

Possible Criteria for Distinguishing between Cyclic and Acyclic Activated Complexes and among Cyclic Activated Complexes in Addition Reactions¹

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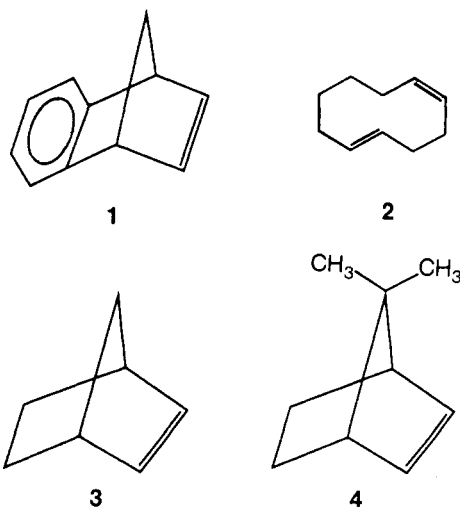
I. Introduction

One of the principal objectives of studying the kinetics and mechanisms of chemical reactions is to acquire relevant data in order to definitively describe the structures and properties of transient intermediates and of *activated complexes* or *transition states*.² Many theoretical calculations and ingenious experiments have been devised and performed in elegant attempts to elucidate the nature of these short-lived species.³⁻²¹ Some of the more recent and more valuable approaches toward elucidating the finer structural details of activated complexes include the "Hammond postulate",³ the kinetic isotope effects studies of Streitwieser,⁴ Swain and Thornton,^{5,6} and Wiberg,⁷ the Haberfield's^{8,21} enthalpies of transfer method from one solvent to another for estimating substituent effects, the determination of absolute thermody-

namic properties by Robertson and coworkers,⁹ the calculations of Kurz and coworkers^{10,11} for acid- and base-catalyzed reactions, the set of symmetry based selection rules (Woodward-Hoffmann rules),^{12,18} the Zimmerman^{13,19,20} topological approach to orbital levels of the transition state, and various molecular orbital calculations.¹⁴⁻¹⁶

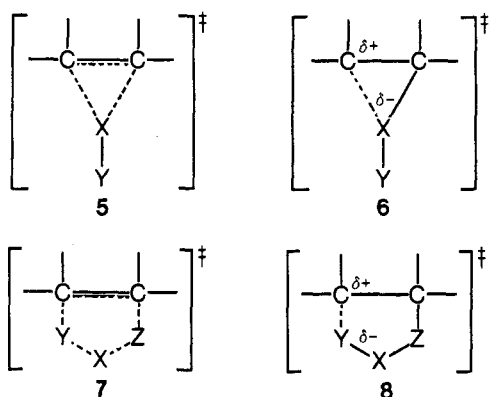
During this current period of refinement of several potentially viable quantitative and semiquantitative models for describing activated complexes and transition states, several qualitative descriptions of these transient species have been postulated. One of the more promising qualitative descriptions, which is based on a comparison of the ratios of relative rates and/or equilibrium constants of selected unsaturated systems, provides possible criteria for distinguishing between cyclic and acyclic activated complexes and for differentiating among the sizes of cyclic activated complexes in electrophilic addition and 1,3-dipolar cycloaddition (2 + 3) reactions of simple alkenes, cycloalkenes, and styrenes.

Several investigations indicate that kinetic and product studies of electrophilic and 1,3-dipolar cycloaddition reactions to certain mono-, bi-, and tricyclic olefins, e.g., benzonorbornadiene (1),²² *cis,trans*-1,5-cyclodecadiene (2),²³ norbornene (3), bicyclo[2.2.1]hept-2-ene,²⁴ 7,7-dimethylnorbornene (4, 7,7-dimethylbicyclo[2.2.1]hept-2-ene),²⁴ can provide a valuable probe for distinguishing between cyclic and noncyclic processes. Also, several inferences concerning symmetrical



and unsymmetrical three-membered and five-membered cyclic activated complexes (5-8) have been deduced from selected comparative rate studies of electrophilic addition and 1,3-dipolar cycloaddition reactions involving cyclopentene, cyclohexene, and 3.²⁵⁻³⁸

The relative reactivities of cyclopentene and 3 with respect to cyclohexene in reactions postulated to proceed via three-



membered cyclic activated complexes are 1.2–4.1 and 1.2–17.0, respectively. For reactions involving four-, five-, and six-membered cyclic activated complexes, the relative reactivities of cyclopentene and **3** with respect to cyclohexene are generally 9.1–110 and 450–8000, respectively.^{25,28,30}

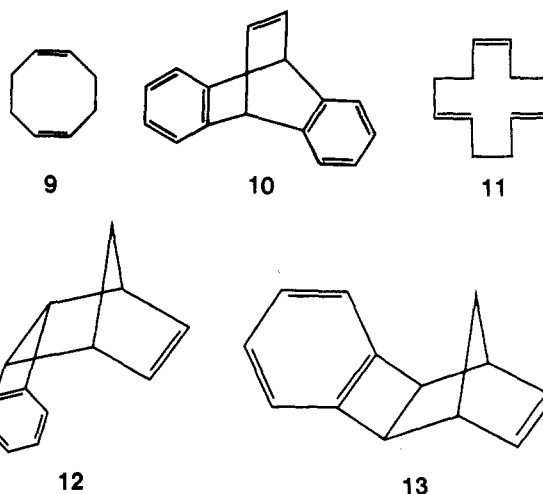
In order to ascertain whether or not a qualitative comparison of the relative reactivities of cyclopentene and **3** with respect to cyclohexene, and other relative reactivity data, can be used in connection with the principles of modern physical organic chemistry to differentiate between cyclic and acyclic activated complexes and among symmetrical and/or unsymmetrical three-, four-, five-, and six-membered cyclic activated complexes, this article will summarize and analyze the most recent kinetic, equilibrium, stereochemical, and product data for electrophilic addition and 1,3-dipolar cycloaddition reactions of simple alkenes, cycloalkenes, polycycloalkenes, and styrenes. Also, in order to present a more complete mechanistic picture, heretofore unreported relationships between ionization potentials and rates and equilibrium constants of electrophilic addition and 1,3-dipolar cycloaddition reactions are examined. Analyses of these data have led to the formulation of the criteria described below. It is hoped that this qualitative evaluation of recent relative rate data in electrophilic addition and 1,3-dipolar cycloaddition reactions of carbon-carbon double bonds will lead to new chemical insights and to new correlations concerning the postulated mechanisms.

The scope of this review, which covers the available literature through 1973, requires a very concise presentation and discussion of each reaction. However, excellent comprehensive reviews on electrophilic addition^{40–51} and 1,3-dipolar cycloaddition reactions^{37,52–55} are available for experimental procedures and additional mechanistic inferences. The discussion will consider the available kinetic and mechanistic data for some electrophilic addition reactions which are postulated to proceed via carbocations, radicals, and three-, four-, five-, and six-membered cyclic activated complexes.

II. Criteria

In attempting to describe the properties of transition states and activated complexes, the scientist encounters what is the ultimate in chemical, mathematical, and physical complexity. Our knowledge of transition states and activated complexes is far from complete and is, in fact, just beginning to accumulate. Although knowledge of reaction mechanisms has grown tremendously over the last 45 years, there is still the need of reliable criteria for obtaining pertinent information concerning the nature of transient species in going from reactants to products. With this objective in mind, the following mechanistic criteria (A–F) are proposed to be used in conjunction with other modern scientific theories for the elucidation of the nature of cyclic and noncyclic activated complexes in electrophilic addition and 1,3-dipolar cycloaddition reactions. After a

brief discussion of the most recent developments in each area of the proposed criteria, they will then be applied to a wide variety of addition reaction of unsaturated hydrocarbons in order to demonstrate their utility. As will be seen below, the rigor with which these relative reactivity rules are obeyed is surprising.



A. Relative reactivities, steric influences, and transannular reactions in monocyclic and polycyclic olefins, e.g., **1–4**, **9–13**.

1. Stereoselective preference for addition.
2. Transannular rearrangements.
3. Relative reactivities of **3** and of **4**.
4. Relative reactivities of cyclopentene and **3** with respect to cyclohexene.

B. Relative reactivities of geometrical isomers.

C. Relative reactivities of 1,1-diphenylethene (**14**) and styrene (**15**).

D. Linear free energy relationships.

E. Molecular orbital theory.

F. Ionization potentials.

As will be shown below, attempts to incorporate the presently available data from secondary deuterium kinetic isotope effects, solvent effects, and thermodynamic parameters (ΔH^\ddagger , ΔS^\ddagger) as part of the mechanistic criteria were not completely successful.

A. Relative Reactivities, Steric Influences, and Transannular Reactions in Monocyclic and Polycyclic Olefins

Two of the intrinsic properties of the norbornene skeleton stem from the extraordinary observations that electrophilic addition reactions occur overwhelmingly on the exo side of the molecule and that appropriately located substituents can play a dominant role in controlling the approach of the electrophile to the double bond. It is generally accepted that a steric factor cannot be the sole governing factor controlling the stereoselective preference shown for exo electrophilic attack on norbornene systems. Indeed, one must also consider, among other factors, the contributions of bridging or rapidly equilibrating classical ions, of bond angle bending, of torsional strain, of nonbonded and transannular effects, of polar effects, and of resonance effects. Fortunately, there are sufficient data available to permit a qualitative understanding of the major factors which contribute to the stereoselective preference and to the reactivity differences among cycloalkenes and bicyclic olefins, and to permit a qualitative mechanistic interpretation and prediction of addition reactions to simple olefinic centers.

TABLE I. Stereochemistry of Additions to Norbornene (3) and 7,7-Dimethylnorbornene (4)⁸⁹

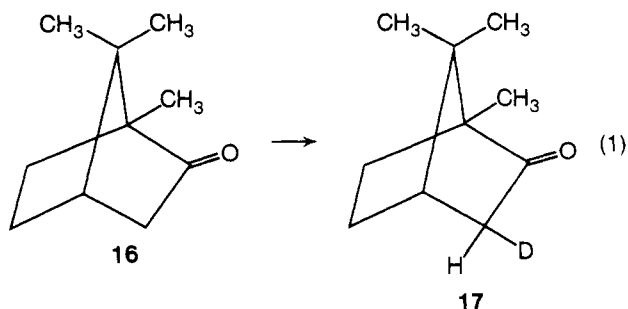
Addend	Proposed size of cyclic activated complex	3		4	
		Exo attack, %	Endo attack, %	Exo attack, %	Endo attack, %
<i>m</i> -Chloroperbenzoic acid	3	99.5	0.5	12	88
Dichlorocarbene	3	~100		NR ^a	
Benzenesulfonyl chloride ⁶⁴	3	~100		4	96
Arenethiosulfonyl chloride	3?	65			50
Silver ion	3	~100		NR ^a	
Hydrogen	4?	90	10	10	90
Nitrosyl chloride	4	~100		NR ^a	
Diborane	4	99.5	0.5	22	78
9-BBN ^b	4	99.5	0.5	3	97
Sulfonyl isocyanate	4?	~100		NR ^a	
Phenyl azide ⁶⁵	5	~100		NR ^a	
Benzonitrile oxide	5	c		34	66
Diphenylnitrilimine	5	d		26	74
Diimide	6	~100		~100	
Mercuric acetate	3?	e		e	
Deuterium chloride	R ⁺	e		e	
Thiophenol ^f	R·	99.5	0.5	95	5

^a No reaction. ^b 9-Borabicyclo[3.3.1]nonane. ^c Addition to 3 is >100 times faster for exo addition than for endo. ^d Addition to 3 is >300 times faster for exo addition than for endo. ^e Addition proceeds to give predominantly exo-cis addition.⁶⁸ ^f The electrostatic and steric interactions between attacking thiyl radicals and several norbornyl systems have been discussed.⁶²

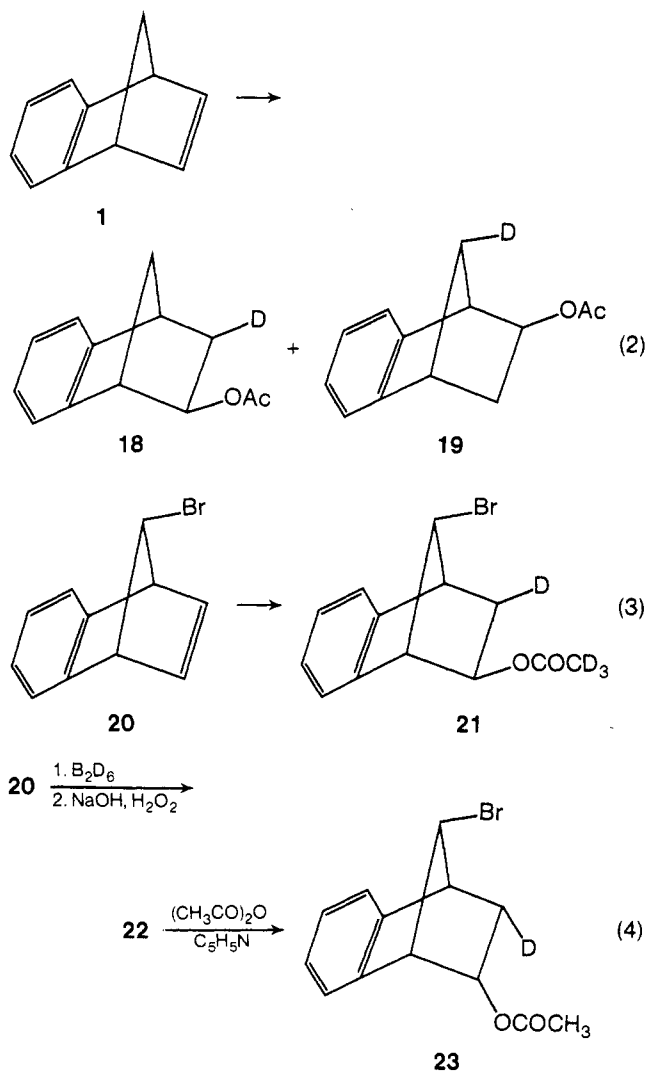
1. Stereoselective Preference for Addition

Brown and coworkers^{39,56-61} have observed that electrophilic addition reactions proceeding through cyclic activated complexes preferentially give exo products with 3 and endo products with 4 (Table I). Presumably, the steric hindrance to exo attack which is exerted by the 7,7-dimethyl groups is comparable to or greater than the steric hindrance to endo attack exerted by the endo-5,6-hydrogen atoms. Thus it is seen from the limited data in Table I that the 7,7-dimethyl groups in 4 reverse the stereochemistry observed with 3. In contrast, this steric control is not noted in reactions which proceed in two stages such as the free-radical addition of thiophenol⁶⁶ and the electrophilic addition of hydrogen chloride.⁵⁶ It is also significant to note from Table I that certain cyclic additions (chlorosulfonyl isocyanate, dichlorocarbene, nitrosyl chloride, phenyl azide, silver ion complexation) occur with 3 but fail with 4. Thus, it can be tentatively concluded from the preliminary data in Table I that: *The 7,7-dimethyl groups in 4 rigorously control the stereoselective preference of electrophiles which add via three- or four-membered cyclic activated complexes. This influence is less rigorous in addition reactions proceeding through five- and six-membered cyclic activated complexes, and in two-stage noncyclic addition processes.*

Other possible examples of the steric influence of norbornene derivatives with groups located at the 7 position include deuterium exchange (eq 1),^{66,67} the sulfuric acid-*d*₂ catalyzed



addition of acetic acid-*d*₄ to benzonorbornadiene (1) and *anti*-7-bromobenzonorbornadiene (20) (eq 2 and 3)^{22,68,69} and the deuterioboration of 20 (eq 4).²² Presumably, the presence of



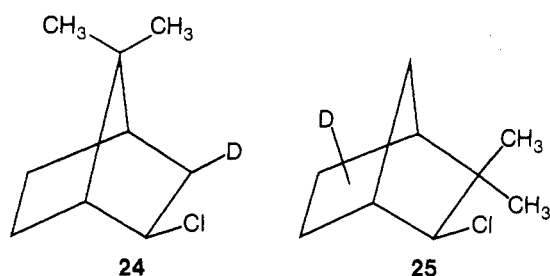
the syn bromine accounts for the stereoselectivity observed in the reactions. The *cis*-exo addition to 20 in eq 3 is compatible with the report of Brown and Liu⁶⁹ that 4 reacts with deuterium chloride to give primarily the *cis*-exo adduct 24 and

TABLE II. Products Resulting from Electrophilic Additions to *cis,cis*-1,5-Cyclooctadiene⁷³

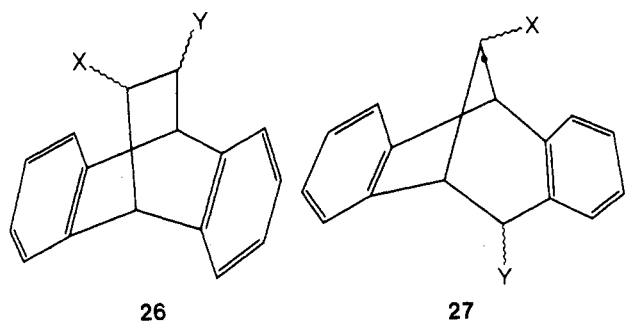
Electrophile	Temp, °C	Solvent	Products	
			1,2-Addition	Bicyclic
HCl	100	CH ₂ Cl ₂	+	—
HBr	—40	CH ₂ Cl ₂	+	—
HI	—20	CH ₂ Cl ₂	+	—
H ₃ PO ₄	150		—	+
HClO ₄	115	CH ₃ CO ₂ H	+	+
HClO ₄	65	CH ₃ OH	+	+
Cl ₂	—30	CH ₂ Cl ₂	+ ^a	+
Cl ₂	0	CH ₃ CN	—	+
Cl ₂	—30	CH ₃ OH	+ ^a	+
2,4-(NO ₂) ₂ C ₆ H ₃ SCl	20	CHCl ₃	+	—
NOCl	—10	Et ₂ O-HCl	+	—
Hg(OAc) ₂	20	CH ₃ CO ₂ H	+	—
Hg(OAc) ₂	20	CH ₃ OH	+	—
INO		CH ₃ OH ⁷⁴	+	—
IN ₃		CH ₃ OH ⁷⁴	+	—
INO ₃		CH ₃ OH ⁷⁴	—	—
I ₂		CH ₃ OH ⁷⁴	—	+
CH ₃ OCH ₂ OCOCH ₃		ClCH ₂ CH ₂ Cl ⁷⁵ (Lewis acid catalysis)	—	+
CH ₃ OCH ₂ Cl		ClCH ₂ CH ₂ Cl ⁷⁵ (Lewis acid catalysis)	—	+
CH ₃ OCH ₂ OCH ₃		ClCH ₂ CH ₂ Cl ⁷⁵ (Lewis acid catalysis)	—	+
HCO ₂ H ⁸¹			—	+
CH ₃ COCI ⁸²			—	+
Br ₂	—30	CH ₂ Cl ₂	+ ^b	—

^a Major product. ^b Free-radical conditions.

10% of the rearranged product **25**. It will be shown below that variable stereochemical results have been obtained from the addition of hydrogen halides to **3**.



The reaction products resulting from dibenzobicyclo[2.2.2]octatriene (**10**) and various reagents can be used to predict whether the reaction involved free radical or ionic processes.⁷⁰⁻⁷² One could predict that radical addition or reactions involving negligible charge development should afford the unrearranged *cis*- or *trans*-disubstituted dibenzobicyclo[2.2.2]octadienes (**26**) and one would expect rearranged

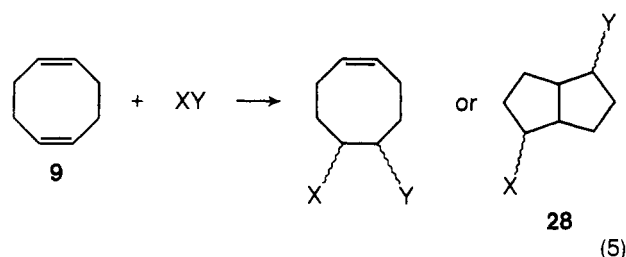


4,8-disubstituted dibenzobicyclo[3.2.1]octadienes (**27**) from reactions involving ionic processes. The high degree of stereoselectivity in the rearrangement will be discussed below.⁷¹

Preliminary studies of electrophilic reactions of *endo*- and *exo*-3,4-benzotricyclo[4.2.1.0^{2,5}]nona-3,7-diene (**12**, **13**) with bromine, chlorine, diborane, and performic acid suggest that rearrangement or lack of rearrangement can be used to differentiate between an ionic or cyclic process.

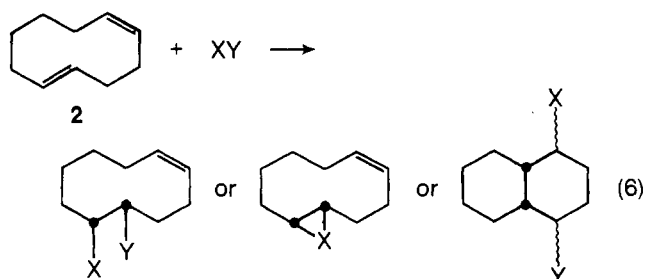
2. Transannular Rearrangements

Carbonium ion solvolyses suggest that unconjugated cyclooctadienes of appropriate configuration and conformation can lead to products resulting from cationic π, π -transannular cyclization. For example, addition of various electrophilic reagents to *cis,cis*-1,5-cyclooctadiene (**9**) can lead to monocyclic products by simple 1,2-addition to one of the double bonds or to bicyclo[3.3.0]octane derivatives (**28**) as a result of transannular π participation.⁷³⁻⁸² Presumably the bicyclic products are formed when cationic species are generated during the reaction. However, Table II clearly shows that transannular cyclizations are very dependent on reaction conditions and that great care must be exercised in generalizing concerning mechanisms based on product studies involving electrophilic additions to **9**. Indeed, a cationic intermediate



formed after the rate-determining step could account for the observed rearranged products.

Preliminary studies^{23,83} indicate that the reactions of *cis,trans*-1,5-cyclodecadiene (**2**) with various electrophiles can be used to distinguish between cyclic and noncyclic processes. A high degree of selectivity for addition to the *trans* double bond in **2** has been observed for reagents which add in one step. In contrast, reagents adding in two stages via radical or ionic mechanisms lead to transannular cycloadditions which yield substituted *cis*-decalins as products. Thus it would appear from the data in Table III that bromine, chlorine, methanesulfonyl chloride, and mercuric acetate react via ionic mechanisms.



Preliminary data also suggest that the reactivity of *cis,trans,trans*-1,5,9-cyclododecatriene (**11**) with electrophiles which add in one stage parallels the reactivity of **2**.⁸⁴⁻⁹¹ Table IV shows that *cis*-addition reactions proceeding via cyclic mechanisms react preferentially with the *trans* double bond in **11**. Similarly, the greater reactivity of the *trans* double bond in cyclononene,^{33,86,92,93} in cyclododecene, and in **2** has been observed with a variety of peroxyacids.^{33,86,92,93} Also, nitro-

TABLE III. Products Resulting from Electrophilic Additions to *cis,trans*-1,5-Cyclodecadiene^{28,83}

Electrophile	Solvent	Ring size of cyclic activated complex	Products	
			1,2-Addition	<i>cis</i> -Decalins
CF ₃ CO ₂ H	CF ₃ CO ₂ H	R ⁺	—	+
H ₂ SO ₄ + CH ₃ CN	CH ₃ CN	R ⁺	—	+
H ₂ SO ₄ + C ₆ H ₅ CN	C ₆ H ₅ CN	R ⁺	—	+
Pb(OAc) ₄	CH ₃ CO ₂ H	R ⁺	—	+
Hg(OAc) ₂	CH ₃ OH	R ⁺ or 3	—	+
Hg(N ₃) ₂	THF-H ₂ O	R ⁺ or 3	—	+
Br ₂	CH ₃ CO ₂ H	R ⁺ or 3	—	+
Br ₂	CCl ₄	R ⁺	—	+
Cl ₂	CCl ₄	R ⁺	—	+
Cl ₂	CCl ₄	R ⁺	—	+
C ₆ H ₅ ICl ₂	CCl ₄	R ⁺	—	+
C ₆ H ₅ ICl ₂	CCl ₄	R ⁺	—	+
CH ₃ SCl	CH ₂ Cl ₂	R ⁺ or 3	—	+
CHBr ₃	CHBr ₃	R ⁺	—	+
CBrCl ₃	CBrCl ₃	R ⁺	—	+
H ₂ C:	(CH ₃ CH ₂) ₂ O	3 ^a	+	—
H ₂ C:	(CH ₃ CH ₂) ₂ O	3 ^b	+	—
Br ₂ C:		3 ^{c,d}	+	—
Cl ₂ C:		3 ^d	+	—
(CH ₃) ₂ C=C:		3 ^e	+	—
<i>m</i> -ClC ₆ H ₄ CO ₂ H	Ethyl acetate	3	+	—
BH ₃	Diglyme	4	+	—
O ₃	CH ₃ CO ₂ H	5	+	—
O ₃	CHCl ₃ or CCl ₄	5 ^f	—	—
N ₂ H ₂	CHCl ₃	6	+	—

^a Generated from diazomethane and copper powder. ^b Generated from methylene iodide and zinc-copper couple. ^c Generated from bromoform and potassium *tert*-butoxide. ^d J. Graefe and M. Muhlstadt, *Tetrahedron Lett.*, 3431 (1969). ^e Generated from lithium 2-ethoxyethoxide and 5,5-dimethyl-*N*-nitrosooxazolidone. ^f Diethylene glycol dimethyl ether. ^g Low molecular weight polymeric ozonides were obtained.

syl chloride and osmium tetroxide add preferentially to the *trans* double bond in cyclododecene.^{33,94}

3. Relative Reactivities of 3 and 4

Preliminary studies suggest that the relative rate of *exo* addition to 3 and 4 is closely related to cyclic or noncyclic nature of the activated complex.^{39,61} The ratio $k_{exo-3}:k_{exo-4}$ is relatively low for additions involving noncyclic activated complexes and is relatively high for additions involving cyclic activated complexes (Table V). Presumably, the relative reactivities are explicable in terms of the steric hindrance resulting from the *syn*-7-methyl group (*vide supra*). In noncyclic processes, the electrophile approaches from the *exo* side at the end of the olefinic bond away from the *syn*-7-methyl group, and in cyclic additions the addend forms a symmetrical bridge with the carbon-carbon double bond under the *syn*-7-methyl group. Consequently, the *syn*-7-methyl group would be expected to exert less steric hindrance on noncyclic additions than on cyclic additions. Of course, the steric requirements of the addend must also be taken into consideration.

In order to contrast the behavior of norbornenes bearing a nonpolar bulky 7-substituent, Baird and Surridge^{97,98} investigated cyclic and noncyclic additions to *syn*- and *anti*-7-*tert*-butylnorbornenes (29 and 30). It was observed that the 7-*tert*-butyl group diminished the reactivity of the *anti* double bond in 30 relative to 3 (Table VI). Presumably nonbonded interactions resulting from the development of repulsive interactions between the *anti*-7-*tert*-butyl group and the *exo,cis*-5,6-hydrogen atoms in the activated complex would retard *exo* attack and favor *endo* addition. It is clearly seen from the limited

TABLE IV. Relative Reactivities of *Cis* and *Trans* Double Bonds in *cis,trans,trans*-1,5,9-Cyclododecatriene⁸⁴

Reagent	Proposed size of cyclic activated complex	Double bond preferentially attacked	
		<i>cis</i>	<i>trans</i>
Br ₂	R ⁺ or 3	+	+
Cl ₂	R ⁺ or 3	+	+
HCl, FeCl ₃	R ⁺	+	+
CH ₃ CO ₂ H, BF ₃	R ⁺	+	+
C ₆ H ₅ CO ₂ H	3	—	+
H ₂ O ₂ , HCO ₂ H	3	—	+
(CH ₃ CH ₂) ₂ BH	4	—	+
NOCl	4	—	+
OsO ₄	5	—	+
KMnO ₄	5	—	+
N ₂ H ₂	5	—	+

TABLE V. Relative Rates of *Exo* Addition to 3 and 4^{39,61,95,96}

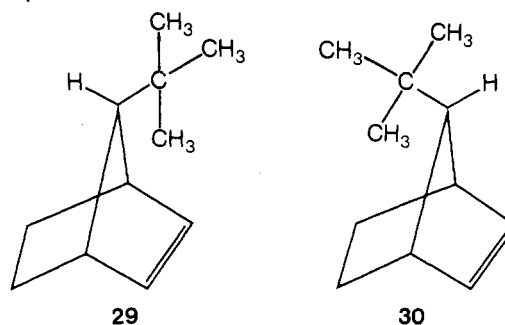
Addend	Proposed size of cyclic activated complex	Rate ratio ^a
HCl	R ⁺	2.2
CH ₃ CO ₂ H	R ⁺	2.8
C ₆ H ₅ SH	R ⁺	30
Hg(OAc) ₂ , H ₂ O	R ⁺ or 3	58
<i>m</i> -ClC ₆ H ₄ CO ₂ H	3	1000
C ₆ H ₅ SCl	3	1820
9-BBN ^b	4	480
N ₂ H ₂	6	950

^a $k_{exo-norbornyl}/k_{7,7-dimethyl-exo-norbornyl}$. ^b 9-Borabicyclo[3.3.1]nonane.

TABLE VI. Relative Rates of Addition to 3 and 30^{97,98}

Reagent	Proposed size of cyclic activated complex	k_3/k_{30}
Hg(OAc) ₂	R ⁺ or 3	5.49
<i>m</i> -ClC ₆ H ₄ CO ₂ H	3	5.16
AgNO ₃	3	2.4
9-BBN	4	3.73
H ₂	4	3.77
N ₂ H ₂	6	1.55

data in Table VI that the relative reactivities of 3 and 30 do not provide a criterion for distinguishing among cyclic activated complexes.



The influence of the *syn*-*tert*-butyl group in 29 is comparable to Brown's results with 4. Although 29 did not react with diimide, silver nitrate, mercuric nitrate, and thiophenol, it reacted with deuterium and 9-BBN to give *endo* products.⁹⁷

The presently available data indicate that relative kinetic studies of nonpolar derivatives of 3, 4, and other norbornenes will provide pertinent information for distinguishing between cyclic and noncyclic addition processes.

4. Relative Reactivities of Cyclopentene and 3 with Respect to Cyclohexene

Heats of hydrogenation show that the double bond in **3** is more strained than that of cyclohexene by about 6 kcal/mol^{80,99-103} (Table VII), and a consideration of torsional strain and bond angle bending strain suggests that cyclopentene and **3** are more strained than cyclohexene by about 3.7 and 9.7 kcal/mol, respectively.³⁵ The latter calculations also suggest that a considerable part of this strain can be alleviated in some cyclic activated complexes leading to cycloalkanes. This is in contrast to cyclohexene which acquires an increase in torsional strain during passage through a similar transition state region. Presumably, relaxation of angular strain in the bicyclic system is a major contributing factor to the high dipolarophilic reactivity of **3** in 1,3-dipolar cycloaddition reactions which proceed via five-membered cyclic activated complexes.^{49,51} Indeed, the higher reactivity of cyclopentene and **3** is also observed in reactions involving four- and six-membered cyclic activated complexes (Table VIII).

In contrast to a significant release of strain in going from an unsaturated system to a four-, five-, or six-membered cyclic activated complex, the transformation of a carbon-carbon double bond in cyclopentene, **3**, or cyclohexene to a considerably strained three-membered cyclic activated complex is not expected to lead to an appreciable relief of strain. Consequently, as seen in Table VIII, the relative reactivities of cyclopentene (0.05-4.1) and **3** (1.0-17) with respect to cyclohexene are generally closer to one for reactions leading to three-membered cyclic activated complexes than for those reactions proceeding via four-, five-, and six-membered cyclic activated complexes (9.4 to 140 for cyclopentene and 4.3 to 8000 for **3**). Thus, this appears to be a very good criterion for distinguishing between three- and five-membered cyclic activated complexes.

B. Relative Reactivities of Geometrical Isomers

Trans isomers are generally more stable than the corresponding cis isomers in alkenes while the reverse is true for medium-size cycloalkenes.⁹⁹⁻¹⁰³ In addition reactions where steric factors are not significant, it is expected that the cis isomer will react faster than the trans isomer. Thus it is seen from Tables IX and X that in addition reactions involving three-membered cyclic activated complexes the cis isomer reacts faster than the corresponding trans isomer while the trans isomer reacts faster in addition reactions proceeding via four-, five-, and six-membered cyclic activated complexes (cf. Table IV).

The higher reactivity of the trans isomer is explicable in terms of van der Waals compression and bond opposition forces. In addition reactions involving the larger cyclic activated complexes the 120° bond angles of the two sp²-hybridized carbon atoms are being transformed to 109.5° bond angles (sp³ hybridization). Although the carbon-carbon bond length is being lengthened (1.34 Å → 1.54 Å), the decrease in bond angles causes increased steric interaction of the eclipsed cis substituents which leads to an increase in the energy of activation and a corresponding decrease in the rate of reaction.

Table IX shows that many of the $k_{cis}:k_{trans}$ values are close to unity and that there are several examples where the ratio is less than unity for reactions proceeding via three-membered cyclic activated complexes. Moreover, it is recognized that this is a very complex question which is difficult to divorce from the steric effects of the substituents of the addends and the extent of perturbation of the alkene during passage through the transition state region. Nevertheless, with very precise and accurate kinetic data it appears that this qualitative criterion can be quite useful.

TABLE VII. Strain Energies of Some Unsaturated Hydrocarbons^{a,80}

Alkene	Strain energy, kcal/mol
Ethene	0.0
Propene	0.0
Methylpropene	0.0
1-Butene	0.87
cis-2-Butene	1.21
trans-2-Butene	0.05
2-Methyl-2-butene	1.60
2,3-Dimethyl-2-butene	4.60
cis-2-Pentene	1.75
trans-2-Pentene	0.90
2-Methyl-2-pentene	1.93
Cyclopentene	6.93
Cyclohexene	2.61
cis-Cycloheptene	7.35
trans-Cycloheptene	27.67
cis-Cyclooctene	8.81
trans-Cyclooctene	17.85
cis-Cyclodecene	11.63
trans-Cyclodecene	11.95
cis,cis-1,5-Cyclooctadiene	13.28
trans,trans-1,5-Cyclooctadiene	27.82
Methylenecyclopentane	8.67
Methylenecyclohexane	2.76
Norbornene	23.62
Bicyclo[2.2.2]octene	15.99

^a Calculated via a force field method using ethene, propene, and methylpropene as the strainless reference compounds.

The greater reactivity of the trans double bond in medium-size cycloalkenes has been demonstrated (vide supra) in the reactions of peroxyacids,^{33,84,86,92,93} iodomethylzinc iodide,¹⁰⁴ potassium permanganate,⁸⁴ nitrosyl chloride,^{84,94} and osmium tetroxide.³³

C. Relative Reactivities of 1,1-Diphenylethene (14) and Styrene (15)

The greater dependence of 1,3-dipolar cycloaddition reactions on steric factors provides another qualitative diagnostic comparison for differentiating between three-membered and five-membered cyclic activated complexes.²⁵ Table XI shows that reactions proceeding via three-membered cyclic activated complexes react faster with **14** than with **15**. It is clearly seen that, in spite of the additional resonance stabilization of the second phenyl group, the steric effects cause a large diminution in rates for reactions proceeding through five-membered cyclic activated complexes.^{25,49} In contrast, stabilization resulting from the extended conjugated system appears to be more favorable in addition reactions involving three-membered cyclic activated complexes.

The rate differences may also be due to the charge density on the benzylic carbon atom (i.e., extent of perturbation of the carbon-carbon double bond). This might explain why this criterion is variable for electrophilic additions and almost constant for 1,3-dipolar cycloadditions in which the increase in positive charge development is probably not that extensive.

