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THE OXYMERCURATION OF ALLENES

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By

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THE OXYMERCURATION
OF
ALLENES

By William Lincoln Waters

A thesis submitted to the Graduate School of the University of Hawaii in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

ABSTRACT

Addition of mercuric acetate to allene and the five possible methyl-substituted allenes was carried out in methanol. The reaction is quite rapid and even quantitative if an equivalent amount of sodium carbonate is added soon after initial mixing of the reagents.

Allene yields exclusively 1,3-bis-(acetoxymercuri)-2-propanone. Methylallene produces an analogous ketone plus one monoadduct. All other allenes form either one or two monoadducts. The original allenes can be regenerated from the monoadducts by shaking a benzene solution with aqueous hydrochloric acid.

The orientation of mercuric acetate addition in at least the cases of methylallene and 1,1-dimethylallene differs from that reported for hydrogen halide addition to the same compounds. Methylallene adds hydrogen chloride to the less substituted double bond, putting hydrogen on the terminal carbon atom. Oxymercuration of this compound gives a similar product (although not stopping at the monoadduct stage) and
a substantial amount of a second product in which Markovnikov addition has occurred across the more highly substituted olefinic bond. In the corresponding reactions of 1,1-dimethylallene, the Lewis acid attacks the center carbon of the allenic system in both cases. However, the halide ion in hydrogen halide addition adds to give the thermodynamically more stable primary halide, while the attack of methanol in oxymercuration appears to be kinetically controlled, i.e., a tertiary ether is produced.

The significance of these differences must reflect either the dissimilarities of the two reaction intermediates involved, i.e., classical carbonium ion in the case of hydrohalogenation and a bridged mercurinium ion in the case of oxymercuration, or some rather unlikely type of rearrangement before or after the addition of the electrophilic reagent to these allenes.

The structural assignments of most of the products were based on detailed NMR analyses. Unambiguous results were obtained when measured \( \text{Hg}^{199}\text{-H}_1 \) spin-spin coupling constants were compared with literature values for similar mercury-proton systems.

Unexplained mercury satellites which consistently appeared in the NMR spectra of some of these allene adducts prompted an investigation of possible long-range \( \text{Hg}^{199}\text{-H}_1 \) spin-spin coupling. The spectra of oxymercuration products from some twenty olefins revealed that coupling through four sigma bonds does exist and can vary in size from 0 to 50 \text{cp.s.},
depending on substituents. In addition to non-bonded steric repulsions, intramolecular electronic attractions between mercury and aromatic or halo substituents appear to be important in determining the magnitude of this coupling.
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I. INTRODUCTION

A. Objective of the Research
   
   The primary objective of this research was to determine if stable addition compounds of mercury salts and allenes exist. This being the case, the orientation and stereochemistry of the products were to be studied, hoping to better define both the mechanism of oxymercuration and the behavior of allenes toward electrophilic reagents.

B. Significance of the Research

1. Mercury

   Mercury salt addition to double bonds is interesting for the following three reasons:

   (a) Hg$^{++}$ electrophilic addition is quantitative and proceeds under very mild (non-acidic) conditions compared to hydrohalogenation. This means rearrangement is unlikely and therefore the results should be more dependable than those from HX addition.

   (b) The pi-complex intermediate is better established (or at least more likely) for Hg$^{++}$ addition than H$^{+}$ addition, resulting in more definite mechanistic conclusions.

   (c) Since a heteratom (Hg) will not exhibit nuclear magnetic resonance at the same frequency as do protons, the orientation of such additions can be easily determined. Moreover, in the special case of mercury, 17% of all mercury atoms have the ability of spin coupling with neighboring hydrogens, allowing a detailed structural analysis by nmr spectroscopy.
2. **Allenens**

Allenens unlike simple olefins have the unique feature of producing two possible unusual intermediate structures upon electrophilic addition. Either a vinyl carbonium ion (a) or a twisted, non-resonance-stabilized allylic carbonium ion (b) can result as shown below.

![Diagram of Allenens](image)

Both structures a and b are of considerable theoretical interest.

C. **Literature Background**

1. **Oxymercuration(a)**

Oxymercuration of olefins is a well-studied reaction. Addition of mercuric acetate to an olefin in methanol usually leads to a β-methoxyalkylmercuric acetate as shown in Fig. 1. The mechanism for such a reaction probably involves an initial Hg complex, followed by a rate-determining attack of the alcohol. Other mechanisms have been proposed but none

(a) The term "oxymercuration" refers to a reaction with any mercuric salt in the presence of a hydroxylic solvent, producing an alkoxyalkylmercuric or hydroxyalkylmercuric (if water is the solvent) compound.
OXYMERCURATION OF OLEFINS

\[ \text{R} \equiv \text{C} \equiv \text{C} \text{R} + \text{Hg(OAc)}_2 \xrightarrow{\text{CH}_3\text{OH}} \text{R} \equiv \text{C} \equiv \text{C} \text{R} + \text{HgOAc} + \text{HOAc} \]

Fig. 1. Oxymercuration of Olefins
seem to fit all the available data. With few exceptions, however, it is known that Markovnikov's Rule is obeyed for these particular addition reactions.

