Electrophilic and Cycloaddition Reactions of 5-methylene-2-norbornene

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ELECTROPHILIC AND CYCLOADDITION REACTIONS
OF 5-METHYLENE-2-NORBORNENE

BY

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Abstract

TOMMY LYNN BARUTH

Under the supervision of Professor Edwin S. Olson

The 5-methylene-2-norbornene system, which contains two double bonds of unequal energies, appears to be a unique tool which can be used in distinguishing the two types of electrophilic and the two types of cycloaddition reactions. Previous experimental evidence as well as the data presented here show that electrophiles which form bridged, three-membered intermediates in their addition to olefins all attack at the higher energy endocyclic double bond. Electrophiles which are not known to form bridged intermediates attack at the exocyclic double bond. In such cases the energy of the endocyclic homoallylic, non-classical carbonium ion formed may be the most significant factor. Cycloaddition reactions can be distinguished in the same manner as the electrophilic additions. Concerted cycloaddition reactions attack at the endo double bond and two-step or highly asymmetrical cycloadditions react at the exo double bond. A brief discussion is also presented on the possible equilibriums and rearrangements which could accompany these reactions.
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TLB
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HISTORICAL

The primary purpose for conducting the experimental work involved in the formulation of this thesis was to examine the interactions between two non-conjugated double bonds during electrophilic and cycloaddition reactions. The history is divided into three parts; the first part dealing with interactions between non-adjacent carbons, the second part describing electrophilic addition characteristics of various electrophiles, and the third part examining cycloaddition reactions and the principles involved.

I. INTERACTIONS OF NON-ADJACENT CARBONS

Some of the first established non-adjacent olefin-carbonium ion interactions noted were in replacement reactions with cholesterol. It was found that when PCl₅, SOCl₂, or SCCl₂ in pyridine was added to cholesterol, retention of configuration at C-3 was observed. An increase in reactivity was also displayed by a chlorine atom attached to C-3. The conclusion reached was that the C-5, C-6 double bond was polarized and interaction occurred between C-3 and C-5. Rate studies of the acetolysis of cholesteryl p-toluenesulfonate revealed that the solvolysis was first-order with a rate 100 times that for the cyclohexyl ester. The driving force was believed to be furnished by participation of the double bond with the formation of an extended homoallylic carbonium ion (1).
Since that discovery, much time and effort has been expended on determining how much interaction exists between the double bond and the developing carbonium ion and what the nature is of the intermediate formed. The norbornenyl and benzonorbornenyl systems were used to a large extent in trying to answer these questions because of their fixed configurations.

Solvolysis studies\(^3\) in 50\% ethanol-20\% water were conducted on exo- and endo-norbomyl (2,4) and exo- and endo-norbornenyl (3,5) halides. Although the rates were run at different temperatures and different halides were used, a qualitative study showed the following rate relationship. Of principal importance shown here is that the exo-compounds solvolyze at a faster rate than the corresponding endo-compounds. The reaction products from the saturated norbornyl systems both showed the \(-\text{OH}\) attached at the exo-position. The unsaturated
norbornenyl halides solvolyzed to a nortricyclyl system which also had the -OH group attached in the exo-position. Therefore, two of the reactions must have proceeded with carbon skeleton rearrangement. The formation of the nortricyclic compound from the norbornenyl systems showed that the double bond was involved in the overall reaction if not in the rate-determining step. Two plausible mechanisms were suggested both of which give the exo-substituted derivative structurally. One could predict that the exo-compound should solvolyze faster if either of these mechanisms were followed.
Of considerable interest was the fact that the unsaturated systems solvolyzed at a slower rate than the saturated systems. This is in direct contradiction to what takes place in the cholesterol system. The geometry of the double bond with regard to the developing carbonium ion center was examined. In cholesterol, and other systems where interaction was known to occur, the carbonium ion is situated more nearly endwise to the double bond than in the case of the norbornenyl cation. However, later work showed that the unsaturated exo-norbornenyl system, in fact, solvolyzed at a rate substantially higher than the saturated exo-norbornyl derivative.

Further acetolysis rate studies showed that the exo-norbornenyl p-bromobenzenesulfonate reacted at a rate 7000 times the rate of the corresponding endo-norbornenyl. This indicates that the double bond provides considerable driving force in the exo-isomer while the endo-species reacts at approximately the same speed as the rate of ionization.
Semi-empirical molecular orbital calculations (LCAO) were carried out on homoallylic (non-classical structures with an intervening methylene group) carbonium ions. For these calculations, the axis of the vacant p-orbital and the p-orbitals of the double bond were considered to lie in the same plane so that the intermediate bond would be of a nature between \( \pi \) and \( \sigma \). The results of the calculations showed that the 1,3-overlap is great enough to be of chemical importance even at a \( C_1-C_3 \) bond distance of 2.5\( \AA \). Greater stabilization was observed when interatomic distances were decreased. The intervening methylene group had very little effect on the amount of interaction.

The foregoing data suggests that there can be considerable interaction between a non-adjacent double bond and a developing carbonium ion. However, the nature of the intermediates formed remained to be elucidated.

Tracer experiments were carried out on the 2-norbornenyl cation in an attempt to distinguish what form of intermediate existed in the reaction. Labels were introduced on \( C_2 \) and \( C_3 \) of both exo- and endo-norbornenyl-6-\( p \)-bromobenzenesulfonates. After acetalolysis, 38% rearrangement in the norbornenyl product was observed from the exo-species and 30% rearrangement in the case of the endo. The difference in the amount of skeletal change was attributed to the direct displacement which occurred in the endo-portion (6-10%). The mechanism of the portion of the reaction leading to rearrangement was considered to be the same regardless of the configuration of the starting material (exo or endo).
Because 50% rearrangement was not observed, Roberts and co-workers believed that the intermediate would not be entirely symmetrical such as 6 but would probably be much like 7 which could be in equilibrium with 8. Intermediate 7 would not give a rearrangement product while 8 would only yield a rearranged product. The possibility also exists of an equilibrium between the symmetrical species, 6, and an unsymmetrical adduct, 7 or 8. This possibility was given merit by a solvolysis study of exo-5-norborn-2- enyl-OBS, 9, and exo-2-nortricyclon-OB$i$, 10. The solvolysis products of these two compounds were the same, although much less of the unsaturated component was formed from nortricyclon-OB$i$. Schmid suggests that unsymmetrical intermediates

9

10

(little)
such as 7 and 8 are not the only ones involved. If the reactions proceeded through the unsymmetrical intermediates, the proportions of products should have been identical for the two reactions. The norbornenyl system is believed to solvolyze through an unsymmetrical intermediate whereas the nortricyclyl system is thought to pass through the symmetrical species.

The acetolysis of exo, cis-3-deuterionorbornen-2-yl p-bromobenzenesulfonate (11) yielded the acetate with about 50% of the deuterium at C7. However, extensive ion pair return resulting in formation of 7-deuterated OB3 also takes place at a rate about 12 times faster than the acetolysis. Therefore, one cannot tell if the intermediate is, indeed, symmetrical.

The 7-norbornenyl species has also been studied extensively to determine the extent of delocalization between the double bond and the
developing carbonium ion at the 7-position. In the saturated analog, the rate of solvolysis of the p-bromobenzenesulfonate is 10,000 times slower than that for n-butyl brosylate indicating extraordinary unreactiveness of the 7-position.\textsuperscript{9} Therefore, one could predict that this system should have an extremely high sensitivity to factors promoting ionization.

Anti-7-norbornenyl systems (12) undergo solvolysis reactions at a rate $10^{11}$ times faster than do the 7-norbornyl systems (14).\textsuperscript{10} Complete retention of configuration was observed in the reaction product indicating that the double bond not only enhanced the ionization but influenced the formation of the product as well. Further studies\textsuperscript{11} involving some 7-substituted 7-norbornenyl p-nitrobenzoates 16 (a) and (b), where rates are enhanced 40 and $3 \times 10^4$ times the respective rates for the saturated 7-norbornyl analogs, show that the
anchimeric assistance from the double bond is a function of the electron demand at the incipient carbonium ion center. Comparing the anti-7-norbornenyl (12) solvolysis rates with exo- and endo-2-norbornenyl shows that the double bond facilitates solvolysis of the 7-position by factors of 24 and $2 \times 10^5$ times, respectively. This indicates that the double bond does participate in solvolysis at the 7-position; even to a greater extent than at the 2-position.

The corresponding syn-isomer (13) has been shown to solvolyze $10^7$ times slower than the anti-7-norbornenyl analog (12)$^{13}$ indicating that the double bond plays a much smaller role in this case. However, syn-7-norbornenyl systems still react $10^4$ times faster than 7-norbornyl systems which suggests that the double bond is important in forming the cation.

7-Norbornadienyl derivatives (15), which have both syn- and anti-double bonds, solvolyze at a rate greater than either the syn- or anti-norbornenyl compounds.$^{13}$ Rate studies show that the 7-norbornadiene systems react $10^{14}$ times faster than the corresponding saturated 7-norbornyl compound. This is a rate enhancement of $10^3$ times faster than the anti-7-system and $10^{10}$ times faster than the syn-7-analog which indicates that both double bonds must participate in the formation of the cation.
The intermediates proposed for these reactions\textsuperscript{14} have been derived from much experimental work but are, in most cases, still quite controversial. Anti-7-norbornenyl compounds are thought to solvolyze through a symmetrical intermediate (18).\textsuperscript{10} However, another proposal\textsuperscript{15} suggested a rapidly equilibrating pair of tricyclic classical ions 19 (a) and (b). The feud which developed from this difference of opinion may never be completely resolved, but intermediate 18 seems to have developed wide-spread usage. Experimental data which seems to point toward the symmetrical intermediate (18) is that the placement of methyl groups in the 2- and 3-positions has cumulative rate-enhancing effects.\textsuperscript{16}

The syn-7-norbornenyl systems rearrange with acetalolysis producing bicyclo-(3.2.0)heptenyl acetates.\textsuperscript{13} The intermediate suggested for this reaction is the bicyclic allylic cation shown in 20.
Many different intermediates have been proposed for the solvolysis of 7-norbornadienyl derivatives. When the compound was first synthesized and initial solvolysis rate studies were run, three intermediates were proposed as plausible; 21, 22, and 23.\(^{17}\)

\[\begin{align*}
&\text{21} \quad \equiv \quad \text{22} \\
&\text{23}
\end{align*}\]

A short time later,\(^{18}\) a nuclear magnetic resonance (n.m.r.) spectrum run on the intermediate showed four peaks which integrated for \(1:2:2:2\). This spectrum implies interaction between \(C_7\) and at least one pair of olefinic carbons. The slight upfield shift of the \(C_5\) and \(C_6\) hydrogens probably indicates only slight interaction of that double bond with \(C_7\). An intermediate such as 21 was suggested.