D. Linear Free Energy Relationships¹⁰⁸⁻¹¹⁹

The effect of substitution on the benzene ring on the rate or equilibrium constants for reactions is generally correlated by the extrathermodynamic Hammett $\rho\sigma$ equation:¹¹⁵

$$\log k = \log k_0 + \rho\sigma \quad (7)$$

To estimate the relative importance of inductive and reso-

TABLE VIII. Relative Reactivities of Cyclopentene and Bicyclo[2.2.1]hept-2-ene (3) with Respect to Cyclohexene

Electrophile	Proposed size of activated complex	Relative rates	
		Cyclopentene/cyclohexene	3/Cyclohexene
Bromine	3, ^a R ⁺ ^b	1.3, ^{c,170} 3.5, ^{d,32}	13, ^{d,32}
Iodine	3 ^e	0.05, ^{f,162} 0.6, ^{g,310} 0.8 ^{h,313}	1.3 ^{h,313}
Iodine isocyanate	3	2.20 ^{i,j,326,328}	4.40 ^{i,326,328}
Iodine thiocyanate	3	2.1 ^{c,32}	7.1 ^{c,32}
Silver nitrate	3	2.0 ^{k,340}	17 ^{k,340}
2,4-Dinitrobenzenesulfonyl chloride	3	3.3 ^{c,32}	12.9, ^{c,355} 33 ^{c,32}
Dibromocarbene	3	1.25 ^{l,398,399}	
Dimethylethylidenecarbene	3	1.1 ^{m,404}	
Iodomethylzinc iodide	3	1.60 ^{n,408}	1.70 ^{n,408}
Peroxyacids (epoxidation)	3	1.5, ^{o,451} 2.2, ^{p,463} 0.92 ^{q,470}	3.8, ^{q,470} 1.2 ^{r,455}
Molybdenum(V) peroxo compounds	3		1.94 ^{s,33}
Chromic acid	3	1.29 ^{t,30}	5.5 ^{t,30}
Chromyl chloride	3?	4.1 ^{u,27,29,523}	511 ^{u,27,29,523}
Nitrosyl chloride	4	88 ^{v,32}	660 ^{v,32}
Diborane	4	2.4 ^{w,558,559}	
Bis-3-methyl-2-butylborane	4	140 ^{x,y,558,559}	
Triethylamine-di- <i>n</i> -propylborane	4	0.05 ^{z,563}	
Bis-tetra- <i>n</i> -propyldiborane	4	0.05 ^{aa,563}	
Diethylaluminum hydride	4	9.4 ⁸⁸⁹	
Osmium tetroxide	5	21.9 ^{bb,31}	72.3, ^{bb,31} ~320 ^{n,33}
Ozone	5	3.9, ^{cc,31} 4.5 ^{dd,625}	4.3, ^{cc,31} 10 ^{dd,625}
Benzonitrile oxide	5	19 ^{ee,638}	1800 ^{ee,638}
Diphenylnitrilimine	5	~12 ^{ff,646}	248 ^{ff,646}
Phenyl azide	5	57, ^{gg,647} 56 ^{v,649}	5700, ^{gg,647} 6500 ^{v,649}
Picryl azide	5	42 ^{v,649}	8000 ^{v,649}
Diimide	6	15.5 ^{hh,35}	450 ^{hh,35}
Mercuric acetate	3?	0.78 ^{ii,672}	3.7 ^{ii,672}
Mercuric acetate	3?	0.73 ^{jj,670}	1.0 ^{jj,670}
Mercuric acetate (transmercuration)	3?	0.3 ^{kk,670}	800 ^{kk,670}
Mercuric trifluoroacetate	R ⁺		13,158 ^{ll,697}
Trifluoroacetic acid	R ⁺	1.16 ⁷⁶⁸	
Hexachlorocyclopentadiene	6	22 ^{mm}	24 ^{mm}

^a For alkene and cycloalkene systems. ^b For styrenes. ^c Acetic acid solvent. ^d Methyl alcohol solvent. ^e Charge-transfer complex formation. ^f Equilibrium constant of I₂ adsorption using a gas-solid chromatographic technique. ^g Equilibrium constant in acetic acid, 25°. ^h Equilibrium constant (reciprocal mole fraction units) in 2,4,4-trimethylpentane solvent. ⁱ Generated in situ. ^j See Table XXV for rates of preformed solutions. ^k Equilibrium constant in ethylene glycol, 40°. ^l *t*-Butyl alcohol solvent. ^m Generated from 5,5-dimethyl-*N*-nitrosooxalidone and lithium alkoxide. ⁿ Diethyl ether solvent. ^o Peracetic acid in acetic acid. ^p Perlauroic acid in chloroform. ^q Peroxybenzimidic acid (C₆H₅C(=NH)OOH) generated in situ from benzonitrile and alkaline hydrogen peroxide. ^r Perbenzoic acid in chloroform. ^s Methylene chloride solvent. ^t 0.002 M H₂SO₄ in 95% w/w acetic acid in the absence of air and light, 25°. ^u Carbon tetrachloride solvent, 10°. ^v Chloroform solvent. ^w NaBH₄·BF₃ in diglyme, 0°. ^x THF, 0°. ^y Disiamylborane dimer. ^z Temperature range 26.8–28°. ^{aa} Temperature 30°. ^{bb} Pyridine solvent, 25°. ^{cc} Ethyl acetate, –78°. ^{dd} Ethanol, –60°. ^{ee} Diethyl ether, 20°. ^{ff} Boiling benzene solvent. ^{gg} Benzene solvent. ^{hh} Diglyme, 80°. ⁱⁱ 50% (v/v) aqueous THF. ^{jj} Methanol, 25°. ^{kk} Methanol, 50°. ^{ll} Equilibrium constants in THF, 25°. ^{mm} A. S. Bailey and J. E. White, *J. Chem. Soc. B*, 819 (1966).

nance effects in aromatic side-chain reactions in which a partial or fully developed positive charge is capable of direct resonance interaction with the benzene ring, one can use the Brown^{108,116} $\rho^+\sigma^+$ relationship:

$$\log k = \log k_0 + \rho^+\sigma^+ \quad (8)$$

A σ^- parameter has also been proposed for reactions involving unshared electron pairs on an atom next to the benzene ring.^{115,117}

In aliphatic systems the participation of polar effects can be treated by the Taft equation:¹⁰⁷

$$\log k = \log k_0 + \rho^*\sigma^* \quad (9)$$

In order to better understand the influences of structural modifications of reactant molecules, Taft¹⁰⁷ developed a procedure for separating polar, resonance, and steric effects on the rates or equilibrium constants.¹¹⁹ Also, application of multiparameter correlations to the Taft equation has met with some success.^{112–119}

Linear free energy relationships are of great value in summarizing and understanding the influences of molecular struc-

ture on chemical reactivity. The magnitude of ρ depends mainly on the ability of the bridging atom to acquire and stabilize charge in the activated complex and not necessarily on the symmetry of the cyclic structure. However, it is seen in Table XII that ρ (ρ^+) values of 0 to –3 are generally characteristic of reactions postulated to proceed via partially positively charged cyclic activated complexes, while ρ^+ values more negative than –5 generally imply a species resembling a fully developed carbonium ion in the rate-determining step (Table XIII). It is also seen from Table XII that generally there appears to be less charge development in 1,3-dipolar cycloadditions than in electrophilic additions (cf. $k_{14}:k_{15}$).

E. Molecular Orbital Theory

In addition to the molecular orbital approaches to elucidate the nature of activated complexes cited above, some of the more recent reports have been directly concerned with electrophilic addition reactions. For example, an attempt has been made to develop a quantitative electrostatic description of the activated complex for additions to carbon-carbon double bonds according to Markovnikov's rule,¹²³ and extended

TABLE IX. Relative Reactivities between Cis and Trans Alkenes for Reactions Involving Cyclic Activated Complexes

Electrophile	Proposed size of activated complex	$k_{cis}:k_{trans}$				
		2-Butene	2-Pentene	3-Hexene	4-Octene	2-Undecene
Bromine	3	1.54 ^{a,177,213}	1.50 ^{a,177,213}	1.76 ^{a,177} 2.08 ^{b,32}	2.21 ^{a,213} 2.42 ^{b,32}	1.61 ¹⁸⁴
Chlorine	3	1.29 ^{c,267}				
Iodine ^d	3	4.0 ^{e,161} 6.0 ^{e,f,161}	5.2 ^{e,161}			
Iodine thiocyanate	3	1.9 ^{g,32}	2.1 ^{g,32}	1.8 ^{g,32}	2.0 ^{g,32}	
Silver nitrate	3	3.86 ^{h,340,344-347} 3.1 ^{i,343-347}	3.91 ^{h,340,344-347} 3.1 ^{i,343-347}	3.9 ^{h,340}		
2,4-Dinitrobenzenesulfonyl chloride	3	9.1 ^{g,32}	10.0 ^{g,32}	15.1 ^{g,32}	12.3 ^{g,32}	
Methanesulfonyl chloride	3	18.1 ^{j,352}	10.9 ^{j,352}			
Bromocarbene	3	0.93 ^{k,430}				
Chlorocarbene	3	2.0 ^{l,395,396} 0.91 ^{k,430}				
Fluorochlorocarbene	3	1.44 ^{m,418-420}				
Methylchlorocarbene	3	1.42 ^{n,417}				
Phenylchlorocarbene	3	1.85 ^{o,418}				
Dichlorocarbene	3	1.53 ³⁹⁰	1.73 ^{p,390,400}			
2,2-Diphenylcyclopropylidene carbene	3	2.74 ^{q,406}				
Iodomethylzinc iodide	3		2.0 ^{r,409}			
<i>m</i> -Chloroperbenzoic acid	3				2.6 ^{s,463}	1.35 ^{t,489}
Peroxybenzimidic acid	3			1.44 ^{u,470}		
Chromic acid	3	1.5 ^{v,30}				
Chromyl chloride	3		0.98 ^{w,523}			
Nitrosyl chloride	4	0.53 ^{x,y,32}	0.57 ^{x,y,32}	0.53 ^{x,y,32}	0.34 ^{x,y,32}	
Bis-3-methyl-2-butylborane	4	6.0 ^{x,558,558}	7.0 ^{x,558,558}	9.5 ^{x,558,558}		
Monochloroborane	4			2.3 ^{y,577}		
Ozone	5		0.86 ^{aa,625}	0.71 ^{bb,626}	0.88 ^{aa,626} 0.56 ^{bb,626}	
Diimide	6		1.02 ^{cc,25}			
Mercuric acetate	3?		3.29 ^{dd,672}	5.6 ^{bb,30,670,673}	6.7 ^{bb,30,670,673}	4.0 ^{bb,673}
Mercuric acetate (trans-mercuration)	3?				12.5 ^{bb,670}	
Mercuric perchlorate	?	3.41 ^{ee,695}				
Thallium(III) acetate	3?	1.71 ^{ff,713}				
Thallium(III) perchlorate	3?	4.26 ^{gg,714}				
Palladium(II) chloride	4?	1.93 ^{hh,729}				
Trifluoroacetic acid	R ⁺			1.52 ⁷⁵⁸		
Oxygen atom		0.74 ^{769,760}				
Bromine atom		0.94 ⁷⁷³				

^a Methyl alcohol containing 0.2 M NaBr solvent. ^b Methyl alcohol solvent. ^c Neat in the presence of oxygen. ^d Charge-transfer complex formation. ^e Equilibrium constant for I₂ adsorption using a gas-solid chromatograph technique. ^f Ratio for perdeuterated isomers. ^g Acetic acid solvent. ^h Equilibrium constant in ethylene glycol, 40°. ⁱ Equilibrium constant in ethylene glycol, 25°. ^j Hydrocarbon solvent, -70°. ^k Thermolysis of XCH₂N₂, 30°. ^l Methylene chloride and *n*-butyllithium between -35 and -40°. ^m (FCI₂C)₂C=O and K⁺ -O-*t*-Bu, 10°. ⁿ Photolysis of methylchlorodiazirine, 25-30°. ^o Photolysis of phenylchlorodiazirine or C₆H₅CHCl₂ and K⁺ -O-*t*-Bu, -10 to -20°. ^p CHCl₃, K⁺ -O-*t*-Bu, -10 to -20°. ^q Generated from *N*-nitroso-*N*-(2,2-diphenylcyclopropyl)urea and Li⁺ -OCH₂CH₃. ^r Diethyl ether solvent. ^s Comparison between *cis*- and *trans*-2,2,7,7-tetramethyl-4-octene in chloroform solvent. ^t Perbenzoic acid. ^u Formed in situ from benzonitrile and alkaline hydrogen peroxide. ^v 0.002 M H₂SO₄ on 95% acetic acid in the absence of air and light, 25°. ^w Carbon tetrachloride solvent. ^x Chloroform solvent. ^y Similar rates obtained for other olefins in CH₂Cl₂ and ClCH₂CH₂Cl. ^z THF, 0°. ^{aa} Ethanol, -60°. ^{bb} Neat, 0°. ^{cc} Diglyme, 80°. ^{dd} 50% (v/v) aqueous THF. ^{ee} 0.01 M HClO₄, 25°. ^{ff} Aqueous acetic acid. ^{gg} 0.25 M HClO₄. ^{hh} Equilibrium constant for π complex formation.

Hückel molecular orbital calculations have been used in an attempt to delineate the nature of the intermediates and activated complexes formed in a variety of electrophilic addition reactions.^{15,124,125} In spite of the elegant approaches of many of these useful calculations, it is still not possible to present an overall theory that adequately treats a wide variety of electrophilic addition reactions. Although it appears that little effort has been expended on applying molecular orbital theories to electrophilic additions to olefins, it is expected that an all-encompassing mechanism for these reactions will be available in the near future.

F. Ionization Potentials

Ionization potentials (IP) are determined by spectroscopic

(S), photoionization (PI), and electron impact (EI) techniques. Ionization potentials determined by PI or S are generally lower than those determined by EI, and variations in the IP values for the same compounds via the EI method are probably attributable to different interpretations of the ion current vs. electron energy graphs (Table XIV).

The lowest IP of a simple alkene corresponds to the removal of one of the less tightly held π electrons in the double bond.¹²⁶⁻¹²⁹ Alkyl substitution for hydrogen at the center of

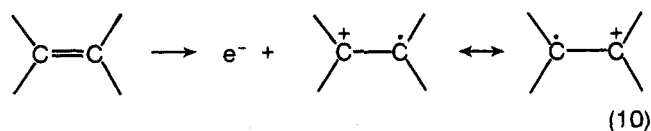


TABLE X. Relative Reactivities between *cis*- and *trans*-Styrenes in Reactions Involving Cyclic and Carbonium Ion Like Activated Complexes

Electrophilic reagent	Size of activated complex	$k_{cis}:k_{trans}$		
		1-Phenyl-propene	1,2-Diphenyl-ethene	2-Phenyl-2-butene
Bromine	R ⁺	0.27 ^{a,178}	1.34 ^{b,178}	4.87 ^{b,187}
		0.72 ^{b,187}	3.0 ²¹⁹	
2,4-Dinitrobenzene-sulfonyl chloride	3	0.47 ^{c,373}	0.59–0.97 ^{e,361}	
		0.19 ^{c,d,370}		
Peracetic acid	3		1.66 ^{e,453}	
Perbenzoic acid	3		2.1 ^{f,453,457}	
Chromic acid	3		0.26 ^{g,30}	
Chromyl chloride	3		1.8 ^{h,25}	
Nitrosyl chloride	4		0.20 ^{i,32}	
Ozone	5		0.074 ^{j,626}	
Diphenylnitrilimine	5		0.04 ^{k,646}	
Mercuric acetate	3?	1.0 ^{l,672}		

^a Methyl alcohol containing 0.2 M NaBr solvent. ^b Acetic acid containing 0.1 M LiBr solvent. ^c 1,1,2,2-Tetrachloroethane solvent. ^d *p*-Methoxy-1-phenylpropenes substrates. ^e Acetic acid solvent. ^f Benzene-diethyl ether solvent. ^g 0.002 M sulfuric acid in 95% w/w acetic acid solvent. ^h Carbon tetrachloride solvent. ⁱ Chloroform solvent. ^j Neat, 0°. ^k Boiling benzene solvent. ^l 50% (v/v) aqueous THF.

unsaturation lowers the IP owing to inductive and hyperconjugative effects. Compatible with the concept of electrophilicity is the expectation that an increase of electron availability at the carbon-carbon double bond should increase the rates of electrophilic addition reactions.^{28,130,131} Good to excellent linear correlations of IP's of unsaturated hydrocarbons with the energies of the highest occupied π -molecular orbitals (HOMO),^{132,133} with the sum of the inductive substituent constants ($\Sigma\sigma_i$),¹²⁶ and with the extended Hammett equation¹³⁴ have been obtained. The influence of structure on IP has been discussed in terms of various molecular orbital theories.^{135,136}

A correlation coefficient (r) of 0.981 is obtained from a plot of IP for 14 olefins against $\Sigma\sigma_i$.¹²⁶ The regression line obtained for the plot is expressed by

$$IP = 10.260 + 11.586\Sigma\sigma_i \quad (11)$$

The slope of the regression line is analogous to ρ_i and is a measure of the sensitivity of the π -bond to the inductive effects of substituents. Experimental IP values are in good agreement with the values calculated from eq 11 or from eq 12,¹²⁶ and it has been suggested that one can use the regression lines (eq 11 and eq 12) to estimate the IP's of olefins for which the experimental values are not known.¹²⁶

$$IP = 6.831 + 3.528HOMO(\beta) \quad (12)$$

Since the IP is closely related to the energy of the highest occupied molecular orbital, it is seen that this criterion is not really different from criterion E (vide supra).

Although numerous examples of linear correlations of the logarithms of rate or equilibrium constants for different series of reactions are well known, there appears to be a dearth of data concerning this potential linear dependence on IP, heats of hydrogenation, strain energies, and spectroscopic excitation energies. In order to help fill this void for IP, tables and graphs are included throughout the discussion. *It should be emphasized that there should not necessarily be a correlation for reactions where disruption of the π system is not rate determining. Indeed, this can be an additional criterion when formation of an "onium" ion is rate limiting. Moreover, those reactions where nucleophilic attack on a reversibly formed π*

TABLE XI. Relative Reactivities of 1,1-Diphenylethene (14) and Styrene (15) in Some Electrophilic Addition Reactions

Electrophile	Ring size of activated complex	k^{a14}/k^{15b}
Bromine	R ⁺	25 ^{c,178}
2,4-Dinitrobenzenesulfonyl chloride	3	0.41 ^{d,32}
Dibromocarbene	3	2.0 ^{e,399}
Dichlorocarbene	3	0.78 ³⁹⁰
Peracetic acid	3	4.3 ^{d,453}
Chromic acid	3	2.2 ^{f,30}
Chromyl chloride	3	12.8 ^{g,25}
Nitrosyl chloride	4	1.55 ^{h,564}
Benzonitrile oxide	5	0.35 ^{i,638}
Diphenylnitrilimine	5	0.07 ^{j,646}
Diphenyldiazomethane	5	0.2 ^{k,654}
C-Phenyl-N-methylnitrone	5	0.08 ⁶⁶²
Diphenylketene	4	0.016 ^{l,m}
Methyl radical	R ⁻	1.9 ^m

^a Rate constant for 1,1-diphenylethene (14). ^b Rate constant for styrene (15). ^c Methanol containing 0.2 M sodium bromide, 25°. ^d Acetic acid solvent. ^e *tert*-Butyl alcohol solvent. ^f 0.002 M H₂SO₄ in 95% acetic acid in the absence of air and light, 25°. ^g Carbon tetrachloride solvent. ^h Chloroform solvent. ⁱ Diethyl ether, 20°. ^j Boiling benzene solvent. ^k *N,N*-Dimethylformamide, 40°. ^l Bromobenzene, 119.96°. ^m J. E. Baldwin and J. A. Kapecki, *J. Am. Chem. Soc.*, **92**, 4868 (1970); *ibid.*, **92**, 4874 (1970).

complex (e.g., oxymetalation) is rate determining should not be controlled by the ground state energy of the olefin.

III. Other Possible Criteria

The following considerations are presented to be used with the above criteria where applicable. They were not included in the proposed criteria because of inadequate theoretical principles, insufficient data, and/or numerous unexplained exceptions.

A. Solvent Effects^{139–147}

The formulation of many reaction mechanisms can be aided by information on the effects of solvents upon the rates, equilibria, and products of reaction. Unfortunately, the scientist's understanding of solvent effects is poor owing to the absence of a satisfactory structural theory for liquids and the lack of a precise molecular model for solvation. However, in spite of these difficulties, several empirical parameters (Table XV) have been developed for estimating solvent polarity in hope of delineating the degree of charge development in the activated complex. Some of these parameters include the dielectric constant, the dipole moment, the Grunwald and Winstein Y values,¹³⁹ the Z scale of Kosower,¹⁴⁰ the E_T scale of Dimroth and coworkers,¹⁴¹ the S values of Brownstein,¹⁴² the F values of Dubois and coworkers,¹⁴³ and the G values of Allerhand and Schleyer.¹⁴⁴

The effects of solvents on equilibria and rates are shown in Table XVI. Development of a small and/or dispersed charge in the activated complex predicts a slight acceleration in rate in more polar solvents for addition of uncharged electrophiles to carbon-carbon double bonds. In reactions where there is substantial charge development in the activated complex, there are large accelerations in rates with increase in solvent polarity.

B. Secondary Deuterium Kinetic Isotope Effects

Secondary deuterium kinetic isotope effects can provide pertinent data concerning the symmetrical or unsymmetrical nature of cyclic activated complexes.^{148–151} These data

TABLE XII. Linear Free Energy Relationships for Electrophilic Addition and Cycloaddition Reactions to Carbon-Carbon Double Bonds

Electrophile	Proposed size of cyclic activated complex	ρ Values		
		Alkenes $\rho^*(r)^a$	Cycloalkenes $\rho^*(r)^a$	Styrenes $\rho^+(r)^a$
Bromine	3, R ⁺	-2.94 (0.988) ^{b, 182} -2.99 (0.966) ^{c, 181} -3.22 ^{c, d, 174, 180, 200}	-2.5 to 5.1 ^{256, 267, 268}	-4.21 (0.988) ^{e, 187} -4.30 (0.993) ^{e, 182} -5.05 ^{c, g, 176, 216, 217} -3.57 ^{d, h, 245} -4.71 ^{e, 188}
Chlorine	3, R ⁺	-4.15 ^{i, 174, 267}		
Iodine thiocyanate	3	-3.42 ^{e, 32}		-2.59 (0.937) ^{e, 32} -3.69 (0.950) ^{e, f, 32}
Silver nitrate	3	-0.93 ^{j, 342}		-0.766 (0.976) ^{f, h, 349, 351}
2,4-Dinitrobenzene-sulfonyl chloride	3	-2.84 ^{e, 286} -1.89 ^{e, 32}	-2.88 ^{e, f, 365, 366}	-2.33 (0.992) ^{e, f, 32} -2.03 (0.978) ^{e, 32} -2.20 (0.999) ^{e, 366} -0.714 ^{e, m, 365, 385} -0.667 (0.956) ^{e, n, 377}
2,4-Dinitrobenzene-sulfonyl bromide	3			1.05 (0.982) ^{f, o, 397}
Cycloheptatrienylidenecarbene	3			
Dichlorocarbene	3	-0.74 ^{p, q, 412} -4.3 ^{r, 400, 402}		-0.378 ^{r, 413} -0.62 ^{s, 401} -3.4 ^{f, t, 404}
Dimethylethylidene-carbene	3			
Ethylzinc carbenoid	3			-1.61 ^{f, u, 407}
Perbenzoic acid	3			-1.2 ^{v, 447} -1.3 ^{f, w, 459}
Chromyl chloride	3?	-2.63 ^{x, 26}	~-2.0 ^{x, 28}	-1.99 ^{x, 26, 27}
Nitrosyl chloride	4	-5.34 ^{w, 32}		-3.84 (0.972) ^{f, v, 32} -2.08 (0.985) ^{y, 32} -0.7 ^{s, 562} -0.5-1.2 ^{f, aa, 565} -0.65 ^{f, aa, 577}
Diborane	4			~0.00 ^{bb, 593c} ~0.00 ^{bb, 593c}
Monochloroborane	4			-0.57(0.72) ^{f, cc, 626} -0.91 ^{f, ff, 626, 636}
Permanganate ion	5	~0.00 ^{bb, 593c}		
Ozone	5	-2.53 ^{cc, 625} +2.60 ^{dd, 626} +3.75 ^{ee, 626}		+0.76 ^{f, aa, 645} +0.8 ^{f, hh, 646}
Benzonitrile oxide	5			
Diphenylnitrilimine	5			
Phenyl azide	5		+0.84 ^{ii, 646} +0.88 ^{ii, jj, 647} 0.90 ^{kk, 647}	+0.90 (0.99) ^{f, ll, 651} +1.3 (1.0) ^{Y, mm, 651} +0.9 ^{f, nn, 662}
Diazomethane	5			
c-Phenyl-N-methyl-nitrone	5			
Mercuric acetate	3?	-1.00 ^{oo, 671}		-2.25 (0.98) ^{f, oo, 680} -1.59 (0.97) ^{oo, 680}
Mercuric perchlorate	?	-3.3 ^{pp, 695}		
Thallium triacetate	?	-4.70 ^{716, 720}		-2.2 ^{oo, 718}

^a Correlation coefficient (r). ^b 70% (w/w) CH₃OH-30% H₂O, 0.2 M NaBr. ^c Methyl alcohol containing 0.2 M NaBr solvent. ^d A variety of ρ^* values have been reported. ^e Acetic acid solvent. ^f Correlated with Hammett σ constants. ^g Bromination of *trans*-stilbenes. ^h Bromination of 1-aryl-1-phenylethenes. ⁱ Neat in the presence of oxygen. ^j Alkenals used as substrates. ^k Water, 25°. ^l Ratio correlated with inductive substituted-2-constant σ_I . ^m Rates of addition of 4-substituted-2-nitrobenzenesulfonyl chlorides to cyclohexene. ⁿ Rates of addition of 4-substituted-2-nitrobenzenesulfonyl bromides to cyclohexene. ^o Generated by photolysis of the sodium salt of 2,4,6-cycloheptatrienone *p*-toluenesulfonylhydrazide in THF. ^p Generated from Cl₂CCO₂Et and NaOMe in pentane. ^q Correlated with σ^+ constants. ^r Generated from CHCl₃ and K⁺O⁻tBu. ^s Generated from C₆H₅HgCCl₃Br in benzene, 80°. ^t Generated from 5,5-dimethyl-N-nitroso-2-oxazolidone and lithium ethoxide. ^u Benzene or *n*-pentane solvent, 24.4°. ^v *trans*-Stilbenes in benzene solvent. ^w Benzene solvent, 20, 30, 40°. ^x Carbon tetrachloride solvent. ^y Chloroform solvent. ^z Diglyme, 20°. ^{aa} THF. ^{bb} Alkenoate and cinnamate ions. ^{cc} Ethanol, -60°. ^{dd} Cis olefins, neat, 0°. ^{ee} Trans olefins, neat, 0°. ^{ff} CCl₄ solvent, 5-25°. ^{gg} Cycloaddition of substituted benzenenitriles to styrene. ^{hh} Boiling benzene solvent. ⁱⁱ Substituted aryl azides added to 3 in ethyl acetate. ^{jj} Benzene solvent. ^{kk} Substituted aryl azides added to cyclopentane. ^{ll} Dioxane solvent. ^{mm} DMF solvent. ⁿⁿ Toluene solvent. ^{oo} Methanol solvent. ^{pp} 0.01 M HClO₄, 25°.

should provide an insight into the differences, if any, between the σ -bond-forming rates during passage through the transition state region. Unfortunately, precise application of these isotope effects is not always clear-cut. Table XVII shows that inverse isotope effects are observed for several electrophilic additions and 1,3-dipolar cycloadditions to carbon-carbon double bonds, and an attempt has been made to correlate kinetic and stereochemical data with the direction and magni-

tude of α -secondary deuterium kinetic isotope effects.^{160, 161}

Unfortunately, in spite of the many theoretical discussions and various detailed molecular orbital calculations, the precise causes of secondary deuterium kinetic isotope effects have not been fully elucidated.^{148, 153} However, the concept of Streitwieser and coworkers¹⁴⁹ suggests that the kinetic isotope effect originates from the zero-point energy differences of the deuterated and protiated molecules in the reac-

TABLE XIII. Reaction Constants (ρ^+) for Some Carbonium Ion Reactions

Reaction	ρ^+	Ref
Bromination of polymethylbenzenes	-10.7	a
Solvolysis of 2-phenyl-2-chloropropanes	-4.30 to -4.54	116
Addition of chlorine to cinnamic acids	-4.01	121
Hydration of styrenes	-3.21 to -4.51	b-e
Solvolysis of benzhydrol chlorides	-4.22	f
Bromination of styrenes	-4.30	122
Solvolysis of benzyltosylates	-6.4	g
Solvolysis of furylmethylcarbinols	-7.5	h
Solvolysis of 1-(2-thienyl)ethyl <i>p</i> -nitrobenzoates	-7.1	i

^a F. Rothenberg, P. Alcais, and J. E. Dubois, *Bull. Chem. Soc. Fr.*, 592 (1971). ^b W. M. Schubert, B. Lamm, and J. R. Keefe, *ibid.*, 86, 4727 (1964). ^c N. C. Deno, F. A. Kish, and H. J. Peterson, *ibid.*, 87, 2157 (1965). ^d W. M. Schubert and J. R. Keefe, *ibid.*, 94, 559 (1972). ^e J. P. Durand, M. Davidson, M. Hellin, and F. Coussemant, *Bull. Soc. Chim. Fr.*, 43, 52 (1956). ^f S. Nishida, *J. Org. Chem.*, 32, 2692 (1967). ^g H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, *J. Am. Chem. Soc.*, 89, 370 (1967). ^h D. S. Noyce and G. V. Kaiser, *J. Org. Chem.*, 34, 1008 (1969). ⁱ D. S. Noyce, C. A. Lipinski, and R. W. Nichols, *ibid.*, 37, 2615 (1972).

tant and activated complex, and that an inverse secondary deuterium kinetic isotope effect is predicted for electrophilic addition reactions in which the carbon-carbon double bond undergoes $sp^2 \rightarrow sp^3$ rehybridization in the rate-determining step.^{148,149} It is also of interest to note that there is considerable ambiguity associated with the probable significance of secondary deuterium kinetic isotope effects in (2 + 2),¹⁵⁵ (2 + 3),¹⁵⁶⁻¹⁵⁸ and (4 + 2)^{157,158} cycloaddition reactions.

C. Entropy of Activation

The entropy of activation (ΔS^\ddagger) is the standard entropy of the activated complex less the standard entropy of the reactants in their ground states. Transition state theory gives the equation

$$k = (kT/h)e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R} \quad (13)$$

which, after taking logarithms, differentiating, and comparing the result with the differential form of the Arrhenius equation (eq 14), shows that

$$d(\ln k)/dT = E_a/RT^2 \quad (14)$$

TABLE XIV. Ionization Potentials of Some Unsaturated Hydrocarbons^a

Unsaturate	Ionization potential, eV				
Ethene	10.48 ^b	10.50 ^c	10.507 ^d	10.515 ^e	10.62 ^f
Propene	9.69 ^c	9.70 ^c	9.73 ^c	9.84 ^f	
Methylpropene	9.17 ^c	9.23 ^c	9.26 ^h	9.35 ^f	
1-Butene	9.58 ^c	9.59 ^c	9.76 ^{f,h}	9.77 ⁱ	
<i>cis</i> -2-Butene	9.12 ^c	9.13 ^c	9.29 ^{f,i}	9.30 ^g	9.34 ^h
<i>trans</i> -2-Butene	9.12 ^c	9.13 ^c	9.24 ^f	9.27 ^{f,h}	
2-Methyl-1-butene	9.12 ^c	9.20 ^h			
3-Methyl-1-butene	9.22 ^f	9.51 ^c	9.52 ^c	9.60 ^h	
2-Methyl-2-butene	8.68 ^c	8.8 ^k	8.85 ^f	8.89 ^h	
2,3-Dimethyl-2-butene	8.30 ^l	8.4 ^m	8.53 ^h	>8.5 ⁿ	
1-Pentene	9.50 ^c	9.66 ^f	9.67 ^h		
<i>cis</i> -2-Pentene	9.11 ^h				
<i>trans</i> -2-Pentene	9.06 ^h				
1-Hexene	9.45 ^l				
1-Heptene	9.54 ^c				
1-Octene	9.43 ^o	9.52 ^f			
1-Decene	9.51 ^c				
2-Methyl-1-pentene	9.076 ^p				
Cyclopentene	9.00 ^c	9.01 ^c	9.09 ⁱ	9.27 ^h	9.3 ^f
Cyclohexene	8.72 ^b	8.945 ^{q-r}	9.18 ^h	9.2 ^{k,m}	9.24 ^f
Cycloheptene	8.81 ^s	8.87 ^u			
<i>cis</i> -Cyclooctene	8.97 ^s	8.82 ⁿ			
<i>trans</i> -Cyclooctene	8.91 ^s				
<i>cis</i> -Cyclononene	8.65 ^s				
<i>trans</i> -Cyclononene	8.73 ^s				
<i>cis</i> -Cyclodecene	8.78 ^s	8.80 ^u			
<i>trans</i> -Cyclodecene	8.74 ^s	8.80 ^u			
<i>cis</i> -Cyclododecene	8.65 ^s				
<i>trans</i> -Cyclododecene	8.70 ^s				
Methylenecyclobutane	9.12 ^r	9.148 ^r	9.160 ^r		
Methylenecyclopentane	8.93 ^r				
Methylenecyclohexane	8.94 ^r	8.984 ^r	8.99 ^r		
Bicyclo[2.2.1]hept-2-ene	8.83 ^v	8.95 ^w	9.05 ^x		
Bicyclo[2.2.2]oct-2-ene	8.97 ^v				
Styrene	8.42 ^v	8.43 ^c	8.47 ^e	8.86 ^t	
2-Phenylpropene	8.35 ^e				

^a Value in bold type used for calculations and for constructing graphs. ^b M. I. Al-Joboury and D. W. Turner, *J. Chem. Soc.*, 4434 (1964). ^c M. J. S. Dewar and S. D. Worley, *J. Chem. Phys.*, 50, 654 (1969). ^d P. G. Wilkinson, *Can. J. Phys.*, 34, 644 (1956). ^e K. Watanabe, T. Nakayama, and J. Mottile, *J. Quant. Spectrosc. Radiat. Transfer.*, 2, 369 (1962). ^f R. E. Honing, *J. Chem. Phys.*, 16, 105 (1948). ^g W. C. Price, *Chem. Rev.*, 41, 257 (1947). ^h J. Collins and F. P. Lossing, *J. Am. Chem. Soc.*, 81, 2064 (1959). ⁱ R. E. Fox and A. Langer, *J. Chem. Phys.*, 18, 460 (1950). ^j S. Oshima, *Bull. Jpn. Petrol. Inst.*, 3, 56 (1961). ^k W. C. Price and W. T. Tuttle, *Proc. Roy. Soc., Ser. A*, 174, 207 (1940). ^l R. Bralsford, P. V. Harris, and W. C. Price, *ibid.*, 258, 459 (1960). ^m J. L. Charlton, C. C. Liao, and P. de Mayo, *J. Am. Chem. Soc.*, 93, 2463 (1971). ⁿ R. J. Cvetanovic, *J. Chem. Phys.*, 30, 19 (1959). ^o D. A. Demeo and M. A. El-Sayed, *ibid.*, 52, 2622 (1970). ^p P. Masclet, D. Grosjean, G. Mouvier, and J. Dubois, *J. Electron. Spectrosc. Relat. Phenom.*, 2, 225 (1973). ^q K. Watanabe, *J. Chem. Phys.*, 26, 542 (1957). ^r D. A. Demeo and A. J. Yencha, *ibid.*, 53, 4536 (1970). ^s H. Remane, J. Graefe, and R. Herzschuh, *Z. Chem.*, 12, 194 (1972). ^t J. D. Morrison and A. J. C. Nicholson, *J. Chem. Phys.*, 20, 1021 (1952). ^u P. Bischof and E. Heilbronner, *Helv. Chim. Acta*, 53, 1677 (1970). ^v N. Bodor, M. J. S. Dewar, and S. D. Worley, *J. Am. Chem. Soc.*, 92, 19 (1970). ^w W. C. Steele, B. H. Jennings, G. L. Botyos, and G. O. Dudek, *J. Org. Chem.*, 30, 2886 (1965). ^x S. Winstein and P. P. Lossing, *J. Am. Chem. Soc.*, 86, 4485 (1964). ^y D. W. Turner, *Adv. Phys. Org. Chem.*, 4, 2 (1966).

TABLE XV. Empirical Measures of Solvent Polarity

Solvent	$\epsilon^{a,b}$	$\mu^{b,c}$	γ^d	Z^e	E_T^f	S^g	$\delta^{h,i}$	$G^{j,k}$	Ω^l	F^m
H ₂ O	78.4		3.493	94.6	63.1	0.1540	23.4			
CH ₃ OH	32.6	2.87 ⁿ	-1.090	83.6	55.5	0.0499	14.45		0.830	0.34
CH ₃ CH ₂ OH	24.3	1.66 ⁿ	-2.03	79.6	51.9	0.0	12.9		0.749	0.25
(CH ₃ CH ₂) ₂ O	4.2	1.15 ⁿ			34.6	-0.277	7.74			0.07
1,4-Dioxane	2.21	0.45			36.0	-0.179	9.73	86		0.10
HCONH ₂	109.45	3.37 ^{o,p}	0.60	83.2	56.6					
HCON(CH ₃) ₂	37.8	3.86 ^{p,q}		68.5	43.8					0.09
Pyridine	12.3	2.37 ^{q,r}		64.0	40.2	-0.1970	10.6	94	0.595	
CH ₃ CN	36.2	3.44 ⁿ		71.3	46.0	-0.1039	11.8	93	0.703	0.16
[(CH ₃) ₂ N] ₃ PO	~30	5.54 ^{p,q}		62.8						
Sulfolane	~44	2.04 ^{p,q}		77.5	44.0					
(CH ₃) ₂ SO	46.6	3.9 ^{p,q}		71.1	45.0					
CS ₂	2.64	0.06 ^{p,q}			32.6	-0.240	10.0	74		
CH ₂ Cl ₂	8.9	1.14		64.2	41.1	-0.179	9.88	100		
CHCl ₃	4.64	1.15 ^{p,q}		63.2	39.2			106		0.08
CCl ₄	2.22	0.00			32.5			69		
C ₆ H ₆	2.27	0.00 ^{n,o,q}		54	34.5			80		-0.05
n-C ₆ H ₁₄	1.89	0.085 ^q			30.9			44		0.00
Cyclohexane	2.023					-0.324	8.18			-0.01
Toluene	2.37	0.31 ^{n,o,q}			33.9	-0.237	8.91	74		
CH ₃ Cl	5.62	1.54 ^{p,q}			37.5					
CH ₃ COCH ₃	20.7	2.69 ⁿ			42.2	-0.1748	9.66			
C ₆ H ₅ COCH ₃		1.82 ^{o,p}			41.3					
CH ₃ CO ₂ H	~6.17	1.68 ^{o,p}	-1.68	79.2						
CF ₃ CO ₂ H	8.32	2.28 ^s	~4.5	~88						
HCO ₂ H	58.5	1.82 ^{o,p}	2.054							
Ethyl acetate	6.02	1.88 ^{o,p}			38.1	-0.210	9.04			

^a Dielectric constant. ^b J. A. Riddick and W. B. Bunger, "Organic Solvents," Vol. II of "Techniques of Organic Chemistry," A. Weissberger, Ed., Wiley-Interscience, New York, N.Y., 1970. ^c Dipole moment. ^d Reference 139. ^e Reference 140. ^f Reference 141. ^g Reference 142. ^h Solubility parameter. ⁱ H. F. Herbrandson and F. R. Neufeld, *J. Org. Chem.*, **31**, 1140 (1966). ^j Solvent shift parameter. ^k Reference 144. ^l J. A. Berson, Z. Hamlet, and W. A. Mueller, *J. Am. Chem. Soc.*, **84**, 297 (1962). ^m Reference 143. ⁿ 20°. ^o 30°. ^p Benzene solvent. ^q 25°. ^r Carbon tetrachloride solvent. ^s Gaseous state, 100°.