Once prepared, the $R\_\text{Hg}\_\text{OAc}$ compound can be readily converted into the mercuric chloride, bromide, or iodide derivative by addition of the appropriate potassium or sodium halide in water. While the acetoxy derivatives are usually oils, the halides are fairly stable solids which may be re-crystallized from ethanol-water solutions. The organomercuric iodide can in turn be transformed into an organic iodide by the following reaction:

$$R\text{HgI} + I_2 \xrightarrow{\text{(red)}} RI + \text{HgI}_2$$

The olefin itself can usually be regenerated by addition of dilute HCl to any of the organomercurials.

$$\begin{align*} &\text{HgX} \\ \text{OCH}_3 \end{align*} + \text{HCl} \rightarrow \text{C=CH}_3 + \text{CH}_3\text{OH} + \text{HgXCl}$$

2. **Electrophilic Addition to Allenes**

The products formed from mercuric acetate and allenes were expected to be similar to those obtained by electrophilic addition of hydrogen halides to these 1,2 - dienes.

According to Griesbaum, allene itself adds hydrogen halide in the following manner at ambient temperatures:
The fact that no cyclic compound is formed in the case of HI may be explained by the greater nucleophilicity of the iodide ion. In the case of methoxymercuration, cyclization is not expected because alkylation of another allene molecule to give cyclobutane products is less likely for the intermediate olefin-mercury complex (I) in which it appears there is much less free carbonium ion character.

Oxymercuration of substituted allenes may proceed via the most stable carbonium ion, i.e., according to the Markovnikov Rule. Jacobs and Johnson noted methylallene reacts with HCl in the following fashion:

\[
\begin{align*}
\text{CH}_3\text{CH}=\text{C}=\text{CH}_2 + \text{HCl} & \rightarrow \text{CH}_3\text{CH}==\text{C}-\text{CH}_3 + \text{CH}_3\text{C}=\text{C}==\text{CH}_3 \\
\text{at } -78^\circ \text{C (neat)} & \quad \text{50% (cis and trans)} \quad \text{40%}
\end{align*}
\]

M. Bouis and A. V. Fedorova added HBr to another monosubstituted allene and noted similar results.

\[
\begin{align*}
\text{Pr-CH}=\text{C}=\text{CH}_2 + \text{HBr} & \xrightarrow{\text{Et}_2\text{O}} \text{Pr-CH}=\text{C}-\text{CH}_3 \\
\text{5 days} & \quad \text{Pr-CH}=\text{C}-\text{CH}_3 \quad \text{Br}
\end{align*}
\]
Hennion and Sheehan\(^7\) obtained the same compound with the above 1,2-diene and HCl plus some diadduct similar to the allene product. In conclusion, it would therefore seem in the addition of hydrogen halide to monosubstituted allenes, H\(^+\) always adds to the terminal methylene producing what appears to be an intermediate vinyl carbonium ion.

Kondakov\(^4\) and later Jacobs and Johnson\(^4\) discovered that unsymmetrically di-substituted allenes, on the other hand, give quite different products with HCl.

\[
\begin{align*}
\text{CH}_3\text{C}═\text{C}-\text{CH}_2 & \quad \xrightarrow{\text{HCl, } -78^\circ\text{C}} \quad \text{CH}_3\text{C}═\text{CH}-\text{CH}_2\text{Cl} + \text{CH}_3\text{C}═\text{CH}═\text{CH}_2 \\
\text{CH}_3\text{C}═\text{C}═\text{CH}_2 & \quad 66\% \quad \text{CH}_3\text{C}═\text{CH}═\text{CH}_2 & \quad 33\%
\end{align*}
\]

The second product is believed to have originated from HCl addition to isoprene produced by allylic isomerisation of the starting material. A. V. Fedorova\(^6\) carried out the HBr addition on this compound as follows:

\[
\begin{align*}
\text{CH}_3\text{C}═\text{C}═\text{CH}_2 & \quad + \quad \text{HBr} \quad \xrightarrow{\text{Et}_2\text{O, } 5 \text{ days}} \quad \text{CH}_3\text{C}═\text{CH}═\text{CH}_2\text{Br}
\end{align*}
\]

In these latter reactions the proton adds to the center carbon of the allenic system resulting in an unsymmetrical allylic carbonium ion which goes on to give predominately the thermodynamically more stable product.\(^8\)

Other types of allenes give a mixture of products of unpredictable geometry.\(^9\)
3. NMR Spectra of Organomercurials

The problem of primary concern in this research was to accurately determine the geometry of all the products. Chemically, this would have been a long and arduous task. Fortunately, there are some data in the literature on the nmr spectra of organomercurials and this method of analysis proved to be the quickest as well as the most unambiguous.