Later work\(^{19}\) on the 7-methyl-7-norbornadienyl cation revealed that an unsymmetrical intermediate exists at \(-45^\circ\text{C}\) but that the vinyl proton signals coalesce at \(-14^\circ\text{C}\). Above \(-5^\circ\text{C}\) rearrangement occurs to the 2-methylnorbornadienyl cation. The chemical shifts of the \(C_7^-\) and \(C_2^-\) methyl ions supports the view\(^{20}\) that more positive charge resides on the \(C_2\) and \(C_3\) atoms than on the \(C_7\). They also argue strongly against the formation of rapidly equilibrating tricyclic "classical" carbonium ions as was postulated for anti-7-norbornenyl cations, 19 (a) and (b).
Solvolysis studies were also run on exo- and endo-2-benzonorbornenyl, syn- and anti-9-benzonorbornenyl, and syn- and anti-9-benzonorbornadienyl compounds. As a general rule, these compounds have an opposition to ionization because the aromatic ring resists the strain imposed by the bicycloheptene during bond movements. However, if this opposition were cancelled out, the aromatic ring would be almost identical to the double bond in its ability to assist ionization at the 2-position. The benzene ring is vastly inferior to the double bond in assisting ionization at C7 because the intermediate needed would have to develop from a realignment of the atomic orbitals causing complete absorbance of a double bond but loss of some aromatic stabilization energy.
The intermediates formed in the solvolysis of the benzonorbornenyl compounds correspond to those produced from the similar norbornenyl analogs. The symmetrical non-classical structures are again favored because placing substituents on the 6- and 7-positions of the benzene ring has a cumulative effect on the rate of solvolysis.\(^2\)

Now that we have examined some interactions between non-adjacent double bonds and developing carbonium ions, let us focus our attention on the interaction of non-adjacent double bonds in norbornyl systems. Two compounds of interest are norbornadiene and 5-methylene-2-norbornene because each has two double bonds although the orientation of the double bonds with regard to each other is different. In norbornadiene (24), the double bonds lie side-by-side; whereas in 5-methylene-2-norbornene (25), they are more nearly end-to-end.

![Diagrams of norbornadiene (24) and 5-methylene-2-norbornene (25)]

In norbornadiene (24), interaction between the double bonds in the excited state is suggested by comparing its ultraviolet absorption spectrum with that of norbornene and that of butadiene.\(^2\) Norbornene shows an absorption at 195 nm, butadiene at 210, and norbornadiene at 211 with considerable fine-splitting between 226 and 199 nm.

Semi-emperical molecular orbital calculations were conducted\(^2\) on norbornadiene to determine the amount of interaction between the olefinic groups in the ground state and in the first excited state.
The calculations were made using three different wave-mechanical methods; the simple Linear Combination of Atomic Orbitals (LCAO), and the more refined methods of Pariser-Parr and Longuet-Higgins. The LCAO method used ignored configuration interaction and specific electron repulsion while the more refined procedures accounted for the electron spin and included specific terms for electron-electron repulsions.

The ground state for norbornadiene is described\(^{25}\) by all three of the methods to have no \(\text{C}_2-\text{C}_6\) bond order between the double bonds. Experimental heats of hydrogenation observed for this compound also gave no indication of homoconjugative stabilization. For the lowest excited state, the refined molecular orbital calculations predicted an energy transition at 2.14 nm which is very close to the observed absorption at 2.11 nm. Because of this quantitative agreement, these methods were believed to provide a reasonably accurate description of the \(\pi\)-electron interactions. A bond order of approximately 0.12 was calculated to exist between the double bonds in the excited state.

Extended Huckel (EH) M.O. calculations\(^ {26}\) agree with these results indicating interaction between the double bonds of the excited state. The EH calculations show that the erstwhile degenerate \(\pi\)-bonding orbitals are split by 0.43 eV. Photoelectron spectroscopy varifies the splitting but gives a much larger value, 0.35 eV, to the energy difference between the two \(\pi\)-bonding orbitals.

Very little effort seems to have been directed toward investigating the 5-methylene-2-norbornene system. However, a comparison of the
ultraviolet absorption spectra of norbornene (195 nm), 2-methylene norbornene (195 nm), and 5-methylene-2-norbornene (207 nm) reveals that interaction may also occur between these two double bonds. Reactions of 5-methylene-2-norbornene indicate homoconjugative interaction similar to that observed in norbornadiene. Therefore, one might expect a bond order between C2 and C6 of approximately the same magnitude as in the case of norbornadiene.

II. ELECTROPHILIC ADDITIONS

Even though a great deal of work has been carried out trying to determine the mechanism of electrophilic additions to olefins, no one mechanism has been found which encompasses all of these reactions. Generally, one utilizes a bridged intermediate (26) for some reactions and a carbonium ion intermediate (27) for most of the other reactions. However, for "borderline" electrophiles, those which would form "onium" ions (26) of intermediate stability, one may choose to use either of these intermediates or a combination of the two.

In the next portion we will examine some typical electrophiles and the mechanisms proposed for their additions to olefins.

Proton Addition:

The mechanism for the protonation of olefins is still not
completely understood. Rate studies conducted on the acid-catalyzed hydration of olefins followed Hammett's acidity factor, $K_o$, more closely than $[H^+]$, the concentration of the hydronium ion.\textsuperscript{23} This implied, on the basis of the Hammett-Zucker hypothesis, that the reaction must be specific-acid catalyzed and the following mechanism was proposed.

\[
\begin{align*}
\text{C} = \text{C} + \text{H}^+ & \xrightleftharpoons{K_1} \text{[} \text{C} \text{= C} \text{]} \\
\text{[} \text{C} \text{H} \text{]}^+ & \xrightleftharpoons{K_2} \text{C} \text{H} \\
\text{C} \text{H} + \text{H}_2\text{O} & \xrightleftharpoons{K_3} \text{C} \text{H}_2\text{O} \\
\text{[} \text{C} \text{H}_2\text{O} \text{]}^+ & \xrightleftharpoons{K_4} \text{C} \text{H}_2\text{O} + \text{H}^+
\end{align*}
\]

Studies were then carried out to determine the slow-step of the reaction. Equilibria 3 and 4 were eliminated because the rate of exchange of isotopic oxygen by tertiary alcohols was found to be several times the rate at which it dehydrated\textsuperscript{23,30} showing that the free energy of the transition state between carbonium ion and olefin must be greater than that between carbonium ion and alcohol. The formation of the carbonium ion was found to be irreversible\textsuperscript{31} when hydration of 2-methyl-1-butene or 2-methyl-2-butene was stopped after 5\textsuperscript{1} reaction and none of the other isomer was detected. If the rate-determining transition state occurred after the carbonium ion formation, then a mixture of the olefin isomers should have been formed.
Therefore, the proton transfer must be the slow step of the reaction which would imply general-acid catalysis. Solvolysis isotope effect studies involving deuterated water also suggest general-acid catalysis. However, the entropy of activation in the hydration of the olefins was found to be quite small indicating only a slight increase of organization in the transition state, or a unimolecular isomerization. Bimolecular transition states, which a general-acid catalyzed reaction would involve, generally have quite a large entropy of activation. Thus, equilibrium 2 was chosen as the slow step since general-acid catalysis had not been directly observed by kinetics.

General-acid catalysis was established for protonation of double bonds by the formate buffered hydration of p-methoxy-α-methylstyrene. This implied that one molecule of water was needed in the rate-determining step. The acidity dependence for the reaction was found to be approximately halfway between $H_0$ and $H_R^+$ based on an anilinium ion and a carbonium ion equilibrium, respectively.
It was also suggested that the slope of the line, -0.6, obtained from the plot of log k, vs $H^+$ was typical for bimolecular reactions with water in the transition state. The calculated Bronsted $\alpha$ of 0.42 implies that the proton is transferred to the olefin from the acid in the transition state. It was suggested that the transition state resembled a carbonium ion more than an encumbered carbonium ion which was postulated by Taft to explain general-acid catalysis.

The existence of the initial $\pi$-complex proposed has never been proven. However, $\pi$-complexes are thought to occur when the carbon-electrophile bond is weak, such as in the cases of C-Br$^+$ and C-I$^+$. Their existence is also favorable in nonpolar solvents or when unstable carbonium ions would form. In polar solvents, however, or when a carbonium ion can be stabilized by substituents or by delocalization, no $\pi$-complex should form. Semi-empirical self-consistent field molecular orbital calculations show that the $\pi$-complex species, formed by protonation of ethylene, is less stable than the "open" carbonium ion by 9 kcal/mole.

Hydrogen Halide Addition:

The existence of a bridged $\pi$-complex (28) in the hydrogen halide addition to olefins is based largely upon the observation of
trans-addition products.²⁹ However, kinetic studies showed that two or more molecules of the hydrogen halide must be present in the rate-determining step of the reaction.²⁹,⁴⁰ Experimental evidence indicates that no interconversion of olefins occurs and, with the exception of styrene, no deuterium from the solvent is incorporated into the olefin.⁴¹,⁴²,⁴³ This seems to rule out the formation of a π-complex as the rate determining step although the transition state may still occur via ion-pairs (29) or from simultaneous electrophilic and nucleophilic attack (30).

![Chemical Diagram](image)

The mechanism involving simultaneous attack by the electrophile and nucleophile was ruled out because of the rearrangement which occurred when hydrogen chloride was added to isopropyl ethylene.⁴⁴

![Chemical Reaction](image)

A similar rearrangement was observed in the hydrogen iodide addition to t-butyl ethylene.⁴⁵ It was felt that this hydride migration could only evolve from a carbonium ion. Therefore, a mechanism involving an intermediate such as 29 was postulated as most probable.

Further studies involving hydrogen chloride addition to cyclohexene yielded results which contrasted those expected from a
mechanism involving a carbonium ion (29). The products obtained from the addition in acetic acid showed a much lower $\frac{\text{Cl}^-}{\text{C}^-\text{Ac}^-}$ ratio (0.3) than was observed from t-butylethylene ($\sim 2$) and styrene ($\sim 13$). This product ratio was found to be largely dependent upon the concentration of dissociated chloride ion in the case of cyclohexene whereas the Cl\textsuperscript-- concentration played a much smaller role in the cases of t-butylethylene and styrene. Furthermore, the chloride ion concentration was found to be associated with the amount of stereospecific trans-addition observed with cyclohexene.\textsuperscript{47}

Therefore, hydrogen halide addition to olefins was proposed to proceed by either of two mechanisms depending on the nature of the alkene.\textsuperscript{47} One of the mechanisms involves the formation of a carbonium ion intermediate (29) while the other mechanism involves simultaneous electrophilic and nucleophilic attack (30).

I. $\text{C}=$O + HCl $\xrightarrow{\text{Slow} \text{ECAC}}$ $\xrightarrow{\text{Cl}^-}$ $\text{Cl}^-$ $\rightarrow$ C\textsuperscript{\text{OAc}} + C\textsuperscript{\text{OAc}}

II. $\text{C}=$O + HCl + Cl\textsuperscript-- $\xrightarrow{\text{or}}$ $\text{Cl}^-$ $\rightarrow$ C\textsuperscript{\text{OAc}} + C\textsuperscript{\text{OAc}}
In the first mechanism, only cis-hydrohalogenation should occur along with the formation of some trans-alkylacetate product. In the second mechanism, exclusive trans-addition products should form although a very small amount of cis-adducts may appear because of the molecular addition of hydrogen chloride.