TABLE XVI. Effects of Solvents on Rates, Equilibria, and Products in Addition Reactions to Carbon-Carbon Double Bonds

Electrophile	Proposed size of activated complex	Observations
Bromine	3	Solvent effects are very important. ^{164-166,176,179,183,185,186,192,199,201,205,249} Large solvent effects with 1-pentene indicate that the charge-transfer complex probably rearranges unimolecularly. ²⁰⁷
	R ⁺	Rate increases with increased solvent polarity, but there are very complex effects with styrenes. Loss of stereospecificity occurs as solvent polarity increases. ^{185-187,198,204,210,212,223}
Chlorine	3, R ⁺	Results with pentenes infer initial formation of chloronium ion-chloride ion intimate pairs. ²⁷³
2,4-Dinitrobenzenesulfonyl chloride	3	Rates are much faster in polar solvents than nonpolar solvents, ³⁵⁹ and the presence of sodium perchlorate in acetic acid also enhances the reaction rate. ³⁶⁴
Dichlorocarbene	3	Small solvent effects on relative rates. ^{402,437}
Ethylzinc carbenoid	3	Rates are faster in n-pentane than in benzene or ether. ⁴⁰⁷
Peroxyacids (epoxidation)	3	Moderate increase in rates with an increase in solvent polarity. The highest rates are observed in halogenated solvents (CHCl ₃ , CH ₂ Cl ₂ , C ₆ H ₅ Cl) and the slowest rates in solvents capable of intermolecular association (ethers, alcohols). The strength of intermolecular peracid-solvent interaction increases with increasing solvent basicity. ^{455,483-485,487,488} Polarizabilities and steric requirements of solvents may also influence the rate.
Chromyl chloride	3?	Small increase in rates with slight increase in solvent polarity. ²⁵⁻²⁹
Nitrosyl chloride	4	Rates tend to increase slightly with the polarity of the solvent. Unusually slow rates are observed in diethyl ether. ^{32,554}
Osmium tetroxide	5	Rates appear to be faster in diethyl ether than in pyridine. ^{31,33}
1,3-Dipolar cycloadditions	5	Negligible solvent effects. ⁶⁴⁵

The energy of activation (E_a) is given by eq 15. Rewriting eq 13

$$E_a = \Delta H^\ddagger + RT \quad (15)$$

with reference to eq 15, one obtains

$$k = (ekT/h) \exp(-E_a/RT) \exp(\Delta S^\ddagger/R) \quad (16)$$

which simplifies to

$$\frac{\Delta S^\ddagger}{4.576} = \log k - 10.753 - \log T + \frac{E_a}{4.576T} \quad (17)$$

TABLE XVII. Secondary Deuterium Kinetic Isotope Effects for Some Electrophilic Reactions

Electrophile	Proposed size of cyclic deactivated complex	$k_H : k_D$		
Bromine	R ⁺		0.91 ^{a,159}	0.97–1.00 ^{b,160}
Chlorine	3, R ⁺ ?		0.97–1.00 ^{b,160}	
Iodine	3	0.62 ^{c,d,162}	0.77 ^{c,e,162}	0.93 ^{c,f,162}
Silver nitrate	3	0.86 ^{d,341,343}	0.90 ^{e,341,343}	0.89 ^{f,341,343}
2,4-Dinitrobenzene-sulfonyl chloride	3	0.95 ^{b,160}	0.87 ^{g,159}	
Peracetic acid	3	0.91 ^{h,159}		
Osmium tetroxide	5	0.88 ^{i,159}		
Permanganate ion	5	0.88 ^{j,159}	0.76 ^{k,594}	
Ozone	5	0.93 ^{i,159}		
Chromyl chloride	3	0.98 ^{m,15}	0.88 ^{n,25}	
43.4% Perchloric acid	R ⁺	0.98 ^{o,p}	1.03 ^{p,q}	
49.3% Perchloric acid	R ⁺	0.97 ^{p,r}	1.01 ^{p,s}	

^a *trans*-Stilbenes in ether, –78°. ^b α -Deuteriostyrene in dry acetic acid, 40°. ^c Equilibrium constants of I₂ adsorption using a gas solid chromatographic technique. ^d Propene and propene-d₆. ^e *cis*-2-Butene and *cis*-2-butene-d₆. ^f *trans*-2-Butene and *trans*-2-butene-d₆. ^g *trans*-Stilbenes in acetic acid, 25°. ^h *trans*-Stilbenes in chloroform-acetic acid, 29.7°. ⁱ *trans*-Stilbenes in ether, 25°. ^j *trans*-Stilbenes in acetone, –5°. ^k *trans*-Cinnamic acid- α - or β -d in 0.99 M HClO₄, 30°. ^l *trans*-Stilbenes in ethanol, 25°. ^m α -Deuteriostyrene in carbon tetrachloride, 0°. ⁿ β , β -Dideuteriostyrene in carbon tetrachloride, 0°. ^o α -Deuteriostyrene, 25°. ^p W. M. Schubert and B. Lamm, *J. Am. Chem. Soc.*, **88**, 120 (1966). ^q β , β -Dideuteriostyrene, 25°. ^r α -Deuteriostyrene, 10°. ^s β , β -Dideuteriostyrene, 10°.

TABLE XVIII. Enthalpies and Entropies of Activation for Some Electrophilic Reactions Involving Cyclic Activated Complexes

Electrophile	Proposed size of activated complex	ΔH^\ddagger , kcal/mol			$-\Delta S^\ddagger$, eu		
		Alkenes	Cycloalkenes	Styrenes	Alkenes	Cycloalkenes	Styrenes
Bromine	3, R ⁺	6.00–6.96 ^{a,219}	3.5–4.5 ^{b,c,257,266}	12.5–12.8 ^{a,219} 6.1–9.0 ^{a,188}	22.9–25.6 ^{a,219}	21.5–26 ^{b,c,257,266}	21.5–24.1 ^{a,219} 39–42 ^{a,188}
Iodine thiocyanate	3	5.0 ^{a,32}	5.9 ^{a,32}	7.7 ^{a,32}	53 ^{a,32}	46 ^{a,32}	44 ^{a,32}
2,4-Dinitrobenzene-sulfonyl chloride	3	9.0–13.5 ^{a,32}	11.1–12.8 ^{a,32,387}	9.4–16.9 ^{a,b,32,356,361}	29–37 ^{a,32}	23–32.7 ^{a,32,387}	24.4–41.5 ^{a,32,356,361}
2,4-Dinitrobenzene-sulfonyl bromide	3		11.2 ^{a,387}			30.7 ^{a,387}	
Perbenzoic acid	3		12.7–14 ^{c,d,457,476}	14.2 ^{d,457} 14.0–16.6 ^{d,e,457}		24.0 ^{d,457}	24.8 ^{d,457} 21.1–22.8 ^{d,e,457}
Chromyl chloride	3?	5.7–7.2 ^{f,26}	3.21–10.6 ^{f,28}	2.0–9.0 ^{f,28,27}	27.4–40.7 ^{f,26}	23.5–42.7 ^{f,28}	23.8–42.4 ^{f,26,27}
Nitrosyl chloride ^e	4		8.1 ^{g,32,554}	9.1 ^{g,32,554}		43 ^{g,32,554}	37 ^{g,32,554}
Monochloroborane	4	9.2 ^{h,577}					27 ^{h,577}
Permanganate ion	5	4.8–7.5 ^{i,593c}		3.3 ^{j,593c}	24–32 ^{i,593c}		36 ^{j,593c}
Benzonitrile oxide	5			12–14 ^{k,645}			27–29 ^{k,645}
Phenyl azide	5		12.5–14.9 ^{l,48} 15.2 ^l			29.4–34.9 ^{l,48} 29.0 ^{l,647}	
Picryl azide	5	14.2 ^{l,649}	12.3 ^{l,649}	14.0 ^{l,649}	35.5 ^{l,649}	35.5 ^{l,649}	34.2 ^{l,649}
Mercuric perchlorate	?	9.6–12.0 ^{m,695}			3–10 ^{m,695}		
Thallium triacetate	?			7.9 ^{n,718}			41 ^{n,718}

^a Acetic acid solvent. ^b Data for *cis*- and *trans*-stilbene. ^c Includes other peroxyacids. ^d Benzene-diethyl ether solvent. ^e *trans*-Stilbenes. ^f Carbon tetrachloride solvent. ^g Chloroform solvent. ^h THF solvent. ⁱ Alkenoate ions. ^j Cinnamate ion. ^k Substituted benzonitrile oxides. ^l Chloroform solvent. ^m 0.01 M HClO₄. ⁿ Acetic acid solvent.

The rate constant (k) must be based on the second as the unit of time and ΔS^\ddagger has units of cal deg^{–1} mol^{–1} (entropy units, eu). ΔS^\ddagger also depends on the absolute values of the rate constants and on the unit of concentration used for rate constants for reaction order greater than one.

Determination of ΔS^\ddagger involves measurement of the temperature coefficient of the rate constant. In order to obtain meaningful values for small changes in ΔS^\ddagger , one must obtain kinetic data of high precision. For example, a probable 3% error in k_1 and k_2 at a 25–35° temperature interval can lead to a statistical error of ± 2.6 eu in ΔS^\ddagger , and a probable error of 15% can lead to a statistical error of 13 cal mol^{–1} deg^{–1}.

ΔS^\ddagger may be negative or positive depending on the difference in the number and character of the rotational, translational, and vibrational degrees of freedom between activated complex and reactants. A semiempirical generalization about ΔS^\ddagger is that if the activated complex has a high degree of or-

ganization, then the resulting ΔS^\ddagger is large and negative. Electrophilic addition and 1,3-dipolar cycloaddition reactions at the carbon-carbon double bond which proceed via cyclic activated complexes require strict orientation of the reactants in the rate-limiting step. Consequently, many of these reactions are generally characterized by low values for ΔH^\ddagger and large negative ΔS^\ddagger values (Table XVIII).

Table XVIII shows examples where ΔS^\ddagger appears to be more negative for 1,3-dipolar cycloadditions (five-membered cyclic activated complexes) than for electrophilic additions proceeding via three-membered cyclic activated complexes. However, if an average is taken, it is seen that there is no significant difference in $-\Delta S^\ddagger$ for three- and five-membered cyclic addition reactions. However, it is possible that a judicious selection of olefins, electrophiles, and solvents could provide sufficiently accurate ΔS^\ddagger values to distinguish among ring sizes in cyclic processes.

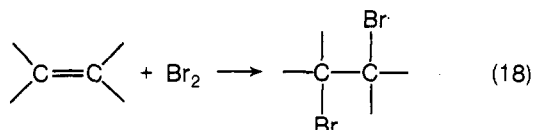
D. Strain Energy

Although it is reasonable to expect the strain energy^{80,99-103} of the olefin to be a significant factor in electrophilic addition reactions to the carbon-carbon double bond, many addition reactions do not parallel the relative ground-state strain energies of the alkene or the relative difference between reactant and product strain energies. However, as with ionization potentials (IP), one might expect a correlation only when the rate-determining step involves disruption of the π system. That is, if there is a rate-limiting attack on a π complex intermediate, one should not expect the rate to be related to the ground state energy of the alkene.

IV. Three-Membered Cyclic Activated Complexes

A. Bromine Addition^{22,32,68,164-266}

Although the exothermic addition of bromine to carbon-carbon double bonds has been studied extensively for many years, the mechanisms have remained somewhat obscure until recently. The kinetics of the electrophilic addition are

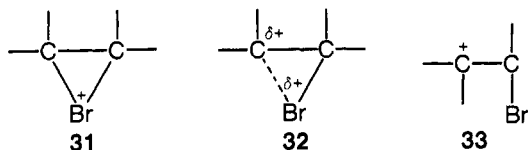


very complex and are generally described (depending on the solvent) by part or all of eq 19 where U represents the unsaturated compound. Consequently, much difficulty has been en-

$$-d[\text{Br}_2]/dt = k_2[\text{Br}_2][\text{U}] + k_3[\text{Br}_2]^2[\text{U}] + k_3'[\text{Br}_2][\text{Br}^-][\text{U}] \quad (19)$$

countered in various kinetic systems in trying to separate the respective rate constants for the contributions of bromide ion, bromine, and tribromide ion.

Until recently it was generally accepted that bromine adds stereospecifically anti to most acyclic and monocyclic alkenes in polar solvents via an intermediate bromonium (bromiranium) ion (31).²⁵¹ This belief has been supported by kinetic, spectroscopic, stereochemical, and thermochemical evidence. However, it is now clear that brominations can show variable stereoselectivity and that the nature of the intermediate is dependent on the structure of the reactant olefin and on the solvent. Also, the intermediate bromonium ion could be strongly bridged (31) or weakly bridged (32). The

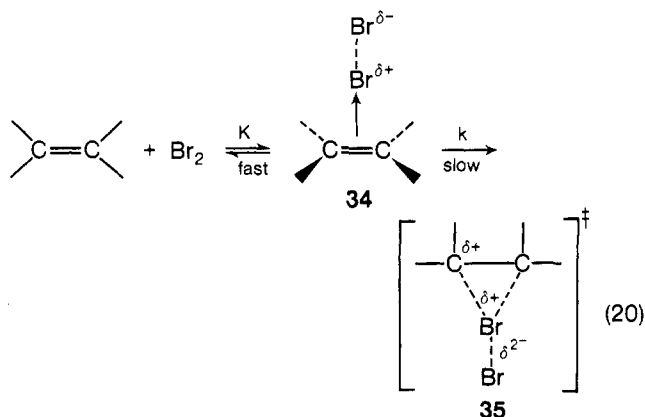


PMR^{169,221,222} and electronic absorption spectra²¹⁴ of some three-membered cyclic bromonium and iodonium (iodiranium) ions from alkenes have been reported under experimental conditions that are different from the kinetic systems generally used for bromination studies.

It has proved difficult to obtain unequivocal kinetic evidence in order to distinguish between an AdE2 and an AdE3 mechanism for the electrophilic addition of bromine to carbon-carbon double bonds. However, it is probable that an AdE2 mechanism is involved with alkenes and more reactive olefins.²⁵⁰ Also, it is difficult to evaluate the importance of bromonium ion structures and of stereochemical studies which only give information about the structure of the product determining intermediates.^{164,165,219} Yates and co-workers,^{164,165,219} using a combined thermochemical-kinetic product study approach, have attempted to assess the impor-

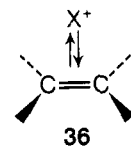
tance of bromonium ions as intermediates and as activated complexes.

The rapid preequilibrium formation of transitory charge transfer complexes (CTC) between alkenes and bromine (34) has been demonstrated (ref 191, 203, 207, 208, 226, 228, 244, 262). Presumably 34 could rearrange to an activated complex resembling 33 or 35. Subsequent formation of the



bromonium ion and/or product determining intermediates would then lead to the observed products.

Extended Hückel calculations for the bromine-ethene system show that the symmetrical intermediate bromonium ion is stable and that little energy is required in going from a symmetrical to an unsymmetrical bromonium ion.^{196,198,209} It has been suggested that the halonium ion intermediate could also be described as a π complex (36) in which the empty valence orbital of the acceptor X^+ forms a dative bond by interaction with the π orbital of the alkene.²⁵¹⁻²⁵⁵



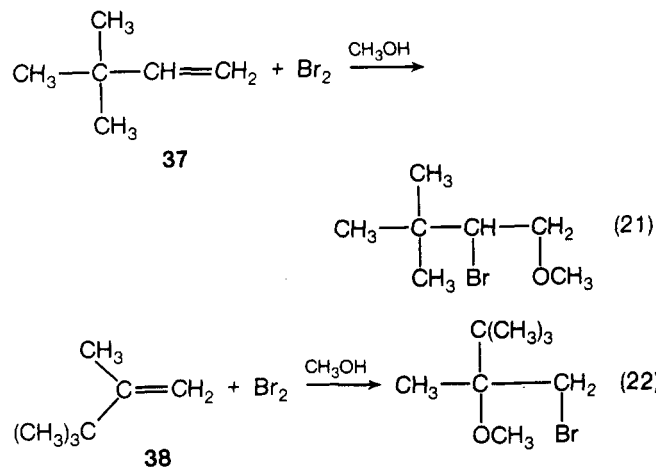
Rolston and Yates^{186,187} have presented evidence for symmetrical bridging, with no solvent incorporation, in the bromonium ions from *cis*- and *trans*-2-butene, and Heublein and coworkers^{211,218} observed that solvation of the cationic intermediates is greater with alkenes than with arylalkenes. Thus it is clear that more data concerning the influence of structures and of solvents on product distribution in the bromination of alkenes are necessary in order to ascertain the influence of solvent on the degree of bromine bridging in bromonium ions.

It can be concluded from the small $k_{\text{cyclohexene}}:k_3$ value (Table VIII), the $k_{\text{cis}}:k_{\text{trans}}$ value greater than one (Table IX), the $k_{14}:k_{15}$ greater than one (Table XI), the ρ^* value of approximately -3 (Table XII), the solvent effects (Table XVI), and the entropy of activation (-22.9 to -25.6 eu) that according to the proposed criteria the activated complex for the addition of bromine to alkenes probably has a close resemblance to 32 or 35.

The ρ^* value of -3 implies a high degree of positive charge localization (approaching carbonium ion character) on the more highly substituted carbon atom in the activated complex. It is also of interest to note that variable ρ^* values have been reported for the bromination of alkenes, and that σ^* and E_s are not independent (ref 174, 181, 182, 184, 204, 213, 220). Thus, it appears that the question for the bromination of alkenes is how the positive charge is distributed between the carbon atom and the bromine atom in the activated complex.

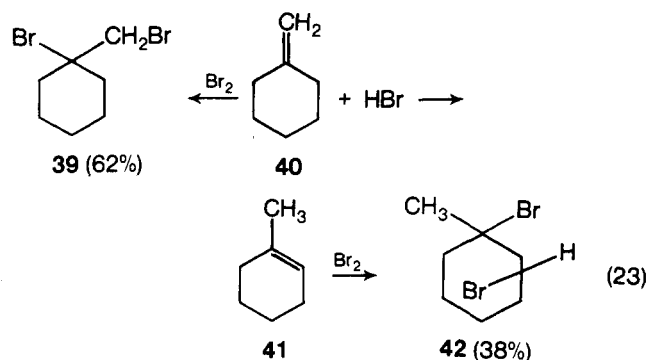
Presumably, bromination of mono-, *cis*-1,2-di-, tri-, and tetrasubstituted olefins¹⁸⁰ involves an activated complex in

which the charge distribution is approximately symmetrical (35), and bromination of *gem*-disubstituted compounds, e.g., methylpropene and 2-methyl-1-butene, involves an activated complex in which the positive charge is displaced toward the more highly substituted carbon atom. These postulates are consistent with the regiospecific anti-Markovnikov addition of bromine to 3,3-dimethyl-1-butene (37), and the regiospecific Markovnikov addition of bromine to 2,3,3-trimethyl-1-butene (38).^{180,186,187,258}



It can be seen from Figure 1 that a good correlation (root mean squared deviation (rms) = 0.3904) is obtained when $\log k_{\text{rel}}$ for the bromination of alkenes (Table XIX) is plotted against ionization potential. This correlation indicates that the effect of alkyl substituents on the π -electron density during passage through the transition state region is primarily an inductive one, and that the slope of the regression line (-2.89) is similar to the reaction constant ($\rho^* = -3.0$) and is a measure of the susceptibility of the π bond to substituent effects (cf. eq 7, 9, and 11) in the rate-determining step.

The addition of bromine to cycloalkenes, which is anti stereospecific, has been thoroughly studied (ref 166, 167, 195, 206, 232, 233, 259). In systems where free-radical brominations at allylic positions compete with bromine addition to the carbon-carbon double bonds, the hydrogen bromide so formed can isomerize the exocyclic cycloalkenes to the corresponding endocyclic cycloalkenes which then can add bromine to yield 2,3-dibromides²³⁴⁻²³⁶ (eq 23).



The cationic nature of the reaction of bromine with cycloalkenes is demonstrated in the transannular products from 2 and from cyclodecene,^{237,243} in the predominant formation of the *cis*-dibromide from cyclooctatetraene,²³⁸ and in the formation of 2,7-dibromobicyclo[2.2.1]heptane from 3.^{239,240-243} Also, addition of bromine to 12 gives a mixture of dibromo derivatives (43, 44). In contrast, addition to 13 to give the normal anti addition product 45.²⁶¹ Additional evidence for the cationic character of the bromination of cycloalkenes is obtained from the bromination of benzonorbornadiene (1) and *anti*-7-bromobenzonorbornadiene (20).^{22,68,263-265} (eq 26).

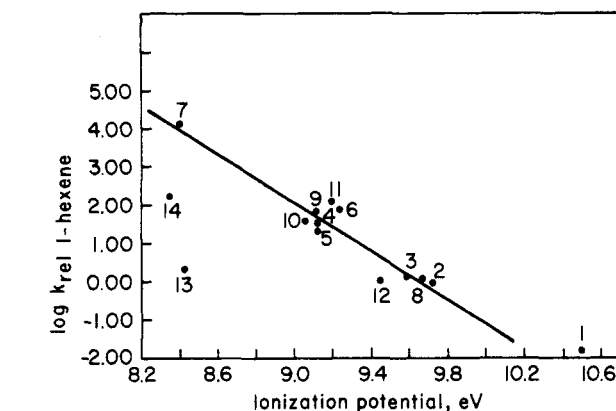
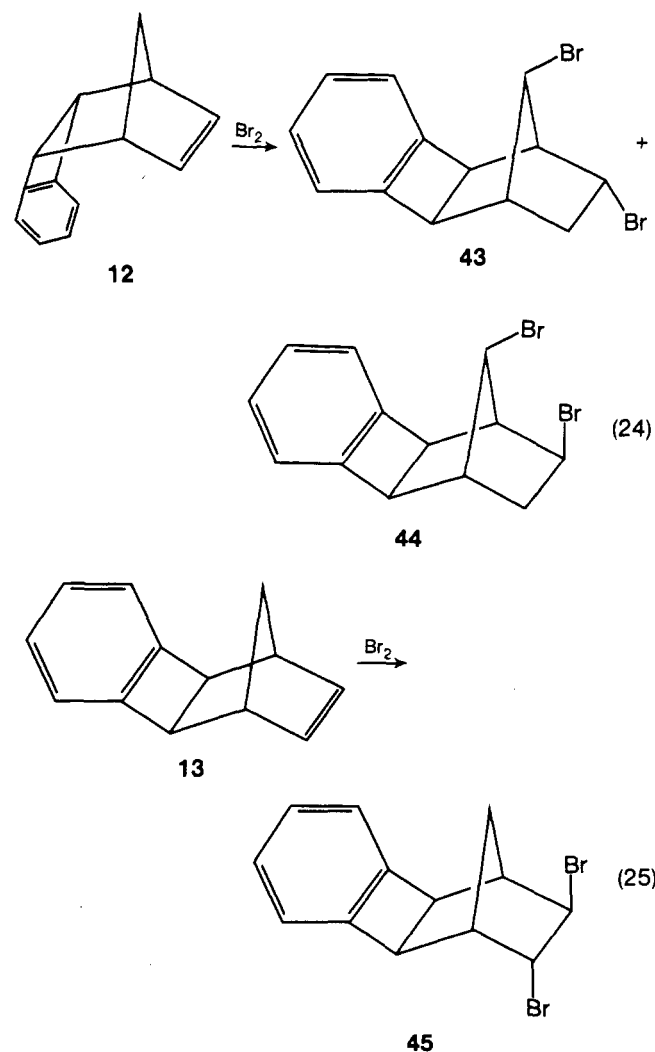


Figure 1. Relation between log relative rates (to 1-hexene) of bromine addition to alkenes and ionization potentials in methanol solvent containing 0.2 M NaBr.^{174,178,213} The slope of points 1-12 = -2.89 , and the root-mean-squared deviation (rms) = 0.3904. The unsaturated compounds for the number points are: (1) ethene, (2) propene, (3) 1-butene, (4) *cis*-2-butene, (5) *trans*-2-butene, (6) methylpropene, (7) 2,3-dimethyl-2-butene, (8) 1-pentene, (9) *cis*-2-pentene, (10) *trans*-2-pentene, (11) 2-methyl-1-butene, (12) 1-hexene, (13) styrene, (14) 2-phenylpropene.



benzonorbornadiene (1) and *anti*-7-bromobenzonorbornadiene (20).^{22,68,263-265} (eq 26).

The $k_{\text{cyclohexene}}:k_{\text{norbornene}}$ value of 13, the ρ^* values of -2.7 , -2.5 , and -3.0 for 1,2-disubstituted cyclopentenones, cyclohexenes, and cycloheptenes, respectively, the small ΔH^\ddagger values, and the large negative ΔS^\ddagger values are consistent with a three-membered cyclic activated complex with

TABLE XIX. Relative Rates of Bromine Addition to Carbon-Carbon Double Bonds in Methyl Alcohol Containing 0.2 M NaBr at 25°

Unsaturate	IP, eV ^a	$k_2 \times 10^{-2}$ l. mol ⁻¹ min ⁻¹	$k_2^b/k_2(1\text{-hexene})^b$	Log ($k_2^b/k_2(1\text{-hexene})^b$)
Ethene	10.50	0.303 ^c	0.015	-1.82
Propene	9.70	18.4 ^d	0.93	-0.03
1-Butene	9.59	29 ^c	1.46	0.16
<i>cis</i> -2-Butene	9.13	787 ^d	39.6	1.60
<i>trans</i> -2-Butene	9.13	508 ^d	25.5	1.41
Methylpropene	9.23	1,640 ^d	82.4	1.92
2,3-Dimethyl-2-butene	8.4	280,000 ^e	14,070	4.15
1-Pentene	9.66	20.9 ^c	1.05	0.02
<i>cis</i> -2-Pentene	9.11	1,260 ^d	63.3	1.80
<i>trans</i> -2-Pentene	9.06	799 ^d	40.2	1.60
2-Methyl-1-butene	9.20	2,680 ^d	134.7	2.13
1-Hexene	9.45	19.9 ^c	1.00	0.00
Styrene	8.42	40.3 ^e	2.03	0.31
2-Phenylpropene	8.35	3,510 ^e	176.4	2.25

^a Ionization potential. ^b Observed second-order rate constant which is probably an undetermined composite of k_2 and k_3' in eq 19. ^c Reference 174. ^d Reference 213. ^e Reference 178.

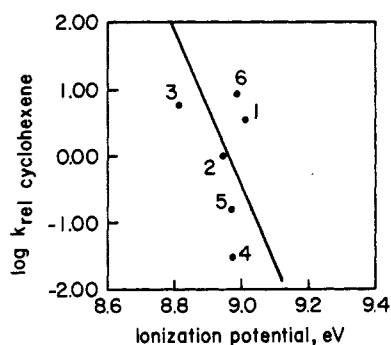
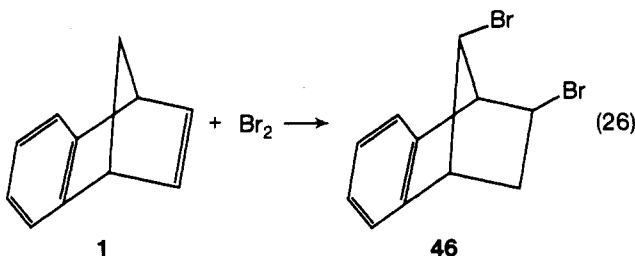


Figure 2. Relation between log relative rates (to cyclohexene) of bromine addition to cycloalkenes in methanol solvent and ionization potentials. The slope = -3.74 (rms = 0.8530). The cycloalkenes for the number points are: (1) cyclopentene, (2) cyclohexene, (3) cycloheptene, (4) *cis*-cyclooctene, (5) bicyclo[2.2.2]oct-2-ene, (6) methylenecyclohexane.



moderate charge development on the carbon atom (47). The ρ^* value of -5.1 for *cis*-cyclooctenes is consistent with a more cationic activated complex which could resemble structure 48.

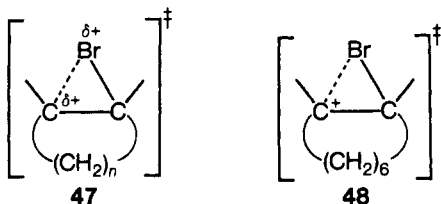


Figure 2 (slope = -3.7, rms = 0.853) shows the plot of log k_{rel} vs. IP for bromine addition to several cycloalkenes (Table XX).³² A slope of -4.58 (rms = 0.786) is obtained from the data of Dubois and Fresnet^{256,257,268} for cyclohexene, cyclopentene, cycloheptene, and *cis*-cyclooctene. If *cis*-cyclooctene is omitted from the latter plot, the slope of the three point line is -1.83 (rms = 0.3828).

TABLE XX. Relative Rates of Bromine Addition to Carbon-Carbon Double Bonds in Methyl Alcohol Solvent^{252,256,267,268}

Unsaturate	IP, eV ^a	$k/k_{\text{cyclohexene}}$	Log $k/k_{\text{cyclohexene}}$
Cyclopentene	9.01	3.5	0.54, ^b 0.77 ^c
Cyclohexene	8.945	1.00	0.00, 0.00 ^{c,d}
Cycloheptene	8.81	5.7	0.76, ^b 0.95 ^c
<i>cis</i> -Cyclooctene	8.97	0.03	-1.52, ^b -1.23 ^c
Bicyclo[2.2.2]oct-2-ene	8.97	0.15	-0.82 ^b
1-Methylcyclohexene		7.3	0.86 ^b
Methylenecyclohexane	8.98	8.6	0.93 ^b

^a Ionization potential. ^b Reference 32. ^c References 256, 257, 266. ^d $k = 0.474$ l. mol⁻¹ min⁻¹.

Bromine addition to ring and side-chain substituted styrenes,¹⁸⁵⁻¹⁸⁷ to triarylpropenes,²²⁴ to *cis*- and *trans*-1-phenylpropene (49, 50),²¹⁰ to *p*-methoxy-*trans*-1-phenylpropene (51),²¹⁰ and to *cis*- and *trans*-stilbene (52, 53)^{168,204,206,223} is nonstereospecific although *trans* addition is favored. The products are dependent on the presence of added salts, solvent polarity, and temperature which suggests the involvement of intimate as well as solvent-separated ion pairs in weakly nucleophilic solvents.^{211,218}

A potentiometric rate study¹⁸⁷ of the bromination of ring- and side-chain methyl-substituted styrenes suggests that the activated complex has a highly unsymmetrical charge distribution with most of the positive charge being located on the benzylic carbon atom. The kinetic study also revealed that 2-phenylpropene (54) is more reactive than 49 or 50, and that there is no simple relationship between the rate of bromine addition and the number of methyl groups (Table X).^{187,188} Also, the nonadditivity of substituent effects in the kinetics for the bromination of 1,1-diphenylethenes has been demonstrated (ref 171, 175, 215, 216, 229, 241, 246, 247), and a dual path addition mechanism has been proposed for the bromination of 52 and 53.¹⁶⁸

The postulate of a carbonium ion-like activated complex (55) for the bromination of styrenes is further supported by the k_{14}/k_{15} value of 25 which is much larger than any of the values in Table XI for reactions proceeding via cyclic activated complexes, and by the ρ values of -4.2 to -5.1 (Tables XII and XII).

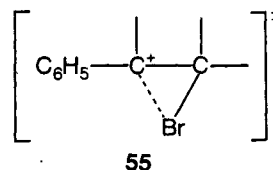


TABLE XXI. Relative Rates of Chlorine Addition to Alkenes in the Presence of Oxygen^{a,267}

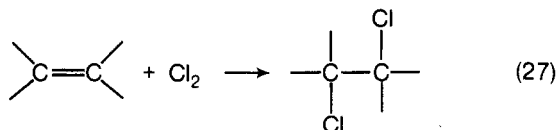
Unsaturate	$k/k_{1\text{-butene}}$	Log $k/k_{1\text{-butene}}$	IP, eV
1-Butene	1.00	0.00	9.59
<i>cis</i> -2-Butene	6.3	1.80	9.13
<i>trans</i> -2-Butene	5.0	1.70	9.13
Methylpropene	5.8	1.76	9.23
2-Methyl-1-butene	160	2.20	9.20
2-Methyl-2-butene	11,000	4.04	8.8
2,3-Dimethyl-2-butene	430,000	5.63	8.40
Cyclohexene	5.0	1.70	8.945

^a Competitive chlorination in mixed olefins as solvent.

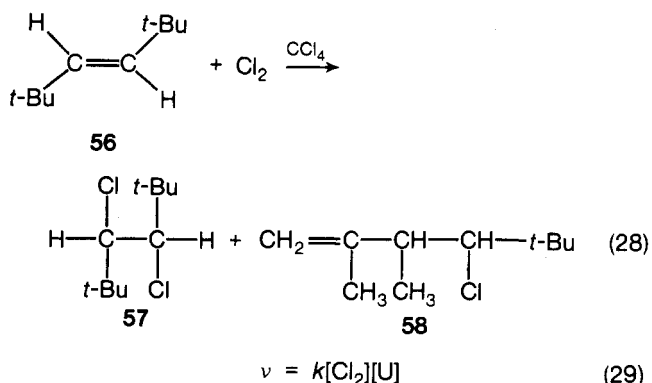
The secondary deuterium kinetic isotope effect for the bromination of *trans*-stilbene (**53**) is 0.91 and of α -deuteriostyrene is 0.97–1.00.^{159,160} It is also seen from Table XVII that other reactions which proceed via carbonium ion mechanisms have k_H/k_D values closer to one than those reactions proceeding via cyclic activated complexes.

B. Chlorine Addition^{73,83,267–308}

The liquid-phase chlorination of unsaturated hydrocarbons, which can occur by both heterolytic and homolytic pathways, has not received the extensive study accorded to bromine addition. Although the mode of reaction is also dependent on the



concentration and structure of the unsaturate, one can isolate the ionic pathway under dark conditions with radical inhibitors.^{270,271} Skeletal rearrangements and allylic chloride formation are competing side reactions in the heterolytic pathway (ref 249, 268, 271, 275, 280–282), and the limited kinetic data are consistent with a bimolecular mechanism (Table XXI, Figure 3).²⁷⁴



Evidence for the formation of transitory charge-transfer complexes between chlorine and alkenes (**59**) has been reported.^{208,271,272} As in bromine addition, and consistent with the observed reaction products, it is reasonable to expect the charge-transfer complex to rearrange to a three-membered cyclic activated complex (**60** or **61**) which subsequently leads to a product-determining chloronium (*chloriranium*) ion or to a fully developed carbonium ion (**62**).

As indicated above, the question of intermediate three-membered halogenonium ions in electrophilic addition reactions to unsaturated hydrocarbons has not been fully resolved. Bromine is considered a better bridging atom than chlorine,^{281,284} and if one assumes that polar solvents stabilize the open carbonium ions from *cis*- or *trans*-stilbene (**52**,

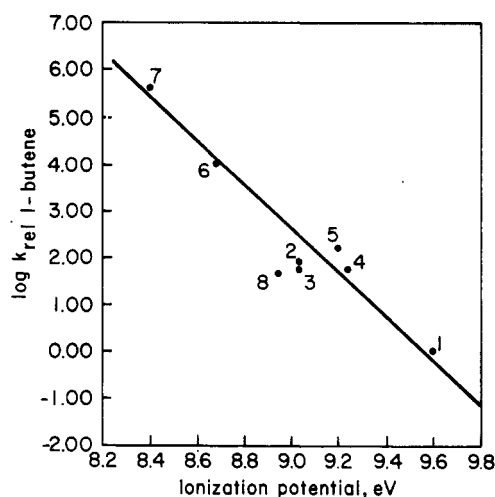
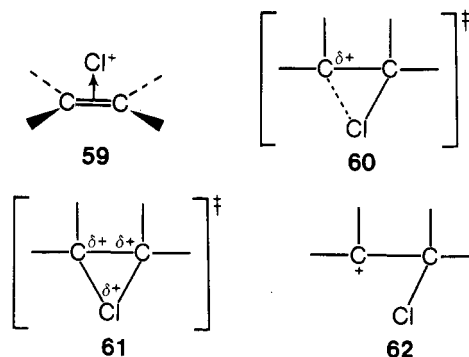
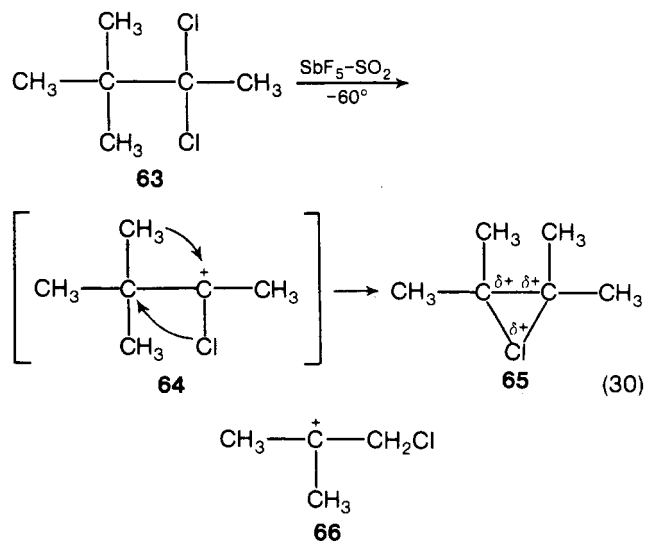


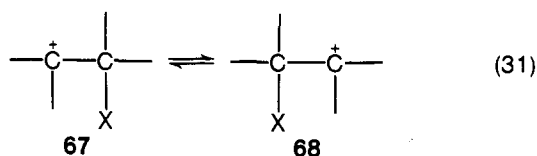
Figure 3. Relation between log relative rates (to 1-butene) of chlorine addition to olefins and ionization potentials. The slope = -4.82 (rms = 0.2876) excluding point 8, and the unsaturated compounds for the number points are: (1) 1-butene, (2) *cis*-2-butene, (3) *trans*-2-butene, (4) methylpropene, (5) 2-methyl-1-butene, (6) 2-methyl-2-butene, (7) 2,3-dimethyl-2-butene, (8) cyclohexene.



53), then the tendency for halogens to form intermediate halonium ions is $\text{Cl}_2 < \text{Br}_2 < \text{I}_2$.¹⁹⁸ Isolation of the bromonium²⁴⁷ and chloronium²⁸⁵ ions of sterically hindered adamantylideneadamantane in carbon tetrachloride at low temperatures has been accomplished. Also, the elegant PMR studies of Olah and Bollinger^{221,222} indicate that the 2,3-dimethyl-2-butene and 2-methyl-2-butene chloronium ions have bridged structures, and that the methylpropene chloronium ion has an open structure (**66**). The concept of three-membered halogenonium ion intermediates is consistent with the *trans* stereospecificity observed in bromine and chlorine addition reac-



tions. This concept assumes that molecular rotation in a halonium carbonium ion is much more rapid than attack by an external nucleophile. However, rapidly equilibrating classical ions such as **67** and **68** could also lead to the observed stere-

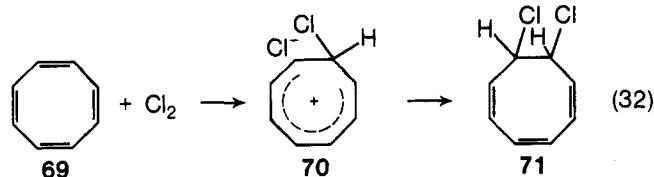


ospecificity. Although there is a need for more systematic studies, the kinetic and stereochemical arguments are strong for bridged halogenonium ions under a variety of experimental conditions.