Mercury-199 has a nuclear spin of 1/2, and thus can spin couple with hydrogen nuclei on nearby carbon atoms. Since the natural abundance of Hg$^{199}$ is 16.92%, protons neighboring mercury show symmetrical satellite peaks whose combined area approximates 17% of the total area of the central peaks and satellites combined. These satellite peaks have been used in the correlation of structure. Specifically, Moy, Emerson, and Oliver$^{10}$ assigned mercury-proton coupling constants ($J_{\text{Hg}^{199}-\text{H}^1}$) to the different protons in the following systems:

\[
\begin{align*}
\text{RHg} & \quad \text{CH}_3(1.933\delta) & \quad \text{RHg} & \quad \text{H}_2(5.592\delta) & \quad \text{CH}_3 & \quad \text{C} = \text{C} & \quad \text{H}_2(6.932\delta) & \quad \text{RHg} & \quad \text{H}_1(4.807\delta) \\
(1) & & (2) & & (3) & & & & \\
\end{align*}
\]

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<th>Cpd.</th>
<th>$J_{\text{Hg}^{199}-\text{H}^1}$</th>
<th>$J_{\text{Hg}^{199}-\text{H}_2}$</th>
<th>$J_{\text{Hg}^{199}-\text{CH}_3}$</th>
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<td>(1)</td>
<td>134 c.p.s.</td>
<td>244</td>
<td>12</td>
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<tr>
<td>(2)</td>
<td>125</td>
<td>140</td>
<td>5</td>
</tr>
<tr>
<td>(3)</td>
<td>128</td>
<td>256</td>
<td>88</td>
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This data proved useful since most allenes added mercury (like hydrogen) to the center carbon of the allenic system, producing geometry analogous to the above.

Other reported\textsuperscript{11-13} Hg\textsuperscript{199}-H\textsuperscript{1} spin-spin coupling phenomena include the fact that coupling through two sigma bonds (\(\alpha\) - coupling) usually results in a \(J_{\text{Hg}199-\text{H}1}\) value of 100-150 c.p.s. and that through three sigma bonds (\(\beta\) - coupling) = 200-250 c.p.s. for dialkyl mercurials. Hence, it was simple to discern the position of mercury in the product from the spin-coupling through single bonds alone.
II. EXPERIMENTAL

All carbon and hydrogen analyses were done at the Berkeley Analytical Laboratory, Berkeley, California.

Melting points were taken in sealed glass capillaries and not corrected for partial immersion. A silicone oil bath was used as the heat source.

All infrared (IR) spectra were recorded for potassium bromide discs, using a Beckman IR-5 Infrared Spectrometer.

All vapor-phase chromatography (vpc) was performed on Aerograph (Wilkins Instrument and Research Inc., Walnut Creek, California) Models 90-P3, A-700, and A-90P, each employing a thermal conductivity detector. (Several different columns were used, the nature of each to be listed wherever they appear in connection with actual experiments.)

Nuclear magnetic resonance (nmr) spectra were recorded on a Varian Associates Model A-60 Analytical NMR Spectrometer. Probe temperatures for all spectra were between 41 and 43°C. Solutions were generally 25% in carbon tetrachloride to insure easy observation of the Hg^{199} satellite peaks. No attempt at extrapolating chemical shifts to infinite dilution was made since coupling constants were of primary interest in these spectra.

A. oxymercuration of Allenes

1. Preparation of the Allenes

(a) allene was obtained commercially from Matheson Company, Inc. The gas was found to contain less than 1% propyne by vpc and nmr analyses, and was used without further
purification.

(b) Methylallene was obtained commercially (Technical Grade) from Columbia Organic Chemicals Company, Inc. The suppliers specified up to 30% contamination by 1-butyne and 1,3-butadiene. Vpc analysis on a 20' x 3/8" dimethylsulfolane (25% on 60/80 "chromasorb P") preparatory column revealed a total of seven compounds. The last peak of the chromatogram proved to be methylallene and accounted for about 70% of the total peak area. The allene was purified on this column employing a column temperature of 40-50°C. and flow rate of 150 ml./min. The purified methylallene showed no contaminants either on a 20' x 1/8" apiezon L (25% on 60/80 "chromasorb W") or on the dimethylsulfolane column.