**Halogen Addition**

The halogenation of olefins has been established as an electrophilic addition by the effect various substituents have on the rate. Electron-donating groups enhance the rate of reaction while electron-withdrawing substituents retard the rate. Preliminary work by Bartlett and Tarbell revealed that the first step of the reaction produced a negative halide ion and a positive organic ion. The stereochemistry of the halogenation additions was known to be generally trans and kinetic studies indicated that the reaction was first order in olefin and first order in halogen. Therefore, a symmetrical, bridged intermediate (31) was proposed. The stereospecificity of the reaction was then explained by the "configuration holding" effect of the electrophilic halogen. The nucleophile, whether halide or solvent, would then only be able to attack the positive organic ion from the side opposite the electrophilic halogen (32). The mechanism involves initial π-complex formation (31) which dissociates to an ion-pair in the rate-determining step.
The propensity for bridging or the stability of the three-membered intermediate formed by each halide can be determined by the extent of participation in the solvolysis of α-neighboring groups. Trans-configuration of halogen to leaving group was found to be favored for maximum participation. These studies, involving trans-cyclohexyl p-bromobenzenesulfonate halides, also revealed that iodine participated to a greater extent than bromine which, in turn, participated more than chlorine. A study concerning 1→2 halogen shifts in carbonium ion intermediates agrees with this by showing iodine > bromine > chlorine in shifting ability.

Thus, one would expect the iodonium ion to be more stable than the bromonium ion which would be more stable than the chloronium ion. Low temperature NMR studies were conducted on each of the possible "onium" ions. Deshielding of the tetramethylethylene protons increased in going from I⁺→Cl⁺ indicating more positive charge exists on the carbon in the case of the chloronium ion.
At −60°C, chlorine, bromine, and iodine each showed a stable "onium" ion. Fluorine, on the other hand, existed as rapidly equilibrating classical carbonium ions which suggests it to be a poor bridging group.

A stable bromonium ion was thought to have been isolated when bromine was added to a carbon tetrachloride solution of adamantylidene-adamantane. The yellowish solid produced could not be recrystallized from polar solvents. Because it was insoluble in non-polar solvents, it was believed to be a salt. Infrared and mass spectrographic data suggest a structure such as 33.

The 1,2-addition of bromine to piperylene showed the reaction to be stereoselective; occurring preferentially at the less-substituted double bond in a trans-manner. The initial step of
the addition seemed to be the formation of the n-complex as occurred in mono-olefins. The high portion of 1,2-addition indicates that the initial bridged intermediate must be quite stable.

When the double bond at which addition occurs is conjugated with a continuing unsaturated center, styrene, for example, cis-addition occurs predominantly. This is explained by the fact that the carbonium ion center formed is conjugated with the unsaturated system, thus lowering its energy with respect to the cyclic "onium" ion.

\[
\begin{array}{c}
\text{\textbf{X}} \\
\text{C} \quad \text{C} \\
\text{H} \quad \text{H} \\
\end{array}
\]

The attacking nucleophile can then attack the carbonium ion from either of the two sides. The steric hindrance of the phenyl group may cause the nucleophile to attack from the same direction as the electrophile yielding cis-addition products or a racemic mixture if bond rotation occurs.

The solvent also plays a role in determining the nature of the reaction intermediate. As solvent polarity increases, the stereospecificity decreases because polar solvents induce polar intermediates. Thus, in the absence of substituent effects, "onium" type intermediates, where the charge is spread over three atoms, would be expected to exist in non-polar solvents whereas classical carbonium ions, with the charge on only one atom, should predominate in polar solvents.

Extended Hückel molecular orbital calculations were carried out to determine the nature of the intermediate formed from the
halogenation of ethylene. The results of these calculations also show that iodine is the best bridging group followed by bromine and then chlorine. A bridged intermediate was calculated to be highly unlikely in the case of fluorine.

**Sulfur Addition:**

Sulfur addition to olefins was believed to involve homolytic, free radical, attack because oxygen tended to act as a biradical. However, the relative rates of reaction were observed to increase with greater electron-release to the reaction center by the olefinic substituents. Also, the reactions were accelerated by increasing the polar character of the medium. Therefore, the addition of sulfur to olefins was established as an electrophilic addition.

Much of our knowledge of electrophilic sulfur additions and the intermediates involved comes from sulfonyl halide additions to olefins. Kinetic studies involving addition of 2,4-dinitrobenzenesulfonyl chloride to styrene and cyclohexene showed the addition to be second order. Addition of sodium perchlorate to the reaction increased the rate which indicated the rate-determining transition state was formed in the initial step.

The stereochemistry of the addition is almost exclusively trans. This was taken as evidence for a cyclic episulfonium ion intermediate (34) where the sulfur is bonded to both carbons until the nucleophile

![Diagram of episulfonium ion intermediate](image-url)
attacks from the opposite direction and completes the addition. The cyclic episulfonium ion intermediate theory was strengthened when p-chlorobenzenesulphenyl chloride was added to cis and trans-2-butene.\textsuperscript{55} Exclusive trans addition products were observed in both cases; even over a wide temperature range. If an open carbonium ion existed as the intermediate, then the activation energy for rotation must be the same as the activation energy for chloride ion attack. Further evidence which was believed to imply a cyclic intermediate comes from methane- and benzenesulphenyl chloride addition to 1,3-dienes.\textsuperscript{66} 1,2-Addition was observed which was followed by post-isomerization to the thermodynamically more stable 1,4 products. The lack of 1,4-adducts in the initially formed products indicated a carbonium ion was not formed. Also, benzenesulphenyl chloride products had little or no propensity to rearrange to the 1,4 adducts. This was attributed to the electron-withdrawing effect of the benzene ring which lowered the availability of the unshared electrons on sulfur for anchimeric assistance in the migration.

A detailed study of sulphenyl halide addition to olefins suggested that no single mechanism would encompass all the reactions.\textsuperscript{67} Rather, it seemed as if the substituents on the olefin and the sulphenyl chloride influenced the course of reaction. Both electronic and steric factors play a role in the formation of the products.

Methane- and benzenesulphenyl chloride addition to alkyl-substituted terminal olefins yielded anti-Markownikoff products which
rearranged to the more stable Harkownikoff adducts. Electronic effects of the olefin would strive to form Harkownikoff addition products; so, apparently, the episulfonium ion ring opening could not be predicted from electronic effects. This would signify that little charge is developed on carbon and that steric factors control the formation of the products. Other olefins which are electronically biased, i.e., styrene, form Harkownikoff addition products. However, as in the case of 1,1-diphenyl ethylene, where electronic and steric effects both exist in high magnitude, competition may exist yielding both the Harkownikoff and the anti-Harkownikoff adducts. This phenomenon also supports the bridged ion intermediate theory.

Conjugated olefins react with sulfenyl chloride to give Harkownikoff addition adducts. This is explained by the ability to delocalize the positive charge on the allylic carbon. Electronegative substituents on the olefin, particularly those with carbonyl groups, also favor formation of Harkownikoff products because the incoming nucleophile can form partial bonds with the α-carbon and the carbonyl carbon. It may also be that the electron-withdrawing effect of the carbonyl group may simply stabilize the adjacent carbon toward attack from the nucleophile.
Substituents bonded to sulfur play a similar role in influencing the orientation of the products.\textsuperscript{67} Electron-donating groups in the para position of 2-nitro-4-benzenesulfenyl chloride systems accelerate the rate of reaction with olefins\textsuperscript{70} by stabilizing the positive charge which develops on sulfur. Anti-\textsuperscript{1}arkownikoff adducts may form from these cyclic intermediates. Electron-withdrawing groups bonded to the sulfur destabilize cyclic intermediates and lead to carbonium ion formation.\textsuperscript{67} \textsuperscript{1}arkownikoff addition products result.

In an attempt to determine the relative stability of the cyclic sulfonium ion intermediate, optically active 2,2-dimethyl-3,4-hexadien-1-ol was reacted with 2,4-dinitrobenzenesulfenyl chloride and with bromine.\textsuperscript{71} If a stable cyclic intermediate existed, then optically active products should result. A racemic mixture, however, would form from a carbonium ion intermediate. Results showed an optically active product formed from sulfenyl chloride addition whereas bromination yielded a racemic mixture. Thus, sulfur forms a more stable bridged intermediate than bromine.

Molecular orbital calculations\textsuperscript{37} also show the intermediate formed in sulfenyl halide addition to olefins to be a symmetrical, three-membered cyclic species. Substituents which create a greater positive charge on carbon were calculated to destabilize the episulfonium ion intermediate.

\textbf{Oxymercuration:}

The oxymercuration of olefins has been studied since the beginning of the 20th Century when it was found that, of all the metallic salts,
mercury formed the most stable addition adducts with unsaturated substrates.\textsuperscript{72} Kinetic studies indicated that the oxymercuration of olefins was second order; first order in olefin and first order in mercuric salt although the olefin and its substrates helped to determine the speed of the reaction. Trans-olefins were found to react slower than the cis-isomers\textsuperscript{73} and electronegative substituents hindered and, in some cases, prevented addition.

A cyclic intermediate (35) was proposed to exist in the reaction mechanism because the oxymercuration of olefins yielded nearly exclusive trans-addition products.\textsuperscript{72} Further evidence for a cyclic intermediate resulted from the additions to 1,3-butadiene and isoprene.\textsuperscript{75} The products obtained were the saturated heterologs resulting from separate Markownikoff 1,2-addition to each double bond.

\[
\begin{align*}
\text{H}_2\text{C} \equiv \text{C} & \equiv \text{C} \equiv \text{C} \equiv \text{H} + \text{Hg(Cyclical)}_2 \rightarrow \text{H}_2\text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{H} \quad \text{HgCac} & \rightarrow \text{H}_2\text{C} \equiv \text{C} \equiv \text{C} \equiv \text{C} \equiv \text{H} \quad \text{HgCac}
\end{align*}
\]

Extensive studies of the mechanism of oxymercuration were begun after observing an exo-cis product from the addition to norbornene.\textsuperscript{75}
The previously proposed intermediate should have given a trans-addition adduct so it was believed that other factors must have altered the course of the reaction. The mechanism proposed for the oxymercuration of norbornene\textsuperscript{77} consists of formation of an initial π-complex by displacement of one of the ligands on mercury with ultimate front-side opening by ligand migration or ion-pair collapse. Normal back-side attack by the solvent, as occurs in unstrained olefins, was suggested to be unlikely since it would require a 30° twist about the C—C axis. A strained olefin, such as norbornene, would prevent such a twist.

The nucleophilicity of the solvent was also suggested to be a deciding factor in product determination.\textsuperscript{73} Evidence of this was shown when dibenzobicyclo (2.2.2) octatriene was reacted with mercuric acetate in acetic acid and in aqueous acetone.\textsuperscript{79} In the less nucleophilic acetic acid solvent, only the cis-addition adduct...
was formed; however, both cis- and trans-products resulted from the addition in aqueous acetone.

Product stereochemistry was also found to be dependent upon the ligands attached to the mercury. If the ligand is highly electronegative, a great deal of positive charge forms on the adjacent carbon atom. This carbonium ion character tends to reduce the stereospecificity of the reaction toward exclusive trans-addition.