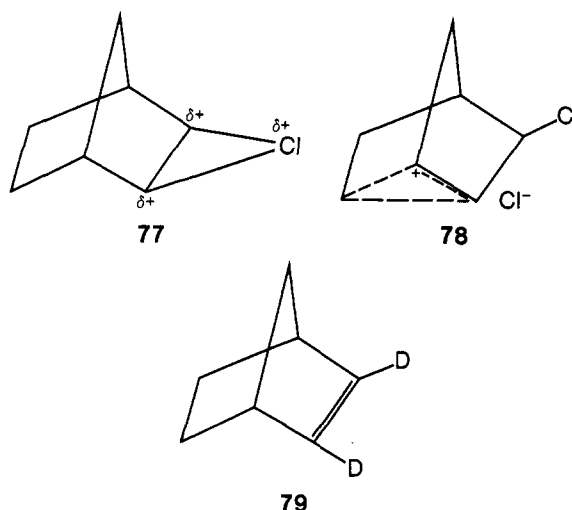
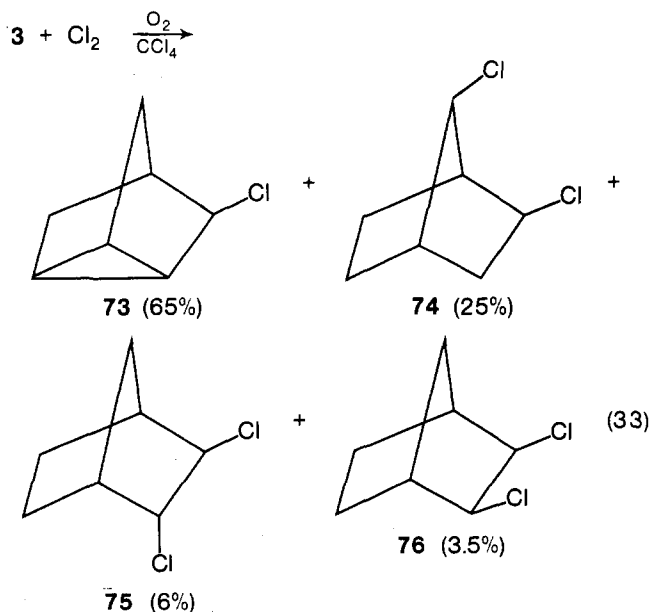
It is of interest to note that chloronium ions formed from alkenes react with benzene²⁸⁶ and with nitriles.^{286,287}

The greater reactivity of *cis* isomers (Table IX) might suggest that chlorine adds to nonconjugated alkenes via a three-membered cyclic activated complex (**60** or **61**). Although the relatively large ρ^* value of -4.15 mitigates against structure **61**, the formation of rearranged products in the chlorination of alkenes suggests that carbonium ion intermediates are formed in the reaction. A plot of $\log k_{\text{rel}}$ vs. IP (Figure 3) gives a slope of -4.82 ($\text{rms} = 0.288$), and alkenes capable of forming relatively stable carbonium ion correlate quite well. These data are consistent with substantial partial positive charge development on the more highly substituted carbon atom.

Chlorine adds stereospecifically (1,2-*cis*) to cyclooctatetraene (**69**) via the homoaromatic 8-chlorohomotropylum ion (**70**) to give **71**.^{288,289} *trans*-1,2-Dichlorocyclooctane (**72**) is



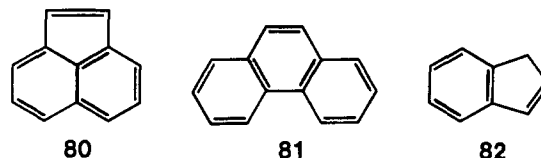
obtained when chlorine is added to *cis*-cyclooctene,²⁹⁰ and the products (**73–76**) which arise from the ionic reaction of chlorine and **3** are explicable by invoking a chloronium ion (**77**) or a nonclassical or rapidly equilibrating pair of classical ions (**78**).^{267,268} Similar results have been obtained from the chlorination of 2,3-dideuteriobicyclo[2.2.1]hept-2-ene (**79**),²⁴² and the chlorination of **2** and **9** in acetonitrile, methyl alcohol,



or methylene chloride gives transannular products in the reaction mixture.^{73,83} Chlorine shows no selectivity in its reaction with **11**⁸⁴ and gives rearranged products on reaction with **10**³⁰⁷ and **12**.²⁶¹ The above data are consistent with the formation of cationic species during the heterolytic chlorination (addition-rearrangement) of cycloalkenes. Owing to the absence of kinetic data concerning the addition of chlorine to cycloalkenes, the proposed mechanistic criteria cannot be applied.

As with alkenes, treatment of styrenes with chlorine can give products resulting from both addition and substitution reactions.^{277,293} The results of the chlorination of **49** and **50** are complicated²⁷⁷ but are compatible with an open carbonium ion intermediate. A systematic investigation of the kinetics, product distributions, and stereochemistry of the chlorine addition to styrenes is in progress.²⁹²

The *cis* and *trans* addition of chlorine to arenes and polyenes has been discussed.²⁹⁴ *Cis* addition of chlorine has been observed with acenaphthylene (**80**),²⁹⁵ phenanthrene (**81**),^{296,297} indene (**82**),²⁹⁸ and cyclooctatetraene.^{288,289}



Depending on the properties of the precursors, different and competing intermediates and activated complexes can be postulated for addition of various chlorinating agents to carbon-carbon double bonds. For example, the pseudohalogen 1-chlorobenzotriazole adds to alkenes by initial electrophilic attack of the chlorine atoms on the double bond,³⁰¹ and the addition of chlorine (using CuCl , 320°) to *cis*- and *trans*-2-butene is largely *trans* owing to competing bridged ion and radical pathways.³⁰³ The reaction of iodobenzene dichloride ($\text{C}_6\text{H}_5\text{ICl}_2$) with **3** proceeds by an ionic or a free radical mechanism.^{249,302} In the presence of oxygen (ionic addition), the product distribution is similar to that from molecular chlorine in acetic acid. In contrast, chloroacetate formation by the direct addition of chlorine acetate to styrenes is less stereoselective and more independent of added acetate ion than by use of chlorine in acetic acid.³⁰⁰ Also, the contributions of chloronium ions, intimate or solvent-separated ion pairs, and open carbonium ions have been reinvestigated in the addition of chlorine to cinnamic acids.^{304–306}

C. Iodine Addition^{32,74,162,169,308–338}

It has been shown, as for bromine addition, that the solvent-dependent kinetics of iodine addition to carbon-carbon

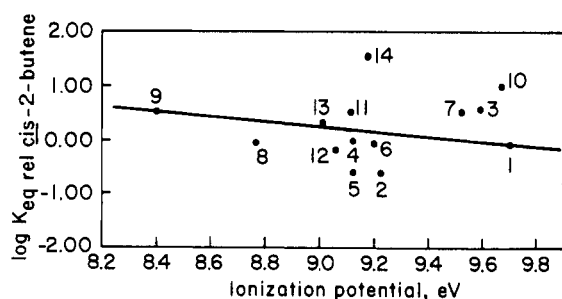
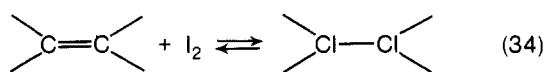


Figure 4. Relation between log relative equilibrium constants (to *cis*-2-butene) for solid iodine to form charge-transfer complexes with alkenes and ionization potentials. The slope = 0.24 (rms = 0.4727) excluding points 13 and 14. The unsaturated compounds for the number points are: (1) propene, (2) methylpropene, (3) 1-butene, (4) *cis*-2-butene, (5) *trans*-2-butene, (6) 2-methyl-1-butene, (7) 3-methyl-1-butene, (8) 2-methyl-2-butene, (9) 2,3-dimethyl-2-butene, (10) 1-pentene, (11) *cis*-2-pentene, (12) *trans*-2-pentene, (13) cyclopentene, (14) cyclohexene.

TABLE XXII. Secondary Deuterium Kinetic Isotope Effects for Complex Formation of Alkenes on a Iodine-Coated Silanized Firebrick Column at 0°¹⁶²

Alkene	$K_{eq\ H}:K_{eq\ D}$	Alkene	$K_{eq\ H}:K_{eq\ D}$
$CH_3CD=CH_2$	0.85	$CD_3CD=CD_2$	0.63
$CH_3CH=CD_2$	0.74	<i>cis</i> - $CD_3CD=CD_2$	0.81
$CH_3CD=CD_2$	0.67	<i>trans</i> - $CD_3CD=CD_2$	0.96
$CD_3CH=CH_2$	1.1		



double bonds is complicated and involves a mobile preequilibrium complex formation (83) step.³⁰⁸⁻³¹⁰ Equilibrium constants for formation of olefin-iodine charge-transfer com-

$$-d[I_2]/dt = k_3[I_2]^2[U] + k_4[I_2]^3[U] \quad (35)$$

plexes have been evaluated by several investigators under diverse experimental conditions and compared with olefin-silver ion systems.^{162,310-313,321} The polar addition of iodine to cyclohexene is overall second order in a variety of solvents, and, curiously, in some chloro solvents the reaction rates appear to decrease with an increase in temperature.³²²

The principal observations in the equilibrium constants (K_{eq}) for adsorption (electron donor-acceptor interactions) of gaseous alkenes on solid iodine deposited on silanized firebrick include the greater complexation with *cis* isomers, an inverse secondary deuterium kinetic isotope effect (Table XXII), an insensitivity to ionization potentials (Tables XXIII, and XXIV; Figures 4 and 5), and a small relative reactivity value of 1.3 between 3 and cyclohexene. These data suggest that a three-membered cyclic activated complex, which probably

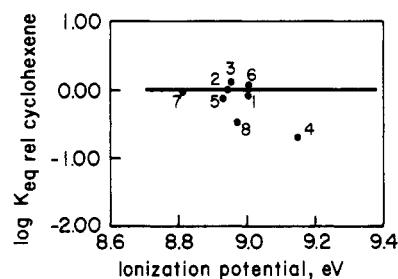
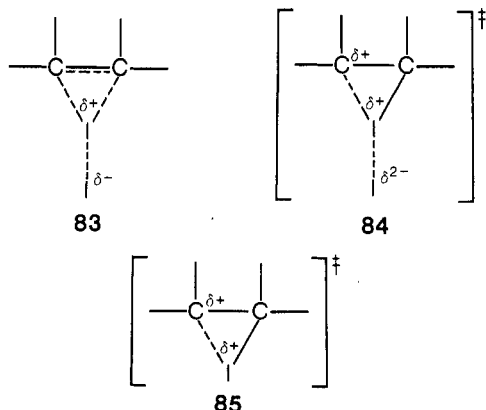


Figure 5. Relation between log relative equilibrium constants (to cyclohexene) for cycloalkene-iodine charge-transfer complex formation and ionization potentials. The slope = -0.16 (rms = 0.1660). The cycloalkenes for the number points are: (1) cyclopentene, (2) cyclohexene, (3) bicyclo[2.2.1]hept-2-ene, (4) methylenecyclobutane, (5) methylenecyclopentane, (6) methylenecyclohexane, (7) cycloheptene, (8) *cis*-cyclooctene.

TABLE XXIII. Relative Equilibrium Constants at 0° for Solid Iodine to Form Charge-Transfer Complexes with Alkenes¹⁶²

Unsaturate	IP, eV ^a	$K_{eq}^b /$ $K_{eq(cis-2-butene)}^b$	$\log K_{eq}^b /$ $\log K_{eq(cis-2-butene)}^b$
Propene	9.70	0.8	-0.097
Propene- <i>d</i> ₆		1.3	0.114
Methylpropene	9.23	0.26	-0.585
1-Butene	9.59	4.2	0.623
<i>cis</i> -2-Butene	9.13	1.0	0.000
<i>cis</i> -2-Butene- <i>d</i> ₃		1.3	0.114
<i>trans</i> -2-Butene	9.13	0.26	-0.585
<i>trans</i> -2-Butene- <i>d</i> ₃		0.28	-0.553
2-Methyl-1-butene	9.20	0.92	-0.036
3-Methyl-1-butene	9.52	3.5	0.544
2-Methyl-2-butene	8.8	1.0	0.000
2,3-Dimethyl-2-butene	8.4	3.5	0.544
1-Pentene	9.66	10.4	1.02
<i>cis</i> -2-Pentene	9.11	3.6	0.556
<i>trans</i> -2-Pentene	9.06	0.69	-0.161
Cyclopentene	9.01	2.1	0.322
Cyclohexene	8.945	41	1.61
Cycloheptene	8.81	7.0	0.845

^a Ionization potential. ^b Equilibrium constant of adsorption of gaseous olefin molecules on solid iodine deposited on a Chromosorb P, AW, DMCS column.

TABLE XXIV. Relative Equilibrium Constants for Iodine Charge Transfer Complex Formation with Endocyclic and Exocyclic Cycloalkenes⁸¹³

Cycloalkene	IP, eV ^a	$K_{eq}^b /$ $K_{eq(cyclohexene)}^b$	$\log K_{eq}^b /$ $\log K_{eq(cyclohexene)}^b$
Cyclopentene	9.01	2.80	0.85
Cyclohexene	8.945	3.30	1.00
Cycloheptene	8.81	3.05	0.92
<i>cis</i> -Cyclooctene	8.97	1.09	0.33
Bicyclo[2.2.1]hept-2-ene	8.95	4.33 ^c	1.31
Methylenecyclobutane	9.15	2.78	0.84
Methylenecyclopentane	8.93	2.61	0.79
Methylenecyclohexane	8.98	3.65	1.10
Methylenecycloheptane		2.67	0.81

^a Ionization potential. ^b Equilibrium constant (reciprocal mole fraction units) in 2,2,4-trimethylpentane, 25°. ^c Single determination.

has a close resemblance to 84 or 85, is involved in the electrophilic addition of iodine to carbon-carbon double bonds.

Although it is difficult to delineate all the factors which contribute to the pronounced inverse secondary deuterium kinetic isotope effects and the absence of a β -isotope effect with $CD_3CH=CH_2$, some characteristics of alkene-iodine complexation are similar to charge-transfer complex formation in alkene-silver ion systems.¹⁶²

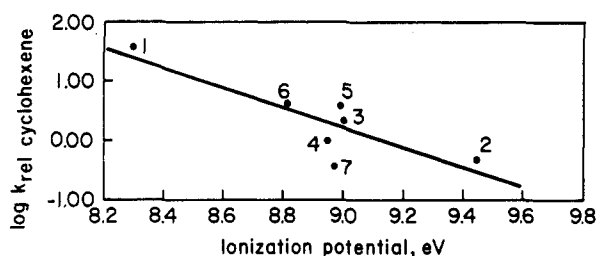
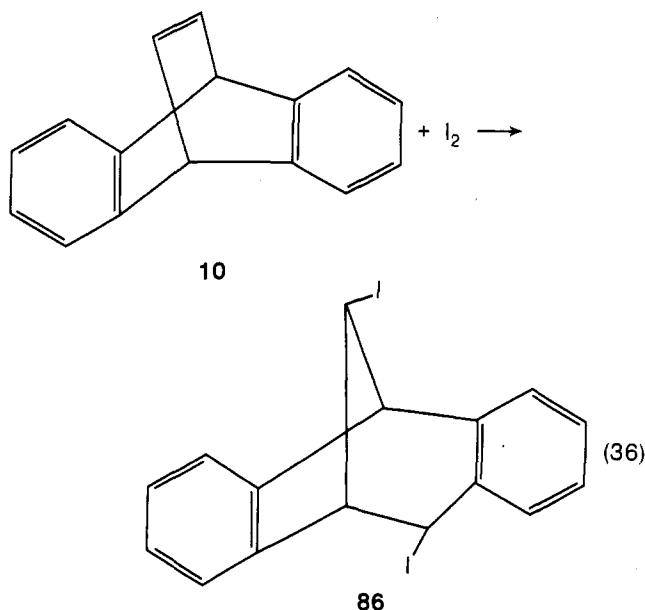


Figure 6. Relation between log relative rates (to cyclohexene) of iodine isocyanate (in situ) addition to unsaturates and ionization potentials. The slope = -1.84 (rms = 0.3653), and the compounds for the number points are: (1) 2,3-dimethyl-2-butene, (2) 1-hexene, (3) cyclopentene, (4) cyclohexene, (5) bicyclo[2.2.1]hept-2-ene, (6) cycloheptene, (7) *cis*-cyclooctene.

In contrast to alkenes, it appears that the characteristics of cycloalkene-iodine complex formation differ from the cycloalkene-silver ion complex formation.³¹³ An ionic mechanism appears to be operative in the addition of iodine to 9,10-dihydro-9,10-ethenoanthracene (**10**) in nonpolar sol-



vents. The sole product is *endo*-4-*syn*-8-diiododibenzobicyclo[3.2.1]octadiene (**86**) which slowly isomerizes at room temperature to an equilibrium mixture of the reactants, to *trans*-7,8-diiododibenzobicyclo[2.2.2]octadiene (**87**), and to its thermodynamically less stable isomer *exo*-4-*anti*-8-diiododibenzobicyclo[3.2.1]octadiene (**88**).²⁰² Also, addition of iodine in methanol to **9** gives *endo,endo*-2,6-diiodo-9-oxabicyclo[3.3.1]nonane (**89**) as the sole product.⁷⁴ Presumably the iodonium ion is the precursor to an intermediate iodine-methoxy adduct which leads to **89** as a result of transannular π participation.³²³

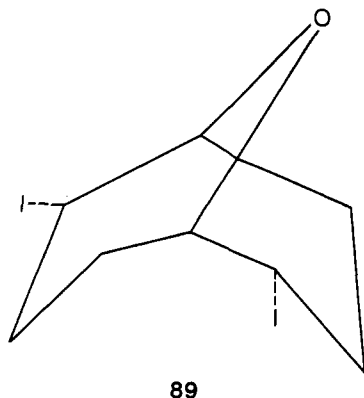
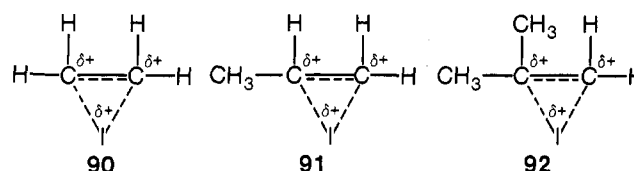


TABLE XXV. Relative Reactivities of Unsaturated Compounds with Iodine Isocyanate Generated in Situ under Heterogeneous Conditions^{a,325,328}

Unsaturate	$k/k_{\text{cyclohexene}}$	$\text{Log } k/k_{\text{cyclohexene}}$
2,3-Dimethyl-2-butene	38.0	1.58
1-Hexene	0.5	-0.30
<i>trans</i> -3-Hexene	5.7	0.76
2-Methyl-1-pentene	12.5	1.10
Cyclopentene	2.20	0.34
	(6.85) ^b (10) ^c	
Cyclohexene	1.00	0.00
Cycloheptene	4.30	0.63
<i>cis</i> -Cyclooctene	0.35	-0.46
Bicyclo[2.2.1]hept-2-ene	4.40	0.64

^a $\text{I}_2 + \text{AgOCN} \rightarrow \text{IOCN} + \text{AgI}$. ^b Competitive in situ method.³²⁵
^c Competitive preformed method.³²⁵

A comparison of the PMR shifts of several iodonium ions (**90-92**) and the corresponding protonated oxides and sulfides has been made.¹⁶⁹ Additional kinetic studies are necessary in

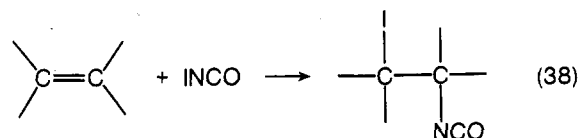


order to determine the degree of iodonium ion participation in the electrophilic reactions of I_2 , ICl ,^{315,316} INO_2 ,³¹⁷ INO_3 ,^{319,320} IBr ,³¹⁴ IF ,³²⁰ and IN_3 .^{323,325,326} However, it is of interest to note that ICl , IF , INCO , and IN_3 add stereospecifically *trans*, and that the addition of ICl follows second-order kinetics.³¹⁵

$$v = k[\text{ICl}][\text{U}] \quad (37)$$

D. Iodine Isocyanate Addition

The pseudohalogen iodine isocyanate (INCO) adds stereospecifically *trans* to straight-chain and cyclic alkenes, and *trans*-diaxially to steroid alkenes to give vicinal iodoisocyanates.^{74,324-338} Although it is possible to use preformed iodine



isocyanate solutions, many synthetic procedures generate the reagent *in situ* from iodine and silver cyanate.³³⁰⁻³³⁶ Kinetic studies have shown that iodine isocyanate is an electrophilic agent in homogeneous preformed solutions or when it is generated *in situ*,^{326,332,338} and that, in spite of several anomalies, the reaction follows second-order kinetics in both systems.³³²

$$v = k[\text{INCO}][\text{U}] \quad (39)$$

Hassner and coworkers³²⁴ have examined the steric and electronic effects, the regioselectivity, and the stereospecificity of the INCO addition to *cis*- and *trans*-2-butene, and β -deuteriostyrene. The relative reactivities of cyclopentene, cyclohexene, and **3**, the electrophilicity of INCO (Table XXV, Figure 6), and the rearrangement of the carbon skeleton³²⁵ are consistent with the intermediacy of a cyclic three-membered iodonium ion (**84** or **85**). In contrast to iodine, INCO , INO_3 , and IN_3 add to **9** to give only 1,2-addition products.

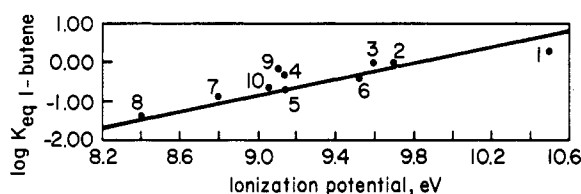


Figure 9. Relation between log relative equilibrium constants (to 1-butene) and ionization potentials for silver ion-alkene electron donor-acceptor complexes. The slope = 0.79 (rms = 0.2186), and the alkenes for the number points are: (1) ethene, (2) propene, (3) 1-butene, (4) *cis*-2-butene, (5) *trans*-2-butene, (6) 3-methyl-1-butene, (7) 2-methyl-2-butene, (8) 2,3-dimethyl-2-butene, (9) *cis*-2-pentene, (10) *trans*-2-pentene.

TABLE XXVIII. Relative Equilibrium Constants of the Electron Donor-Acceptor Complexes between Alkenes and Silver Ions

Alkene	$K_{eq}^{a,340}$	$K_{eq}^{b,343}$	$K_{eq}^b / K_{eq}(1-butene)^b$	$\text{Log } K_{eq}^b / K_{eq}(1-butene)^b$
Ethene	22.3	17.5	1.99	0.30
Propene	9.1	7.5	0.85	-0.069
1-Butene	7.7	8.8	1.00	0.00
<i>cis</i> -2-Butene	5.4	4.9	0.56	-0.25
<i>trans</i> -2-Butene	1.4	1.6	0.18	-0.74
3 Methyl-1-butene	5.1	8.0	0.91	-0.41
2-Methyl-2-butene	0.8	1.01	0.11	-0.94
2,3-Dimethyl-2-butene	0.1	0.34	0.04	-1.41
<i>cis</i> -2-Pentene	4.3	5.6	0.64	-0.20
<i>trans</i> -2-Pentene	1.1	1.8	0.20	-0.69
Cyclopentene	7.3	10.2	1.16	0.06

^a Equilibrium constant in ethylene glycol, 40°. ^b Equilibrium constant in ethylene glycol, 25°.

TABLE XXIX. Deuterium Kinetic Isotope Effects for Alkene-Silver Ion Complex Formation^{341,343}

Alkene	$K_{eq} H^a : K_{eq} D^a$	
	25°	40°
<i>trans</i> -CHD=CHD	0.94	0.93
CH ₃ CD=CH ₂	0.96	
CH ₃ CH=CD ₂	0.94	0.95
CH ₃ CD=CD ₂	0.91	0.93 ^b
CD ₃ CH=CH ₂	0.98	0.99 ^b
CD ₃ CD=CD ₂	0.86	0.91 ^b
<i>cis</i> -2-Butene-d ₃	0.90	0.92
<i>trans</i> -2-Butene-d ₃	0.89	0.90 ^b

^a Equilibrium constant in ethylene glycol on a 1 M AgNO₃ column. ^b 2 M AgNO₃ column used.

the carbon-carbon double bond. This trend is probably a result of steric factors and the relative importance of the $2p\pi \rightarrow 5s$ and the $4d \rightarrow 2p\pi$ charge transfer.

One must exercise some caution when trying to decide whether a three-membered cyclic activated complex is involved. The basic difficulty lies in whether one uses a MO or VB point of view to describe the π complex. For example, **99** could be considered a three-membered ring, but when a highly polarizable carbon-metal bond is involved, the energy difference between **100** and **101** is quite small. **101** is stabilized to the extent of 80% by $\sigma-\pi$ conjugation and could readily form an unsymmetrical π complex. However, on a time-average basis, it probably resembles a three-membered ring with

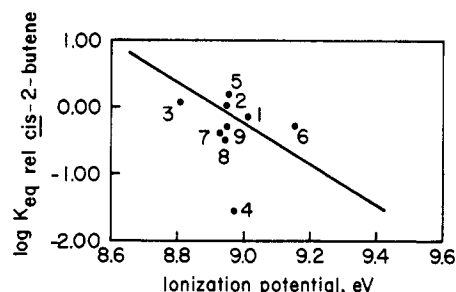
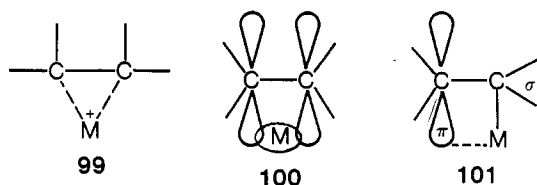


Figure 10. Log relative equilibrium constants to cyclohexene of silver ion complex formation with cycloalkenes vs. IP's. The slope (excluding point 4) = -1.05 (rms = 0.2507), and the cycloalkenes for the number points are: (1) cyclopentene, (2) cyclohexene, (3) cycloheptene, (4) *cis*-cyclooctene, (5) bicyclo[2.2.1]hept-2-ene, (6) methylenecyclobutane, (7) methylenecyclopentane, (8) methylenecyclohexane, (9) methylenecycloheptane.

TABLE XXX. Relative Equilibrium Constants for Silver Ion Complex Formation with Endocyclic and Exocyclic Cycloalkenes^{313,339}

Cycloalkene	K_{eq}^a	$K_{eq}^a / K_{eq}(\text{cyclohexene})^a$	$\text{Log } K_{eq}^a / K_{eq}(\text{cyclohexene})^a$
Cyclopentene	0.119	0.65	-0.19
Cyclohexene	0.184	1.00	0.00
Cycloheptene	0.212	1.15	0.06
<i>cis</i> -Cyclooctene	0.005	0.03	-1.57
Bicyclo[2.2.1]hept-2-ene	0.268	1.46	0.164
Methylenecyclobutane	0.090	0.49	-0.31
Methylenecyclopentane	0.067	0.36	-0.44
Methylenecyclohexane	0.060	0.33	-0.49
Bicyclo[2.2.2]oct-2-ene	0.096	0.52	-0.29
1-Methylcyclohexene	0.008	0.05	-1.35

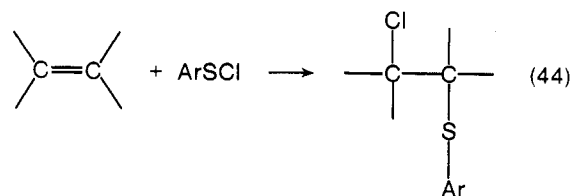
^a Equilibrium constant (l./mol) in CCl₄, 25°.

a partially empty π orbital available for bonding in the activated complex.

It is of interest to note that there is some parallelism between heats of hydrogenation of several olefins and their argentation constants^{313,344-346} and some correlation between the formation constants for silver ion complexes and the estimated strain energies of cycloalkenes.³¹³ Also, a marginally satisfactory correlation for argentation equilibria using a modified Kirkwood-Westheimer cavity model has been discussed.³⁴²

G. Sulfenyl Halide Addition^{15,39,352-388}

Sulfenyl halides react with carbon-carbon double bonds primarily by an ionic mechanism and less frequently by a free radical mechanism to give β -chloro thioether products. The almost exclusive *trans*-stereospecific addition observed with



the isomeric 2-butenes lends further credence to the proposed intermediacy of three-membered cyclic episulfonium ions (thiaranium ions, **102**) in the product-determining step.^{354,364,367-370} The product distribution is dependent on the structures of the sulfenyl halides and the unsaturates, and frequently the addition follows Markovnikov's rule.^{271-275,357} Although the reaction is presumed to be irreversible, the kinetically controlled anti-Markovnikov product can rearrange to

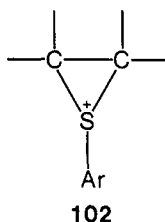
TABLE XXXI. Relative Rate Constants for Addition of 2,4-Dinitrobenzenesulfonyl Chloride to Alkenes³²

Alkenes	$k \times 10^3$ $M^{-1} \text{ sec}^{-1}$	$k/k_{1\text{-hexene}}$	$\text{Log } k/k_{1\text{-hexene}}$
Methylpropene	4.62	3.25	0.51
1-Butene	1.12	1.00	0.00
<i>cis</i> -2-Butene	26.3	18.5	1.27
<i>trans</i> -2-Butene	2.88	2.03	0.31
2-Methyl-1-butene	3.02	2.13	0.33
3-Methyl-1-butene	1.15	0.81	-0.09
2-Methyl-2-butene	21.1	14.9	1.17
<i>cis</i> -2-Pentene	28.4	20.0	1.30
<i>trans</i> -2-Pentene	2.84	2.00	0.30
1-Hexene	1.42	1.00	0.00
1-Hepene	1.41	0.99	0.00
1-Octene	1.52	1.07	0.03

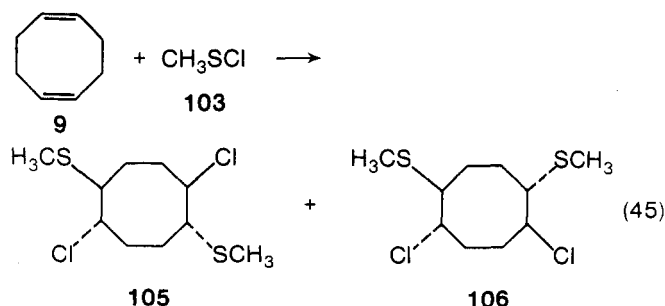
TABLE XXXII. Relative Rate Constants for 2,4-Dinitrobenzenesulfonyl Chloride Addition to Cycloalkenes³²

Cycloalkene	$k/k_{\text{cyclohexene}}$	$\text{Log } k/k_{\text{cyclohexene}}$
Cyclobutene	1.2	0.079
Cyclopentene	3.3	0.518
Cyclohexene	1.00	0.00
Cycloheptene	11	1.04
Bicyclo[2.2.1]hept-2-ene	33	1.52
Methylenecyclobutane	1.0	0.00
Methylenecyclopentane	2.6	0.41
Methylenecyclohexane	0.84	-0.76
Methylenecycloheptane	3.1	0.49
Methylenecyclooctane	3.7	0.57

the Markovnikov isomer.³⁵² Also, it has been reported that chloroalkyl 4-chlorophenyl sulfides exchange 4-chlorobenzenesulfonyl chloride with 1-octene,^{368,376} and several crystalline episulfonium salts have been prepared.³⁷⁸



Product studies in selected unsaturated cyclic systems infer that the episulfonium ion obtained from methanesulfonyl chloride (103) has more carbonium character than the corresponding ion obtained from 2,4-dinitrobenzenesulfonyl chloride (104). For example, the reaction of *cis,cis*-1,5-cycloocta-



diene (9) with 103 leads primarily to the two diadducts 105 and 106.³⁸⁰ Presumably, a transannular overlapping of the sulfur orbitals with the π bonds (in the monoadduct) enhances the nucleophilicity of the second double bond. In contrast, 104 yields the normal 1,2-addition product with 9.³⁸¹ Transannular

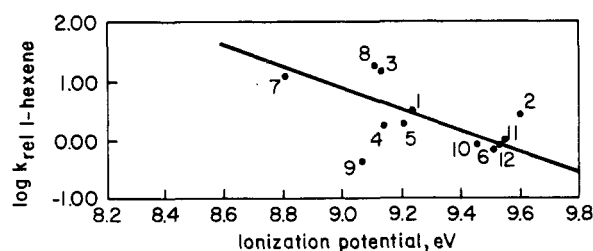


Figure 11. Relation between log relative rates (to 1-hexene) of 2,4-dinitrobenzenesulfonyl chloride addition to alkenes and ionization potentials.²³ The slope = -1.67, (rms = 0.3129), and the alkenes for the number points are: (1) methylpropene, (2) 1-butene, (3) *cis*-2-butene, (4) *trans*-2-butene, (5) 2-methyl-1-butene, (6) 3-methyl-1-butene, (7) 2-methyl-2-butene, (8) *cis*-2-pentene, (9) *trans*-2-pentene, (10) 1-hexene, (11) 1-heptene, (12) 1-octene.

TABLE XXXIII. Relative Rates of Episulfonium Ion Formation for the Reaction of CH_3SCI with Unsaturated Hydrocarbons^{a,352}

Hydrocarbon	$k/k_{\text{methylpropene}}$	$\text{Log } k/k_{\text{methylpropene}}$
Methylpropene	1.00	0.00
1-Butene	1.34	0.13
<i>cis</i> -2-Butene	17.4	1.24
<i>trans</i> -2-Butene	0.96	-0.18
3-Methyl-1-butene	2.60	0.41
2-Methyl-2-butene	11.0	1.04
2,3-Dimethyl-2-butene	17.2	1.24
1-Pentene	3.04	0.48
<i>cis</i> -2-Pentene	24.1	1.38
<i>trans</i> -2-Pentene	2.22	0.35
Cyclopentene	42.4	1.63

^a Dilute paraffin solution, -70°.

participation leading to a substituted *cis*-decalin has been reported for the reaction of 2 and 103.²⁴³ Also, the absence or small amount of rearranged products in bicyclic systems with 104 is consistent with the relatively stable cyclic sulfonium ion intermediate with little cationic character on carbon,^{355,379} and strong evidence has been presented against a nonrotating open carbonium ion.³⁵⁹ The addition of benzenesulfonyl halides to 3^{236,265,382} 4,³⁶³ 80,³⁶³ and bicyclo[2.2.1]hept-2,5-diene (107)³⁸² has been reported to involve the *exo*-episulfonium ions. However, a reexamination of the structure of the 4-104 adduct by Brown and Liu⁵⁷ revealed that the product is *endo*-2-phenylthio-*exo*-3-chloro-7,7-dimethylbicyclo[2.2.1]heptane (108). This latter observation offers strong support for the episulfonium ion concept as it is difficult to form the *exo* sulfonium species in the presence of the bulky 7,7-dimethyl substituents.

Kinetic studies of various sulfonyl halides demonstrated that the reaction is second order,^{359,373,374,377} but in some nonpolar solvents the rate law appears to become more complex.³⁵⁸

$$v = k[\text{ArSCI}][\text{U}] \quad (46)$$

Application of the proposed mechanistic criteria to the electrophilic addition of sulfonyl halides to unsaturated compounds provides very convincing evidence for a three-membered cyclic activated complex with slightly electron-deficient carbon and sulfur atoms (111) (Tables XXXI-XXXIII; Figures 11-13). Extended Hückel calculations on the simulated addition of CH_3S^+ to ethene suggest that the 3p orbitals on sulfur account for the major portion of the bonding.¹⁵ The opposing electronic and steric factors,³⁵² the large solvent effects (Table XII),^{359,384} and the small $k_{14}:k_{15}$ of 0.41 are also noteworthy (*vide supra*).

TABLE XXXIV. Relative Rates of Halocyclopropane Formation from Olefins

Olefin	ClHC: ^a		ClHC: ^b		BrHC: ^b		ClFC: ^c		CH ₃ ClC: ^d		C ₆ H ₅ ClC: ^e	
	<i>k</i> _{rel}	Log <i>k</i> _{rel}	<i>k</i> _{rel}	Log <i>k</i> _{rel}	<i>k</i> _{rel}	Log <i>k</i> _{rel}	<i>k</i> _{rel}	Log <i>k</i> _{rel}	<i>k</i> _{rel}	Log <i>k</i> _{rel}	<i>k</i> _{rel}	Log <i>k</i> _{rel}
Methylpropene	1.00	0.00	1.00	0.000	1.00	0.000	1.00	0.00	1.00	0.00	1.00	0.000
<i>cis</i> -2-Butene	0.91	-0.04	0.99	-0.004	1.02	0.009	0.14 ^f	-0.85	0.74 ^f	-0.13	0.37 ^f	-0.432
<i>trans</i> -2-Butene	0.45	-0.35	1.09	0.037	1.10	0.004	0.097	-1.01	0.52	-0.28	0.20	-0.70
2-Methyl-2-butene	1.78	0.25	1.18	0.072			6.5 ^f	0.81	2.44 ^f	0.39	3.2 ^f	0.51
	(1.76) ^g											
2,3-Dimethyl-2-butene	2.81	0.45			1.18	0.072	31	1.49	3.87	0.59	5.1	0.71
					(1.21) ^g							
1-Pentene	0.23	-0.64										
	(0.24) ^g											
Cyclohexene	0.60 ^h	-0.22										

^a CH₂Cl₂ + *n*-BuLi, -35°, ref 430. ^b Thermolysis of XCH₂N₃, -30°, ref 430. ^c (FCl₂C)₂C=O + K⁺-O-*t*-Bu, 10°, ref 418-420. ^d Photolysis of methylchlorodiazirine, 25-30°, ref 417. ^e Photolysis of phenylchlorodiazirine, 25°, ref 418. ^f Composite of both modes of addition. ^g Measured in competition with *trans*-2-butene. ^h Measured in competition with *cis*-2-butene.

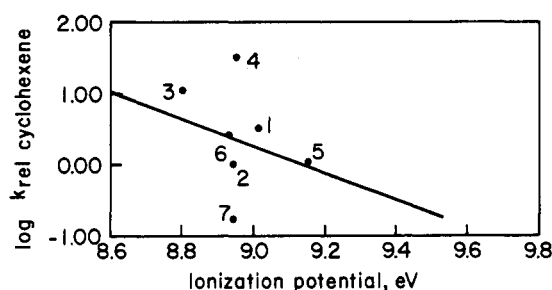


Figure 12. Relation between log relative rates (to cyclohexene) of 2,4-dinitrobenzenesulfonyl chloride addition to cycloalkenes and ionization potentials. The slope = -2.38 (rms = 0.6538), and the cycloalkenes for the number points are: (1) cyclopentene, (2) cyclohexene, (3) cycloheptene, (4) bicyclo[2.2.1]hept-2-ene, (5) methylenecyclobutane, (6) methylenecyclopentane, (7) methylenecyclohexane.

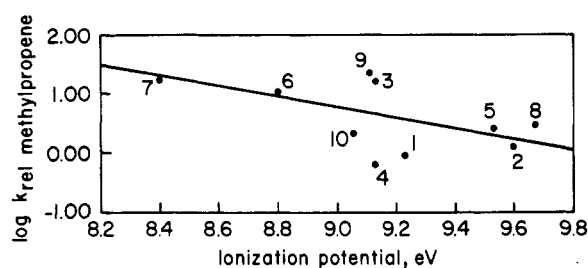
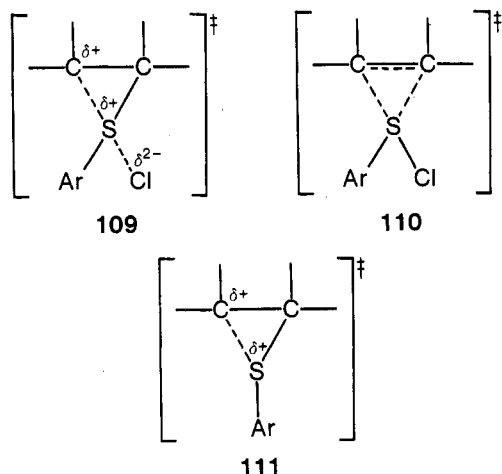
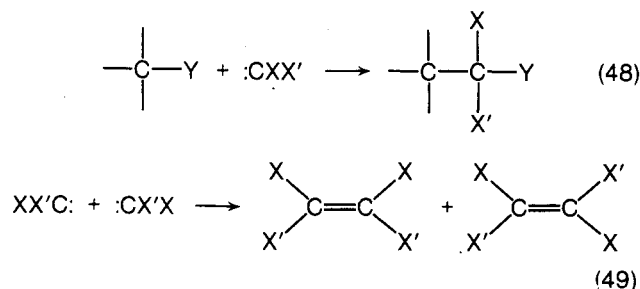
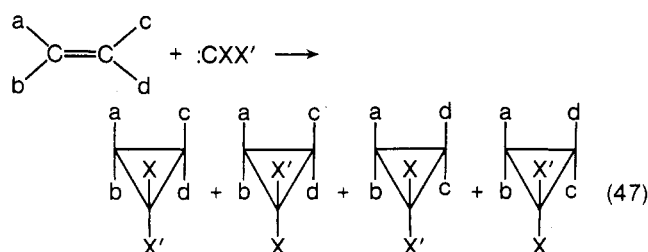


Figure 13. Relation between log relative rates (to methylpropene) of episulfonium ion formation from methanesulfonyl chloride and alkenes and ionization potentials.²³³ The slope = -0.80 (rms = 0.4588), and the alkenes for the number points are: (1) methylpropene, (2) 1-butene, (3) *cis*-2-butene, (4) *trans*-2-butene, (5) 3-methyl-1-butene, (6) 2-methyl-2-butene, (7) 2,3-dimethyl-2-butene, (8) 1-pentene, (9) *cis*-2-pentene, (10) *trans*-2-pentene.