(c) 1,1-Dimethylallene was prepared by lithium aluminum hydride (LAH) reduction of 3-chloro-3-methyl-1-butyne.14 Following the authors' procedure, 276g. of 3-methyl-1-butyne-3-ol was converted to 263g. (78%) of 3-chloro-3-methyl-1-butyne. The chloride was then reduced with LAH (66g.) in tetrahydrofuran (800ml.) to 30g. of the 1,1-dimethylallene (17% yield from the chloride; Bailey and Pfeifer, 51% from the carbinol). By vpc analysis the allene was approximately 94% pure and used for oxymercuration without any further purification.

(d) 1,3-Dimethylallene was prepared by the method of Doering and La Flamme,15 the starting material being obtained by the method of Doering and Hoffmann.16 Trans-2-butene (14g., 0.250 moles) and potassium t-butoxide
(25g., 0.223 moles) were stirred in 50ml. of dry hexane at -10-0°C. Bromoform (63g., 0.250 moles) was slowly added and the resultant mixture stirred for one hour. Water was then added and the product extracted with several portions of ether. After rapid removal of the ether the residue was distilled and product collected at 80-83°C. and 50mm. Vpc analysis of this distillate on the 20' apiezon column showed only two compounds; the desired cyclopropane derivative and an appreciable amount of unreacted bromoform which unfortunately distills in the same temperature range as the dibromocyclopropane. Using a 20' x 3/8" silicon SE-30 (20% on 60/80 firebrick) preparatory column, the desired product was separated from bromoform giving 19.0g. (33.2% yield) of analytically pure \textit{trans}-1,1-dibromo-2,3-dimethylcyclopropane.

The cyclopropane (0.083 moles) was then added dropwise to a stirred mixture of 9.6g. (0.40g.-atom) of magnesium in 30 ml. of ether and worked up according to the procedure of Doering and La Flamme.\textsuperscript{15} Distillation through a 10" column packed with metal helices afforded a fraction, b.p. 35-50° which contained about 1.5g. of 1,3-dimethylallene (b.p. 48.5°C.) contaminated by ether and a small amount of 2-pentyne (b.p. 56°C.) as determined by vpc. Further purification by vpc on the 20' silicon preparatory column removed both impurities and gave 1.35g. of product. The yield of this last step (26.2%) compares favorably with Doering and La Flamme's 16% from \textit{cis}-1,1-dibromo-2,3-dimethylcyclopropane.
(e) **Trimethylallene** was also prepared using the Doering-La Flamme-Hoffmann procedure. Thus 2-methyl-2-butene (67.2g., 0.96 moles) was reacted with potassium t-butoxide (108g., 0.96 moles) and bromoform (243g., 0.96 moles) to give 156.6g. (0.645 moles) of 1,1-dibromo-2,2,3-trimethylcyclopropane (b.p. 63-66°/15mm.), representing a yield of 68% (Doering and La Flamme: 15 53%).

This intermediate (18.1g., 0.075 moles) in 10 ml. of dried tetrahydrofuran (THF) was slowly added to 5g. of magnesium turnings (0.20g.-atom) in 25 ml. of dry THF. After hydrolysis and repeated washing to remove solvent, a distillation gave 1.9g. (ca. by vpc) of trimethylallene (b.p. reported: 15 72.5°C.), using isoctane as a chaser. The yield for this second step was 31% (Doering and La Flamme: 15 53%) while overall from olefin was 24%.

(f) **Tetramethylallene** was obtained commercially from Aldrich Chemical Company, Inc. Analyses by vpc and nmr showed no impurities in this reagent.

(g) A synthesis of 1,1-Diphenylallene was attempted following the procedure of Skattebøl. 18 The compound itself probably formed in fairly high yield but decomposed rapidly during the final distillation step.

Using Skattebøl's modification of the Doering and La Flamme dibromocyclopropane synthesis, 18 6.2g. (0.0344 moles) of 1,1-diphenylethene (prepared by Grignard addition of methylmagnesium iodide to benzophenone with subsequent
dehydration) was mixed with 4g. (0.0358 moles) of potassium t-butoxide and 8.7g. (0.0344 moles) of bromoform. The reaction gave 6.45g. of 1,1-dibromo-2,2-diphenylcyclopropane (white crystals, m.p. 154.5-155.2°C.). The yield from olefin (53.2%) compares favorably with Skattebøl's 54% for the same reaction.

All attempts at reaction of this compound with magnesium in ether or THF failed, even upon prolonged refluxing of the mixtures.

Because of the inertness to magnesium under the specified conditions, a Skattebøl synthesis employing n-butyllithium was attempted. Following the author's instructions, 0.1 moles of the alkyllithium in pentane (Foote Mineral Company) was slowly added to an equimolar amount of the cyclopropane derivative in dry ether at -40°C. After the usual workup, a final distillation was tried at 0.02mm. pressure, using a 6" vigreaux head. A clear liquid of b.p. 85°C. (0.02mm.) was observed condensing in the column but due to column holdup could not be isolated and unfortunately quickly polymerized in the distillation flask. (The author claims distilling conditions of 80°C. and 0.01mm. for 1,1-diphenyllallene, but makes no mention of the instability of this compound.)

