene. Since $\varphi^* \sim 60^\circ$ for the a-approach to VIII ($R = H$ or CH_3), k_a for methylcyclohexene is taken to be equal to $k_a = k_b$ for cyclohexene. From the stereoselectivity of reduction of 4-*t*-butyl-1-methylcyclohexene (no. 10, Table V), $k_b = 0.435k_a$ for this molecule, and a correction factor of $1.435k_a/2k_a = 0.72$ is applied to $k_{\text{rel}}^{\text{calcd}}$ for 1-methylcyclohexene, giving a corrected $k_{\text{rel}}^{\text{calcd}} = 0.15$ which is to be compared with $k_{\text{rel}}^{\text{obsd}} = 0.11$. The correction applied to $k_{\text{rel}}^{\text{calcd}}$ for 1,2-dimethylcyclohexene is equal to $0.87k_a/2k_a = 0.43$ and gives a corrected $k_{\text{rel}}^{\text{calcd}} = 0.018$, which is to be compared with $k_{\text{rel}}^{\text{obsd}} = 0.012$.

Entries no. 6-8 in Table V show that 1-substituted cyclohexenes (A) are about 50% more reactive than the corresponding 4,4-dimethyl-1-substituted cyclohexenes (B). This reduction of reactivities of alkenes B relative to alkenes A may originate in part from a hindered approach of diimide past the axial C-4 methyl

group in the former; however, in view of the dissimilar values of k_a/k_b (equal to *trans/cis* product) for no. 10-13 of Table V and the practically identical relative rate values for no. 6-8, it is most likely that other factors are involved also. Slight deformations from the ideal chair conformations of the 4,4-dimethylcyclohexene rings may account for the small reactivity differences discussed above, although large deformations leading to boat or twisted boat ring conformations are not considered likely as k_A/k_B values would be expected to be considerably less than one.

9. Summary

Diimide reductions of alkenes exhibit a high degree of selectivity—bicyclo[2.2.1]heptene and 1-pentene being more reactive than 1,2-dimethylcyclohexene by factors of about 38,000 and 1900, respectively. The close correspondence between calculated and observed relative rates that is observed for the cyclic, acyclic, and exocyclic alkenes leads to the conclusion that alkene reactivities are dominated by a combination of torsional strain (E_φ), bond angle bending strain (E_ω), and α -alkyl substituent (E_ψ) effects. Steric effects appear not to make important contributions to relative reactivity differences.

Cyclohexene confined to the boat conformation (bicyclo[2.2.2]octene) is predicted and found to be over an order of magnitude more reactive toward diimide reduction than the chair form of cyclohexene. This reactivity difference may serve as a useful probe for evaluating conformational deformations in cyclohexene ring systems. Bicyclo[2.2.1]heptene is predicted and found to be over two orders of magnitude more reactive than cyclohexene toward reduction by diimide. Comparable relative reactivities may be expected for electrophilic additions to these two molecules and, consequently, their observance should not be interpreted to support the intervention of nonclassical norbornyl carbonion intermediates.⁵⁷ The diimide reductions of bicyclo[2.2.1]heptene, cyclopentene, and cycloheptene through cyclononene are predicted to experience stereotorsional control (stereoselectivities originating from approaches to the olefinic center which lead to *trans*-

(57) H. Kwart and L. J. Miller, *J. Am. Chem. Soc.*, **83**, 4552 (1961).

sition states of different torsional energies); however, additional experiments are necessary to evaluate its importance. Diimide reductions of substituted cyclohexenes are moderately stereoselective in some instances, and the stereoselectivities may derive from stereotorsional controls.

Experimental

Olefins. Unless indicated otherwise, the olefins used were >98% pure as judged by g.l.c. and n.m.r. The majority of the olefins used were obtained from commercial sources and purified, when necessary, by gas chromatography. *cis*-Cyclododecene and *cis*-cyclododecene were supplied by Dr. G. V. Smith (IIT, Chicago). 1,2-Dimethylcyclohexene,⁵⁸ 1-phenyl-4,4-dimethylcyclohexene,⁵⁹ 1-phenyl-4-*t*-butylcyclohexene,⁵⁹ 1-phenylcyclohexene,⁵⁹ 1-methyl-4-*t*-butylcyclohexene,⁶⁰ bicyclo[2.2.2]octene,⁶¹ 2-methylenebicyclo[2.2.1]heptane,⁶² methylenecyclopentane,⁶³ methylenecycloheptane,⁶⁴ methylenecyclooctane,⁶⁴ 4-*t*-butylcyclohexene,⁶⁵ and *cis*-cyclononene⁶⁶ were prepared following directions given in the literature and purified further, when necessary, by gas chromatography.