H. Carbene Addition^{39,389-450}

Carbenes and carbenoids⁴³¹⁻⁴³⁴ are generally considered as transient electrophilic intermediates which undergo addition to carbon-carbon double bonds (cyclopropanation), insertion reactions, and dimerization to form olefins. This dis-



cussion will be primarily concerned with the cycloaddition of "free" singlet carbenes and carbenoids in solution, and no attempt will be made to survey all of the considerable recent structural, stereochemical, and mechanistic papers in this exciting area of chemistry. Several excellent reviews are available concerning all aspects of carbene chemistry (ref 389, 391-394, 410, 411, 414, 421-424, 428).

Linear free energy graphs correlating alkene relative reactivities toward halocarbene addition give a carbene selectivity order F₂C: > ClFC: > Cl₂C:⁴²⁶ Other comparisons give a selectivity order of ClFC: > Cl₂C: > C₆H₅ClC: > CH₃ClC:, and of F₂C: > ClFC: > Cl₂C: > (CH₃)₂C=C=C: > Br₂C: > O atoms > H₂C:⁴⁰² Thus, there appears to be an inverse relation between electrophilicity^{402,435} and selectivity. Also, an increase in carbene ground state stability should be reflected in a greater selectivity among carbon-carbon double bonds.

Table XXXIV and Figure 14 show that ClHC: generated by a base-induced α -elimination from methylene chloride is more selective (less reactive or less electrophilic) than ClHC: from chlorodiazomethane (112).⁴³⁰ This difference in reactivity has been attributed to the intermediacy of "free" carbenes from halodiazomethanes and to the intermediacy of carbenoids in α -eliminations. A possible three-membered cyclic activated complex for the carbenoid reaction is depicted in 113.⁴³⁰ It is

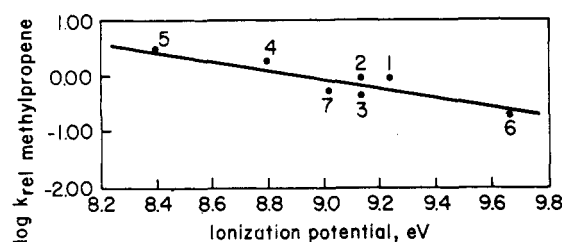


Figure 14. Relation between log relative rates (to methylpropene) of chlorocarbene ($\text{CH}_2\text{Cl}_2 + n\text{-BuLi}$) addition to alkenes and ionization potentials. The slope = -0.83 ($\text{rms} = 0.3631$), and the olefins for the number points are: (1) methylpropene, (2) *cis*-2-butene, (3) *trans*-2-butene, (4) 2-methyl-2-butene, (5) 2,3-dimethyl-2-butene, (6) 1-pentene, (7) cyclohexene.

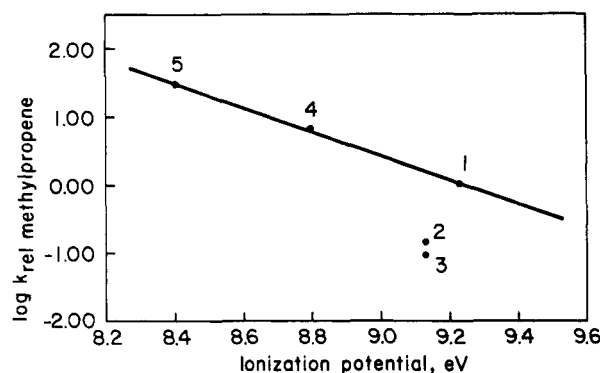
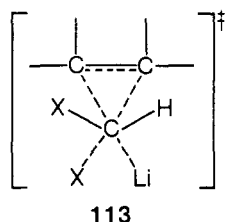


Figure 15. Relation between log relative rates (to methylpropene) of chlorofluorocarbene addition to alkenes and ionization potentials. The slope = -1.80 ($\text{rms} = 0.0179$) excluding points 2 and 3. The alkenes for the number points are: (1) methylpropene, (2) *cis*-2-butene, (3) *trans*-2-butene, (4) 2-methyl-2-butene, (5) 2,3-dimethyl-2-butene.



also seen from Table XXXIV that halodiazomethane generated $\text{CH}_3\text{ClC:}$ and $\text{C}_6\text{H}_5\text{ClC:}$ are more discriminating than the halodiazomethane generated BrHC: and ClHC: . In contrast, recent studies of the kinetic selectivity of $\text{C}_6\text{H}_5\text{BrC:}$, $\text{C}_6\text{H}_5\text{ClC:}$, and $\text{C}_6\text{H}_5\text{FC:}$ revealed that $\text{C}_6\text{H}_5\text{BrC:}$ and $\text{C}_6\text{H}_5\text{ClC:}$ generated by the photoinduced elimination of nitrogen from phenylhalodiazirines were more selective than when they were generated by the action of potassium *tert*-butoxide on benzal halides.⁴¹⁸ With regard to overall selectivity, these latter data showed only small variations in selectivity as a function of halogen.

The relative rate data for carbene and carbenoid reactions are remarkably compatible with the proposed mechanistic criteria (Figures 15–17). A mechanism consistent with these considerations is an electrophilic process which involves partial bonding of singlet carbene with both termini of the olefinic system with little or negligible positive charge development on the more highly substituted carbon atom (114). This mechanism does not exclude the formation of a loose charge-transfer type complex prior to the rate-determining step.⁴⁰² However, it is probable that the activated complex for most carbene and carbenoid cycloaddition reactions to nonaromatic olefinic systems can be depicted with 113 or 114.

Dibromocyclopropanization of carbon-carbon double bonds via a three-membered cyclic activated complex re-

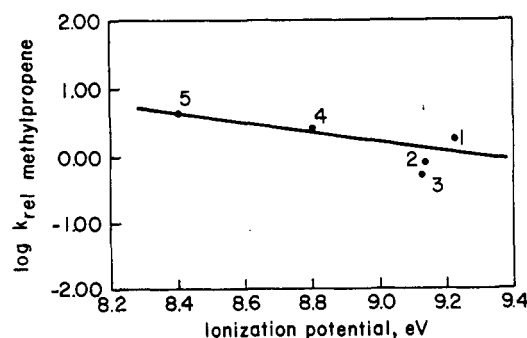


Figure 16. Relation between log relative rates (to methylpropene) of methylchlorocarbene addition to alkenes and ionization potentials. The slope = -0.96 ($\text{rms} = 0.1396$) for all points, -0.84 excluding point 3, and -0.71 excluding points 2 and 3. The alkenes for the number points are: (1) methylpropene, (2) *cis*-2-butene, (3) *trans*-2-butene, (4) 2-methyl-2-butene, (5) 2,3-dimethyl-2-butene.

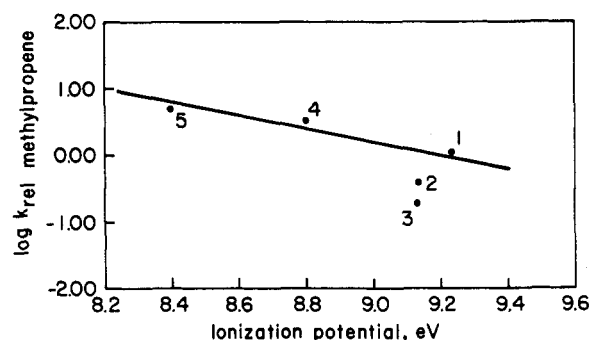
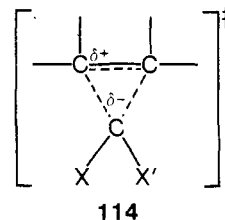


Figure 17. Relation between log relative rates (to methylpropene) of phenylchlorocarbene addition to alkenes and ionization potentials. The slope = -1.18 ($\text{rms} = 0.2282$) excluding point 3, and -0.86 excluding points 2 and 3. The alkenes for the number points are: (1) methylpropene, (2) *cis*-2-butene, (3) *trans*-2-butene, (4) 2-methyl-2-butene, (5) 2,3-dimethyl-2-butene.

TABLE XXXV. Relative Rates of Dibromocarbene Addition to Alkenes^{398–400}

Olefin	$k/k_{\text{methylpropene}}$	$\text{Log } k/k_{\text{methylpropene}}$	$\text{Log } k/k_{\text{cyclohexene}}$
Methylpropene	1.00	0.00	0.57 ^a 0.43 ^b
2-Methyl-2-butene	3.2	0.51	0.87 ^a 0.94 ^b
2,3-Dimethyl-2-butene	3.5	0.54	0.84 ^a 0.97 ^b
1-Pentene			-0.78^a
1-Hexene	0.023	-1.64	$-0.71^{b,c}$
Cyclopentene	0.5	-0.30	
Cyclohexene	0.4	-0.40	0.00
Styrene	0.4	-0.40	

^a Reference 400. ^b References 398 and 399. ^c Measured in competition with methylpropene.



sembling 114 is consistent with the proposed mechanistic criteria. Steric factors could be important in the lack of a simple relation between variation of rates with alkene structures (Table XXXV).

In contrast to chlorocarbenes, the relative reactivity of dichlorocarbene toward carbon-carbon double bonds appears

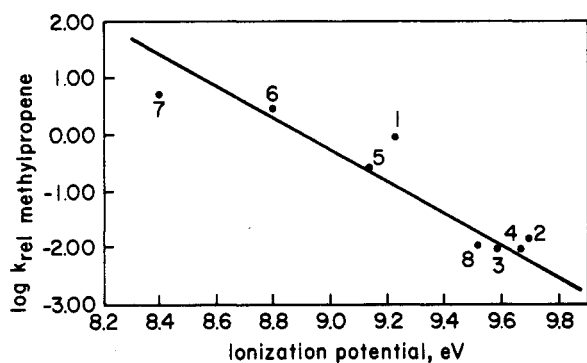


Figure 18. Relation between log relative reactivity (to methylpropene) vs. ionization potential for dichlorocarbene addition to alkenes at -78° . The slope = -1.89 (rms = 0.6749), and the alkenes for the number points are: (1) methylpropene, (2) propene, (3) 1-butene, (4) 1-pentene, (5) *cis*-2-butene, (6) 2-methyl-2-butene, (7) 2,3-dimethyl-2-butene, (8) 1-octene. Under slightly different experimental conditions at -10 to -20° , the slope = -2.14 (rms = 0.3892).

TABLE XXXVI. Relative Rates of Addition of Dichlorocarbene to Alkenes

Alkene	IP, eV ^a	Log $k^b/k_{\text{cyclohexene}}$	Log $k^c/k_{\text{methylpropene}}$
Methylpropene	9.23	0.92 (0.89) ^d	0.00
Propene	9.70		-1.80^e
1-Butene	9.59		-1.99^e
1-Pentene	9.66	-0.86 (-0.78) ^d	-1.98^e
<i>cis</i> -2-Butene	9.13		-0.58^{e-f}
<i>cis</i> -2-Pentene	9.11	0.21	
<i>trans</i> -2-Pentene	9.06	(0.33) ^h	
2-Methyl-1-butene	9.20	0.74	
2-Methyl-2-butene	8.8	1.37	0.48 ^e
2,3-Dimethyl-2-butene	8.4	(1.73) ⁱ	0.72 ^a
1-Hexene	9.45	-0.73	
Cyclohexene	9.18	0.00	-0.86^e
1-Octene	9.52		$-1.92^{e,j}$

^a Ionization potential. ^b Reference 400, -10 to -20° . ^c Reference 402, -78° . ^d Measured in competition with 1-hexene as reference. ^e BuLi + CHCl₃, THF solvent. ^f BuLi-TMEDA + CHCl₃, isopentane solvent. ^g Relative rates independent of solvents (THF or isopentane). ^h Measured in competition with *cis*-2-pentene. ⁱ Measured in competition with 2-methyl-2-butene. ^j *t*-BuOK + CHCl₃, isopentane solvent.

to be independent of the method by which the carbene is generated (Table XXXVI, Figure 18).^{389,394,402,403} Indeed, the similarity of relative rates among dichlorocarbenes generated from various precursors under a variety of experimental conditions is more compatible with a "free" carbene species than with a carbenoid species.^{402,434} Steric hindrance also appears to be an important factor in controlling the rate of dichlorocarbene addition to alkenes,⁴⁰⁵ and the kinetic data are consistent with an almost symmetrically bridged activated complex resembling **114**.⁴⁰² However, it must be noted that the unusually large ρ^* value (-4.3),^{402,405} obtained with the Taft polar-steric relationship,¹⁰⁷ is incompatible with **114** and the reported ρ^* of -0.74 .⁴¹² The latter ρ^* value for dichlorocarbene addition is consistent with an activated complex resembling **114**. **114** is also consistent with the lack of transannular rearrangement in **2** and in **9**, the greater reactivity of the *cis* compound over its *trans* isomer, the greater reactivity of **3** over **4**, and the small solvent effects on relative rates.

The addition of dichlorocarbene generated from phenyl(trichloromethyl)mercury to substituted norbornenes is very sensitive to steric hindrance and depends on the reactivity of the double bond.⁴⁴² No product was obtained with **115**, and a low yield (9%) was obtained with **116** which appears to be unreactive toward dibromocarbene.⁴⁴²

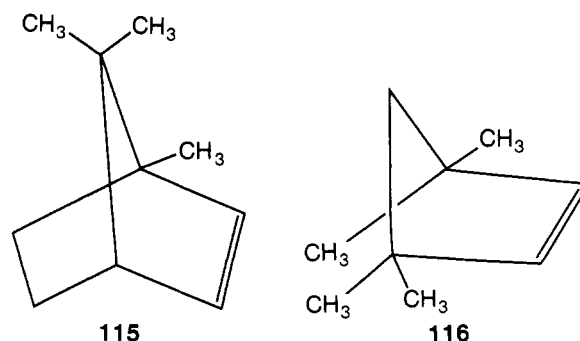
TABLE XXXVII. Relative Rates of Methylenation of Alkenes by Iodomethylzinc iodide⁴⁰⁹

Alkene	$k/k_{\text{1-hexene}}$	Log $k/k_{\text{1-hexene}}$
1-Hexene	1.00	0.00
1-Heptene	1.08	0.03
2-Methyl-1-butene	7.02	0.85
3,3-Dimethyl-1-butene	0.39	-0.41
2-Methyl-2-butene		0.78
2,3-Dimethyl-2-butene	3.6	0.55
<i>cis</i> -3-Hexene	2.3	0.36
<i>trans</i> -2-Hexene	1.17	0.07

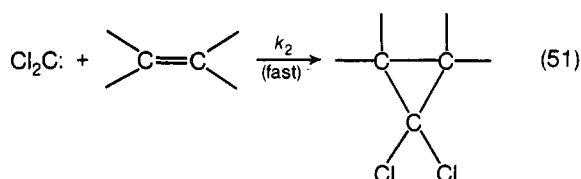
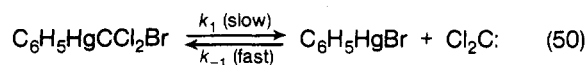
TABLE XXXVIII. Relative Rates of Methylenation of Cycloalkenes with Iodomethylzinc iodide⁴⁰⁸

Cycloalkene	$k/k_{\text{cyclohexene}}$	Log $k/k_{\text{cyclohexene}}$
Cyclopentene	1.60 ^a	0.20
Cycloheptene	1.18	0.07
Cyclohexene	1.00	0.00
Methylenecyclohexane	3.84	0.58
Bicyclo[2.2.1]hept-2-ene	1.70	0.23

^a Measured in competition with cycloheptene.



The slow step in the stereospecific dichlorocyclopropanation of alkenes with phenyl(bromodichloromethyl)mercury compounds has been postulated to be the extrusion of dichlorocarbene from the mercurial (eq 50).^{437,439} Thus, the first-order rate law⁴³⁷ for alkenes appears to rule out an electrophilic addition to the olefinic center in the rate-determining step (**113** or **114**), and differs from the kinetics observed for the dichlorocyclopropanation of styrenes.^{402,413}



Iodomethylzinc iodide (Simmons-Smith reagent),^{409,410} which may be considered a "carbenoid," reacts slowly with carbon-carbon double bonds to yield cyclopropanes. Tables XXXVII and XXXVIII show that reactivity increases with increased substitution at the double bond with alkyl groups. Although the relative importance of electrical and steric effects has not been assessed with certainty, it appears that the rate-enhancing electronic effects of alkyl substituents is countered by steric hindrance in the cyclopropanation of 2,3-dimethyl-2-butene. In the absence of C-H insertion products and consistent with the proposed criteria, it is reasonable to represent the activated complex for the nucleophilic displacement on the reagent by olefin with structure **117**. Except for

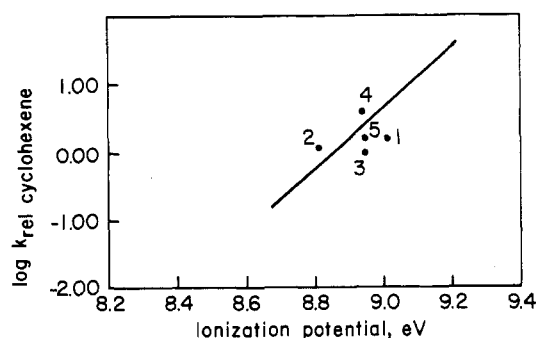


Figure 19. Relation between log relative reactivity (to cyclohexene) and ionization potentials for addition of iodomethylzinc iodide to cycloalkenes. The slope = 1.31 (rms = 0.1785), and the cycloalkenes for the number points are: (1) cyclopentene, (2) cycloheptene, (3) cyclohexene, (4) methylenecyclohexane, (5) bicyclo[2.2.1]hept-2-ene.

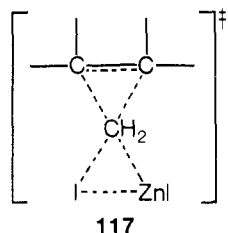
TABLE XXXIX. Relative Rates of Addition of 2,2-Diphenylcyclopropylidene to Alkenes⁴⁰⁶

Alkene	$k/k_{\text{methylpropene}}$	$\text{Log } k/k_{\text{methylpropene}}$
Methylpropene	1.00	0.00
1-Butene	0.22	-0.66
cis-2-Butene	1.15	0.06
trans-2-Butene	0.42	-0.38
2,3-Dimethyl-2-butene	0.41	-0.39
Cyclohexene	1.23	0.09

TABLE XL. Relative Rates of Addition of Dimethylethylidenecarbene to Unsaturates^{2,404}

Unsaturate	$k/k_{\text{cyclohexene}}$	$\text{Log } k/k_{\text{cyclohexene}}$
2,3-Dimethyl-2-butene	0.02	-1.70
1-Octene	0.2	-0.70
Cyclopentene	1.1	0.04
Cyclohexene	1.0	0.00
Cycloheptene	0.6	-0.22
Cyclooctene	0.7	-0.15
Styrene	6.2	0.79
1-Methylcyclopentene	0.3	-0.52

symmetry along the double bond axis, **117** resembles the spirano-oxygen activated complex for peracid epoxidation of olefins (vide infra).



Although a positive slope of 1.31 (Table XXXVIII, Figure 19) is calculated by the method of least squares for the addition of iodomethylzinc iodide to cycloalkenes, it could be possible that the rates of reaction are insensitive to ring size.

Thermally unstable *N*-nitroso-*N*-2,2-diphenylcyclopropylurea (**118**) reacts with lithium ethoxide to give 2,2-diphenylcyclopropylidene (**119**).

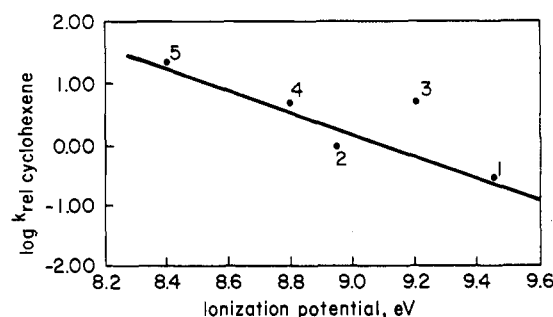
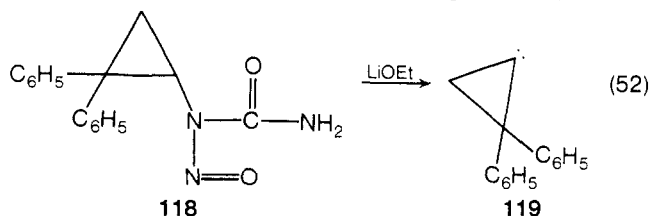


Figure 20. Relation between log relative rates (to cyclohexene) and ionization potentials for addition of dimethylallenidenecarbene to olefins. The slope = -1.38 (rms = 0.4128 excluding point 3), and the olefins for the number points are: (1) 1-hexene, (2) cyclohexene, (3) 2-methyl-1-butene, (4) 2-methyl-2-butene, (5) 2,3-dimethyl-2-butene.

TABLE XLI. Relative Rates of Dimethylallenidenecarbene to Olefins⁴³⁸

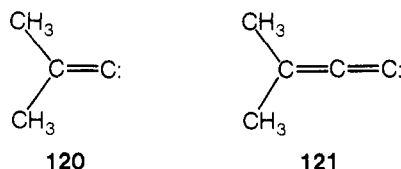
Olefin	$\text{Log } k/k_{\text{cyclohexene}}$
1-Hexene	-0.60
Cyclohexene	0.00
2-Methyl-1-butene	0.70
2-Methyl-2-butene	0.67
2,3-Dimethyl-2-butene	1.3

TABLE XLII. Relative Rates of Addition of Cyclopentadienylidene to Olefins^{448,449}

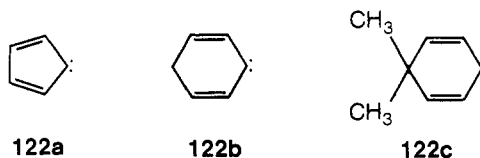
Olefin	Rel rate	Log rel rate
Cyclohexene	1.00	0.000
Styrene	0.94	-0.027
1-Hexene	0.94	-0.027
2-Methyl-2-butene	0.75	-0.125
2,3-Dimethyl-2-butene	0.74	-0.131
3,3-Dimethyl-1-butene	0.70	-0.155

cyclopropylidene (**119**).⁴⁰⁶ Table XXXIX shows that both electronic and steric factors contribute to the relative reactivity of **119**. The limited available data are not inconsistent with a symmetrical activated complex resembling **114**.

Steric factors are also important in the stereospecific addition of dimethylethylidenecarbene (**120**) to alkenes (Table XL, Figure 20).⁴⁰⁴ In contrast, electronic factors appear to predominate in the stereospecific addition of dimethylallenidenecarbene [(**121**), dimethylvinylidenecarbene].⁴³⁸



Cyclopentadienylidene (**122a**)^{448,449} and cyclohexadienylidene (**122b**)^{339,450} show a minimal selectivity and exhibit a mild sensitivity to steric hindrance on addition to tri- and tetrasubstituted olefins. More discrimination is shown in the addition of **122c**.⁴⁵⁰



Although little is known about the kinetic isotope effects of carbene reactions, several reports suggest that the magni-

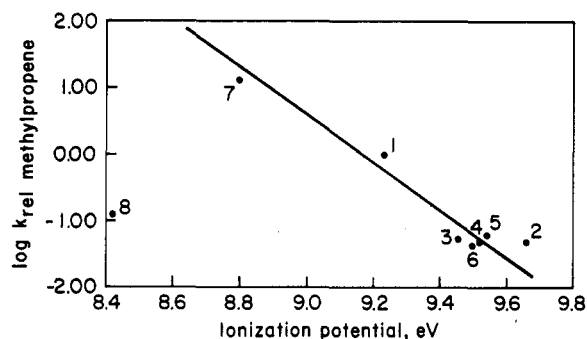
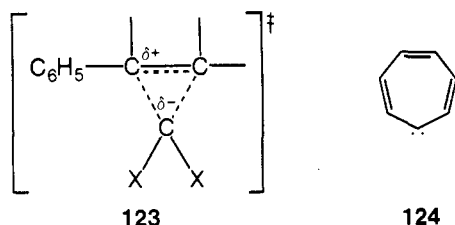


Figure 21. Relation between ionization potentials and addition of peracetic acid to olefins. The slope = -3.23 (rms = 0.2062) excluding point 8, and the olefins for the number points are: (1) methylpropene, (2) 1-pentene, (3) 1-hexene, (4) 1-heptene, (5) 1-octene, (6) 1-decene, (7) 2-methyl-2-butene, (8) styrene.

tude of k_H/k_D can be used as a diagnostic probe for differentiating between a complexed carbene and a "free" carbene.^{443,446}

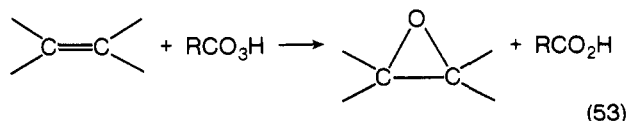
Very little kinetic data have been published concerning carbene addition to cycloalkenes. In one of the few reports^{404,408} it is noted that the relative rates of cyclopropane formation using iodomethylzinc iodide are explicable in terms of a balance between small inductive and steric factors (Table XXXVIII, Figure 19). The small 3:cyclohexene rate ratio (Table VIII) is compatible with an activated complex similar to **117**. It is highly probable that symmetrical three-membered cyclic activated complexes similar to **114** are involved in the addition of "free" singlet carbenes to cycloalkenes.

Kinetic studies of the addition of various carbenes to styrenes suggest that the rate-determining step involves a three-membered cyclic activated complex with only small or negligible development of a partially positive charge at the benzylic carbon atom (**125**) as compared to the ground state.^{401,407,413} The ρ value of -3.4 for the cyclopropanation of styrenes with **120** is surprisingly large and negative,⁴⁰⁴ while the ρ value of -1.61 for ethylzinc carbenoid⁴⁰⁷ and ρ^+ values of -0.62 ⁴⁰¹ and -0.378 ⁴¹³ for dichlorocarbene are more consistent with structure **123**. The ρ value of $+1.05$ for cycloheptatrienyldienecarbene (**124**) addition to styrenes is in agreement with the proposed nucleophilicity of a carbocyclic aromatic carbene.^{397,422}



I. Peroxy Acids (Epoxidation)^{39,86,92,93,451-489}

Oxidation of carbon-carbon double bonds by organic peracids is the most general and widely used reaction for introducing the oxirane group into unsaturated organic compounds. The yields are generally excellent to quantitative under a wide



range of experimental conditions. Epoxidation of pure unsaturated hydrocarbons is a second-order reaction, first order in olefin and first order in peroxy acid. Electron-withdrawing groups in the peroxy acid enhance the rate of epoxidation.^{457,476,477}

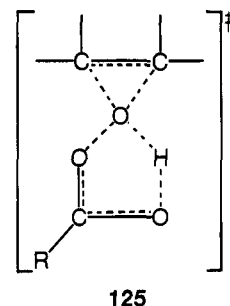
TABLE XLIII. Relative Reactivity of Peracetic Acid Epoxidation of Alkenes and Styrenes^{a,451,453,478-481}

Unsaturate	$k \times 10^3$ $M^{-1} \min^{-1}$	$k/k_{\text{methylpropene}}$	$\log k/k_{\text{methylpropene}}$
Ethene	0.19	0.002	-17.69
Propene	4.2	0.046	-1.34
Methylpropene	92	1.00	0.00
1-Pentene	4.3	0.047	-1.33
1-Hexene	5.0	0.054	-1.26
1-Heptene	5.5	0.06	-1.22
1-Octene	4.7 ^b	0.05	-1.29
1-Decene	4.1 ^b	0.045	-1.35
2-Methyl-2-butene	1240	13.5	1.13
Styrene	11.2	0.12	-0.914
1,1-Diphenylethene	48	0.52	-0.28
Triphenylethene	5.76	0.06	-1.20

^a Temperature 25.8°. ^b Temperature 25.0°, ref 453.

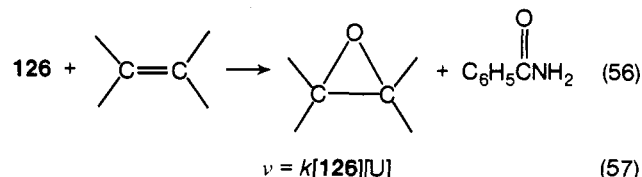
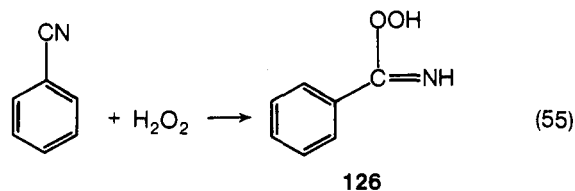
$$v = k[RCO_3H][U] \quad (54)$$

In spite of the vigorous discussions concerning the nature of the activated complex in the bimolecular electrophilic addition of peracids to carbon-carbon double bonds (Figure 21),⁴⁶¹ it is now generally accepted that Bartlett's⁴⁶⁷ original proposal of a symmetrical three-membered cyclic structure (**125**) correctly depicts the activated complex. Structure **125**



is also consistent with the proposed mechanistic criteria, and it is of interest to note that cis double bonds in straight-chain alkenes are epoxidized faster than the trans double bond isomers, while the reverse is true for geometrical isomers of cycloalkenes.^{92,93,489}

The limited available data for epoxidation with peroxybenzimidic acid (**126**) are also consistent with an almost symmetrical three-membered cyclic activated complex resembling **127**.^{470,471} **126** appears to be a less selective reagent for the

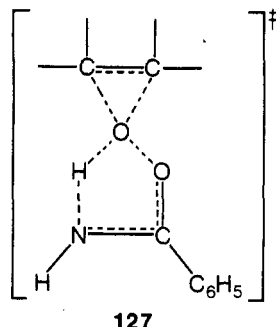


epoxidation of carbon-carbon double bonds than are peracids, and the relative insensitivity of **126** and peracetic acid to π -electron availability (IP) is shown in Tables XLIV and XLV.

Table XLIV. Relative Reactivity of the Peroxyacetic Acid^{451,463,478-481} Epoxidation of Cycloalkenes

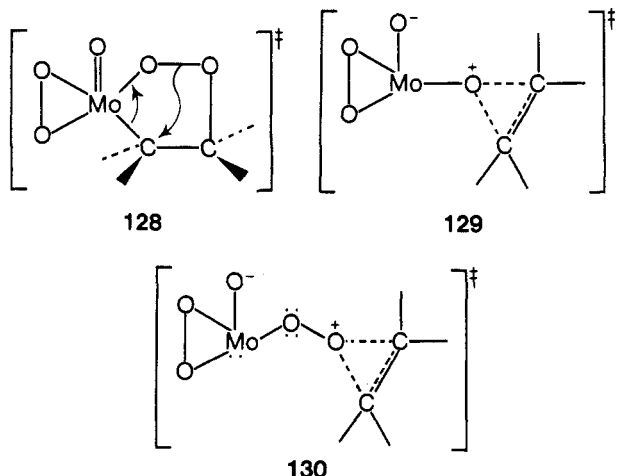
Cycloalkene	$k \times 10^3$ $M^{-1} \text{ min}^{-1}$	$k/k_{\text{cyclohexene}}$	$\text{Log } k/k_{\text{cyclohexene}}$
Cyclobutene	21.0	0.16	-0.79
Cyclopentene	19.0	1.47	0.17
Cyclohexene	129	1.00	0.00
Cycloheptene	175	1.36	0.13
1-Methylcyclopentene	2220	17.2	1.24

^a Temperature 25.8°.



J. Hydroperoxides and Oxo Transition Metal Compounds^{33,490-501}

A five-membered peroxy structure similar to **128** has been proposed for the epoxidation of alkenes by oxo transition metal compounds.^{491,492,500} Recent ¹⁸O studies with molybdenum(VI) peroxy compounds and a comparison of the 3: cyclohexene reactivity ratio (1.9, Table VIII) suggest that alternate mechanisms involving three-membered cyclic activated complexes (**129**, **132**) should also be considered as well as the possibility of rate-determining π complex formation.³³ The slightly greater reactivity of *cis*-cyclododecene over the *trans* isomer is also consistent with a three-membered cyclic activated complex (**129**, **130**).³³

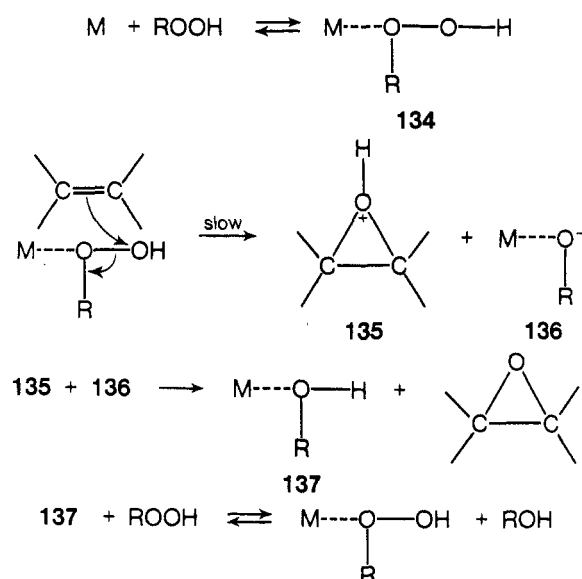


Epoxidation of alkenes, cycloalkenes, and styrenes by organic hydroperoxides in the presence of catalytic amounts of molybdenum and vanadium compounds has received limited kinetic study.⁴⁸³⁻⁴⁹⁸ The kinetics of epoxidation of 1- and 2-octene in the presence of molybdenum hexacarbonyl (**131**), and naphthenate (**132**) and vanadium acetylacetonate (**133**) with organic hydroperoxides suggest that the reaction is generally first order in catalyst and in unsaturated.⁴⁹³ A heterolytic mechanism for epoxidation by **131**-**133** is shown in Scheme I.^{493,496} The available kinetic data do not permit a differentiation among possible activated complexes which are similar to **138** and **139**. More recent studies of the epoxidation of 1-oc-

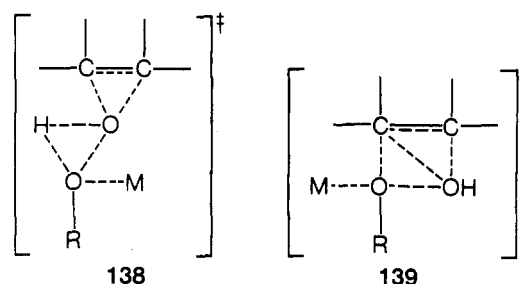
TABLE XLV. Relative Rates of Epoxidation of Some Representative Olefins with Peroxybenzimidic Acid⁴⁷⁰

Olefin	$k/k_{\text{cyclohexene}}$	$\text{Log } k/k_{\text{cyclohexene}}$
Methylpropene	2.1	0.32
2,3-Dimethyl-2-butene	3.5	0.54
1-Hexene	0.4	-0.40
<i>cis</i> -3-Hexene	1.3	0.11
<i>trans</i> -3-Hexene	0.9	-0.05
Cyclohexene	1.0	0.00
Cyclopentene	0.92	-0.04
Cycloheptene	2.03	0.31
Methylenecyclohexane	1.46	0.16
Bicyclo[2.2.1]hept-2-ene	3.8	0.58

SCHEME I



tene by *tert*-butyl and cumene hydroperoxide in the presence of **131** as catalyst provides additional information on the reversible inhibition by the coproduct alcohol.⁴⁹⁰



A mechanistic pathway involving an allylic hydroperoxide intermediate has been proposed for the mild oxidation of 2,3-dimethyl-2-butene in the presence of oxygen-carrying iridium(I) and rhodium(I) complexes.⁴⁹⁹

K. Chromic Acid Oxidation^{30,502-515}

Chromic acid, which is one of the most versatile of the readily available oxidants, oxidizes carbon-carbon double bonds to acids, aldehydes, epoxides, glycols, ketols, and ketones. Under controlled reaction conditions one can obtain a desired product in good yield.⁵⁰²⁻⁵⁰⁷ Studies of the mecha-

$$v = k[\text{H}_2\text{CrO}_4][\text{U}] \quad (58)$$

nisms of chromic acid oxidations have been complicated by secondary oxidations involving intermediate chromium(IV) and chromium(V) species. Although these intermediate valence

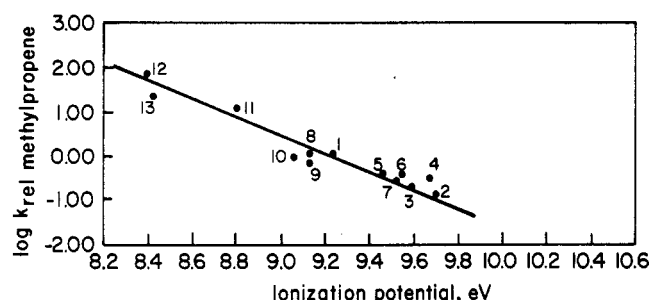


Figure 22. Relation between log relative rates (to methylpropene) for the chromium(VI) oxidation of olefins. The slope = -1.92 (rms = 0.1957) excluding point 13, and the olefins for the number points are: (1) methylpropene, (2) propene, (3) 1-butene, (4) 1-pentene, (5) 1-hexene, (6) 1-heptene, (7) 3-methyl-1-butene, (8) *cis*-2-butene, (9) *trans*-2-butene, (10) *trans*-2-pentene, (11) 2-methyl-2-butene, (12) 2,3-dimethyl-2-butene, (13) styrene.