It was recently noted that Jones, et. al. have developed a chromatographic method of isolating this thermally sensitive allene. Future preparations of the compound should include this method of purification.
2. **Reaction of the Allenes with Mercuric Acetate in Methanol**

   (a) **Reaction of Allene**

   Allene was oxymercurated by three different methods, thus encouraging the formation of more than one product.

   (i) Allene was bubbled through a solution of 1.6g. (0.005 moles) of mercuric acetate in 25 ml. of methanol at 27° until a drop of the solution failed to give a positive test for mercuric ion (formation of yellow mercuric oxide on addition of a drop of solution to a few mg. of sodium carbonate on a watchglass.)

   (ii) In the closed system of Fig. 2 allene was absorbed by a stirred solution of 1.6g. (0.005 moles) of mercuric acetate in methanol (25ml.) at 27° C. until the water manometer ceased to record any more uptake of gas. The amount absorbed (45ml., 0.0018 moles) may be subject to some error due to the necessary preliminary "flushing" of the system. However, it remains obvious that less than half an equimolar amount of allene is absorbed in such an experiment.

   (iii) Allene was condensed at -78°C. and weighed. A double molar amount of mercuric acetate in methanol was cooled to 0°C. and slowly added to the allene. The entire mixture, under constant stirring, was allowed to attain room temperature.
Fig. 2. Apparatus for Allene Absorption
In all three methods a voluminous white precipitate separated from the solution. After filtration and evaporation of the methanol, a substantial second crop could be isolated. The solid (compound I, Fig. 16) after repeated washing with methanol, melted 176.6-177.5°C. (decomp.) and was insoluble in all solvents tried except water. The yield of I (1,3-bis-(acetoxymercuri)-2-propanone) was 95% based on mercuric acetate.

In an attempted isolation of the reaction intermediate, a carbon tetrachloride solution of the immediate product of oxymercuration was quickly filtered into an nmr tube and its spectrum immediately recorded. A strong singlet in the methoxy region rapidly disappeared while methanol peaks suddenly appeared and grew at an equally fast rate. After another filtration of the mixture and reinvestigation by nmr, the same phenomenon was noted accompanied again by precipitation of I.

The infrared spectrum of I (Fig. 3) shows a strong carbonyl stretching bond at 1616 cm\(^{-1}\) as well as the acetate function at 1570 and 1410 cm\(^{-1}\). (a)

The nmr spectrum in deuterium oxide (Fig. 4) shows two singlets at 2.08 and 3.03 \(\delta\) with an area ratio of 6 to 2.8 respectively (Table 1). About the low field peak are two sets of mercury satellite peaks with J=338 and 20 c.p.s. In support of the structure for I, an nmr spectrum of

(a) The IR spectrum of mercuric acetate has only these two intense peaks.
Fig. 3. Infrared Spectrum of 1,3-Bis-(acetoxymercuri)-2-propanone
Fig. 4. NMR Spectrum of 1,3-Bis-(acetoxymercuri)-2-propanone (in D₂O)
bromomercuriaceton(a) in carbon tetrachloride shows satellites about the CH₂ and CH₃ singlets with JHg-H values of 296.5 and 12.0 c.p.s. respectively (Table 1).

The infrared spectrum of this monomercuri compound shows carbonyl absorption at 1633 cm⁻¹.

Anal. Calcd. for C₁₀H₁₀O₂Hg₂: C, 14.61; H, 1.75.
Found: C, 14.63, 14.63; H, 1.78, 1.90.

Compound I was converted to the chloromercuri, bromomercuri, and iodomercuri derivatives by shaking an aqueous solution of I with the appropriate sodium or potassium halide. These derivatives are all solids and insoluble in all solvents tested including water.

An IR spectrum of the bromomercuri derivative (Fig. 5) illustrates the loss of acetate function. The remaining sharp carbonyl peak still appears at 1616 cm⁻¹.

As a final structural proof for cpd. I, 0.1459g. (0.00205 moles) of the iodomercuri derivative was stirred with 0.1120g. (0.00440g.-atom) of iodine in 25ml. of benzene for two hours. The clear solution was then decanted from the solid mercuric iodide and combined with 5ml. of benzene used to wash the red inorganic salt. After careful removal of the solvent under vacuum, solid 1,3-diiodoacetone (m.p. 65-66°C. after sublimation; lit.²⁰, 65-66°C.) was isolated in a yield of 0.0560g. (88%). Authentic 1,3-diiodoacetone was prepared by reaction of 1,3-dichloroacetone

(a) The sample was kindly supplied by L. L. Schaleger, Department of Chemistry, University of Hawaii.
Fig. 5. Infrared Spectrum of 1,3-Bis-(bromomercuri)-2-propanone
with potassium iodide in water. The two samples gave identical IR spectra (a) and melting points, and a mixed m.p. was not depressed.