The nature of the transition state involved in the oxymercuration of olefins has been a controversial issue for several years. Exclusive Markownikoff addition products suggests much carbonium ion character must be present in the product-determining step of the reaction. However, a carbonium ion intermediate can be eliminated because no rearrangement occurs from the addition to 3,3-dimethyl-1-butene or norbornene. However, a considerable amount of positive
charge must reside on one of the carbon atoms, the one which can best
stabilize the charge, because oxymercuration of methylenecyclopropane
results in ring opening.

\[
\begin{align*}
\text{CH}_3\text{CH}_3\text{H} + \text{Hg}(\text{OAc})_2 \overset{\text{NaCl, EtOH}}{\longrightarrow} & \text{CH}_3\text{CH}_3\text{Cl} \\
\end{align*}
\]

The existence of a bridged mercurinium ion has never been
established. Oxymercuration of 7,7-dimethyl-2-norbornene yields an
exo-eis addition product, whereas the addition of benzylsulfenyl
chloride gives the trans-product in which the benzylsulfenyl cation
added from the endo direction. If a cyclic mercurinium ion were
involved in the addition, one would expect to obtain the same stereo-
chemical oxymercuration product as obtained from the sulfenyl halide
addition. The importance of a mercurinium ion, if formed, was studied
by the methanolysis of trans-2-hydroxycyclohexyl mercuric acetate
in the presence of 1-methylecyclohexane. It was felt that if forma-
tion of the mercurinium ion was the rate determining step, the principle
product would be methoxycyclohexene (Path A). If the mercurinium ion
was a low energy intermediate, the products would be expected to
consist of mostly 1,1-di-thoxymethylcyclohexane or an equal amount of
the two adducts. After ten minutes an examination of the products
showed that 10% of the 1,1-di-thoxymethylcyclohexane had formed

\[
\begin{align*}
\text{CH}_3\text{HgCl} \\
\text{Cl} \\
\text{CH}_3 \\
\text{Cl} \\
\end{align*}
\]
compared to less than 1% of the methoxycyclohexane adduct. It was felt, then, that if a mercurinium ion did form, it merely represented a "shallow well" between the reactants and the transition state. They suggest that the rate-determining step was the formation of an intermediate (37) in which there would be simultaneous electrophilic and nucleophilic attack.
Evidence suggesting the existence of a mercurinium ion was shown by the products formed from the oxymercuration of 4-tert-butyl-1-cyclohexenyl compounds. The same products were obtained from the bromination of these compounds whereas addition of HBr gave the syn- and anti-ADZ products. It was suggested that the oxymercuration proceeded by the fast, reversible formation of a mercurinium ion which could then be opened by trans-attack of the nucleophile to give the diaxial products. In the case of the 4-tert-butyl-1-methylcyclohexene, only one product was formed because the formation
of the other expected product would require either an anti-Markownikoff or a trans-disequatorial adduct. Such products are less likely to occur.

Several instances have been reported dealing with spectroscopic isolation of mercurinium ions. One of the first was a room temperature NMR spectrum of the mercury (II) complex with ethylene. This report was later determined to be incorrect. More recently, however, Claib and Clifford announced the discovery of a mercury complex of cyclo-hexene from the NMR spectrum of a solution at -60°C. They also reported similar complexes with 1,2-dimethyl-ethylene, norbornene, and ethylene at low temperatures.

The intermediate formed in the rate-determining step of the oxymercuration of olefins is still undecided. Several intermediates have been proposed: a bridged mercurinium ion (35), a carbonium ion, a four-center reaction intermediate (36), and a simultaneous electrophilic-nucleophilic attack intermediate (37). Experimental evidence indicates that formation of either of the first two independently is unlikely. However, the formation of an intermediate (38) which would be a combination of a mercurinium ion and a carbonium ion may not be unlikely. In this type of intermediate, much of the positive charge would reside on the adjacent carbon atom which could be stabilized.
by the substituents bonded to that atom and by the non-bonding electrons on the mercury atom. This type of intermediate would tend to hold the configuration from charge delocalization and give considerable \( \alpha \)-bond character to the transition state.\(^{30}\) Evidence for this type of unsymmetrical intermediate was presented by Brown and Kawakami\(^ {34}\) to explain the \textit{exo-cis} addition product obtained from the oxymercuration of 7,7-dimethylnorbornene.

Extended Hückel molecular orbital calculations\(^ {37}\) indicate that oxymercuration of olefins proceeds to a symmetrical \( \pi \)-complex (35) which readily polarizes to the unsymmetrical form (38) with developing positive charge on the adjacent carbon atom. The calculations show that little energy is needed to move the mercuric salt along the C—C axis in forming the unsymmetrical intermediate from the symmetrical intermediate.

\textbf{Epoxidation Reactions:}

The epoxidation of olefins by peroxy acids has been found to be an electrophilic addition which is first order in olefin and first order in acid.\(^ {93}\) One of the first mechanisms proposed for the addition involved free hydroxyl cations.\(^ {94}\) However, an ionic reaction

\[
\text{RCO}_3\text{H} \rightarrow \text{RCO}_2^- + \overset{+}{\text{OH}} \quad \overset{\text{C}^+}{\text{C}} \quad \overset{\text{C}^-}{\text{C}} \quad \rightarrow \text{C} \quad \text{C} + \text{H}^+.
\]

such as this was rendered as highly unlikely because the rate of epoxidation was found to be faster in benzene than in ether.\(^ {25}\)
Bartlett suggested a mechanism whereby a molecule of the peracid attached the double bond. This mechanism agrees with the findings of Badger when he suggested that perbenzoic acid acts as a "double bond agent" in that it attacks the double bond not one of the constituting carbons.

In order to establish that the molecular mechanism proposed by Bartlett could, indeed, be the mechanism of epoxidation, rates of epoxidation of various olefins by substituted perbenzoic acids were reported. It was found that electron-withdrawing substituents on the olefin increased the free energy and heat of activation. The opposite effect was found to be true for the substituted perbenzoic acids. This trend is in accord with the characters of the olefins and peracids as nucleophilic and electrophilic reagents, respectively. Because the rates did not change when anions or benzoic acid was added, it was felt that the reaction was not general-acid catalyzed.

Epoxidation of ethyl crotonate with m-chloroperbenzoic acid showed the rates of epoxidation to be identical in non-hydrogen-bonding solvents even though the dielectric constants of the solvents varied. This conflicted with previous results which showed the rates of epoxidation, where intramolecular hydrogen-bonding was
intact, roughly paralleled the dielectric constant of the solvent. It was felt that the consistency of rates in solvents with differing dielectric constants may be due to disruption of the ground state resonance in the olefin so only a slight difference in polarity would exist between the ground state and the transition state. The cons-

sistency of rates was considered as evidence against the formation of a hydrogen-bonded complex between the peracid and ethyl crotonate in the rate-determining step. It was felt that if such a complex did form to any great extent, then addition of excess peracid would increase the rate.

The epoxidation of ethyl crotonate in acetonitrile was found to be a zero-order reaction. Therefore, a scheme was proposed in which $k_2 > k_{-1}$, $k_2 > k_{-1}$, and $k_2 >> k_2$. If this were true, it was felt
An investigation of the reactivity parameters and kinetic characteristics of epoxidation reactions revealed that they also parallel the properties of 1,3-dipolar additions. In addition, the fact that the $\Delta S$ value for the reaction did not increase as the solvent polarity increased was cited as evidence against a 1,1-addition and support for a concerted 1,3-dipolar addition mechanism. Therefore, a 1,3-dipolar transition state mechanism was proposed which relates to the mechanism proposed by Creigee for ozonolysis.
It was also suggested that a mechanism such as this may explain the formation of some of the by-products formed during ozonolysis reactions. The five-membered 1,3-dipolar transition state proposed was suggested to break apart easily because the lone pairs of electrons on the oxygens would have to line up in the formation of the transition state. Their repulsion would cause the transition state to quickly decompose to the products.

This 1,3-dipolar addition mechanism was later denounced\(^{102}\) because the rates of epoxidation of norbornene and cyclohexene were found to be very similar. If the rate-determining step for epoxidation was the attack of the 1,3-dipole, then the epoxidation of norbornene should have been much faster than the epoxidation of cyclohexene because of the relief of strain in the norbornenyl system. Kwart\(^{103}\) then proposed a new mechanism for epoxidation but this new pathway also involved a 1,3-addition to the olefin. However, it seems as though this new mechanism was unnecessary since these additions are known to occur at a much faster rate with norbornene than with cyclohexene.\(^{102}\)

Pariser-Parr-Pople self-consisting field molecular orbital calculations were carried\(^{104}\) out to determine which atom of the peracid was most electrophilic and which of the two mechanisms proposed, 1,1-addition or 1,3-dipolar addition, was most likely to occur. The calculations showed the oxygen atom next to the hydrogen to be most reactive. Because a small total energy difference was found for the two mechanisms, it was suggested that 1,1-addition may occur in non-polar solvents and 1,3-dipolar addition may occur in polar solvents.
In an attempt to systematize the effects of various solvents on the rates of epoxidation, the reaction kinetics were related to the spectroscopic characteristics of various peracids. A lowering and broadening of the O-H stretching frequency in various oxygen-containing solvents compared to the intramolecular hydrogen-bonded O-H frequency in inert solvents showed that peracids exist as intermolecularly bonded adducts in oxygen-containing solvents. It was found that

\[ \begin{array}{c}
\text{R} \\
\text{C} \\
\text{O} \\
\text{H} \\
\text{R}
\end{array} \]

the strength of the intermolecular association increased as the basicity of the solvent increased which caused the reaction rate to decrease. Therefore, the strength of the peracid-solvent interaction was considered to be one of the major factors influencing the kinetics of epoxidation. Polarizabilities and steric requirements of solvents were also suggested to influence the rate when differences in basicity of solvent pairs are small.

Thus, one can see that the mechanism for epoxidation is still not known. It does appear as if a 1,1-addition mechanism may be the "most probable" method. Whether or not such a mechanism is correct, one still does not know if the addition occurs as a concerted process or if the two new bonds form at different rates.
III. CYCLOADDITION REACTIONS

Cycloaddition reactions may be defined as a combination of two or more molecules of n and m atoms to give a ring structure of n + m atoms. In the formation of these cyclic compounds, no sigma bonds are broken, although, new sigma bonds are formed at the expense of π-bonds or non-bonding electrons. Classification of cycloaddition reactions is based upon the number of new sigma bonds formed and the number of ring atoms which each reactant contributes.

Through the combination of molecular orbital theory and symmetry principles, Woodward and Hoffmann have formulated a set of rules governing concerted cycloaddition reactions. Correlation diagrams were devised for the various cycloaddition reactions which compared the symmetry elements of the orbitals of approaching reactants with the symmetry elements of the cycloaddition products. If the same symmetry elements composed the bonding orbitals of the reactants and products, then the cycloaddition was considered to be an "allowed" process. However, if one of the symmetry elements which was bonding in the reactants turned out to be anti bonding in the products, then the addition was considered to be a "forbidden" process. Cycloadditions which are "forbidden" according to these rules may still occur by a two-step mechanism where one sigma bond forms at a time and a dipolar intermediate forms.

The cycloaddition rules may be generalized in the following manner: if K is the number of electrons involved in any manner in the formation
of the new sigma bonds or the displacement of \( \pi \) bonds, then \( 4K \) electron cycloadditions are symmetry "forbidden" in the ground state and \( 4K + 2 \) electron cycloadditions are symmetry allowed in the ground state. It should be noted that those rules only apply for ground state concerted cycloadditions. The reverse is true for excited state reactions.