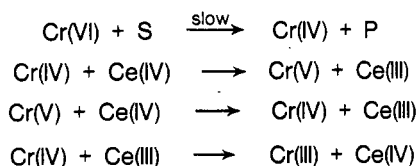
TABLE XLVI. Relative Rates of the Chromium(VI) Oxidation of Alkenes^{a,30}

Alkene	$k \times 10^3$ $M^{-1} \text{ min}^{-1}$	$k/k_{\text{methylpropene}}$	$\text{Log } k/k_{\text{methylpropene}}$
Methylpropene	7.28	1.00	0.00
Propene	0.95 ^b	0.13	-0.88
1-Butene	1.53	0.21	-0.68
1-Pentene	2.22	0.30	-0.52
1-Hexene	2.94	0.40	-0.39
1-Heptene	2.77	0.38	-0.42
3-Methyl-1-butene	2.02	0.28	-0.56
<i>cis</i> -2-Butene	8.42	1.16	0.06
<i>trans</i> -2-Butene	5.55	0.76	-0.12
<i>trans</i> -2-Pentene	7.24	0.99	0.00
2-Methyl-2-butene	91.9	12.6	1.10
2,3-Dimethyl-2-butene	469	64.4	1.81
Styrene	167	22.9	1.36
1,1-Diphenylethene	363	49.9	1.70

^a 0.002 M sulfuric acid in 95% w/w acetic acid in the absence of air and light. ^b Estimated rate constant.

states appear to be more powerful oxidants than chromium(VI), their potency can be frequently diminished by the addition of cerous, ceric, or manganous ions (Scheme II).^{502,514,515}

SCHEME II



The proposed symmetrical three-membered cyclic activated complex (140–142) for the chromic acid oxidation of alkenes and cycloalkenes in 0.002 M sulfuric acid in 95% w/w acetic acid in the absence of air and light is consistent with the proposed mechanistic criteria.³⁰ Isolation of epoxides in the chromic acid oxidation of allylic alcohols,⁵⁰⁸ cyclohexene,⁵⁰⁹ and styrenes^{510–512} provides further support for the proposed epoxide-like activated complexes 140–142, and the electrophilic character of chromic acid is suggested by the plots of log relative rates vs. ionization potentials (Figures 22 and 23).

Although epoxides are formed in the oxidation of styrenes,^{510–512} the occurrence of rearrangements indicates that a positively charged product-determining species may be formed during the reaction. Also, the initially formed epoxide may rearrange under the acidic reaction conditions to the ob-

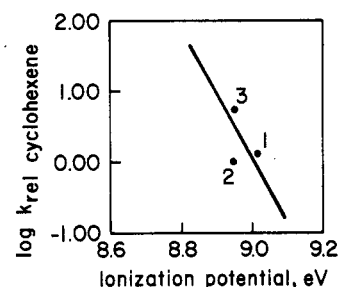
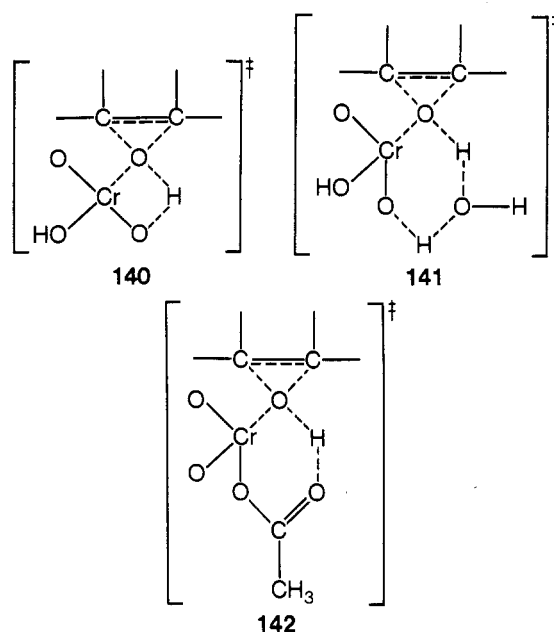


Figure 23. Relation between log relative rates (to cyclohexene) for the chromic acid oxidation of cycloalkenes and ionization potentials. The slope = -3.43 (rms = 0.3099) and the cycloalkenes for the number points are: (1) cyclopentene, (2) cyclohexene, (3) cycloheptene.

TABLE XLVII. Relative Rates of the Chromium(VI) Oxidation of Cycloalkenes^{a,30}

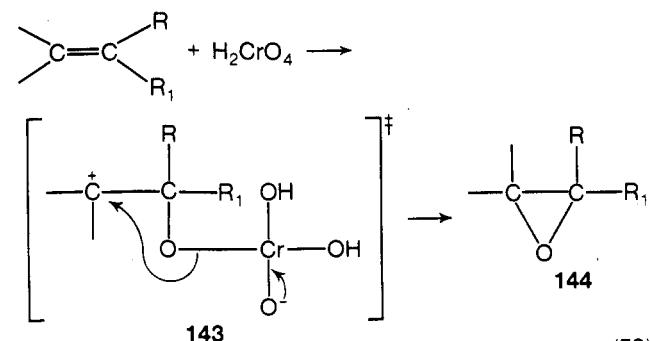
Cycloalkene	$k \times 10^3$ $M^{-1} \text{ min}^{-1}$	$k/k_{\text{cyclohexene}}$	$\text{Log } k/k_{\text{cyclohexene}}$
Cyclopentene	93.1	1.29	0.11
Cyclohexene	72.4	1.00	0.00
Bicyclo[2.2.1]hept-2-ene	397	5.48	0.74

^a 0.002 M sulfuric acid in 95% w/w acetic acid in the absence of air and light.

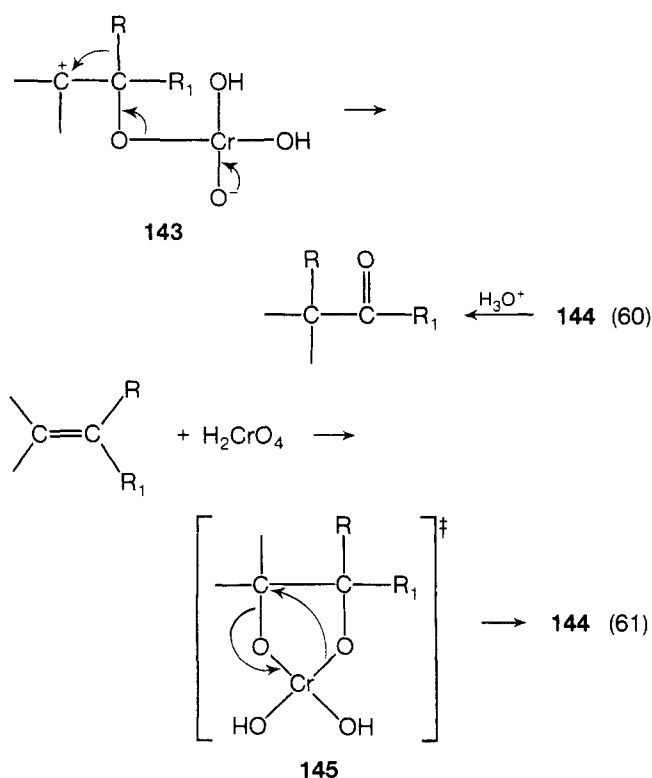


served carbonyl products. Several plausible reaction pathways are shown in eq 59–61.

Consideration of the reaction in light of the Zimmerman treatment of electrocyclic reactions suggests 143 or a similar



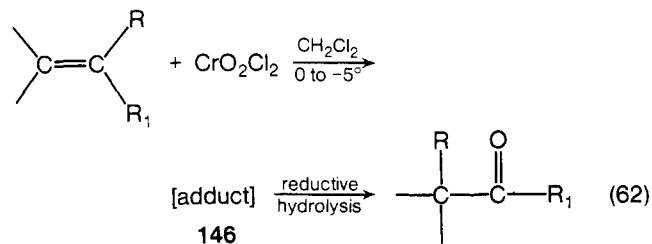
(59)



structure more closely resembles the activated complex than **8** or **145** for the chromic acid oxidation styrenes.^{20,513} In contrast, the small reactivity ratio (2.2) of **14** and **15** and the excellent fit of **15** in the ionization potential graph (Figure 22) argue against a change in mechanism in going from alkenes and cycloalkenes to styrenes. Unfortunately, the presently available data are not adequate to permit a differentiation among the plausible mechanisms for the chromic acid oxidation of styrenes.

L. Chromyl Chloride Oxidation^{25-29,516-541}

Conversion of carbon-carbon double bonds to carbonyl compounds can be achieved in good yields with chromyl chloride.^{519-521,523} Aldehydes are obtained from disubstituted ethenes, while tetrasubstituted ethenes are oxidized to ketones. Presumably the first step involves an electrophilic attack of chromyl chloride to give a 1:1 unsaturate-chromyl chloride adduct (**146**).⁵²³⁻⁵³⁴ The structurally rearranged products could result from a 1,2-hydride, -alkide, or -aride shift.⁵²¹ An



interesting rearrangement during the oxidation of tetraphenyl-ethene (**147**) affords 9,10-diphenylphenanthrene (**148**) in

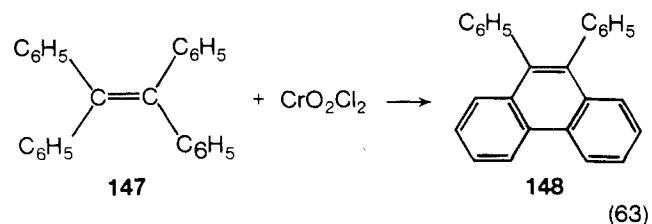


TABLE XLVIII. Relative Rates of Chromyl Chloride Oxidations of Alkenes and Styrenes^{a, 26-27,523}

Alkene	$k \times 10^2$ $M^{-1} \text{ sec}^{-1}$	$k/k_{\text{1-hexene}}$	$\text{Log } k/k_{\text{1-hexene}}$
2-Methyl-2-butene	1,480	201	2.303
2,3-Dimethyl-2-butene	28,750	3912	3.592
3,3-Dimethyl-1-butene	39.3	5.35	0.728
1-Pentene	8.99	1.22	0.087
cis-2-Pentene	111	15.1	1.178
trans-2-Pentene	101	13.7	1.138
2-Methyl-1-pentene	58.8	8.00	0.903
1-Hexene	7.35	1.00	0.000
1-Octene	5.69	0.77	-0.111
1-Decene	6.49	0.88	-0.054
Styrene	29.3	3.99	0.601
2-Phenylpropene	219 ^b	29.8	1.47
1,1-Diphenylethene	376.8	51.3	1.71
Triphenylethene	11.8	1.61	0.21
Tetraphenylethene	0.32	0.04	-1.36

^a Carbon tetrachloride solvent, 10°. ^b Average of several determinations. It is possible that polymerization of 2-phenylpropene may be a factor in the oxidation.

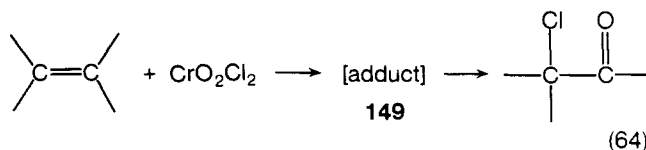
TABLE XLIX. Relative Rates of the Chromyl Chloride Oxidations of Cycloalkenes^{a, 28,29,517,523}

Unsaturate	k , $M^{-1} \text{ sec}^{-1}$	$k/k_{\text{cyclohexene}}$	$\text{Log } k/k_{\text{cyclohexene}}$
Cyclopentene	4.51	3.70	0.568
Cyclohexene	1.22	1.00	0.000
Cycloheptene	4.72	3.87	0.587
Cyclooctene	4.84	3.97	0.598
Cyclododecene ^b	1.26	1.03	0.014
1-Methylcyclopentene	48.6	39.8	1.60
1-Methylcyclohexene	12.1	9.92	0.996
1-Methylcycloheptene	182	149	2.17
Bicyclo[2.2.1]hept-2-ene	547	448	2.65

^a Carbon tetrachloride solvent, 10°. ^b Mixture of cis and trans isomers.

70% yield.⁵³³ Freeman and coworkers have postulated that epoxides are possible intermediates in the oxidation of carbon-carbon double bonds (ref 25-29, 521-523, 538-540), and preliminary studies indicate that chromyl chloride might prove to be the preferred chromium(VI) oxidant for one-step high-yield conversions of 2,2-disubstituted alkenes to aldehydes.^{520,523}

The importance of experimental conditions and the technique for decomposing the organochromium adduct is again demonstrated in the chromyl chloride oxidation of olefins at -70 or -5° in acetone. Hydrolysis of the adduct with aqueous sodium bisulfite solution affords α -chloro ketones in good yields.^{523,541} Although kinetic studies of this procedure have not been published, it is possible that the oxidant is some form of the $\text{CrO}_2\text{Cl}_2 \cdot 2\text{CH}_3\text{COCH}_3$ addition (complex) compound.⁵²³



Several norbornenes have been oxidized with chromyl chloride at -80°. Decomposition of the adduct with 10% aqueous sodium bicarbonate solution gives products which could arise from the initial formation of an *exo-cis*-chlorohydrin. These investigators suggested, in the absence of kinetic data, that the reaction involved a 1,3-dipolar type addition of

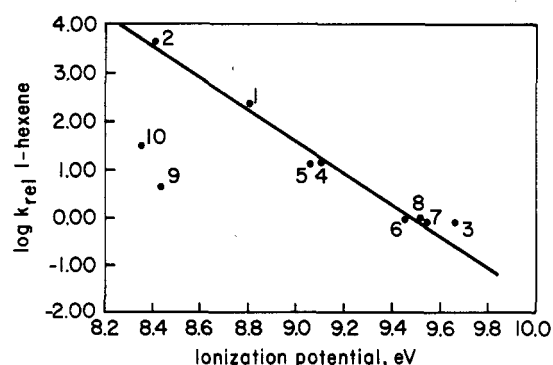
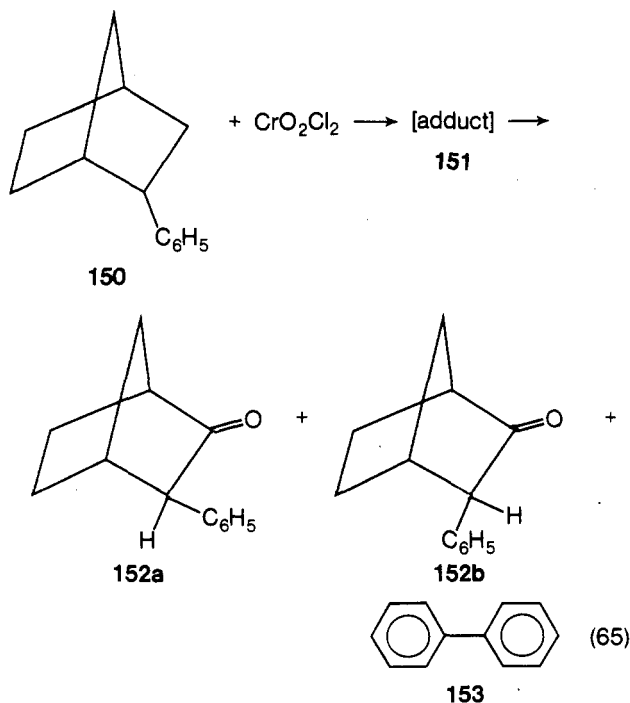


Figure 24. Relation between log relative rates (to 1-hexene) for the chromyl chloride oxidation of alkenes. The slope = -3.06 (rms = 0.2363) excluding points 9 and 10, and the alkenes for the number points are: (1) 2-methyl-2-butene, (2) 2,3-dimethyl-2-butene, (3) 1-pentene, (4) *cis*-2-pentene, (5) *trans*-2-pentene, (6) 1-hexene, (7) 1-octene, (8) 1-decene, (9) styrene, (10) 2-phenylpropene.

oxygen and chlorine from the oxidant to the carbon-carbon double bond or a free radical mechanism.⁵⁴⁰ Evidence for the possibility of a dual mechanistic pathway has been obtained by Freeman and Sing⁵³⁹ in the chromyl chloride oxidation of 2-phenylnorbornene (**150**) in methylene chloride at 0 to 5°. The adduct was decomposed with finely powdered zinc dust, and the products were steam-distilled from the reaction mixture. The 5% yield of biphenyl (**153**), which does not appear to be present in the starting material (**150**), could arise via a free radical mechanism. Under slightly different conditions the chlorohydrin (**154**) is obtained from the oxidation of **3**.⁵³⁹



The kinetics of the rapid oxidation of unsaturated hydrocarbons with chromyl chloride has been studied by Freeman and coworkers via spectrophotometric stopped-flow techniques.^{25-29,503}

$$v = k[\text{CrO}_2\text{Cl}_2][\text{U}] \quad (66)$$

Application of the proposed mechanistic criteria to the data from the chromyl chloride oxidation of alkenes suggests a rate-determining step involving a slightly unsymmetrical three-membered cyclic activated complex (**155**) with partial positive charge development at the more highly substituted carbon

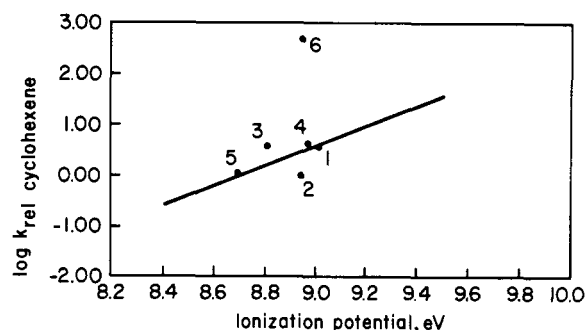
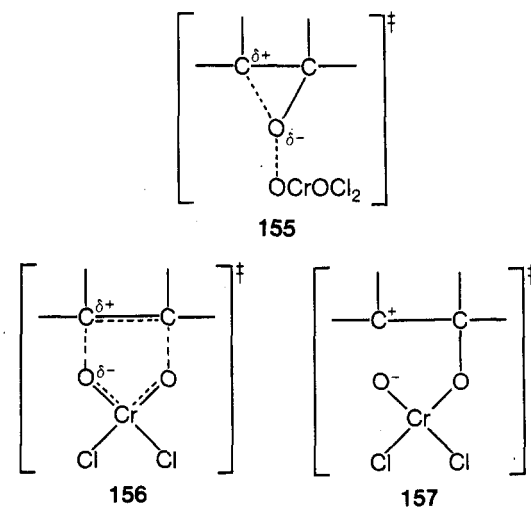


Figure 25. Relation between log relative rates (to cyclohexene) for the chromyl chloride oxidation of cycloalkenes and ionization potentials. The slope = 1.06 (rms = 0.2520) excluding point 6, and the cycloalkenes for the number points are: (1) cyclopentene, (2) cyclohexene, (3) cycloheptene, (4) *cis*-cyclooctene, (5) *cis*- and *trans*-cyclododecene, (6) bicyclo[2.2.1]hept-2-ene.

atom.²⁶ The rapid reaction does not appear to be very sensitive to steric hindrance, and the large negative entropies of activation indicate a rigid orientation of reactants in the activated complex.

155 could also represent the activated complex for the chromyl chloride oxidation of cycloalkenes. This conclusion does not necessarily hold for the oxidation of bicyclic systems, and the presently available data from the oxidation of **3** does not exclude consideration of structures resembling **156** and **157** or a free radical mechanism. The deviation of **3** in Figure 25 might also imply the possibility of a different mechanism than the one proposed for oxidation of simple cycloalkenes.⁵²³ As with chromic acid oxidations, Figures 24 and 25 suggest that chromyl chloride is an electrophilic reagent.

Data for the chromyl chloride oxidation of styrenes suggest that the activated complex is slightly polar with a small partial positive charge at the benzylic carbon atom.^{25,27} Although **155** or **156** is consistent with the data, the relative reactivity of **14** and **15** argues for a three-membered cyclic activated complex (**155**). Steric factors play a role in the oxidation as the rate decreases as phenyl substitution at the carbon-carbon double bond increases.²⁵

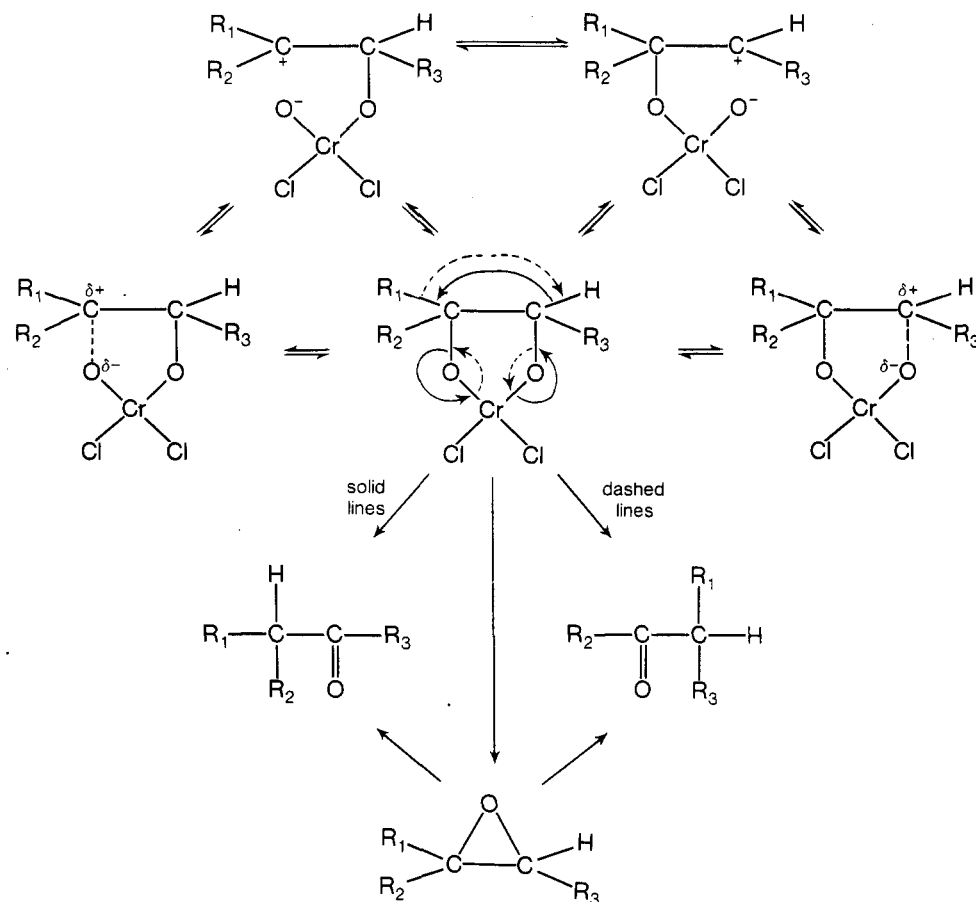


Scheme III shows some of the mechanistic possibilities for the chromyl chloride oxidation of alkenes, cycloalkenes, and styrenes. The oxidation of polycyclic systems is under investigation.⁵³⁹

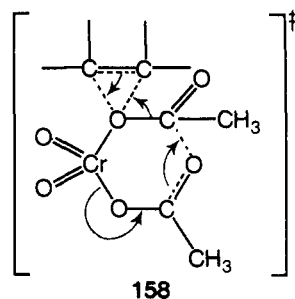
M. Chromyl Acetate Oxidation^{510,511,542-548}

Chromyl acetate, which is easily prepared from chromium trioxide and acetic anhydride,⁵⁴² oxidizes carbon-carbon dou-

SCHEME III



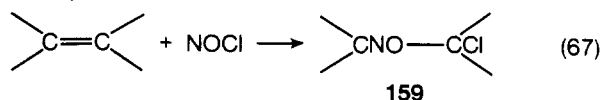
ble bonds to carbonates, epoxides, acids, diols, and carbonyl compounds.^{510,511,543-546} Although the presently available data are not adequate to support a definitive structure for the activated complex, a three-membered cyclic activated complex (158) resembling 142 or 155 could be involved in the chromyl acetate oxidation of carbon-carbon double bonds. A similar mechanism is probably involved in the chromyl trichloroacetate oxidations of cycloalkenes to dialdehydes.⁵⁴⁸



V. Four-Membered Cyclic Activated Complexes

A. Nitrosyl Chloride^{32,39,84,85,94,549-557}

Nitrosyl chloride (NOCl) adds to carbon-carbon double bonds according to the Markovnikov rule to give 1:1 adducts (159).^{549,550} Competing side reactions include dimerization or



$$v = k[\text{NOCl}][\text{U}] \quad (68)$$

TABLE L. Relative Rate Constants for Nitrosyl Chloride Addition to Alkenes^{32,554}

Alkene	$k/k_{1\text{-hexene}}$	$\log k/k_{1\text{-hexene}}$
Methylpropene	44.4	1.65
1-Butene	0.94	-0.025
<i>cis</i> -2-Butene	77.7	1.89
<i>trans</i> -2-Butene	146.3	2.16
2-Methyl-1-butene	53.7	1.73
3-Methyl-1-butene	0.44	-0.35
2-Methyl-2-butene	3333	3.52
1-Hexene	1.00	0.00
1-Octene	1.11	0.46

isomerization of 159 to oximes. A first-order dependence is observed for NOCl and for unsaturate.^{32,554}

Very little is consistently clear concerning the stereochemistry of NOCl additions. The ratio of *cis* to *trans* adducts is not consistent and appears to be solvent dependent.^{84,85,94,554,557} Electrophilic addition of nitrosyl bromide (NOBr) and NOCl to 3 gives the respective *cis*-exo adduct in good yields.⁵⁵²

The relative reactivity (660) of addition to 3 and cyclohexene, the *exo* addition to 3, the absence of transannular rearrangement in the addition to 10, the greater reactivity of the *trans* double bond in 11, the greater reactivity of *trans* alkenes over the corresponding *cis* isomers, the greater reactivity of *trans*-stilbene (53) over *cis*-stilbene (52), and the large negative entropies of activation are all consistent with a cyclic activated complex for the electrophilic addition of nitrosyl chloride to carbon-carbon double bonds (Tables L and LI; Figures 26 and 27). Although a molecular addition complex resembling 160 has been proposed, it appears that the large

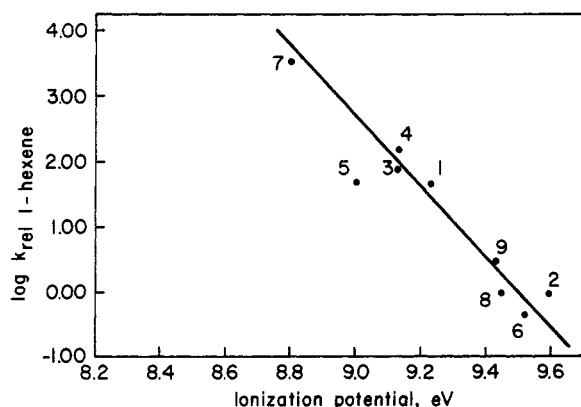
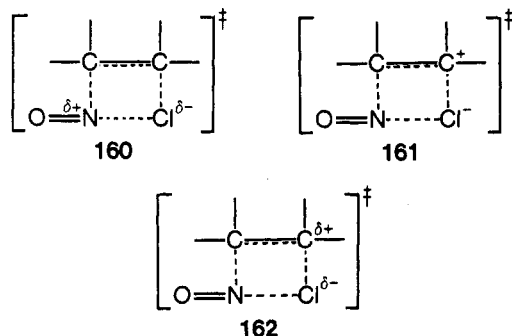


Figure 26. Relation between relative rates (to 1-hexene) for nitrosyl chloride addition to alkenes and ionization potentials. The slope = -4.88 (rms = 0.2667), and the alkenes for the number points are: (1) methylpropene, (2) 1-butene, (3) *cis*-2-butene, (4) *trans*-2-butene, (5) 2-methyl-1-butene, (6) 3-methyl-1-butene, (7) 2-methyl-2-butene, (8) 1-hexene, (9) 1-octene.

TABLE LI. Relative Rate Constants for Nitrosyl Chloride Addition to Cycloalkenes³²

Cycloalkene	$k/k_{\text{cyclohexene}}$	$\text{Log } k/k_{\text{cyclohexene}}$
Cyclobutene	72	1.86
Cyclopentene	88	1.94
Cyclohexene	1.00	0.00
Cycloheptene	29	1.46
<i>cis</i> -Cyclooctene	27	1.43
Bicyclo[2.2.1]hept-2-ene	660	2.28
Methylenecyclobutane	2.0	0.30
Methylenecyclopentane	16	1.20
Methylenecyclohexane	3.0	0.48
Methylenecycloheptane	5.9	0.77
Methylenecyclooctane	18	1.26

negative ρ values are more compatible with substantial positive charge development on the more highly substituted carbon atom (161 or 162).



It is of interest to note that the relative reactivities of cyclopentene and cyclohexene (88) and of 3 and cyclohexene (660) for the addition of nitrosyl chloride are much larger than the values observed above for reactions proceeding via three-membered cyclic activated complexes.

B. Hydroboration^{39,558-588}

The reaction of diborane with simple alkenes in the gas phase to produce trialkylboranes was discovered by Hurd in 1948,⁵⁶¹ and the hydroboration of alkenes in diglyme solution was discovered by Brown and Rao⁵⁶⁰ in 1956. Since boron is more positive than hydrogen, the stereoselective *cis* addition conforms to Markovnikov's rule. Alkylboranes (163) are very useful intermediates which can be easily converted to a wide variety of products.^{560,566,582,587} The hydroboration reaction

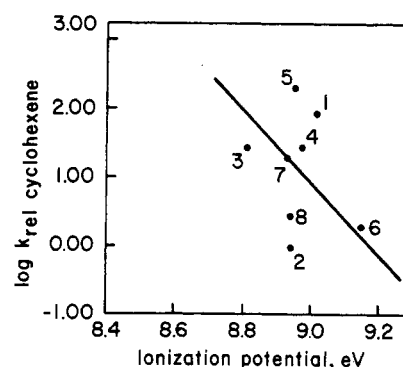
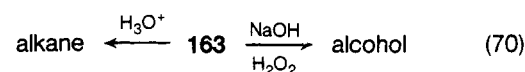
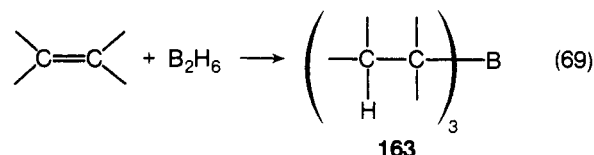


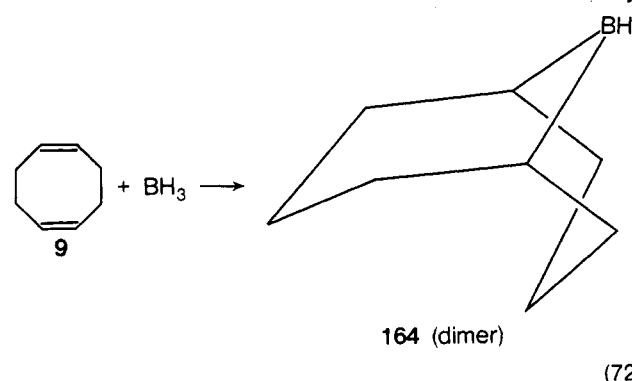
Figure 27. Relation between relative rates (to cyclohexene) for nitrosyl chloride addition to cycloalkenes and ionization potentials. The slope = -2.35 (rms = 0.7269), and the cycloalkenes for the number points are: (1) cyclopentene, (2) cyclohexene, (3) cycloheptene, (4) *cis*-cyclooctene, (5) bicyclo[2.2.1]hept-2-ene, (6) methylenecyclobutane, (7) methylenecyclopentane, (8) methylenecyclohexane.



is bimolecular,^{558,559} and despite its great synthetic utility and its wide applicability, it has not received a thorough kinetic and mechanistic investigation.

$$v = k[B_2H_6][U] \quad (71)$$

Dialkylboranes have many advantages over diborane for selective hydroborations. For example, 9-borabicyclo[3.3.1]nonane (9-BBN, 164), which exists as a dimer in the chair-chair conformation, is a stable, convenient, and selective hydroborating agent. 164 is prepared by the transannular reaction of borane and 9 in THF.^{563,569-574,582} Yields of hy-



droboration-oxidation products in the reaction of unsymmetrical olefins with diborane, 164, and bis-3-methyl-2-butylborane (disiamylborane, 165) have been compared.⁵⁷⁰ Other hydroborating reagents include 4,4,6-trimethyl-1,3,2-dioxaborinane (166),⁵⁷⁵ 1,3,2-benzodioxaborole (167),⁵⁷⁶ monochloroborane (168),⁵⁷⁷ and triethylamine-di-*n*-propylborane (169).⁵⁶³

Diborane addition to 2, and the limited reaction of 4 with 164³⁹ are consistent with a cyclic activated complex in hydroboration reactions. A four-membered cyclic activated complex (170), which is consistent with the proposed mechanistic criteria, has been suggested.⁵⁷⁸ A model involving a triangular π complex between borane and olefin has also been suggested.⁵⁷⁹ Similarly, consideration of orbital symmetry has

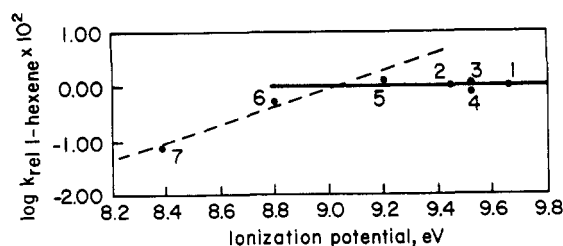
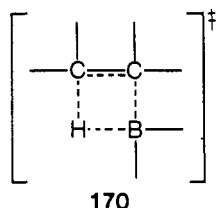
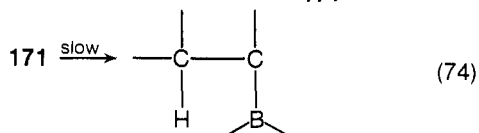
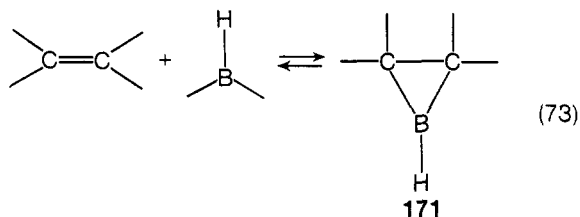


Figure 28. Relation between ionization potentials and relative rates of borane addition to alkenes. The slope (solid line) = -0.24 (rms = 0.0526) excluding points 6 and 7, and the alkenes for the number points are: (1) 1-pentene, (2) 1-hexene, (3) 1-octene, (4) 3-methyl-1-butene, (5) 2-methyl-1-butene, (6) 2-methyl-2-butene, (7) 2,3-dimethyl-2-butene.



led to the postulate of a two-step mechanism for hydroboration.⁵⁸⁶ Presumably the first step is an equilibrium resulting in a three-center-two-electron π complex intermediate (171), and the second step is a concerted conversion of 171 to products by a hydride transfer to the "more stable carbonium ion". It is important to note that this concerted symmetry-allowed process does not involve the buildup of any significant hydridic character on the boron hydrogens.⁵⁸⁸ However, the nearly identical internal and terminal kinetic isotope effects (H-D, ^{10}B - ^{11}B) for the addition of monochloroborane (168)⁵⁷⁷



to styrenes, the ρ value, and the proposed mechanistic criteria appear to argue against the π complex intermediate mechanism. These data do not preclude a possible pretransition state π complex in the hydroboration reaction.

Application of the possible mechanistic criteria to hydroboration with diborane or 9-borabicyclo[3.3]nonane (9-BBN, 164) again demonstrates the strong stereoselective control exercised by the 7,7-dimethyl groups in 4 (Table I) for reactions proceeding via three- or four-membered cyclic activated complexes. Also, the preferential attack of diethylborane at the trans double bond in 11, the 1,2-addition product from 2 and diborane, and the relative rates of exo addition to 3 and 4 with 164 (Table V) are consistent with a concerted four-center mechanism.

Figure 28 shows that diborane appears to be insensitive to the availability of electrons at the carbon-carbon double bond. Inclusion of 2-methyl-2-butene (point 6) and 2,3-dimethyl-2-butene (point 7) in Figure 28 gives a line of slope $+0.81$ (rms = 0.1996).

Figure 29 (Table LII) shows that a positive slope is obtained when bis-3-methyl-2-butylborane reacts with alkenes. In contrast, a slope of -5.39 (rms = 1.416) is obtained from a plot

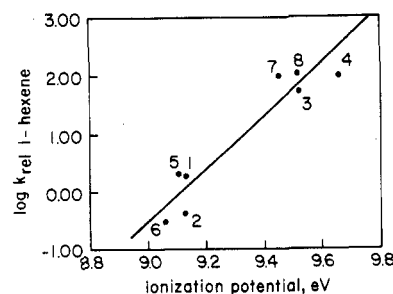


Figure 29. Relation between ionization potentials and relative rates of bis-3-methyl-2-butylborane addition to alkenes. The slope = $+4.45$ (rms = 0.3462), and the alkenes for the number points are: (1) *cis*-2-butene, (2) *trans*-2-butene, (3) 3-methyl-1-butene, (4) 1-pentene, (5) *cis*-2-pentene, (6) *trans*-2-pentene, (7) 1-hexene, (8) 1-octene.

TABLE LII. Relative Rates of Borane Addition to Olefins^{a,558}

Olefin	$k/k_{1\text{-hexene}}$	$\text{Log } k/k_{1\text{-hexene}}$
1-Pentene	0.98	0.00
1-Hexene	1.00	0.00
1-Octene	1.02	0.00
3-Methyl-1-butene	0.75	-0.12
2-Methyl-1-butene	1.21	0.08
2-Methyl-2-butene	0.50	-0.3
2,3-Dimethyl-2-butene	0.07 ^b	-1.15
2-Pentene	0.34 ^c	-0.47
Cyclopentene	0.72	-0.14
Cyclohexene	0.30	-0.52
1-Methylcyclopentene	0.52	-0.28
1-Methylcyclohexene	0.15 ^b	-0.82
Styrene	0.19	-0.72

^a Hydroboration by $\text{NaBH}_4 \cdot \text{BF}_3$ in diglyme at 0° . ^b Relative reactivity to cyclopentene. ^c Geometrical isomer not specified.

TABLE LIII. Relative Rates of Bis-3-methyl-2-butylborane to Olefins^{a,559,569}

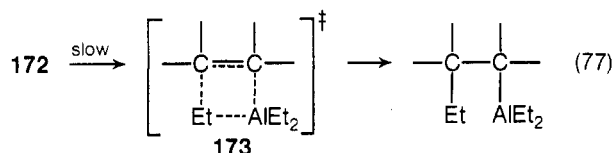
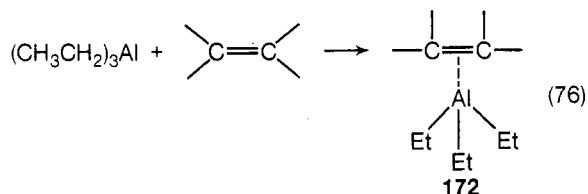
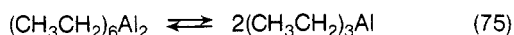
Olefin	$k/k_{1\text{-hexene}}$	$\text{Log } k^b/k_{1\text{-hexene}}^b$
<i>cis</i> -2-Butene	0.023	0.36
<i>trans</i> -2-Butene	0.004	-0.40
3-Methyl-1-butene	0.57	1.75
1-Pentene	1.05	2.02
<i>cis</i> -2-Pentene	0.02	0.30
<i>trans</i> -2-Pentene	0.003	-0.52
1-Hexene	1.00	2.00
1-Octene	1.08	2.03
2-Phenylpropene	0.023	0.36
Cyclopentene	140 ^c	2.15
Cyclohexene	1.00 ^c	0.00
Cycloheptene	2600 ^c	3.41
<i>cis</i> -Cyclooctene	5700 ^c	3.76

^a THF, 0° . ^b Second-order rate constant $\times 10^2$. ^c Relative to cyclohexene.