(b) Reaction of Substituted Allenes

Besides allene itself, the five possible methyl-substituted allenes were also oxymercurated. The general procedure employed for these reactions was to stir equimolar amounts of mercuric acetate and the allene in methanol at 27°C. After five minutes a half-molar amount of sodium carbonate was added, stirred, then filtered. Methanol was evaporated from the filtrate under vacuum and the resultant oil extracted from the inorganic residue with benzene. The benzene was then also evaporated and the oily acetate either analyzed by nmr or added directly to an aqueous solution of a potassium or sodium halide. The water-insoluble β-methoxyalkylmercuric halides, which were usually solids, could be easily recrystallized from ethanol-water mixtures and showed larger J_Hg-199_H values compared to the acetates.

All the adducts were fairly light-sensitive and therefore were stored in foil-wrapped vials in the refrigerator.

(1) Methylallene (0.14g., 0.0025 moles) was cooled to -76°C. and added to mercuric acetate (0.80g., (0.0025 moles) in 25 ml. of methanol at 27°C. After five

(a) As expected, on removal of the two mercury atoms, the carbonyl stretching peak was displaced to a more normal wave number (1720 cm.-1).
minutes the clear solution began to precipitate a white solid. The mixture was stirred magnetically for 24 hours and then filtered. The clear filtrate was worked up in the usual manner (see above) and gave 0.52g. (0.0015 moles) of 2-acetoxymercuri-3-methoxy-1-butene (compound IIA - see Fig. 17, page 50), an oil, in 60% yield.

An IR spectrum of the chloromercuri derivative (m.p. 122-123°C.) of IIA appears in Fig. 6.

The nmr spectrum of the chloromercuri derivative of IIA in benzene (Fig. 7) shows the following peaks:

<table>
<thead>
<tr>
<th>Group</th>
<th>Peak Type</th>
<th>Area</th>
<th>Chem. Shift (δ)</th>
<th>J_{Hg199-H1}(c.p.s.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>doublet</td>
<td>3</td>
<td>0.90</td>
<td>≤2</td>
</tr>
<tr>
<td>OCH₃</td>
<td>singlet</td>
<td>3</td>
<td>2.89</td>
<td>0</td>
</tr>
<tr>
<td>H</td>
<td>quartet</td>
<td>1(-17%)</td>
<td>3.40</td>
<td>not measured</td>
</tr>
<tr>
<td>cis H</td>
<td>singlet</td>
<td>1(-17%)</td>
<td>4.52</td>
<td>290</td>
</tr>
<tr>
<td>trans H</td>
<td>singlet</td>
<td>1(-17%)</td>
<td>5.21</td>
<td>565</td>
</tr>
</tbody>
</table>

Compound IIA and its halide derivatives are soluble in most organic solvents but insoluble in H₂O.

The white solid which had separated from the methanol solution after 24 hours of stirring was washed with fresh methanol and dried. IR and elemental analysis proved it to be 1,3-bis-(acetoxymercuri)-2-butanone (cpd. IIB, 35% from mercuric acetate).

The IR spectrum of the mercuric chloride derivative of this compound (Fig. 8) is quite similar to that of compound I. The strong carbonyl stretching peak again appears exactly at 1616 cm⁻¹.
Fig. 6. Infrared Spectrum of 2-Chloromercuri-3-methoxy-1-butene
Fig. 7. NMR Spectrum of 2-Chloromercuri-3-methoxy-1-butene (in benzene)
Fig. 8. Infrared Spectrum of 1,3-Bis-(chloromercuri)-2-butanone
Compound IIb (like I) is soluble only in water, while its halide derivatives appear to be insoluble in all the usual solvents.

In another reaction an equimolar amount of water was added to a stirred solution of the allene and mercuric acetate immediately after initial mixing of the reagents. In this case a 35% yield of IIb precipitated after only a few minutes.

(2) 1,1-Dimethylallene (0.2085g., 0.00306 moles) and mercuric acetate (0.7877g., 0.00247 moles) were reacted to give 0.7480g. (0.00208 moles) of 2-acetoxymercuri-3-methyl-3-methoxy-1-butene (compound III, Fig. 18) representing an 84% yield of the oil, based on mercuric acetate.

The IR spectrum of the bromomercuri derivative of III (m.p. 90-92°C.) appears in Fig. 9.