Three types of cycloadditions are illustrated below and the mechanisms found to occur in each case are discussed.

\[ [2 + 2] \text{ Cycloadditions} \]

\[
\begin{array}{c}
\text{C} \\
\text{C}
\end{array}
+ \begin{array}{c}
\text{C} \\
\text{C}
\end{array} \rightarrow \begin{array}{c}
\text{C}^+ \\
\text{C}^-
\end{array} \rightarrow \begin{array}{c}
\text{C} \\
\text{C}
\end{array}
\]

Four electrons are involved in these cycloadditions which eliminates the possibility for a thermally allowed \([2s + 2s]\) concerted mechanism although a \([2s + 2a]\) concerted addition is allowed. Many of these reactions have been shown to be two-step, dipolar intermediate additions\(^{109}\) (like the mechanism illustrated). Other reactions, which appear to be concerted, are thought to involve a "near-concerted" or quasi-type mechanism where no intermediate is believed to form although dipolar charges are formed along the reaction pathway\(^{110}\). In other \([2 + 2]\) cycloadditions, such as the addition of 1,1-dichloro-2,2-difluoroethylene to alkenes\(^{111}\), a diradical mechanism is favored because of the nonstereospecificity of the reaction.
[2 + 3] Cycloadditions

C + C\[+\]C\[\rightarrow\]N

These additions have been termed 1,3-dipolar cycloadditions by Huisgen and co-workers.\(^1\) Most of the research on this type of cycloaddition involves 1,3-dipoles which have (1) a double bond and a non-bonding pair of electrons, as shown above, (2) a non-bonding pair of electrons, or (3) a double bond.\(^2\) The modest solvent effects and the stereospecificity exhibited by these cycloadditions suggest a concerted addition. This agrees with the prediction of Woodward and Hoffmann\(^3\) since six electrons are employed in the course of the reaction.

[2 + 4] Cycloadditions

The principle [2 + 4] cycloaddition is the Diels-Alder reaction which has been studied to a great extent.\(^4\) The mechanism proposed for the Diels-Alder cycloaddition is a concerted addition because of the small solvent effects\(^5\) and the stereospecificity of the reaction.\(^6\) Six electrons

\[\]
addition to occur. In some other cases, six-membered rings appear to result from \([2 + 4]\) diradical cycloadditions. The possibility also exists for the formation of six-membered rings from \([2 + 4]\) dipolar, two-step mechanisms although this type of product should only be a minor contribution if the diene is not held in a fixed cis-conformation.

Now let us examine two specific cycloadditions and the principles involved in their mechanisms.

**Dibromocarbene Addition:**

Since very few insertion reactions of dibromocarbenes are known, the addition of dichloro- and dibromocarbenes to alkenes have been studied quite extensively. Despite this, however, the ground state of dibromocarbenes has only been inferred from Skell's Theory to be a singlet species with one vacant p-orbital on the carbon. These addition reactions have shown the dibromocarbenes to be strong electrophiles which always react to give stereospecific cis-addition products. Because the stereometric relationships of the reactants were maintained in the products, a concerted, three-center mechanism was believed to be involved.

A study of the rates of addition of dibromocarbene with various alkenes showed a remarkable parallelism with the rates of bromination of these olefins. This discovery was interpreted as evidence for a concerted-type addition mechanism similar to that observed in the
formation of three-centered bromonium ions. However, the observation that dibromocarbene was more discriminative than bromine was suggested to result from higher dipolar character in the transition state of the carbene addition. Therefore, a "near-concerted", quasi-type mechanism was proposed where the sigma bonds do not form at the same rate and some carbonium ion character is formed on one of the olefinic carbons even though no intermediate seems to exist. This mechanism would be quite similar to the "asymmetric attack" mechanism later proposed\textsuperscript{121} and would be an "allowed" process according to the rules for cycloaddition reactions.\textsuperscript{108} Later work showed that dibromocarbene is, indeed, highly discriminatory in only attacking the more highly alkylated double bond of 1,2-dienes.\textsuperscript{122}

Thus, although the mechanism for dihalocarbene additions to olefins has never been completely proven, experimental evidence seems to point toward the "near-concerted", quasi-type process with formation of some carbonium ion character on one of the carbons of the erstwhile double bond. The amount of carbonium ion character and, therefore, the amount of discrimination displayed by the carbene depends upon the halogens attached to the central carbon atom.\textsuperscript{117} The greater the stability of the dihalocarbene, by back-bonding between an unshared pair of electrons on the halogen and the vacant p-orbital on the carbon, the more selective the carbene is toward addition with various alkenes or double bonds of polyenes.
Dichloroketene Addition:

Ketenes add to alkenes and polyenes to give nearly exclusive [2 + 2] cycloaddition products although higher adducts have been isolated in certain cases. The mechanism proposed for the addition of diphenyl ketenes to olefins was considered to be a "near-concerted", multi-center pathway where the two new sigma bonds do not form at the same rate and there is some charge formation. Considerable evidence supporting a concerted or "near-concerted" mechanism has been published. Some of the most conclusive data require that the reaction (1) must have a high negative entropy of activation, (2) must have only modest rate dependence on solvent polarity, and (3) must maintain stereometric relationships between reactants and products. Woodward and Hoffmann also propose a concerted, one-step mechanism for ketene additions to olefins.

In some other cases, however, such as with enamines and carbodiimides, a two-step mechanism appears to compete with and, in the latter case, predominate over the one-step, concerted mechanism. It should be noted that the conditions given above, suggesting a one-step mechanism, may also be satisfied by a two-step mechanism if the second step is rate-determining. It is felt that this possibility should not be overlooked. The discovery that the second step is the slow step in the ketene addition to carbodiimides allows that a two-step mechanism may be plausible in any ketene reaction. This mechanism would still show the reaction to be second order which agrees with the experimental value.
A general mechanism for the addition of ketenes to olefins does not seem likely, but rather it appears that the mechanism is influenced significantly by the substituents of the alkene. Dipolar character seems to develop during the course of the addition\textsuperscript{125} which causes the reaction to be somewhat selective in its orientation when forming the products. It has also been shown that the reaction is selective between double bonds when double bonds with different substituents are present in the same molecule.\textsuperscript{110}
RESULTS AND DISCUSSION

Nearly all of the reactions discussed here were carried out on the 5-methylene-2-norbornene system (25) which is prepared commercially by the reaction shown.\textsuperscript{129}

\begin{align*}
\text{endo} & \rightarrow \text{exo} \\
25
\end{align*}

This compound, 5-methylene-2-norbornene, is a unique diene because it contains two double bonds of different energies. The endo double bond is strained because of the geometry of the bicyclic ring and undergoes addition reactions very rapidly if the transition state formed is less strained.\textsuperscript{130} The exo double bond, which is not incorporated in the bicyclic ring, should not be nearly as strained and, therefore, should not enter into these reactions as rapidly as its counterpart.

Another distinguishing feature of the 5-methylene-2-norbornene system is that electrophilic attack could result in the formation of two homoallylic non-classical carbonium ions which can have unequal
energies. Electrophilic attack on the exo double bond would give rise to an endo carbonium ion (39) which could be postulated to be of lower energy because the positive charge would reside on secondary and tertiary carbon atoms. Electrophilic attack at the endo double bond would result in the formation of an exo carbonium ion (40) which should be higher in energy because it involves a primary carbon atom.

**Electrophilic Additions:**

Von Schleyer\textsuperscript{131} reported the addition of formic acid, hydrochloric acid, and hydrogen chloride to 5-methylene-2-norbornene. In each case
the initial attack of the hydrogen electrophile is at the exo double bond. A non-classical carbonium ion was suggested to account for the rearranged nortricyclane products obtained from the formic acid and hydrochloric acid additions.

The addition of activated amorphous sulfur to 5-ethylidene-2-norbornene, which may be electrophilic, was found to occur exclusively at the endocyclic double bond.\textsuperscript{132} The reaction was also observed to be stereospecific. Iodination of 5-methylene-2-norbornene, through the use of iodine isocyanate, also showed initial electrophilic attack on the endo double bond.\textsuperscript{133} An intermediate iodonium ion was suggested for the reaction which may have rearranged to an exo carbonium ion (40). Nucleophilic attack could then be focused at the exo methylene group which would give rise to the more stable\textsuperscript{130} tricyclic product. A similar addition involving iodine azide gave the same results.\textsuperscript{134}
The bromination of 5-methylene-2-norbornene, using N-bromo-
succinimide (NBS) in moist dimethylformamide (DMF) resulted in the
formation of three products.\(^{135}\) Initial electrophilic attack by

\[
\text{I-N}_3 \quad \xrightarrow{\text{NBS, moist DMF}} \quad \text{products}
\]

the bromine is evident in each of the products. In accordance with
other bromination mechanisms, an exo bromonium ion intermediate was
suggested to form in the initial step. Since 1,2-addition products
were not observed, the collapse of the bromonium ion to the homoallylic
carbonium ion must have been rapid. Attack occurs at the exo
methylene of the homoallylic carbonium ion because of less strain in
the nortricyclane structure and less steric hindrance of the nucleo-
phile. That the products are equilibrium controlled, i.e., formed
by rearrangement of a 1,2-addition adduct, is unlikely because of the
expected difficulty of rearrangements of a 1,2-bromohydrin under these
conditions. A mechanism involving the rate determining attack of a nucleophile on a charge transfer complex of NBS with the diene is unlikely. 51

From the reactions discussed above, a pattern seems to be evident in these electrophilic additions to 5-methylene-2-norbornene. Sulfur, iodine, and bromine, which add exclusively to the endo double bond of 5-methylene-2-norbornene, are all thought to add through a three-membered, "onium" type intermediate. Electrophilic protonation additions, which add to the exocyclic double bond of 5-methylene-2-norbornene, are not believed to involve a bridged "onium" ion intermediate. Therefore, the hypothesis that electrophiles which favor formation of three-membered, "onium" intermediates will all attack the endocyclic double bond was proposed. In this case, the relative energies of the double bonds and the three-membered intermediate are more important in determining the relative rates of addition to the double bonds of 5-methylene-2-norbornene than the energies of the homoallylic carbonium ions (39 and 40). Electrophiles which form highly unsymmetrical "onium" ions or do not form stable "onium" ions at all should attack at the exo double bond. For these additions, there is more positive charge on the adjacent carbon and the energy of the homoallylic carbonium ion formed seems to be more significant than the energy of the olefinic site. To test this hypothesis an examination of the additions of other electrophiles was carried out.
The suggestion that oxymercuration additions to olefins may not involve a mercurinium intermediate34 caused this electrophile to be of interest. If a three-membered mercurinium ion doesn't exist, then addition should occur on the exocyclic double bond. However, if the addition takes place on the endocyclic double bond, then a mercurinium ion would be implied by the hypothesis presented. Oxymercuration of 5-methylene-2-norbornene resulted in 1,2-addition at the exocyclic double bond indicating the absence of a symmetrical mercurinium ion in the mechanism of the addition. The occurrence of the 1,2-addition product rather than a rearranged 1,5-nortricyclic addition is attributed to \( \sigma-\pi \) stabilization of the positive charge on the adjacent carbon by the mercury as well as the endocyclic double bond.37

Reactions of tertiary butyl chloride were also examined using 5-methylene-2-norbornene and 5-ethylidene-2-norbornene.135 One may predict that tertiary butyl carbonium ions would not be good bridging groups because of the directional character of the vacant \( \pi \)-orbital.

Two important facts were shown by these additions. First, the initial
Electrophilic attack occurred at the exocyclic double bond which suggests that the prediction above is correct. The second important fact shown is that the first step of the reaction, the attack of the electrophile on the exo double bond, is the rate-determining step. This is shown by the higher temperature requirement and the slower rate of addition exhibited by 5-ethylidene-2-norbornene.