1-*t*-Butylcyclopentene, 1-*t*-butylcyclohexene,⁶⁷ 1-*t*-butylcycloheptene, 1-*t*-butyl-4-methylcyclohexene, 1-*t*-butyl-4,4-dimethylcyclohexene, and 1,4-di-*t*-butylcyclohexene were synthesized by distillation of the tertiary carbinols, prepared from the appropriate Grignard reaction, from sodium hydrogen sulfate⁶⁷ under reduced pressure. The products were purified by liquid adsorption chromatography on silica gel followed by fractional distillation and finally by gas chromatography. The over-all yields rarely exceeded 5%. The n.m.r. spectra of the purified alkenes exhibited single vinyl-*t*-butyl proton resonances at τ 8.95–9.00 and were void of any detectable isomeric or other impurities (aliphatic *t*-butyl proton resonances are generally found at τ >9.10). 1,5-Di-*t*-butylcyclohexene and *cis*-3,5-di-*t*-butylcyclohexene will be described in detail elsewhere.

(58) S. Siegel and G. V. Smith, *J. Am. Chem. Soc.*, **82**, 6082, 6087 (1960).

(59) E. W. Garbisch, Jr., *J. Org. Chem.*, **27**, 4243 (1962).

(60) S. Siegel and B. Dmuchovsky, *J. Am. Chem. Soc.*, **84**, 3132 (1962).

(61) J. Hine, J. A. Brown, L. H. Zalkow, W. E. Gorden, and M. Hine, *ibid.*, **77**, 594 (1955).

(62) O. Diels and K. Alder, *Ann.*, **470**, 62 (1929).

(63) R. T. Arnole, R. W. Amidon, and R. M. Dodson, *J. Am. Chem. Soc.*, **72**, 2871 (1950). This procedure lead to a mixture of 87% of methylenecyclopentane and 13% of 1-methylcyclopentene.

(64) M. Vilkas and N. A. Abraham, *Bull. soc. chim. France*, 1196 (1960).

(65) S. Winstein and N. J. Holness, *J. Am. Chem. Soc.*, **77**, 5562 (1955).

(66) A. C. Cope, P. T. Moore, and W. R. Moore, *ibid.*, **82**, 1744 (1960).

(67) R. Filler, B. R. Camara, and S. M. Nagvi, *ibid.*, **81**, 658 (1959).

Competitive Reductions. Reaction solutions consisting of *p*-toluenesulfonylhydrazine (*ca.* 0.1 g.), triethylamine (*ca.* 0.1 g.), 1.0 ml. of diglyme,⁶⁸ and two alkenes (*ca.* 0.02 g. each) were sealed in 8 mm. \times *ca.* 15 cm. Pyrex tubes (changing the length of the tubes did not lead to variant relative rates with the more volatile alkenes). The tubes were suspended in refluxing reagent grade benzene for 16–24 hr. and then removed, cooled in Dry Ice–acetone, and opened carefully. The contents were poured into *ca.* 1.0 ml. of *n*-pentane (99%) and the pentane extracts were washed with 5% sulfuric acid, 5% sodium hydroxide, and finally with water. The extracts were dried with Linde-3A Molecular Sieves and then analyzed by gas chromatography utilizing a 15-ft. QF-1, or a 5- or 7-ft. silver nitrate–benzyl cyanide (20% on 60/80 mesh firebrick) column. In those instances where the *n*-pentane interfered with the product analyses, other solvents such as benzene and toluene were employed. Peak areas were determined by planimeter integration and were taken as being proportional to molar concentrations. Calibrations of many of the alkene–alkane pairs showed that in only several instances were small corrections necessary. Relative rates, then, are given by eq. 7. In general two or more runs were made on each olefin pair and the average of the results is shown in Tables III–V. The average error, with few exceptions, is less than $\pm 5\%$ of the values reported. Relative rates in Table III given for *cis*- and *trans*-2-pentene were determined on a mixture of 74% *cis* and 26% *trans* isomers. Relative rates reported for methylenecyclopentane and methylenecyclooctane were determined on mixtures containing 12.7 and 7.8% of 1-methylcyclopentene and 1-methylcyclooctene, respectively.

Characterizations of the *cis*- and *trans*-disubstituted cyclohexanes (Table V) were accomplished by palladium-catalyzed equilibrations, at elevated temperatures, of the hydrocarbon mixtures resulting from catalytic (Pt) hydrogenations of the alkenes. The isomer predominating at equilibrium was taken as being the *trans*-1,4- (or *cis*-1,3-) disubstituted cyclohexane. Characterization of the *cis*- and *trans*-1,2-dimethylcyclohexanes was accomplished by catalytic hydrogenations of 1, 2-dimethylcyclohexene under conditions that are known to give mixtures consisting of predominantly *trans*- or predominantly *cis*-1,2-dimethylcyclohexanes.⁶⁸

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(68) H. C. Brown and G. Zweifel, *ibid.*, **83**, 1241 (1961).