The nmr spectrum of the chloromercuri derivative of III (Fig. 10) shows the following peaks:

<table>
<thead>
<tr>
<th>Group</th>
<th>Peak Type</th>
<th>Area</th>
<th>Chem. Shift (δ)</th>
<th>J_Hg199-H1(c.p.s.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>singlet</td>
<td>6(-17%)</td>
<td>1.32</td>
<td></td>
</tr>
<tr>
<td>OCH₃</td>
<td>singlet</td>
<td>3</td>
<td>3.22</td>
<td>-</td>
</tr>
<tr>
<td>cis H</td>
<td>singlet</td>
<td>1(-17%)</td>
<td>5.35</td>
<td>315</td>
</tr>
<tr>
<td>trans H</td>
<td>singlet</td>
<td>1(-17%)</td>
<td>5.73</td>
<td>620</td>
</tr>
</tbody>
</table>

Anal. Calcd. for C₆H₁₁OBr₂Hg: C, 18.98; H, 2.92.

Found: C, 19.19, 19.33; H, 2.84, 3.00.
Fig. 9. Infrared Spectrum of 2-Bromomercu ri-3-methyl-3-methoxy-1-butene
Fig. 10. VARIAN A-60 N. M. R. SPECTRUM OF 3-METHYL-3-METHOXO-2-CHLOROMERCURIC IODIDE. 25% IN CC14. PROBE TEMP = 41°C.
An nmr spectrum (Fig. 11) was taken of the product formed by the reaction of the iodomercuri derivative of III and iodine. The mercury satellites had disappeared, accompanying a general downfield shift of all peaks. The vinyl hydrogen were also spin-coupled with one another (J=2 c.p.s.).

(3) 1,3-Dimethylallene (0.17g, 0.0025 moles) was added to mercuric acetate (0.80g, 0.0025 moles) in 25 ml of methanol. The reaction yielded 0.832g (0.00232 moles, 93%) of two monoadducts, both isomers of 3-acetoxymercuri-4-methoxy-2-pentene (cpd. IV, Fig. 19).

The major product (IVA) of this reaction is the compound in which mercury lies cis to the olefinic methyl, forming in about a 4:1 preference over IVB in which the methyl group is trans to mercury.

An nmr spectrum of nearly pure chloromercuri derivative of IVA appears in Fig. 12. The impurity (IVB derivative) shows as two weak doublets at 1.18  and 1.77  and one weak singlet at 3.24 . This spectrum was obtained after four recrystallizations of the compound from hexane.

<table>
<thead>
<tr>
<th>Group</th>
<th>Peak Type</th>
<th>Area</th>
<th>Chem. Shift (δ)</th>
<th>J_{Hg^{199}}-{H}^{1}(c.p.s.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>doublet</td>
<td>3</td>
<td>1.20</td>
<td>≤2</td>
</tr>
<tr>
<td>cis CH₃</td>
<td>doublet</td>
<td>3(-17%)</td>
<td>1.91</td>
<td>38</td>
</tr>
<tr>
<td>OCH₃</td>
<td>singlet</td>
<td>3</td>
<td>3.22</td>
<td>--</td>
</tr>
<tr>
<td>H</td>
<td>quartet</td>
<td>1(-17%)</td>
<td>3.88</td>
<td>not found</td>
</tr>
<tr>
<td>trans H</td>
<td>quartet</td>
<td>1(-17%)</td>
<td>6.29</td>
<td>523</td>
</tr>
</tbody>
</table>
Fig. 11. NMR Spectrum of 2-Iodo-3-methyl-3-methoxy-1-butene
Fig. 12. NMR Spectrum of 3-Chloromercuri-4-methoxy-2-pentene (mercury cis to methyl)
Figure 13 is the nmr spectrum of the residue from the hexane filtrates used in the previous recrystallizations. An enrichment of the chloromercuri of IVB is evident.

The following peaks correspond to the chloromercuri of IVB:

<table>
<thead>
<tr>
<th>Group</th>
<th>Peak Type</th>
<th>Area</th>
<th>Chem. Shift (δ)</th>
<th>J_{Hg^{199}-H^1}(c.p.s.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>doublet</td>
<td>3</td>
<td>1.18</td>
<td>2</td>
</tr>
<tr>
<td>trans CH₃</td>
<td>doublet</td>
<td>3(-17%)</td>
<td>1.77</td>
<td>35</td>
</tr>
<tr>
<td>OCH₃</td>
<td>singlet</td>
<td>3</td>
<td>3.24</td>
<td>--</td>
</tr>
<tr>
<td>H</td>
<td>quartet</td>
<td>1(-17%)</td>
<td>4.33</td>
<td>not found</td>
</tr>
<tr>
<td>cis H</td>
<td>quartet</td>
<td>1(-17%)</td>
<td>5.68</td>
<td>318</td>
</tr>
</tbody>
</table>

As observed in Fig. 13, the long range allylic H¹-H¹ coupling in the case of IVA is about 1.0 c.p.s., whereas in IVB Jallylic=1.5 c.p.s.