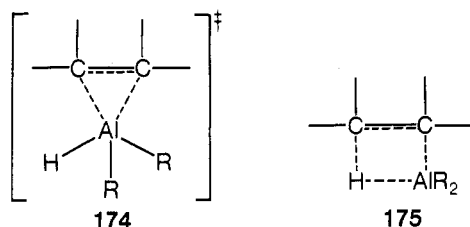
of log relative rates of bis-3-methyl-2-butylborane addition to cyclopentene, cyclohexene, cycloheptene, and *cis*-cyclooctene (Table LIII).

C. Diethylaluminum Hydride^{589,590}

Conflicting mechanisms have been proposed for the addition of alkyl aluminum compounds to carbon-carbon double bonds.^{589,590} A reasonable mechanism for diethylaluminum hydride requires a prior dissociation of the dimer (eq 75) to the monomer which can then form a π complex (172). Rearrangement of 172 could lead to a four-membered cyclic activated complex (173). The relative cyclopentene:cyclohexene



ratio for diethylaluminum hydride addition implies a three-membered cyclic activated complex which could resemble 174. Rearrangement of 174 to a four-center intermediate resembling 175 could then lead to the observed products. However, more data are necessary before a definitive mechanism can be discussed.

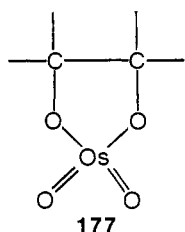
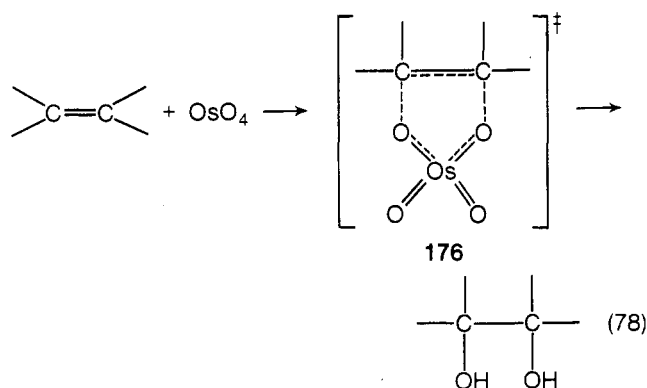


Although limited data are available, it can be seen from the reactions discussed above that judicious application of the proposed mechanistic criteria can be used to differentiate among reactions proceeding via three-membered and four-membered cyclic activated complexes.

VI. Five-Membered Cyclic Activated Complexes

A. Osmium Tetroxide Oxidation

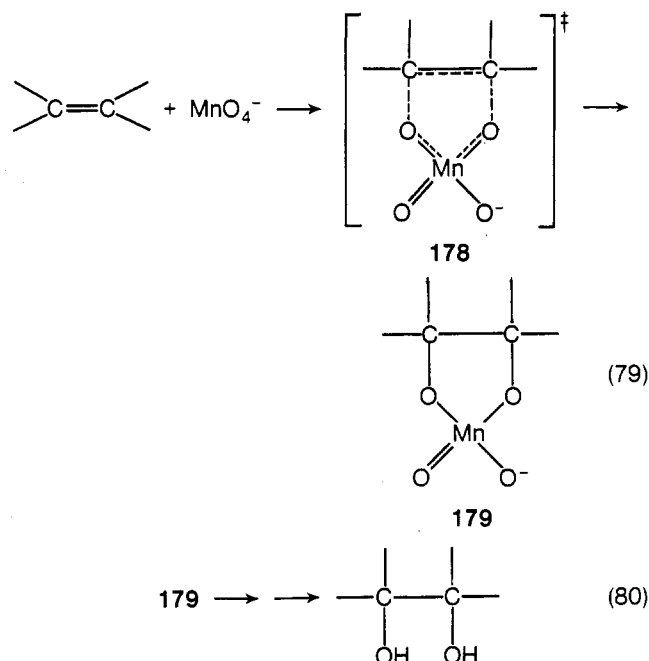
Osmium tetroxide oxidizes carbon-carbon double bonds to cis glycols, and the reaction has been presumed to proceed via a five-membered cyclic activated complex (176). The lim-



ited available data are not inconsistent with 176, and the rate of oxidation appears to be very sensitive to solvent changes.^{31,33} The intermediate osmate ester 177 has been isolated by Criegee and coworkers.^{591,592}

B. Permanganate Ion Oxidation⁵⁹³⁻⁶⁰³

Permanganate ion oxidizes carbon-carbon double bonds to cis glycols and, depending on the reaction conditions, to hydroxycarbonyl compounds.^{598,599,604,605} A five-membered cyclic activated complex (178) has been proposed as a result of kinetic, stereochemical, and ¹⁸O studies.^{598,599,604,605} Recently, the proposed cyclic manganese(V) intermediate 179 and other organomanganese intermediates have been observed spectrophotometrically in the permanganate ion oxidation of thymine,⁵⁹⁷ uracil,⁵⁹⁷ 2-furanacrylic acid,⁵⁹⁵ 2-thiopheneacrylic acid,⁵⁹⁶ crotonic acid,⁵⁹³ and cinnamic acid.⁵⁹⁴



The available data are consistent with the proposed mechanism (ref 593, 594, 597-599, 604, 605). Manganese(VII) is reduced to tetrahedral hypomanganate and, according to the Zimmerman method, the d electrons must be in a d_{z²} orbital. The orbital is locally symmetric whether one or both main lobes are involved in maximizing bonding overlap with reacting orbitals. Consequently, this treatment predicts cis hydroxylation of carbon-carbon double bonds which is consistent with the observed oxidation products.

It is also of interest to note that a five-membered cyclic activated complex resembling 178 has been postulated for the permanganate ion oxidation of nitronate anions,⁵⁹⁹⁻⁶⁰³ and that ruthenium tetroxide probably reacts with carbon-carbon double bonds via an activated complex resembling 176 and 178.

C. 1,3-Dipolar Cycloaddition

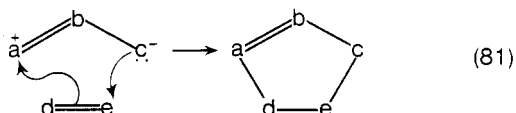
Reactions^{37,54,55,604-654}

Although Smith⁶⁰⁴ published a comprehensive review of open-chain and cyclic 1,3-additions in 1938, it was not until a study of the mechanism of addition of diazoalkanes to double bonds by Huisgen and coworkers^{37,54,55} that the concept of 1,3-dipolar cycloadditions was developed. Experimental investigations by Huisgen and collaborators^{37,54,55} have established a concerted mechanism for 1,3-dipolar cycloaddition reactions. In contrast, Firestone⁶⁰⁵⁻⁶⁰⁷ has proposed a two-step mechanism involving a polarized spin-pair diradical inter-

mediate. Presently it appears that the diradical hypothesis is incomplete or untenable since it provides no explanation for the relative reactivities of various 1,3-dipoles with a series of dipolarophiles. Also, the diradical hypothesis predicts, in contrast to the experimental facts, that the direction of addition of dipoles to monosubstituted alkenes is not influenced by the nature of the substituent.⁶¹² Harcourt⁶⁰⁸ has attempted to reconcile this difference using the valence bond and increased valence bond theory for the cycloaddition of *N*-methyl-*C*-phenylnitrene (**180**) to methyl methacrylate.

Molecular orbital calculations have been performed by extended Hückel and CNDO/2 methods in order to generate a set of frontier orbital coefficients and energies for dipolarophiles and 1,3-dipoles.⁶¹⁰⁻⁶¹⁵ This perturbation model accounts for the reactivity, regioselectivity, and periselectivity in 1,3-dipolar cycloaddition reactions.

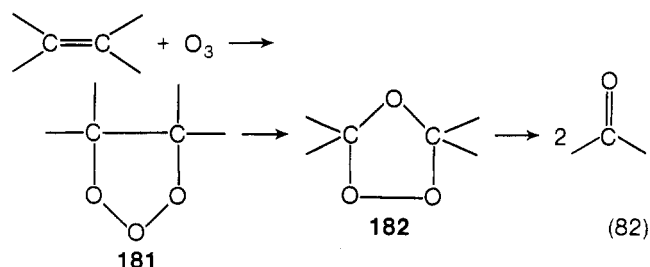
The monumental work of Huisgen and coworkers supports the general concept that 1,3-dipolar cycloaddition reactions involve zwitterionic molecules (the 1,3-dipole) which undergoes 1,3-addition to a dipolarophiles (alkene or alkyne). It is generally accepted that 1,3-dipolar cycloadditions are stereospecifically suprafacial and proceed via a concerted cyclic five-membered activated complex. The cycloadditions



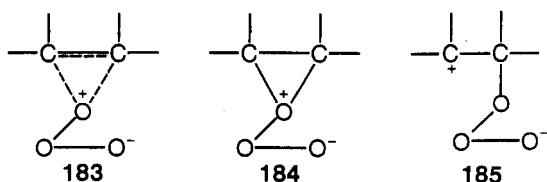
are generally insensitive to solvent polarity and are characterized by small activation enthalpies and large negative activation entropies.

1. Ozone

Ozone reacts with carbon-carbon double bonds to give very unstable intermediate 1,2,3-trioxolanes (**181**) which presumably rearrange to ozonides (**182**).^{624,628-631} **182** has one ether and one peroxy bridge between the two carbon atoms originally bearing the unsaturation, and reductive cleavage of **182** leads to aldehydes and ketones. Structures **183-185**



have been proposed as possible intermediates when one of the ozonolysis products is the epoxide derived from the olefin.^{616,620,632,633} The π complex **183** and σ complex **184** appear^{622,634,635} to be more reasonable than **185**. Extended

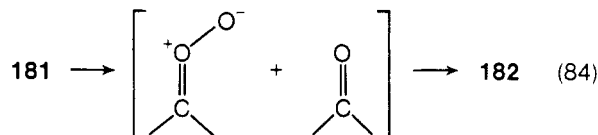


Hückel LCAO-MO calculations indicate that the primary ozonide (**181**) is more stable in the half-chair conformation.^{613,615,623,637}

Ozonolysis leading to normal ozonides is first order in unsaturate and first order in ozone.

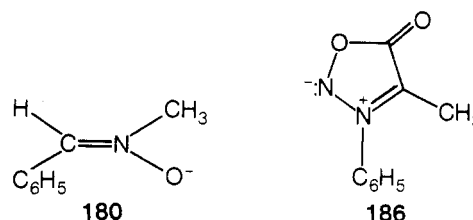
$$v = k[O_3][U] \quad (83)$$

The Criegee mechanism proposes that the primary ozonide **181** collapses to a carbonyl compound and a zwitterion which can recombine to the ozonide **182**. In order to explain

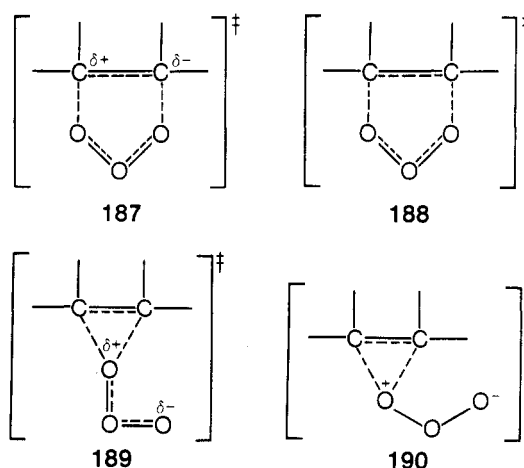


the exciting observation that the cis-trans ratios of cross ozonides obtained from cis and trans unsymmetrical olefins often differ, Story and coworkers^{628,633} proposed a competing "aldehyde interchange" mechanism. Subsequently, Bailey and coworkers revised the original Criegee mechanism by suggesting that the zwitterion intermediate is capable of existing in anti and syn forms which thereby determine the stereochemistry of the reaction. Possible revisions to the Bailey mechanism have recently appeared.⁶¹⁵

Before applying the proposed mechanistic criteria to the ozonolysis of olefins, it is of interest to note that 1,3-dipolar cycloaddition reactions involving class II dipoles [e.g., ozone, **180**, *N*-phenyl-*C*-methylsydnone (**186**)] do not show marked rate enhancements with **3**.⁶⁴⁰⁻⁶⁴² Although the $k_3:k_{\text{cyclohexene}}$



ratio is small (Table VIII), application of the proposed mechanistic criteria suggests that ozonolysis of alkenes proceeds via an unsymmetrical five-membered cyclic activated complex^{625,626} [**187**, $\rho^* \approx +2.60$ (cis), $+3.75$ (trans)] and the ozonolysis of styrenes ($\rho \approx -1.0$)^{625,627} proceeds via a more symmetrical five-membered cyclic activated complex (**188**). However, one has also to consider the possibilities of



three-membered cyclic activated complexes resembling **189** and **190**. Either **187**, **188**, **189**, or **190** could lead to intermediate **181**, **182**, or **183** which can then undergo the Criegee-zwitterion-carbonyl recombination pathway to ozonide formation.

It is of interest to note that a plot of log relative rates of ozone addition to alkenes and IP's (Table LIV, Figure 30) has a negative slope (-1.0), while the corresponding plot for cycloalkenes (Table LIV, Figure 31) has a positive slope $+1.0$.

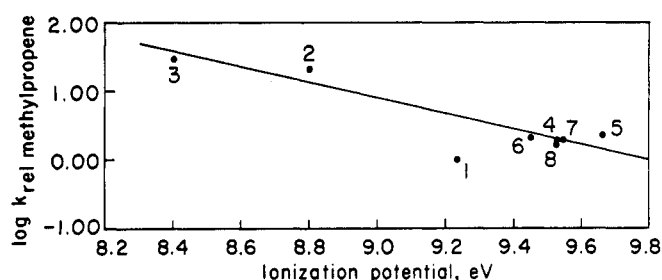


Figure 30. Relation between ionization potentials and relative rates of ozone addition to alkenes. The slope = -1.1 (rms = 0.2586), and the alkenes for the number points are: (1) methylpropene, (2) 2-methyl-2-butene, (3) 2,3-dimethyl-2-butene, (4) 2-methyl-1-butene, (5) 1-pentene, (6) 1-hexene, (7) 1-heptene, (8) 1-octene.

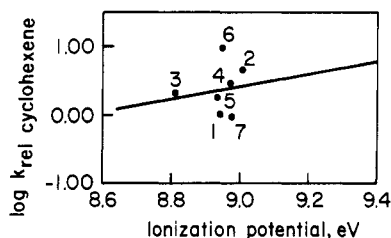


Figure 31. Relation between ionization potentials and relative rates of ozone addition to cycloalkenes. The slope = $+1.02$ (rms = 0.3308), and the cycloalkenes for the number points are: (1) cyclohexene, (2) cyclopentene, (3) cycloheptene, (4) *cis*-cyclooctene, (5) methylenecyclopentane, (6) bicyclo[2.2.1]hept-2-ene, (7) bicyclo[2.2.2]oct-2-ene.

2. Benzonitrile Oxide

Application of the proposed mechanistic criteria suggests an almost symmetrical five-membered cyclic activated complex (7) for the cycloaddition of benzonitrile oxide to carbon-carbon double bonds.

3. Diphenylnitrilimine

The proposed mechanistic criteria are compatible with an activated complex resembling 7 for the 1,3-dipolar cycloaddition of diphenylnitrilimine to carbon-carbon double bonds.

4. Phenyl and Picryl Azide

The proposed mechanistic criteria are also consistent with an almost symmetrical five-membered cyclic activated complex (1) for the cycloaddition reactions of phenyl^{647,648} and picryl^{644,650} azide.

5. Other 1,3-Dipoles

Diazomethane,^{613,651,652} diphenyldiazomethane,^{613,653,654} *C*-phenyl-*N*-methylnitrone,^{640-642,652} and ethylcyclohexylnitrone⁶⁴⁰⁻⁶⁴² are consistent with various aspects of the proposed mechanistic criteria. However, more data are required for a more meaningful comparison.

It is clear from Table VIII that the relative reactivities of cyclopentene and 3 relative to cyclohexene can be used as a criteria to distinguish between three-membered and five-membered cyclic activated complexes. Tables IX and X show that the relative reactivities of *cis* and *trans* isomers can also be used to distinguish between three-membered and five-membered cyclic activated complexes. In the latter group, the *trans* isomer reacts faster than the corresponding *cis* isomer while the reverse is true for the former group. Table XI reveals that 15 reacts faster than 14 in reactions involving five-membered cyclic activated complexes and that 14 generally reacts faster than 15 in reactions proceeding via three-membered cyclic activated complexes.

TABLE LIV. Relative Rates of Ozone Addition to Olefins^{a,625}

Olefin	$k/k_{\text{methylpropene}}$	$\log k/k_{\text{methylpropene}}$
Methylpropene	1.00	0.00
2-Methyl-2-butene	20	1.3
2,3-Dimethyl-2-butene	28.3	1.45
2-Methyl-1-butene	2.3	0.36
1-Pentene	2.4	0.38
1-Hexene	2.25	0.35
1-Heptene	2.16	0.34
1-Octene	1.83	0.26
1-Nonene	1.83	0.26
1-Decene	1.75	0.24
Styrene	2.5	0.40
2-Phenylpropene	2.16	0.34
Cyclohexene	1.00 ^b	0.00
Cyclopentene	4.5 ^b	0.65
Cycloheptene	2.0 ^b	0.30
<i>cis</i> -Cyclooctene	2.8 ^b	0.45
Methylenecyclopentane	1.9 ^b	0.28
Bicyclo[2.2.1]hept-2-ene	10 ^b	1.00
Bicyclo[2.2.2]oct-2-ene	0.93 ^b	-0.03
1-Methylcyclohexene	1.2 ^b	0.08

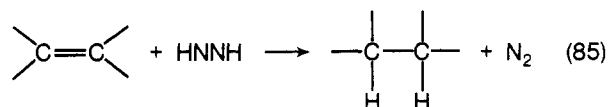
^a Ethanol, -60° . ^b Relative to cyclohexene.

Comparable secondary deuterium kinetic isotope effects are observed for both three-membered and five-membered cyclic activated complexes (Table XVII). Tables XII and XVI show that reactions proceeding via three-membered cyclic activated complexes are generally more unsymmetrical (polar) than those going through five-membered cyclic activated complexes. As expected, Table XVIII reveals that reactions proceeding via cyclic activated complexes are characterized by large negative entropies of activation.

VII. Six-Membered Cyclic Activated Complexes

A. Diimide Reduction^{35,655-664}

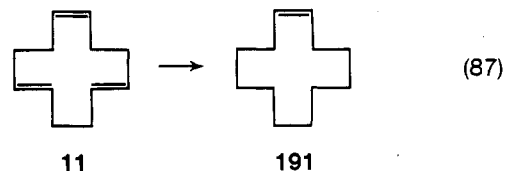
The diimide molecule is the simplest possible azo compound and is isoelectronic to ethene. Presumably the geometry is an idealized sp^2 hybridization at each nitrogen with a N-N double bond distance of 2.30 Å and a N-H bond of 1.011 Å.⁶⁵⁵ The transient azo compound reduces unsaturated hydrocarbons stereospecifically *cis* with no *cis*-*trans* isomeriza-



tion or migration of double bonds.⁶⁶¹⁻⁶⁶³ Steric factors are significant as illustrated by the greater ease of hydrogenation

$$v = k[\text{HNNH}][\text{U}] \quad (86)$$

of *trans* double bonds. This discriminating ability is exemplified in the selective formation of *cis*-cyclododecene from *cis*,-*trans*,*trans*-cyclododeca-1,5,9-triene (11)⁶⁵⁶ and in the faster reduction of fumaric acid as compared to maleic acid.⁶⁵⁷



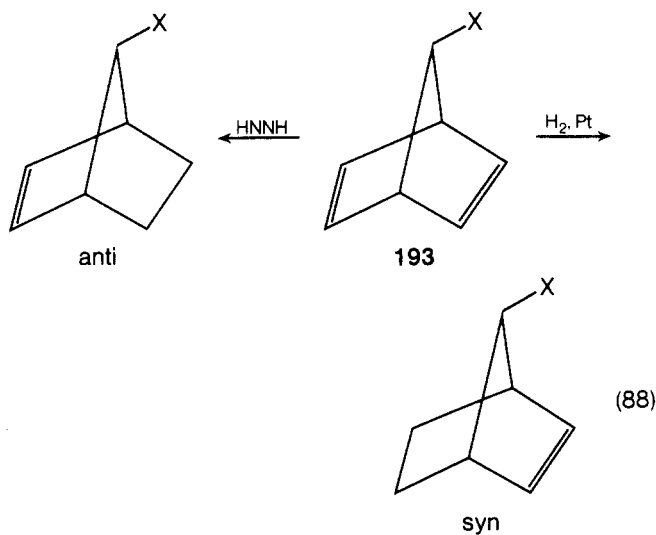
Steric approach control in diimide reductions is demonstrated in its reaction with bicyclo[2.2.1]hept-2-ene-2,3-dicarboxylic acid (192) to give only the *endo*-*cis* isomer via *exo*-*cis* addition of hydrogen. It is also instructive to note that in

TABLE LV. Relative Rates for Diimide Reductions of Alkenes and Cycloalkenes in Diglyme^{a,35}

Unsaturate	$k/k_{1\text{-pentene}}$	$\log k/k_{1\text{-pentene}}$
1-Pentene	1.00	0.00
2-Methyl-1-pentene	0.1	-1.00
<i>cis</i> -2-Pentene	0.13	-0.88
<i>trans</i> -2-Pentene	0.13	-0.89
2-Methyl-2-butene	0.014	-1.86
2,3-Dimethyl-2-butene	0.02	-1.60
Cyclohexene	1.00 ^b	0.00 ^b
Cyclopentene	15.5 ^b	1.19 ^b
Cycloheptene	12.1 ^b	1.08 ^b
<i>cis</i> -Cyclooctene	17.0 ^b	1.23 ^b
Cyclononene	5.70 ^b	0.76 ^b
Cyclodecene	0.85 ^b	-0.07 ^b
Cyclododecene	0.64 ^b	-0.19 ^b
Bicyclo[2.2.1]hept-2-ene	450 ^b	2.65 ^b
Bicyclo[2.2.2]oct-2-ene	29 ^b	1.46 ^b
Methylenecyclohexane	3.27 ^b	0.51 ^b
Methylenecycloheptane	3.6 ^b	0.56 ^b
Methylenecyclopentane	4.0 ^b	0.60 ^b
Methylenecyclooctane	2.4 ^b	0.38 ^b

^a 80°. ^b Relative to cyclohexene.

contrast to the platinum-catalyzed hydrogenation of 7-substituted bicyclo[2.2.1]hept-2,5-dienes (**193**) to syn 7-substituted bicyclo[2.2.1]hept-2-enes, the diimide reduction gives anti 7-substituted bicyclo[2.2.1]hept-2-enes.^{659,664} Although stere-

X = OAc, O-*t*-Bu, OH

ochemical and theoretical principles predict a preferential reaction at the anti double bond, this unusual reduction suggests that a potent electronic stabilizing effect involving the electron-donating oxygen atom in the 7 position suppresses the adverse steric factors.

As with chromyl chloride and with other postulated *cis*-addition reactions (e.g., diethylaluminum hydride addition, diisiamylborane addition), the relative reactivities of diimide reductions do not parallel either the relative ground-state strain energies of the cycloalkanes or the relative differences between product and reactant strain energies.³⁵

The available data are consistent with a concerted *cis* addition of hydrogen to the carbon-carbon double bond via a symmetrical six-membered cyclic activated complex of negligible ionic character (**194**).^{35,660} Garbisch and coworkers³⁵ have measured the relative rates of diimide reductions for nearly 40 acyclic, endocyclic, and exocyclic alkenes, and suggested that the major reactivity differences arose from

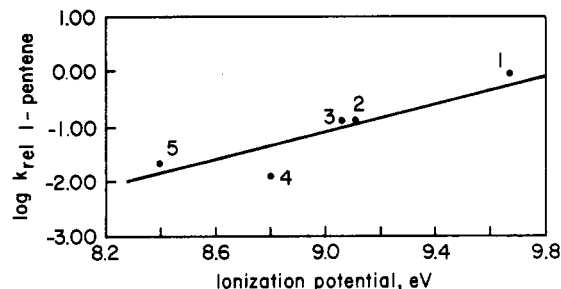


Figure 32. Relation between relative rates of diimide reduction of alkenes and ionization potentials. The slope = +1.43 (rms = 0.2779), and the alkenes for the number points are: (1) 1-pentene, (2) *trans*-2-pentene, (3) *cis*-2-pentene, (4) 2-methyl-2-butene, (5) 2,3-dimethyl-2-butene.

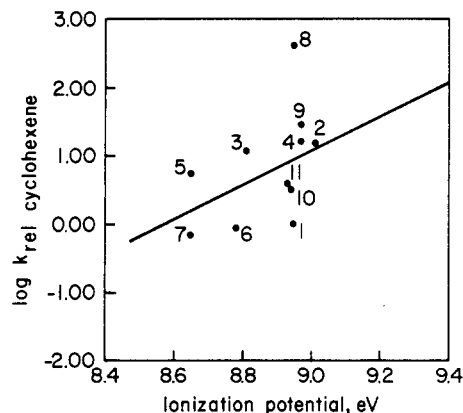
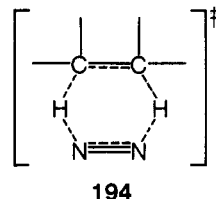


Figure 33. Relation between relative rates of diimide reduction of cycloalkenes and ionization potentials. The slope = +3.00 (rms = 0.6902), and the cycloalkenes for the number points are: (1) cyclohexene, (2) cyclopentene, (3) cycloheptene, (4) *cis*-cyclooctene, (5) cyclononene, (6) cyclodecene, (7) cyclododecene, (8) bicyclo[2.2.1]hept-2-ene, (9) bicyclo[2.2.2]oct-2-ene, (10) methylenecyclohexane, (11) methylenecyclopentane.



bond angle bending strain, α -alkyl substituent effects, and torsional strain.

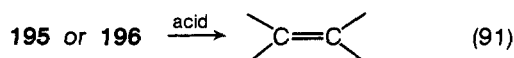
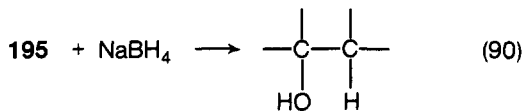
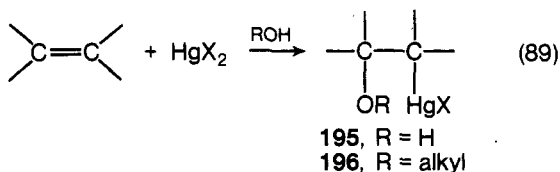
Table VIII shows that the relative reactivities of diimide reduction of cyclopentene and 3 relative to cyclohexene are distinctly different from the reactions proceeding via three-membered cyclic activated complexes and are similar to reactions involving five-membered cyclic activated complexes, and Figures 32 and 33 reveal that plots of log relative rates of diimide reduction of alkenes and cycloalkenes vs. IP's give positive slopes.

VIII. Other Possible Cyclic and Acyclic Activated Complexes

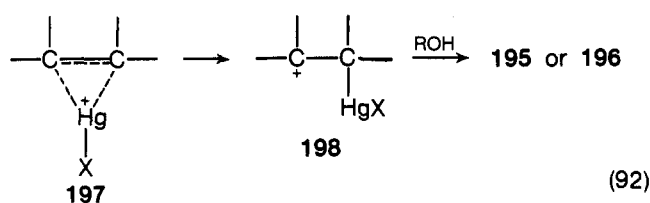
A. Oxymercuration

Mercuric salts readily add to carbon-carbon double bonds to give relatively high yields of unrearranged 1:1 adducts.^{665-667,674} Stoichiometrically the oxymercuration reaction consists of the addition of a mercuric salt, or a mixed mercuric salt involving solvent, to the olefinic center. Reductive replacement of the HgX group in **195** affords high yields of the corresponding alcohol.^{674,682} The reverse of oxymer-

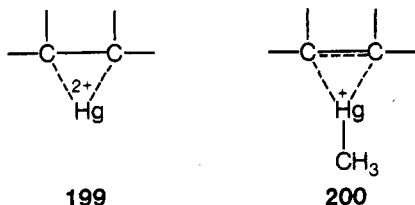
curation, which stereospecifically regenerates the olefin, is called demercuration.



Oxymercuration has been postulated to proceed via a mercuronium (mercurinium) ion (197) intermediate. This postulate is in accord with recent molecular orbital calculations¹⁵ and



the direct observation of stable mercuronium (mercurinium) ions (199) in $\text{FSO}_3\text{H-SbF}_5\text{-SO}_2$ solution⁶⁷⁵⁻⁶⁷⁹ and in the gas phase (200) by ion cyclotron resonance.⁶⁸¹



Three-membered, four-membered, and six-membered cyclic activated complexes have been postulated for the bimolecular oxymercuration reactions by various mercuric salts, and oxymercuration reactions occur faster with an increase in the ionic character of the Hg-X bond [$\text{Hg}(\text{ClO}_4)_2 > \text{Hg}(\text{OAc})_2 \gg \text{HgCl}_2$]. Since it appears that no single mechanism can accommodate the diverse oxymercuration data, the discussion below will treat each mercuric salt individually.

The small relative reactivities of cyclopentene and 3 with respect to cyclohexene (Table VIII) imply that the electrophilic addition of mercuric acetate to carbon-carbon double bonds in aqueous tetrahydrofuran and in methanol proceeds via a three-membered cyclic activated complex resembling 201 or 202. Sufficient data are not available to definitely exclude four-membered and six-membered cyclic activated complexes (203, 204). Support for 201 or 202 is also obtained from the greater reactivity of cis isomers (Tables IX and X), and the small ρ values argue against structures resembling 205. Transformation of 201 or 202 to product-determining intermediates is consistent with the cis-exo addition to derivatives of 3,⁶⁸³⁻⁶⁸⁵ the solvent- and salt-dependent cis:trans adduct ratios with bicyclo[2.2.2]oct-2-ene,⁶⁸³ and the stereochemistry of addition to monocyclic olefins.⁶⁸⁶⁻⁶⁸⁹ The regioselective and stereochemical effects of methyl substituents on the oxymercuration-demercuration of norbornyl derivatives have been studied.^{39,694} Predominant exo-cis addition was observed in the reaction of mercuric acetate with 3 and with 4. Also, it was shown by PMR that the intermediate kinetic mercurial adducts in 3 and 4 have the cis-exo structure.

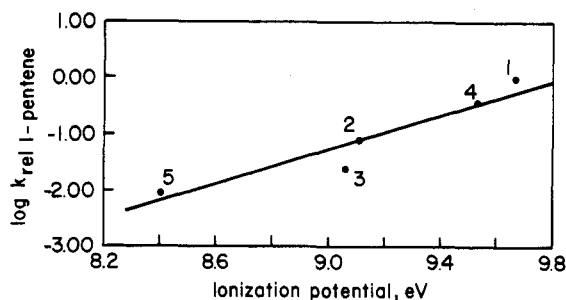
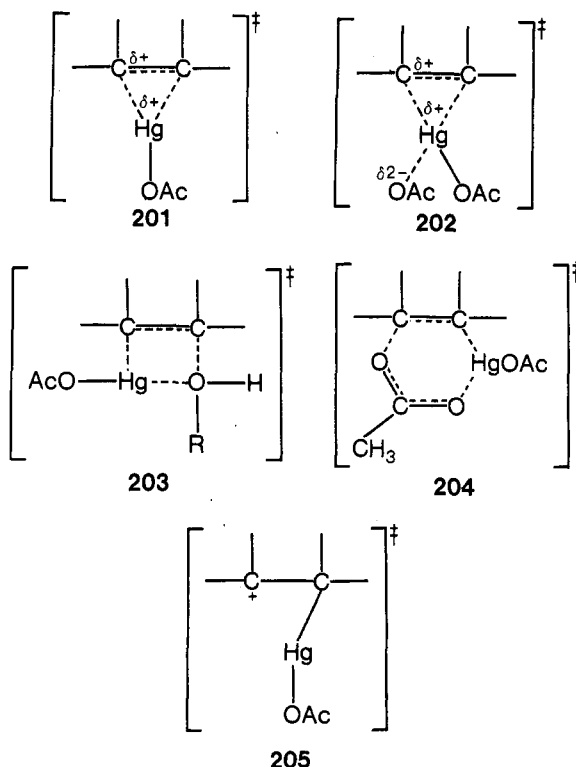


Figure 34. Relation between relative rates of mercuric acetate addition to alkenes and ionization potentials in 50% (v/v) aqueous THF. The slope = +1.60 (rms = 0.2278), and the alkenes for the number points are: (1) 1-pentene, (2) *cis*-2-pentene, (3) *trans*-2-pentene, (4) 3-methyl-1-butene, (5) 2,3-dimethyl-2-butene.



These data have been interpreted as casting doubt on the existence of a cyclic symmetrical mercurinium (mercuronium) ion as the activated complex in oxymercuration.^{39,694}

Additionally, rearranged products from the addition of mercuric acetate and mercuric azide to unsaturated centers suggest that a mercury-substituted carbonium ion is involved in the reaction. However, it is reasonable that a three-membered cyclic activated complex resembling 201 could easily rearrange to a σ -bridged species or to an intermediate resembling 205. Such a mercury-substituted carbonium ion could retain much of the charge on mercury and react rapidly with solvent from the *cis* or *trans* direction in order to lead to the observed products.⁴³ As indicated above, the energy difference among species 99, 100, and 101 is quite small.

Bach and Richter¹⁶³ have presented evidence which implies that neither the rate of oxymercuration nor the degree of π complex formation with silver ion is related to the ground-state energies of olefins. These workers¹⁶³ concluded that the rate-determining step in oxymercuration involves attack by solvent on a mercurinium (mercuronium) ion intermediate. As has been pointed out by T aylor,⁴³ steric effects and torsional or twist strain effects in the activated complex are the significant factors which determine the rate of reaction.

Figure 34 shows the correlation (slope = +1.60) between the relative rates of mercuric acetate addition to alkenes and

TABLE LVI. Relative Rate Constants for Mercuric Acetate Addition to Alkenes and Cycloalkenes in Methanol^{a,30,670,671}

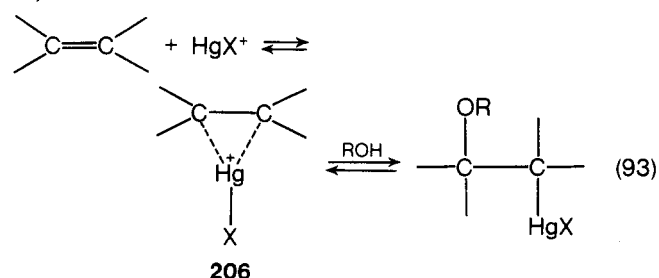
Olefin	$k/k_{1\text{-hexene}}$	$\log k/k_{1\text{-hexene}}$
2-Methyl-1-pentene	0.25	-0.59
1-Hexene	1.00	0.00
1-Heptene	0.95	-0.02
1-Octene	0.95	-0.02
2-Methyl-1-butene	1.77	0.25
2-Methyl-2-butene	0.38	-0.42
2,3-Dimethyl-2-butene	0.0017	-2.77
Cyclohexene	1.00 ^b	0.00 ^b
Cyclopentene	0.73 ^b	-0.14 ^b
Cycloheptene	0.25 ^b	-0.60 ^b
Cyclooctene	0.004 ^b	-2.40
Bicyclo[2.2.1]hept-2-ene	1.0 ^b	0.00 ^b
Bicyclo[2.2.2]oct-2-ene	0.03 ^b	-1.52
Methylenecyclopentane	17 ^b	1.23
Methylenecyclohexane	13 ^b	1.11

^a 25°. ^b Relative to cyclohexene.**TABLE LVII. Relative Rate Constants for Mercuric Acetate Addition to Alkenes and Cycloalkenes**^{a,672}

Olefin	$k/k_{1\text{-pentene}}$	$\log k/k_{1\text{-pentene}}$
1-Pentene	1.00	0.00
2-Methyl-1-pentene	7.27	0.86
<i>cis</i> -2-Pentene	0.08	-1.07
<i>trans</i> -2-Pentene	0.026	-1.59
3-Methyl-1-butene	0.38	-0.42
2,3-Dimethyl-2-butene	0.009	-2.03
Cyclohexene	1.00 ^b	0.00 ^b
Cyclopentene	0.78 ^b	-0.11 ^b
<i>cis</i> -Cyclooctene	0.002 ^b	-2.69 ^b
Methylenecyclopentane	58 ^b	1.76 ^b
1-Methylcyclopentene	1.86 ^b	0.27 ^b
Bicyclo[2.2.1]hept-2-ene	3.7 ^b	0.57 ^b
Bicyclo[2.2.2]oct-2-ene	0.01 ^b	-1.99 ^b

^a 50:50 (v/v) mixture of H₂O and THF. ^b Relative to cyclohexene.

IP's in aqueous tetrahydrofuran. No correlation was obtained for the corresponding oxymercuration of cycloalkenes^{672,693} in the same solvent system and for olefins in methanol (Tables LVI-LVIII). As suggested above, there should not necessarily be a correlation between log relative rates and IP's for those reactions in which disruption of the π system is not the rate-determining step.¹⁶³ Perhaps the data in Tables LVI and LVII are compatible with a rate-limiting step involving nucleophilic attack by solvent on a reversibly formed π complex (eq 93).



Activated complexes resembling **203** and **204** have been proposed to explain alkoxymercuration reactions which result in *cis* addition to some strained and/or bicyclic olefins. Acetoxymercuration of bicyclo[2.2.2]oct-2-ene in acetic acid solvent affords both *cis*- and *trans*-2-acetoxymercuric acetates and could involve an activated complex similar to **207**.⁶⁹⁰ A transoxymercuration mechanism involving **208** is not unreasonable.