The chlorination of 5-methylene-2-norbornene in DMF gave two products depending upon which of the double bonds the initial attack of the electrophile was focused. The ratio of exo/endo double bond attack is approximately 1.6/1.0, mostly exocyclic attack. When the same reaction was run using tertiary butyl hypochlorite in DMF, the ratio
of exo/endo attack by the chlorine was about 0.9/1.0. Because attack of the chlorine is observed at both double bonds, one may infer that the chloronium ion does not have as great a propensity to form in reactions as do the bromonium and iodonium ions. Because of this, the relative energies of the double bonds would have less significance. Experimental evidence shows that, although the stability of the chloronium ion is less than those from bromine and iodine, some bridging character is evident in chlorine additions. Therefore, one may predict both exo- and endo- attack.

Several methods were employed in trying to form the epoxide of 5-methylene-2-norbornene. The first method tried involved the use of peroxyc formic acid. Two products were formed but were not absolutely identified. The evidence available suggests one of the products to be the formate ester produced from the addition of formic acid to 5-methylene-2-norbornene. The other product appears to be either

\[
\text{5-methylene-2-norbornene} + \text{HCOH} + \text{H}_2\text{O}_2 \rightarrow \text{formate ester} + \text{product 2}
\]

2-hydroxy-5-methylnor tricyclane or 5-methyl-2-nortricyclone. The observation that 5-methylene-2-norbornene reacts essentially at the same rate as the rate of mixing with formic acid lends considerable
support for the probability of one of the products as being the formate ester. The second product is probably formed from the addition of H₂O, the solvolysis of the formate ester, or the acid catalyzed addition of peroxyformic acid followed by the loss of formic acid.

When the reaction was carried out under non-acidic conditions, epoxidation of 5-methylene-2-norbornene was found to occur at both double bonds. Moreover, the exo/endo double bond ratio changes with the conditions used. In the method of Lumb,¹³⁷ using acetonitrile, hydrogen peroxide, and bicarbonate in methanol, a product ratio exo/endo of 1/4 was observed, mostly endocyclic epoxide. When m-chloroperoxybenzoic acid was added to 5-methylene-2-norbornene in a Na₂CO₃ buffered solution of methylene chloride, the product ratio exo/endo was about equal, 1/1. Although the mechanism for
epoxidation reactions is still not known, one may expect similar bridging characteristics between oxygen and chlorine atoms. Therefore, attack at both double bonds would be expected to occur. In the case of Lumb's procedure, where methanol is used as the solvent, intermolecular hydrogen bonding probably weakens the electrophilic character of the oxygen, causing the relative energies of the double bonds to become more important. This would shift the reaction in favor of the endocyclic attack.

In order to determine if the nucleophile played a role in determining the formation of the products, iodine monochloride was added to 5-methylene-2-norbornene. In previous additions to 5-methylene-2-norbornene involving chloride ion nucleophiles, nucleophilic attack was focused on the endocyclic double bond or, because of the solvent cage effect in the hydrogen chloride addition, the tertiary carbon atom. The product obtained from iodine monochloride showed exclusive electrophilic attack at the endocyclic

\[
\begin{align*}
\text{5-methylene-2-norbornene} + \text{ICl} & \rightarrow \text{iodine mono-Cl} \\
& \begin{array}{c}
\text{I} \\
\text{Cl}
\end{array}
\end{align*}
\]

double bond and nucleophilic attack by the chloride at the exocyclic double bond. This observation, that the same nucleophile will attack
at either of the double bonds depending upon the electrophile used, is taken as evidence against product determining effects by the nucleophiles.

**Cycloaddition Reactions:**

Because of the apparent pattern displayed by the electrophilic additions to 5-methylene-2-norbornene, the possibility of using this compound to distinguish concerted from two-step cycloaddition reactions was also explored. The formation of three-membered "onium" ions from electrophilic additions is believed to be quite analogous to concerted cycloaddition reactions while carbonium ion energies should be one of the most significant factors in determining the location and orientation of two-step cycloadditions. Therefore, by extending the hypothesis proposed, one may predict concerted cycloadditions to occur on the endocyclic double bond and two-step, dipolar-intermediate cycloadditions to occur on the exocyclic double bond.

The addition of chlorosulfonyl isocyanate to 5-ethylidene-2-norbornene resulted in exclusive addition on the exo double bond. From the observed reactions of similar isocyanates, it is reasonable
to assume this reaction to be an example of a two-step cycloaddition with an intermediate such as 41.

Tetraphenylcyclopentadienone is known to undergo concerted $[2 + 4]$ cycloaddition reactions with alkenes.\textsuperscript{140} When it was added to 5-methylene-2-norbornene, two products were observed which resulted from addition to the endocyclic double bond.\textsuperscript{135} Product B formed by the loss of CO from product A.

Thus, it appeared as though the 5-methylene-2-norbornene system could be used to distinguish cycloaddition mechanisms. However, better footing for the hypothesis proposed was needed so more cycloaddition reactions of 5-methylene-2-norbornene were examined.

Additions of phenyl azide are known as 1,3-dipolar cycloadditions and are believed to occur via a concerted mechanism.\textsuperscript{141} When 5-ethylidene-2-norbornene was reacted with phenyl azide, the product formed could not be isolated.\textsuperscript{142} However, the addition of p-toluenesulfonyl azide, which reacts in a manner similar to phenyl azide,\textsuperscript{143} resulted in the formation of one product from attack at the endocyclic double bond. This observation is in agreement with the hypothesis proposed.
The controversial issue involving the mechanism of ketene additions to olefins made this addition especially interesting to investigate. The "remodeled" rules for cycloaddition reactions predict the addition to occur by a concerted \([2+2]\) process.\(^{108}\) However, the possibility exists that the addition may be two-step with an intermediate which is tightly bound to restrict rotation.\(^{144}\) It was felt that the addition of dichloroketene to 5-methylene-2-norbornene may help to determine which of the mechanisms is correct.

The product obtained from the addition showed exclusive attack on the exocyclic double bond. This implies that the cycloaddition may proceed through either a two-step mechanism with the formation of a dipolar intermediate or else through an asymmetrical concerted mechanism in which positive charge develops on the tertiary carbon atom to a significant extent.
Dihalocarbenes are also known to undergo cycloaddition reactions with some charge separation formed along the reaction pathway.\textsuperscript{120} Therefore, examining this type of reaction using highly electronegative groups on the carbene to maximize the amount of charge separation seemed advantageous. When dichlorocarbene was added to 5-methylene-2-norbornene, exclusive addition to the exocyclic double bond was observed which indicates a two-step, dipolar mechanism.

That the mechanisms projected here are extremes is noteworthy. Because a compound attacks at the exocyclic double bond, this does not mean that total charge separation is evident in an intermediate. What is suggested is that enough charge separation does exist to allow interaction between the double bonds and possible formation of a homoallylic, non-classical carbonium ion (39). If attack occurs on the endocyclic double bond, then little charge separation is suggested and the energy of the double bond is most significant.

Rearrangements and Equilibriums:

There are two possible rearrangements or equilibriums which may take place in electrophilic additions to 5-methylene-2-norbornene. The first of these may occur if initial electrophilic attack is
focused on the endocyclic double bond with formation of an exo-homoallylic carbonium ion (40). This higher energy carbonium ion

could then decay to an endo-homoallylic carbonium ion (42) by way of a 1,3-hydride shift. The transition state for this hydride migration
would be analogous to an allyl π-system which requires a suprafacial
shift. Such shifts are thermally forbidden by the rules of Woodward
and Hoffmann. No such shifts were observed in any of the reactions
discussed here.

If initial electrophilic attack is on the exocyclic double bond,
an equilibrium may occur between two of the bonds of the three-
membered tricyclic system. Such an equilibrium occurs in the case of
norbornadiene\textsuperscript{145} and the direction of attack by the nucleophile is affected by this equilibrium. If the electrophile is a hydrogen atom, the exo- and endo- products formed are indistinguishable enantiomers.

However, if a similar equilibrium had existed in the 5-methylene-2-norbornene system, we could have readily distinguished the diastereoisomers by the $\delta$ value of the methyl group in the NMR spectrum. When formic acid was reacted with 5-methylene-2-norbornene,

\[
\begin{align*}
\text{norbornadiene} & \rightarrow \text{H}^+ \rightarrow \text{electrophile} \rightarrow \text{NMR spectrum} \\
& \text{hydrolysis} \rightarrow \text{tricyclic alcohol} \rightarrow \text{NMR spectrum} \\
\text{product} & \rightarrow \text{hydroxide} \rightarrow \text{NMR spectrum} \\
\text{reduction} & \rightarrow \text{NMR spectrum} \\
\end{align*}
\]

the NMR spectrum showed one signal for the methyl group. Hydrolysis of the formate ester with potassium hydroxide formed the tricyclic alcohol. The NMR spectrum showed one peak for the methyl group. The product, 4-methyl-2-mortricyclene, obtained by oxidizing the hydroxide, also gave only one peak for the methyl group in the NMR spectrum. However, when the tricyclic was reduced with NaBH\textsubscript{4}, two methyl peaks were present in the NMR spectrum signifying the presence of both the syn- and anti- products. Thus only the anti-diastereoisomer,
derived from exo-attack, was formed in the addition reaction. The amount of steric hindrance involved in the reduction of the tricyclone seems to be quite small because the syn- and anti-diasterio-isomers were formed in approximately equal amounts. Because steric factors were not important in the borohydride reduction of the tricyclone, one would expect to have nucleophilic attack from both the exo- and endo-direction on the tricyclic carbonium ions. The reason both products are not formed then must be electronic rather than...
steric. The homoallylic carbonium ion 43 is probably much less stable than 39 because ion 43 is composed of only secondary carbon atoms while carbonium ion 39 consists of two secondary and one tertiary carbon atom. If an equilibrium does exist between the two homoallylic carbonium ions, it must be shifted almost entirely to the left. It was also possible to distinguish the syn- and anti- chloro isomers by the different δ values of the methyl group. However, the mechanism for this reaction is not clear.

![Chemical structure](image)

\[
\text{syn} \quad \frac{\text{anti}}{\text{syn}} = \frac{1}{1}
\]

Methyl δ values\(^a\)

<table>
<thead>
<tr>
<th>X</th>
<th>exo</th>
<th>endo</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH(^b)</td>
<td>1.13</td>
<td>1.22</td>
</tr>
<tr>
<td>Cl(^b, c)</td>
<td>1.19</td>
<td>1.25</td>
</tr>
</tbody>
</table>

\(^a\) External TMS standard
\(^b\) in CCl\(_4\) solution
\(^c\) Reference 135
Competitive Kinetic Study:

A kinetic study was carried out to determine what effect the electrons of the \( \beta \) double bond had on electrophilic attack at the endocyclic double bond. Because of the fast rate of electrophilic attack on the strained endo double bond, a competitive type kinetics was studied where the rate of attack on 5-methylene-2-norbornene was compared to the rates of attack on norbornene and norbornadiene. By comparing the relative peak areas of the endocyclic olefinic protons from the alkenes before and after the addition, it was possible to determine which of the alkenes reacted faster relative to the other alkene.

<table>
<thead>
<tr>
<th>Olefins</th>
<th>Relative Molar Peak Ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Before</td>
</tr>
<tr>
<td>Norbornene</td>
<td>1.1</td>
</tr>
<tr>
<td>Norbornadiene</td>
<td>1</td>
</tr>
<tr>
<td>5-Methylene-2-Norbornene</td>
<td>1.2</td>
</tr>
<tr>
<td>Norbornadiene</td>
<td>1</td>
</tr>
<tr>
<td>5-Methylene-2-Norbornene</td>
<td>0.5</td>
</tr>
</tbody>
</table>

As shown by the chart above, norbornene reacts the fastest followed by norbornadiene with 5-methylene-2-norbornene reacting the slowest. The reason for the high reactivity of norbornene compared to the others is somewhat obscure, but might be attributed to the localization of the electrons in the \( \pi \)-bond. The other two olefins
each have two double bonds and some electron delocalization may occur by lowering the energy of the ground state. Some other phenomenon may also be taking place between the two double bonds in norbornadiene and 5-methylene-2-norbornene so that less of the strain energy is felt by their endo double bonds.

Norbornadiene reacts faster than 5-methylene-2-norbornene because of a statistical factor, i.e., it has two endocyclic olefinic sites, either of which may be attacked. Norbornadiene is also a slightly more strained olefin which may cause the rate of electrophilic addition to be enhanced over that of the 5-methylene-2-norbornene system.

The main point is that there is no rate enhancement resulting from participation of the \( n \)-electrons of the other double bond during electrophilic attack. This supports the argument that the bromination proceeds directly to a localized bromonium ion (43) rather than a delocalized carbonium ion (44). Thus, the principal

![Diagram 43](image1)

![Diagram 44](image2)

rate factor in the bromination reaction is the energy of the double bond being attacked rather than the stability of a possible carbonium ion intermediate.
EXPERIMENTAL

The work reported herein was done in residence at South Dakota State University, Brookings, South Dakota.

Description of Instrumentation Used:

Infrared spectra were obtained on a Perkin-Elmer Model 700 Infrared Spectrophotometer between sodium chloride plates. All samples were liquids and were run neat.

Nuclear magnetic resonance spectra were obtained on a 60 MHz Varian A-60A Spectrometer using tetramethylsilane (TMS) as an external standard. The spectra are reported or shown in delta (δ) units (parts per million, ppm).

Mass spectra were run on a Varian CH-5 Double Focusing Mass Spectrometer at the University of Wyoming, Laramie, Wyoming.

Gas chromatographs were run on a Beckman GC-2A equipped with an aluminum column packed with 15% SE-30 on 42-60 mesh Chromosorb P.

Carbon-Hydrogen analysis on 1-Methyltricyclo [2.2.1.0] heptan-3-one was run by Miss Margy Pearson at South Dakota State University, Chemistry Department, Brookings, South Dakota.

Formic Acid Addition: 1-Methyl-3-tricyclo [2.2.1.0] heptyl formate

To 1.06 g (0.01 mole) of 5-methylene-2-norbornene in 10 ml of formic acid (ACS grade) were added 0.25 g of boron trifluoride etherate. The solution was stirred rapidly for three hours at room
temperature, during which time it turned dark red. It was poured into 50 ml of water and the product was extracted with ether. The ether extracts were washed twice with saturated sodium bicarbonate solution, once with water, and dried over anhydrous magnesium sulfate. Roto-evaporation of the solvent yielded a wine-colored liquid.

Infrared absorption bands appeared at 3060 (C-H of cyclopropyl), 1720 (C=O of formate), and 1185 cm⁻¹ (C-O of formate ester). NMR peaks from a neat sample occurred at 7.706 (singlet, 1H, formate hydrogen), 4.606 (singlet, 1H, C-3 ring hydrogen), and 1.125 (singlet, 3H, methyl hydrogens). Mass spec (parent peak, m/e 152), P-45 (m/e 107, loss of CHO₂).

Yield = 1.84 g  % Yield = 82%
Spectra pages 82, 83

Hydrochloric Acid Addition 1-Methyl-3-chlorotricyclo [2.2.1.0] heptane

A solution of 2.12 g (0.02 moles) of 5-methylene-2-norbornene in 20 ml of 6N hydrochloric acid was stirred at room temperature for 18 hours. While the solution was stirred it changed from colorless to dark reddish-brown. The solution was then extracted twice with ether and the ether extracts were washed repeatedly with concentrated bicarbonate solution, once with water, and dried over anhydrous magnesium sulfate. The ether was then roto-evaporated leaving a reddish-brown liquid.
Infrared bands at 3060 (C-H of cyclopropyl) and 1770 cm\(^{-1}\) (C-Cl). NMR signals from a neat sample appeared at 3.856 (singlet, 1H, C-3 ring hydrogen) and 1.126 (singlet, 3H, methyl hydrogens).

Mass spec (parent peak, m/e 143),

\[ \text{Yield} = 1.84 \, \text{g} \quad \% \, \text{Yield} = 65\% \]

Spectra pages 84, 85

**Ethereal Hydrogen Chloride Addition: 5-Chloro-5-methyl-2-bicycle[2.2.1] heptene**

Into a solution composed of 1.06 g (0.01 mole) of 5-methylene-2-norbornene and 75 ml of dried diethyl ether was bubbled dry HCl gas, generated by adding concentrated sulfuric acid to sodium chloride and bubbled through concentrated sulfuric acid. When the ether solution was saturated with HCl, it was loosely stoppered and stirred overnight. It was then washed with water, washed repeatedly with saturated bicarbonate solution and once again with water. After drying over anhydrous magnesium sulfate, the ether was roto-evaporated leaving a light yellow liquid product.

Infrared absorption at 3070 cm\(^{-1}\) (C-H of olefin) and 1575 cm\(^{-1}\) (C=C of endocyclic olefin). A neat sample gave NMR peaks at 5.856 (multiplet, 2H, endocyclic olefinic hydrogens) and 1.386 (singlet, 3H, methyl hydrogens).

\[ \text{Yield} = 0.79 \, \text{g} \quad \% \, \text{Yield} = 56\% \]

Spectra pages 86, 87
Peroxyformic Acid Addition:

The procedure used was the same as that used by Schaefer\textsuperscript{136} only the reaction was reduced to 1/4 the amount used there. After drying the organic extracts, the solvent was stripped off and the residue was distilled off under vacuum. Two portions were collected; the first portion was obtained from 50-70\textdegree C at 5 mm and the second portion from 70-105\textdegree C at 4 mm pressure. An undistillable tar remained in the reaction flask after the distillation was complete. Gas chromatography, using an SE-30 column, showed that the same two compounds made up the two portions only in different amounts. Mass spectral evidence showed one of the compounds to be the formate ester with a parent peak at m/e 152, a P-28 peak from loss of CO, and a P-44 peak from the loss of CO\textsubscript{2}. G. C. retention times of an originally prepared sample of 1-methyl-3-tricyclo [2.2.1.0\textsuperscript{2}3.3.0\textsuperscript{2}7.0\textsuperscript{2}12] heptyl formate with this product verified it as being a formate ester. The other product gave a parent peak at m/e 124 along with a P-15 peak. However, only very small P-1, P-16, and P-17 peaks were evident. G. C. retention times suggest this product to be 1-methyltricyclo [2.2.1.0\textsuperscript{2}3.3.0\textsuperscript{2}7.0\textsuperscript{2}12] heptan-3-ol. No N.M.R. or I.R. were run on the individual products.

Lumb's Epoxidation: 2,3-Epoxy-5-methylene-bicyclo [2.2.1] heptane and 5-Bicyclo [2.2.1] heptene-2-spiro-2'-oxirane

The formation of the epoxides was carried out in the same manner as the method employed by Lumb and Whitham\textsuperscript{137} to 4.24 g of 5-methylene-2-norbornene, 4.0 g of potassium bicarbonate and 2.04 g
of acetonitrile in 50 ml methanol was added 5 ml of 30% hydrogen peroxide during a 10 minute time period. The suspension was allowed to stir at room temperature for 22 hours before being heated to 40°C for 3 hours. After cooling, the solution was poured into 100 ml of water. Methylene chloride was added to the milky water solution and the resulting mixture was stirred with a stirring rod. The layers were separated and the organic portion was dried over anhydrous sodium sulfate. Roto-evaporation of the solvent and a small amount of starting material yielded a yellow liquid which was found to contain two epoxides.

Infrared bands at 3000 cm⁻¹ (olefinic and epoxy C=H) and 850 cm⁻¹ (asymmetrical epoxy ring stretching). NMR absorption of a neat sample appeared at 5.906 (multiplet, endocyclic olefinic hydrogens) and at 4.75 and 4.556 (two singlets, exocyclic olefinic hydrogens). Because the NMR spectrum showed a multiplet for the endocyclic olefins, it was assumed that no starting material was present in the products. By comparing the integration of the exo and endocyclic olefinic protons, a ratio of exo/endo epoxide formation of 1/4 was observed.

Yield = 1.33 g

% Yield = 27%

Spectra pages 88, 89
**Buffered Epoxidation**: 2,3-Epoxy-5-methylene-bicyclo[2.2.1]heptane and 5-Bicyclo[2.2.1]heptene-2-spiro-2'-oxirane

A solution of 2.12 g (0.02 moles) of 5-methylene-2-norbornene and 10.60 g of sodium carbonate in 75 ml of methylene chloride was stirred rapidly at room temperature during the addition of 3.44 g (0.02 moles) of m-chloroperoxybenzoic acid in small portions. After the addition was completed, about 90 minutes, the reaction vessel was loosely stoppered and stirred for nine hours at room temperature. The solution was then vacuum filtered through two fine-pore filter papers and the solid washed with clean methylene chloride. The combined methylene chloride adducts were washed twice with water and dried over anhydrous sodium sulfate. Aromatic impurities were present in the products after roto-evaporation. Further washing failed to remove them. The liquid product which remained contained two epoxide products.

Infrared absorption bands were found at >3000 (olefinic and epoxy C-H) and 850 cm\(^{-1}\) (asymmetrical epoxy ring stretching). NMR peaks from a sample of the neat product occurred at 7.70 and 7.206 (aromatic impurities), 5.956 (multiplet, endocyclic olefinic hydrogens) and at 4.75 and 4.556 (two singlets, exocyclic olefinic hydrogens). Because the NMR spectrum showed a multiplet for the endocyclic olefins, it was assumed that no starting material was present in the products. By comparing the integration of the exo and endocyclic olefinic protons, a ratio of exo/endo epoxide formation of 1/1 was observed.
Yield = 1.33 g  \quad \% \text{Yield} = 54\% \\
Spectra pages 90, 91

**Iodine Monochloride Addition:** 1-Chloromethyl-3-Iodotricyclo [2.2.1.0] heptane

A solution containing 1.80 g of iodine monochloride, 1.06 g (0.01 mole) 5-methylene-2-norbornene and 25 ml acetonitrile was stirred for 5 hours at room temperature. After mixing with water, diethyl ether was added and the solution was washed repeatedly with 5% sodium thiosulfate solution. A light brown solution remained which was dried over anhydrous magnesium sulfate. Roto-evaporation yielded a reddish liquid.

Yield = 1.60 g  \quad \% \text{Yield} = 60\% \\
Spectra pages 92, 93

**Infrared absorption** at 3065 (C-H of cyclopropyl) and 795 cm\(^{-1}\) (C-Cl). NMR peaks of a neat sample occurred at 4.316 (singlet, 1H, C-3 ring hydrogen), 4.186 (singlet, 1.5H, exo methylene hydrogens) and 3.916 (singlet, 0.5H, exo methylene hydrogens).