TABLE LVIII. Relative Rates for Transmercuration of Methoxymercury Acetate with Olefins in Methanol^{a,30,670,671}

Olefin	$k/k_{1\text{-hexene}}$	$\log k/k_{1\text{-hexene}}$
1-Pentene	1.57	0.20
1-Hexene	1.00	0.00
1-Heptene	1.00	0.00
1-Octene	1.00	0.00
2-Methyl-1-pentene	0.02	-1.63
2-Methyl-1-butene	0.09	-1.05
3-Methyl-1-butene	0.37	-0.43
2,3-Dimethyl-2-butene	0.003	-3.48
Cyclohexene	1.00 ^b	0.00 ^b
Cyclopentene	0.3 ^b	-0.52 ^b
Cycloheptene	0.1 ^b	-1.00 ^b
<i>cis</i> -Cyclooctene	0.007 ^b	-2.15 ^b
Bicyclo[2.2.1]hept-2-ene	800 ^b	2.90 ^b
Bicyclo[2.2.2]oct-2-ene	4.0 ^b	0.60 ^b

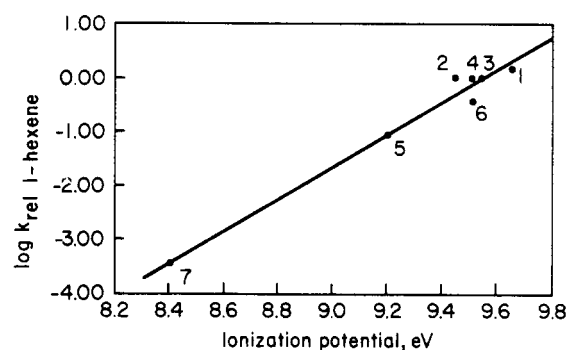
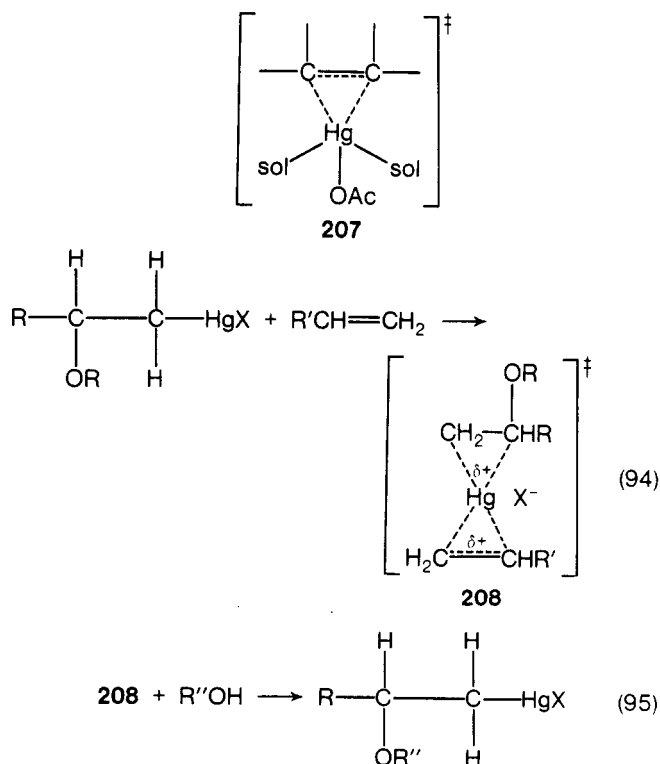
^a 50°. ^b Relative to cyclohexene.

Figure 35. Relation between relative rates of transmercuration of methoxymercury acetate of alkenes in methanol and ionization potentials. The slope = +2.98 (rms = 0.1817), and the alkenes for the number points are: (1) 1-pentene, (2) 1-hexene, (3) 1-heptene, (4) 1-octene, (5) 2-methyl-1-butene, (6) 3-methyl-1-butene, (7) 2,3-dimethyl-2-butene.



Oxymercuration of unsaturated hydrocarbons and alkenols with mercuric perchlorate could proceed via a three-mem-

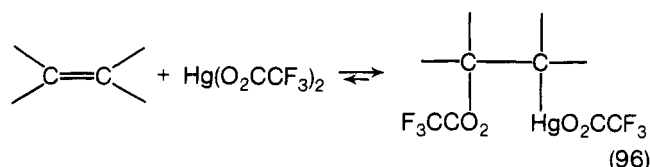
TABLE LIX. Relative Rate Constants for Mercuric Perchlorate Addition to Olefins and Alkenols^{a,695,705}

Substrate	k/k_{ethene}	$\log k/k_{\text{ethene}}$
Ethene	1.00	0.00
Propene	19.6 ^b	1.29
1-Butene	15.7 ^b	1.20
Methylpropene	>200 ^c	>2.30 ^c
<i>cis</i> -2-Butene	1.14	0.06
<i>trans</i> -2-Butene	0.33	-0.48
2-Methyl-2-butene	3.8	0.58
1-Buten-4-ol	1.65	0.22
1-Penten-4-ol	1.20	0.08
1-Penten-5-ol	>200 ^c	>2.30 ^c
Cyclohexene	1.00 ^d	0.00 ^d
Cyclobutene	0.70 ^d	-0.15 ^d
Cyclopentene	0.76 ^d	-0.12 ^d
Cycloheptene	0.18 ^d	-0.74 ^d
Methylenecyclobutane	>400 ^{c,d}	>2.60 ^d
Methylenecyclopentane	>400 ^{c,d}	>2.60 ^d
Methylenecyclohexane	~200 ^d	~2.30 ^d

^a 0.01 M HClO₄, 25°. ^b Low precision due to very fast reaction. ^c Too fast to measure in stopped-flow apparatus. ^d Relative to cyclohexene, ref 705.

bered cyclic activated complex (201 or 202). The ρ^* value of -3.3 implies a reasonable amount of positive charge development at the more highly substituted carbon atom of the reactant olefin during the rate-determining step.⁶⁹⁵ However, the entropies of activation appear to be somewhat small for a cyclic activated complex, and the data in Table LIX (Figure 36) are not simply correlated with IP's.

Mercuric trifluoroacetate reacts rapidly and reversibly with olefins to form molecular addition compounds.⁶⁹⁶⁻⁶⁹⁸ The 1,2-addition gives a *trans* adduct with cyclohexene and *cis*



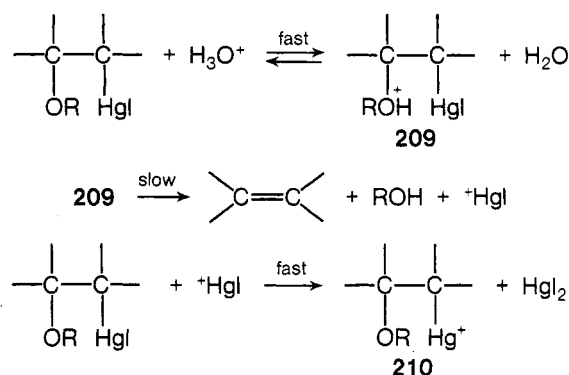
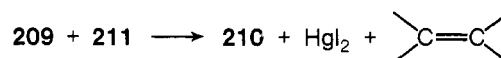
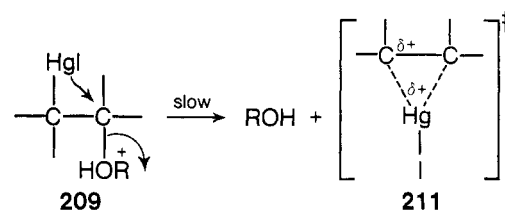
adducts with 3 and 4. The rate ratio $k_{\text{exo-3}}:k_4$ of 73.6 implies that the electrophilic addition is probably noncyclic, and the relative rate ratio of 3 to cyclohexene (13,158) argues against a three- or four-membered cyclic activated complex. Indeed, the rate ratio of 13,158 is larger than the ratio for any reaction postulated to proceed via a cyclic mechanism.

Kreevoy and coworkers have intensely investigated the kinetics of the deoxymercuration of alkoxymercuric iodides under a wide variety of conditions.^{699,702,704} Good first-order kinetics were observed; the slow step involves heterolytic C-O bond cleavage, salt and solvent effects are minimal, and solvent isotope effects of 2-3 are also observed.⁶⁹⁹ ρ^*

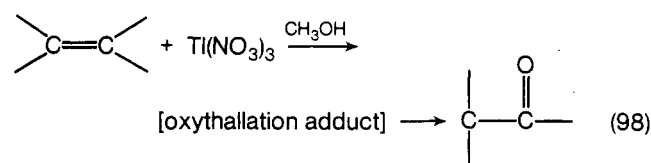
$$v = k[\text{mercurial}][\text{H}_3\text{O}^+] \quad (97)$$

values of -2.77 and -2.93 have been reported for demercuration.^{700,703} These data, but not the secondary deuterium kinetic isotope effects (1.06 ± 0.02) for the demercuration of $\text{CH}_3\text{OCH}_2\text{CH}_2\text{HgI}$ and its 1,1,2,2-tetradeuterio analog,^{702,704} appear to argue against substantial charge development in the activated complex. Scheme IV or Scheme V is compatible with the above kinetic data.

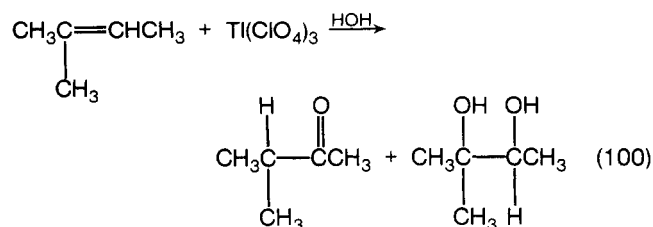
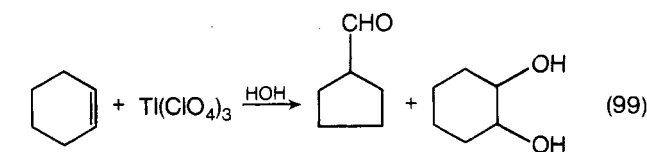
Oxidation of unsaturated hydrocarbons with mercury(II), thallium(III), or lead(IV) can afford a wide variety of products depending on the nature of the anion, the cation, the solvent, and the structure of the unsaturate. Unfortunately, few research results have been reported for the oxidation of

SCHEME IV**SCHEME V**

unsaturated hydrocarbons by toxic thallium(III) compounds.^{665,706-710} One of the few synthetically useful procedures based on oxythallation is a simple method for preparing aldehydes and ketones from olefins with thallium(III) nitrate in methanol.⁷¹⁰⁻⁷¹⁵ (In this respect thallium(III) nitrate appears to be similar to chromyl chloride.) The final oxidation products



depend on the nature of the media; e.g., in aqueous solution the products are 1,2-diols, aldehydes, and ketones, and acetates are also isolated in acetic acid. Structurally rearranged products suggest that product-determining intermediates with some positive charge (thallonium ions) are involved.^{705,711}



Kinetic studies are sometimes difficult because thallium triacetate forms a double salt with thallos acetate which arises from the rapid solvolysis of the oxythallium adduct. The reaction of ethene is first order in ethene and in thallium triacetate with $\rho^* = -4.7$.^{713,720} A ρ^+ value of -2.2 and a ΔS^\ddagger value

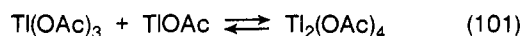
TABLE LX. Relative Rates for the Thallic Ion Oxidation of Various Olefins^{705,713,714}

Olefin	k^a/k_{ethene}^a	k^b/k_{ethene}^b	$\text{Log } k^a/k_{\text{ethene}}^a$
Ethene	1.00	1.00	0.00
Propene	152	167	2.18
Methylpropene	2.3×10^5	$\sim 2 \times 10^5$	5.36
1-Butene	157	162	2.20
cis-2-Butene	60	58	1.78
trans-2-Butene	35	13.6	1.54
Cyclohexene	1.00 ^c		0.00 ^c
Cyclobutene	0.44 ^c		-0.36 ^c
Cyclopentene	0.85 ^c		-0.07 ^c
Cycloheptene	0.14 ^c		-0.85 ^c
Methylenecyclobutane	197 ^c		2.29 ^c
Methylenecyclopentane	3380 ^c		3.52 ^c
Methylenecyclohexane	1169 ^c		3.07 ^c

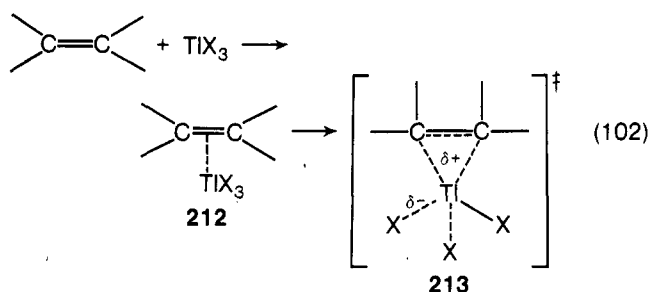
^a $\text{Ti}(\text{OAc})_3$ in aqueous acetic acid, ref 713. ^b $\text{Ti}(\text{ClO}_4)_3$ in 0.25 M aqueous perchloric acid, ref 714. ^c Relative to cyclohexene, ref 705.

TABLE LXI. Relative Equilibrium Constants for Palladium(II) Chloride Oxidation of Alkenes⁷²⁹

Alkene	K/K_{ethene}	$\text{Log } K/K_{\text{ethene}}$
Ethene	1.00	0.00
Propene	0.83	-0.79
1-Butene	0.62	-0.20
cis-2-Butene	0.49	-0.31
trans-2-Butene	0.25	-0.60



of -41 eu for the oxidation of substituted styrenes⁷¹⁸ imply that the activated complex for oxythallation has a high degree of order in which considerable carbon-thallium bond making has occurred. Rearrangement of a π complex to a σ -organothallium species is consistent with stereochemical studies in the cyclohexene systems.^{722,723} These limited data are in agreement with oxythallation proceeding via a cyclic activated complex (213).



It is also possible that the reaction involves the fast reversible formation of a bridged π complex (214) with rate-limiting attack by solvent on thallonium ion intermediate. This would be consistent with the poor correlation between log relative rate for thallation of olefins and ionization potentials (Table

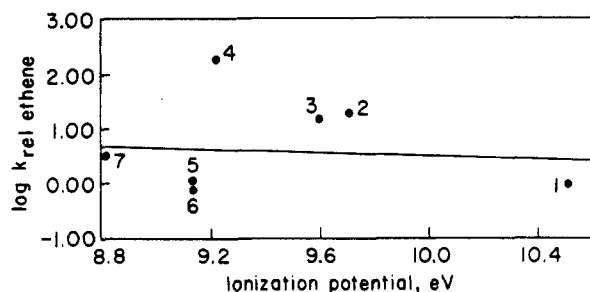
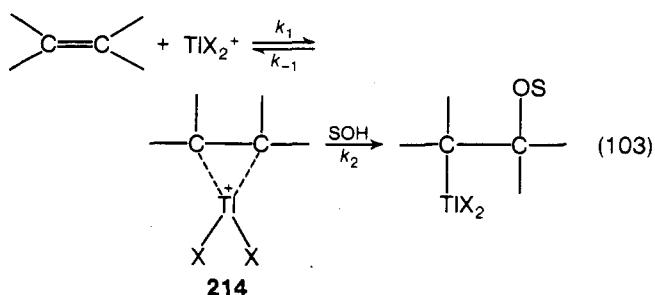


Figure 36. Relation between relative rates of mercuric perchlorate addition to alkenes and ionization potentials in 0.01 M HClO_4 . The slope = -0.11 (rms = 0.8816), and the alkenes for the number points are: (1) ethene, (2) propene, (3) 1-butene, (4) methylpropene, (5) cis-2-butene, (6) trans-2-butene, (7) 2-methyl-2-butene.

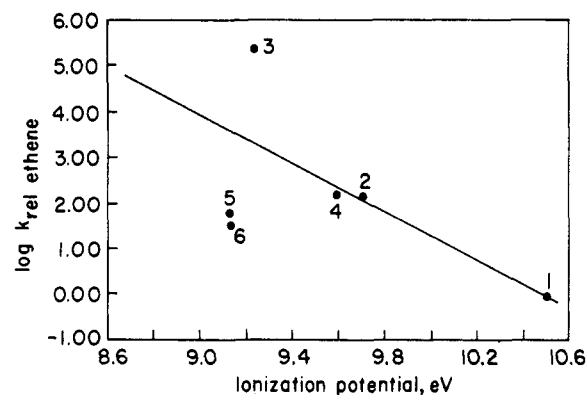
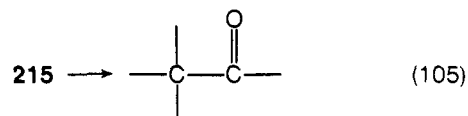
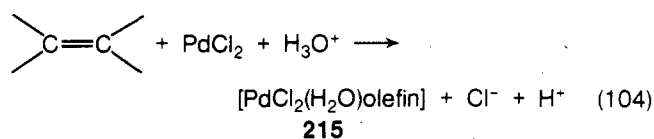


Figure 37. Relation between relative rates of thallic acetate oxidation of alkenes and ionization potentials. The slope = -1.92 (rms = 1.313), and the alkenes for the number points are: (1) ethene, (2) propene, (3) methylpropene, (4) 1-butene, (5) cis-2-butene, (6) trans-2-butene.

LX, Figure 37) since disruption of the π system would not be rate limiting.

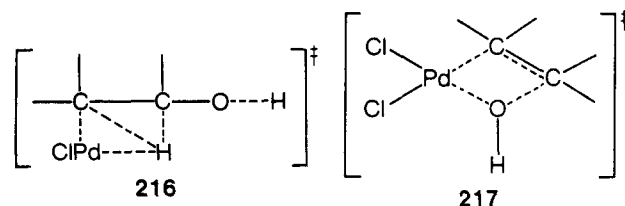
The mechanism of oxypalladation by palladium(II) salts is quite complicated and is not well understood.^{707,726-731} The



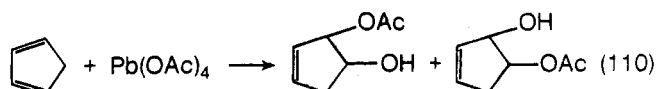
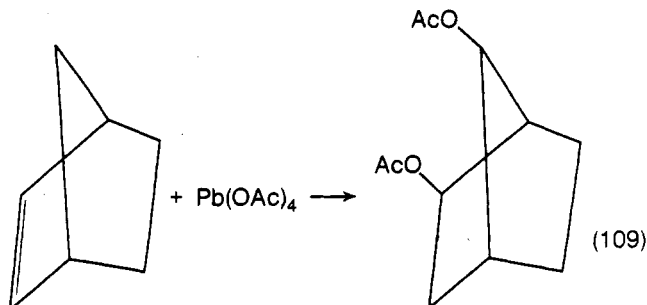
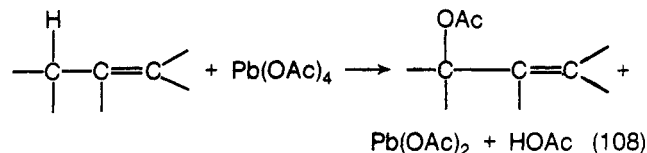
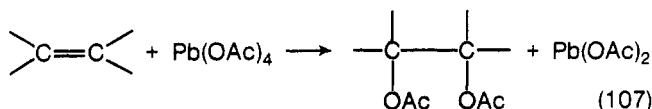
rate expression for the aqueous palladium(II) chloride oxidation of ethene to ethanol is given in eq 106, where K_1 is the equilibrium constant for formation of the ethene-palladium(II) π complex.^{730,731} Unfortunately, sufficient data are not avail-

$$\frac{-d[\text{C}_2\text{H}_4]}{dt} = \frac{K_1 k' [\text{C}_2\text{H}_4] [\text{PdCl}_4^{2-}]}{[\text{Cl}^-]^2 [\text{H}^+]} \quad (106)$$

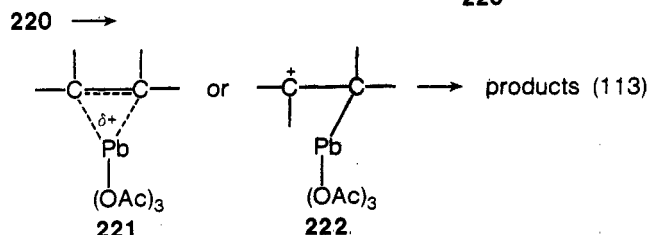
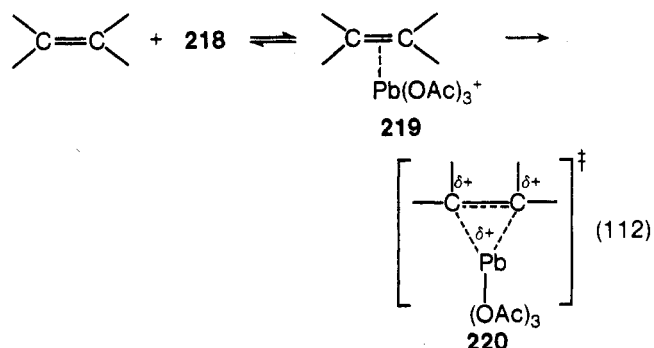
able to support the proposed activated complexes 216 and 217. The limited data in Table LXI show the relative insensitivity of oxypalladation to alkene structure.



The major portion of the reactions of lead(IV) salts with unsaturated compounds involves lead tetraacetate. Lead tetraacetate reacts with carbon-carbon double bonds to give a wide variety of products (eq 107-110). Although lead tetra-



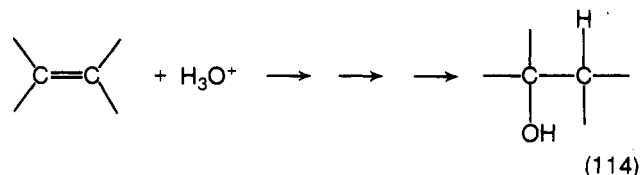
acetate is capable of reacting by a free-radical pathway, it is not unreasonable to expect the lead triacetate cation (**218**) to be an electrophilic oxidant which can reversibly add to a carbon-carbon double bonds to give a π complex (**219**). **219** could rearrange to an activated complex which could resemble **220**, which, depending on the degree of carbon-lead bond formation, could lead to **221** or **222**. This mechanism is anal-



ogous to that proposed above for oxymercuration and oxythallation. However, in contrast to Hg(II) and Tl(III) salts, no acyclic or monocyclic intermediate organolead compounds have been isolated.⁷³² In the absence of pertinent kinetic data, it is not possible to discuss the mechanism of oxyplumbation in detail.

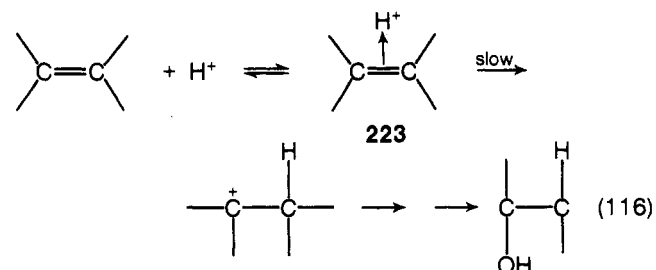
B. Acids^{30,60,737-759}

Carbon-carbon double bonds are weakly basic and form 1:1 and 1:2 hydrogen-bonded molecular complexes with acids. At low acid concentrations, the hydration of olefins is first order in acid concentration and first order in olefin concentration. However, third-order and fourth-order kinetics have been observed in some systems.⁷⁴² Curiously, there is a dearth of kinetic data concerning these hydration and dehydration reactions.

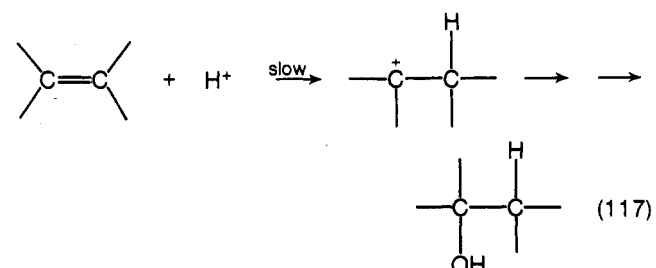


$$v = k[\text{U}][\text{H}_3\text{O}^+] \quad (115)$$

It was once thought that the acid-catalyzed hydration of simple olefins proceeded through the rapid reversible formation of a π complex **223** which subsequently underwent rate-determining collapse to a carbonium ion (A-1 mechanism, eq 116).⁷⁴³⁻⁷⁴⁹ However, more recent studies appear to support an A-SE2 mechanism (eq 117).⁷⁴⁵ Support for the intermediacy of cationic species is obtained from the numerous exam-



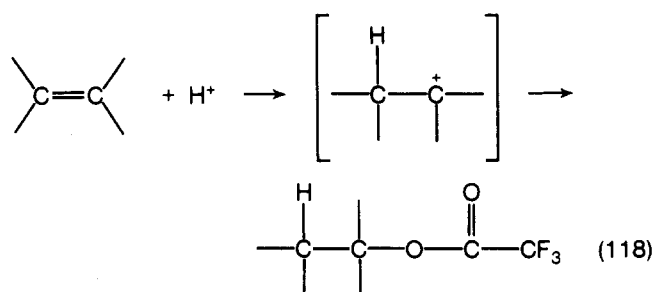
ples of rearrangement observed during acid additions to olefins.^{738,742,750,751}



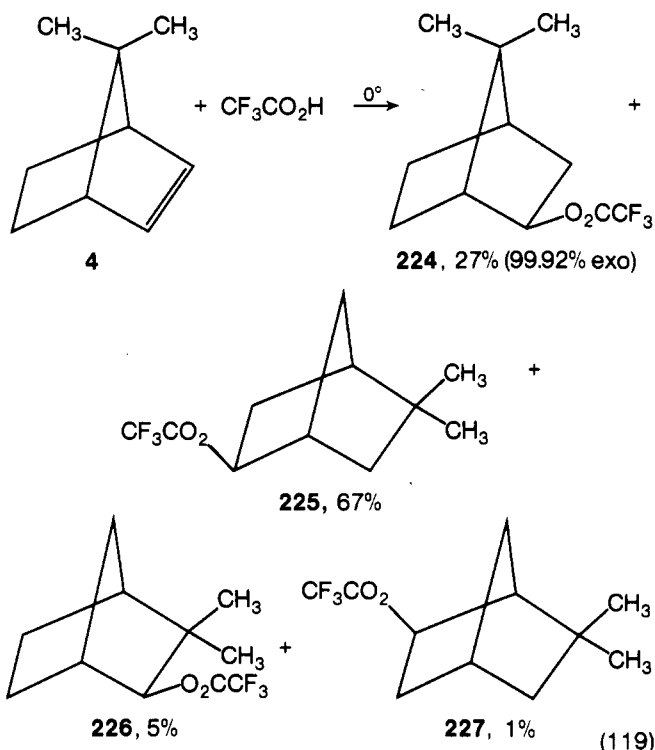
A carbonium ion like activated complex for the hydration of simple olefins appears to be entirely consistent with the proposed mechanistic criteria. The similarity of rates between **3** and **4** for acetic acid and hydrogen chloride (Table V), the large ρ^+ values (Table XIII), the secondary deuterium kinetic isotope effects (Table XVII), and the insensitivity of rates to IP's (Table LXII) are consistent with the postulate of a carbonium ion like activated complex.

Additional data on hydration and dehydration reactions are necessary in order to apply the proposed mechanistic criteria more rigorously and to compare and contrast cyclic and acyclic activated complexes. It would also be of interest to compare the relative rates of addition of alcohols, phenols, thiols, and hydrogen halides to simple olefins.

Presumably trifluoroacetic acid adds to alkenes according to Markovnikov's rule to give trifluoroacetates.^{757,758} An "encumbered" cationic intermediate has been postulated to explain the comparatively small percentage of hydride shift and elimination reactions observed during the addition of trifluo-



roacetic acid to some alkenes.⁷⁵⁸ The addition of perdeuterioacetic acid and deuteriotrifluoroacetic acid to **4** to give *exo*-3-*d*-7,7-dimethylnorbornyl *exo*-acetate-*d*₃ and *exo*-trifluoroacetate, respectively, has been cited as evidence against molecular cyclic addition processes for these two reagents.⁶⁰ Typical carbonium ion characteristics of the addition are exemplified in the great deal of Wagner–Meerwein and hydride shifted products **225–227**. The relative reactivities of several olefins with trifluoroacetic acid are shown in Table LXIII (Figure 38).



C. Free Radicals^{759–773}

Reactions of singlet oxygen are of considerable biological, environmental, and synthetic importance. It is thought that singlet (¹Δ_g) oxygen is an intermediate in the photosensitized 1,4-cycloaddition of oxygen to dienes and 1,2-cycloadditions to electron-rich olefins. Molecular orbital calculations suggest that perepoxides might be involved in the 1,2-cycloaddition reaction which forms 1,2-dioxetanes (**228**).^{768–772} Direct evi-

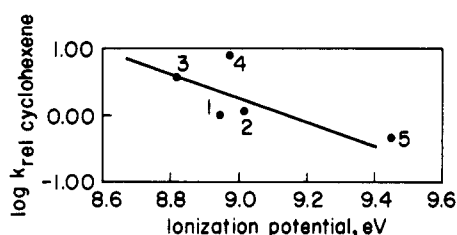
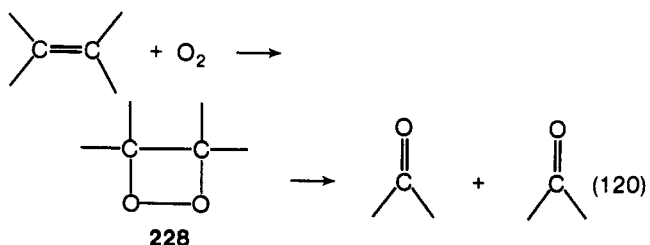


Figure 38. Relation between addition of trifluoroacetate to olefins and ionization potentials. The slope = -1.46 (rms = 0.3590) excluding point 5, and the olefins for the number points are: (1) cyclohexene, (2) cyclopentene, (3) cycloheptene, (4) *cis*-cyclooctene, (5) 1-hexene.

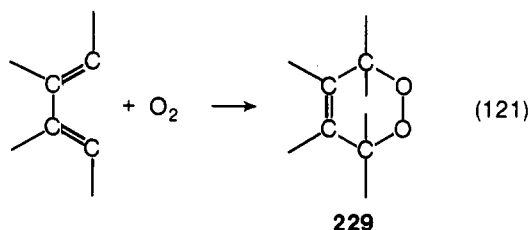
TABLE LXII. Rate Data for the Hydration of Some Olefins^{a,728,744,752}

Alkene	Slope log k_{hydr} vs. $-\text{H}_0$	$k/k_{\text{methylpropene}}$	Log $k/k_{\text{methylpropene}}$
Methylpropene	1.07	1.00	0.00
2-Methyl-1-butene		1.30	0.11
2-Methyl-2-butene	0.98	0.67	-0.17
2,3,3-Trimethyl-1-butene	0.99	1.20	0.08
Methylenecyclobutane	1.11	0.60	-0.22
1-Methyl-1-cyclobutene	1.25	0.1	-1.00
1-Methyl-1-cyclopentene		2.29	0.36

^a Relative rates for the acid-catalyzed hydration of propene (1.00), *cis*-2-butene (1.68), *trans*-2-butene (0.71), methylpropene (10^3 – 10^4), and 2-methyl-2-butene (10^3 – 10^4) have been quoted.^{30,753}

TABLE LXIII. Relative Rates of Addition of Trifluoroacetic Acid to Hexenes and Cycloalkenes⁷⁵⁸

Substrate	$k/k_{\text{cyclohexene}}$	Log $k/k_{\text{cyclohexene}}$
Cyclohexene	1.00	0.00
Cyclopentene	1.16	0.06
Cycloheptene	3.69	0.57
<i>cis</i> -Cyclooctene	8.10	0.91
1-Hexene	0.45	-0.34
<i>cis</i> -2-Hexene	0.58	-0.23
<i>cis</i> -3-Hexene	0.77	-0.11
<i>trans</i> -2-Hexene	0.72	-0.14
<i>trans</i> -3-Hexene	0.51	-0.30



dence for the formation of a perepoxide from the reaction of singlet oxygen and adamantylideneadamantane (**230**) has been reported.⁷⁶⁵ Presumably, the formation of **228** and the cyclic peroxide **229** could involve cyclic activated complexes. Also, a charge-transfer or π complex between olefin and singlet oxygen might be formed in a preequilibrium step prior to the formation of **228**.

It is also of interest to note that oxygen atoms react non-

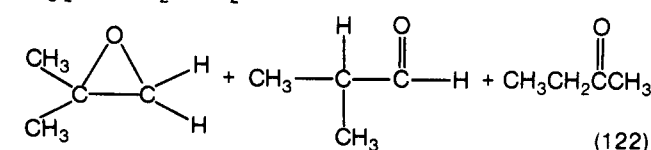


TABLE LXIV. Relative Rates for the Reactions of Alkenes with the Oxygen Atom

Alkene	$k/k_{\text{methylpropene}}$	$\log k/k_{\text{methylpropene}}$
Ethene	0.038	-1.42
Propene	0.23	-0.64
<i>cis</i> -2-Butene	0.84	-0.08
<i>trans</i> -2-Butene	1.13	0.53
Methylpropene	1.00	0.00
2,3-Dimethyl-2-butene	4.18	0.62
Cyclopentene	1.20	0.79

TABLE LXV. Relative Rates of Bromine Atom Addition to Alkenes

Alkene	k/k_{propene}	$\log k/k_{\text{propene}}$
Ethene	0.056	-1.23
Propene	1.00	0.00
Methylpropene	22	1.34
<i>cis</i> -2-Butene	5.4	0.73
<i>trans</i> -2-Butene	5.7	0.76

TABLE LXVI. Comparison of the Slopes^a from Plots of $\log K_{\text{rel}}$ vs. Ionization Potentials and ρ Values

Electrophile	Proposed size of cyclic activated complex	Alkenes		Cycloalkenes	
		ρ^*	Slope ^a	ρ^*	Slope ^a
Bromine	3	-2.94 to -5.22 ^{174,178,181,182,200,213}	-2.89	-2.5 to -3.0 ²⁵⁷	-1.83 ²⁵⁷ -3.74 ³²
Chlorine	3	-4.15 ²⁶⁷	-4.82		
Iodine	3		+0.24		-0.16
Iodine isocyanate	3				-1.84
Iodine thiocyanate	3	-3.42 ³²	-2.2		+0.007
Silver nitrate	3	-0.93 ³⁴²	+0.79	-0.77 ^{349,351}	-1.05
2,4-Dinitrobenzenesulfonyl chloride	3	-1.89 to 2.84 ^{32,356}	-1.67	-2.88 ^{355,356}	-2.38
Methanesulfonyl chloride	3		-0.80		
Chlorocarbene ^b	3		-0.83		
Chlorocarbene ^c	3		-0.17		
Bromocarbene	3		-0.09		
Chlorofluorocarbene	3		-1.80		
Methylchlorocarbene	3		-0.96		
Phenylchlorocarbene	3		-1.18		
Dibromocarbene	3		-0.33		
Dichlorocarbene	3	-0.74 ⁴¹² -4.3 ⁴⁰²	-1.89 -2.14		
Iodomethylzinc iodide	3		-0.52		+1.31
2,2-Diphenylcyclopropylidene	3		-0.09		
Dimethylethylidenecarbene	3				-1.26 ^d
Dimethylallenidenecarbene	3		-1.38 ^e		
Cyclopentadienylidene	3		+0.06 ^f		
Peracetic acid	3		-3.23		-0.02
Peroxybenzimidic acid	3				-0.74 ^g
Chromic acid	3		-1.92		-3.43
Chromyl chloride	3?	-2.63 ^{26-27,523}	-3.06	~2.0 ^{26-27,523}	+1.06
Nitrosyl chloride	4	-5.34 ³²	-4.88		-2.35
Diborane	4		-0.24		
Bis-3-methyl-2-butylborane	4		+4.45		
Ozone	5	-2.53, ⁶²⁵ +2.60, ⁶²⁶ +3.75 ⁶²⁶	+0.40		+1.02
Diimide	6		+1.43		+3.00
Mercuric acetate ^h	3?		+1.60		-27.0
Mercuric acetate ⁱ	3?	-1.00 ⁸⁷¹			-2.53
Mercuric acetate ^j	3?		+2.98		+3.23
Mercuric perchlorate	R ⁺	-3.3 ⁶⁹⁵	-0.11		+7.19
Thallium triacetate	?	-4.70 ^{716,720}	-1.92		+5.84
Palladium chloride	?		+0.29		
Trifluoroacetic acid	?				-0.01
Oxygen atom	?		-1.04		

^a This work. ^b Generated from methylene chloride. ^c Generated from ClHCN₂. ^d Includes 1-octene and styrene. ^e Includes cyclohexene. ^f Includes cyclohexene and styrene. ^g Includes three alkenes. ^h Aqueous THF. ⁱ Methanol. ^j Transmercuration in methanol.

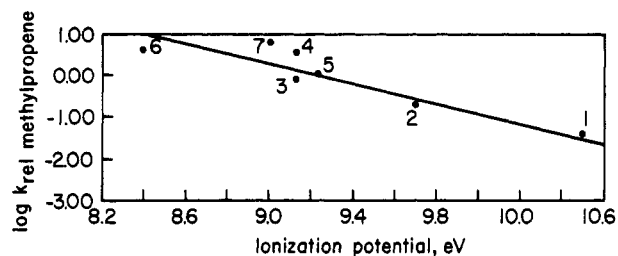


Figure 39. Relation between addition of oxygen to olefins and ionization potentials. The slope = -1.04 (rms = 0.2223) excluding point 7, and the olefins for the points are: (1) ethene, (2) propene, (3) *cis*-2-butene, (4) *trans*-2-butene, (5) methylpropene, (6) 2,3-dimethyl-2-butene, (7) cyclopentene.

stereospecifically with alkenes in the gas phase to give rearranged addition and cleavage products.⁷⁵⁹⁻⁷⁶¹ Presumably the oxygen atom adds predominantly to the less substituted sp^2 -hybridized carbon atom. The relative reactivities (Table LXIV, Figure 39) also suggest that the biradical oxygen atom possesses some degree of electrophilicity. Although a cyclic

activated complex is possible for the addition, there are not sufficient data to apply the proposed mechanistic criteria.

The relative rates of bromine atom addition to alkenes⁷⁶⁰ (Table LXV) are shown for comparison with the relative reactivities of the oxygen atom.

IX. Summary

It is recognized that there are obvious difficulties and limitations associated with an attempt to apply mechanistic criteria to many diverse electrophilic addition and 1,3-dipolar cycloaddition reactions of carbon-carbon double bonds. It would be desirable to determine the lower and upper limits of each criterion, to better define the essential parameters which affect each criterion, to discuss the exceptions in more detail, and to more critically consider the variable nature of the activated complex owing to its position along the reaction coordinate. However, owing to space limitations, incomplete theories, and a dearth of pertinent experimental observations, the data and discussions are presented in the pithy form above.

It would also be desirable to further explore the contributions and influence of heats of hydrogenation, ionization potentials (Table LXVI), spectroscopic excitation energies, and strain energies on the relative rates of additions to carbon-carbon double bonds.

It is clear from the above relative reactivity data that there is promise of establishing objective criteria or sets of criteria to help decide whether electrophilic addition or 1,3-dipolar cycloaddition reactions to carbon-carbon double bonds involve cyclic processes or noncyclic processes, and to help ascertain the ring size of cyclic activated complexes.

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X. References

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