Because the spectra showed several products to be present and because we could not be certain which of the double bonds the electrophile had attacked, the iodo-chloride product was reduced to the iodo-iodide by adding sodium iodide in acetone. The NMR of the resultant product showed no change in the downfield ring proton at 4.316 but showed a significant change in the \(\delta\) value at the exo-methylene protons from 4.186 to 3.916. This showed that the initial
electrophilic attack of the iodine was at the endocyclic double bond. The other products probably originated from some I₂ impurity in the ICl sample used and some water in the reaction solution.

**Dichlorocarbene Addition:** 5-Bicycle [2,2,1] heptene-2-spiro-1'-
(2',2'-dichlorocyclopropane)

A mixture consisting of 1.86 g (0.91 moles) of sodium trichloroacetate, 1.06 g (0.01 moles) of 5-methylene-2-norbornene, 10 ml perchloroethylene, and 2 ml diglyme was refluxed for 12 hours with stirring. The brown solution was then washed repeatedly with water to extract the diglyme. Ether was added to the organic portion and it was dried over anhydrous magnesium chloride. Rotovaporation yielded a brown liquid product.

Infrared bands at 3060 (C-H of olefin and cyclopropyl ring), 1565 (C=C of endocyclic olefin) and 910 cm⁻¹ (cyclopropyl C-Cl). NMR absorptions of the neat product occurred at 6.10 (multiplet, 2H, endocyclic olefinic hydrogens) and at 2.30 and 2.10 (two doublets, 2H, cyclopropyl hydrogens).

Yield = 1.66 g

% Yield = 88%

Spectra pages 94, 95

**Hydrolysis of 1-Methyl-3-tricyclo [2.2.1.0] heptyl formate: 1-
Methyltricyclo [2.2.1.0] heptan-3-ol**

To 2.50 g of 1-methyl-3-tricyclo [2.2.1.0] heptyl formate was added 2.00 g of potassium hydroxide dissolved in 5 ml of ethanol. An
exothermic reaction took place with the formation of a white solid. After standing for about 15 minutes with manual stirring, distilled water was added and the solution was extracted twice with two 25 ml portions of pentane. The pentane extracts were dried over anhydrous sodium sulfate, filtered, and roto-evaporated. A yellow liquid remained.

Infrared absorption bands at 3340 (O-H stretch), 3065 (C-H of cyclopropyl), 1410 and 1340 (C-H bending), 1060 (alcoholic C-O stretch) and 800 cm\(^{-1}\) (asymmetrical cyclopropyl ring stretching).

NMR peaks from a CCl\(_4\) solution of the product appeared at 4.956 (broad singlet, 1H, hydroxyl hydrogen), 3.908 (singlet, 1H, C-3 ring hydrogen) and 1.208 (singlet, 3H, methyl hydrogens).

Oxidation of 1-Methyltricyclo[2.2.1.0\(^2\)heptan-3-ol: 1-Methyltricyclo[2.2.1.0\(^2\)heptan-3-one

A solution of 3.63 g of 1-methyltricyclo[2.2.1.0\(^2\)]heptan-3-ol in 18 ml of acetone was cooled to 0-5°C in a 100 ml 3-necked flask equipped with a stirring bar, thermometer, and dropping funnel with pressure equalizing arm.

The oxidation reagent was prepared by dissolving 2.32 g CrO\(_3\) in 3 ml distilled water. The beaker was immersed in an ice bath and 1.8 ml of concentrated sulfuric acid was added cautiously with manual stirring followed by 6 ml of water. The solution was then cooled to 0-5°C.

When both solutions were cooled, the oxidation reagent was poured into the dropping funnel and added to the alcohol solution
with vigorous stirring at a rate to maintain the temperature of the reaction at about 20°C. A dark green solid formed in the reaction flask during the addition. The solution turned from colorless to green to red. After the addition was complete, the solution was stirred for two hours. Sodium bisulfite was then added in small portions until the brown color in the upper layer of the two layer mixture turned light green. The layers were separated and the lower layer extracted with 6 ml of 30-60° petroleum ether. The ether extract was added to the original upper layer. The lower layer of that mixture was then separated and added to the original lower layer. The combined lower layers were washed three times with 6 ml portions of 30-60° petroleum ether. The extracts were combined with the first extract and washed successively with two 2 ml portions of saturated bicarbonate solution, one 2 ml portion of saturated NaCl solution, and dried over anhydrous magnesium sulfate. Roto-evaporation left a yellow liquid.

Infrared bands occurred at 3025 (cyclopropyl C-H), 1745 (C=O stretch) and 812 cm⁻¹ (asymmetrical cyclopropyl ring stretch).
An NMR spectrum of the neat product showed an absorption at 1.406 (singlet, 3H, methyl hydrogens).

Analysis for \( \text{C}_8\text{H}_{10}\text{O} \)

<table>
<thead>
<tr>
<th></th>
<th>Found</th>
<th>Calc.</th>
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<tbody>
<tr>
<td>C</td>
<td>78.69</td>
<td>78.65</td>
</tr>
<tr>
<td>H</td>
<td>8.20</td>
<td>8.25</td>
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</table>

**Sodium Borohydride Reduction of 1-Methyltricyclo[2.2.1.0]heptan-3-one:**

**syn and anti 1-Methyltricyclo[2.2.1.0]heptan-3-one**

To a solution of 0.19 g of 1-methyltricyclo[2.2.1.0]heptan-3-one
in 2 ml of methanol was added 0.01 g of sodium borohydride in small portions. The temperature of the reaction was maintained at room temperature by the use of an ice bath. When the addition was completed, more methanol was added and the solution was filtered. It was then boiled for three minutes and poured over crushed ice. When the ice had melted, the product was extracted with ether. The ether extract was dried over anhydrous magnesium sulfate and roto-evaporated. A yellow oil remained.

Infrared absorption bands at 3340 (O-H stretch), 3065 (cyclopropyl C-H), 1405 and 1340 (O-H bending), 1065 (alcoholic C-O stretch), and 805 cm\(^{-1}\) (asymmetrical cyclopropyl ring stretch). NMR peaks from a CCl\(_4\) solution of the product appeared at 3.706 (singlet, 1H, C-3 ring hydrogen), 2.885 (singlet, 1H, hydroxyl hydrogen), 1.226 (singlet, 3H, syn-methyl hydrogens) and 1.136 (singlet, 3H, anti-methyl hydrogens).

Oxymercuration Addition: 2-(2-Hydroxy-5-bicyclo[2.2.1]heptenyl) methylmercuric acetate

A solution of 2.16 g (0.01 mole) of mercuric oxide, 2.60 g (0.01 mole) of mercuric acetate, and 2.12 g (0.02 moles) of 5-methylene-2-norbornene in 75 ml of water was stirred at room temperature for 30 hours. The solution was then roto-evaporated to near dryness and extracted with ethyl acetate. The brown liquid was filtered from the solid and allowed to evaporate. Spectral evidence showed the brown oil which remained to be impure so it was extracted with ether and dried over anhydrous magnesium sulfate.
Roto-evaporation gave a yellow oil which contained the impure exo-
cyclic addition product.

Infrared absorption bands showed C=H stretching at 3380 cm\(^{-1}\) olefinic C-H stretching at 3050 cm\(^{-1}\), carbonyl C=O stretching at 1700 cm\(^{-1}\), and C-O stretching at 1025 cm\(^{-1}\). NMR peaks from a CCl\(_4\) solution of the product showed a triplet for the two endocyclic olefinic hydrogens at 5.60\(\delta\), a singlet for the acetate methyl group at 1.99\(\delta\), and a singlet for the hydroxy hydrogen at 3.39\(\delta\).

**Dichloroketene Addition: 5-Bicycle \([2,2,1]\) heptene-2-spiro-3'-
(2',2'-dichlorocyclobutanone)**

To a stirred mixture of 1.95 g (0.03 moles) of activated zinc, 20 ml of dried diethyl ether and 2.12 g (0.02 moles) of 5-methylene-2-norbornene was added dropwise at room temperature a solution containing 1.82 g (0.01 moles) of trichloroacetyl chloride in 10 ml of dried diethyl ether. After the addition was complete, the solution was stirred overnight. The next morning the excess zinc was removed and the filtrate was concentrated by roto-evaporation. The concentrated filtrate was then extracted with hexane which was then concentrated. A reddish-brown liquid remained which contained the impure product.

Infrared absorptions were found at 3070 (olefinic C-H stretch) and 1845 cm\(^{-1}\) (C=O of cyclobutanone). The NMR spectrum obtained from a CCl\(_4\) solution of the product showed peaks at 6.15\(\delta\) (multiplet,
2H, endocyclic olefinic hydrogens) and at 3.24 and 2.958 (two doublets, 2H, cyclobutaneone hydrogens).

Yield = 0.82 g % Yield = 38%

**Competitive Kinetic Study:**

Excess amounts of two of the olefins were weighed out in DMF solvent. An aliquot of this was taken to use as a reference for the unreacted material. Into the remaining DMF-alkene solution was added 10 ml of a previously prepared 0.08M solution of N-bromo-succinimide (NBS) in DMF-water solvent. The combined solutions were stirred at room temperature for approximately 30 minutes before the reaction was quenched with water and the unreacted alkenes extracted with ether or CCl₄. NMR spectra were taken of the aliquot of unreacted alkenes and the extracted alkenes remaining after the reaction. By comparing the relative peak areas of the endocyclic olefinic protons from the alkenes before and after the addition, it was possible to determine which of the alkenes reacted faster relative to the other alkene.

<table>
<thead>
<tr>
<th>Olefins</th>
<th>Relative Observed Molar Peak Ratios</th>
<th>Relative Molar Peak Ratios</th>
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<tbody>
<tr>
<td></td>
<td>Before</td>
<td>After</td>
</tr>
<tr>
<td><strong>Norbornene</strong></td>
<td>17/15</td>
<td>5/15</td>
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<tr>
<td><strong>Norbornadiene</strong></td>
<td></td>
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<tr>
<td><strong>Norbornene</strong></td>
<td>14/12</td>
<td>1.5/15</td>
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<td><strong>5-Methylene-2-Norborne</strong></td>
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<tr>
<td><strong>Norbornadiene</strong></td>
<td>6/12</td>
<td>4/18</td>
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<tr>
<td><strong>5-Methylene-2-Norborne</strong></td>
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</tbody>
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Formic Acid Addition
REMARKS

ORIGIN  Aqueous HCl Addition

PURITY

PHASE  Neat

CONCENTRATION

THICKNESS

DATE

OPERATOR

PERKIN-ELMER
MODEL 700

SPECTRUM NO.

SAMPLE 1

SAMPLE 2

FRQUENCY (CM^-1)

TRANSMITTANCE (%)
**REMARKS**

**ORIGIN** Ethereal HCl Addition

**PURITY**

**PHASE** Neat

**CONCENTRATION**

**THICKNESS**

**DATE**

**OPERATOR**

---

**PERKIN-ELMER**

**MODEL 700**

**SPECTRUM NO.**

**SAMPLE 1**

**SAMPLE 2**

---

**FREQUENCY (CM\(^{-1}\))**

**TRANSMITTANCE (%)**

---

[Graph of the spectrum with frequency ranging from 4000 to 650 and transmittance ranging from 0 to 100.]

---

**THICKNESS**

---

**DATE**

---

**OPERATOR**
Lumb's Epoxide
Buffered Epoxide
REFERENCES


135. E. S. Olson, unpublished work.

142. W. Burkhart, unpublished results.