(4) Trimethylallene (0.205g., 0.0025 moles) and mercuric acetate (0.80g., 0.0025 moles) in 25 ml. of methanol yielded 0.84g. (0.00225 moles) of a mixture of two monoadducts.

The major product was 3-acetoxymercuri-4-methyl-4-methoxy-2-pentene (cpd. VA, Fig. 19, the isomer with mercury cis to the olefinic methyl group), which was formed in a 4:1 preference over 2-methyl-3-acetoxymercuri-4-methoxy-2-pentene (cpd. VB, Fig. 20).

Neither compound was separated, but several nmr spectra were taken of the mixtures in which the percentage of minor product had been progressively increased by repetitive crystalization from ethanol-water solutions. In this
Fig. 13. NMR Spectrum of 3-Chloromercuri-4-methoxy-2-pentene (both geometrical isomers)
The NMR spectrum of the iodomercuri mixture (Fig. 14) could be resolved into the following two sets of peaks:

<table>
<thead>
<tr>
<th>Cpd. VA</th>
<th>Group</th>
<th>Peak Type</th>
<th>Area (%)</th>
<th>Chem. Shift (δ)</th>
<th>J_{Hg^{199}-H^1} (c.p.s.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>singlet</td>
<td>6(-17%)</td>
<td>1.30</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>cis CH₃</td>
<td>doublet</td>
<td>3(-17%)</td>
<td>1.95</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>OCH₃</td>
<td>singlet</td>
<td>3</td>
<td>3.18</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>trans H</td>
<td>quartet</td>
<td>1(-17%)</td>
<td>6.59</td>
<td>566</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cpd. VB</th>
<th>Group</th>
<th>Peak Type</th>
<th>Area (%)</th>
<th>Chem. Shift (δ)</th>
<th>J_{Hg^{199}-H^1} (c.p.s.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₃</td>
<td>doublet</td>
<td>3(-17%)</td>
<td>1.20</td>
<td>not found</td>
<td></td>
</tr>
<tr>
<td>trans CH₃</td>
<td>singlet</td>
<td>3(-17%)</td>
<td>1.80</td>
<td>not found</td>
<td></td>
</tr>
<tr>
<td>cis CH₃</td>
<td>singlet</td>
<td>3(-17%)</td>
<td>2.00</td>
<td>not found</td>
<td></td>
</tr>
<tr>
<td>OCH₃</td>
<td>singlet</td>
<td>3</td>
<td>3.30</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>H</td>
<td>quartet</td>
<td>1(-17%)</td>
<td>4.57</td>
<td>not found</td>
<td></td>
</tr>
</tbody>
</table>

(5) Tetramethylallene (0.3198g., 0.0033 moles) and mercuric acetate (0.8143g., 0.0026 moles) reacted in the usual manner to yield 0.8870g. (0.0023 moles) of 2,4-dimethyl-3-acetoxymercuri-4-methoxy-2-pentene (cpd. VI, Fig. 21), representing a 90% yield from mercuric acetate.

The NMR spectrum of the chloromercuri derivative of VI (Fig. 15) is described by the following peaks.

(a) These values were taken from the spectrum of the chloromercuri derivative.
Fig. 14. NMR Spectrum of 3-Iodo-4-methyl-4-methoxy-2-pentene (iodine cis to methyl)(*) and 2-Methyl-3-iodo-4-methoxy-2-pentene (o)
Fig. 15. NMR Spectrum of 2,4-Dimethyl-3-chloromercuiri-4-methoxy-2-pentene
<table>
<thead>
<tr>
<th>Group</th>
<th>Peak Type</th>
<th>Area</th>
<th>Chem. Shift (δ)</th>
<th>$J_{^{199}Hg-^1H}$ (c.p.s.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH$_3$</td>
<td>singlet</td>
<td>6(-17%)</td>
<td>1.37</td>
<td>9</td>
</tr>
<tr>
<td>trans CH$_3$</td>
<td>singlet</td>
<td>3(-17%)</td>
<td>1.90</td>
<td>24</td>
</tr>
<tr>
<td>cis CH$_3$</td>
<td>singlet</td>
<td>3(-17%)</td>
<td>2.00</td>
<td>38</td>
</tr>
<tr>
<td>OCH$_3$</td>
<td>singlet</td>
<td>3</td>
<td>3.22</td>
<td>--</td>
</tr>
</tbody>
</table>

Although VI is an oil, the three halide derivatives are solids with the following melting points:

<table>
<thead>
<tr>
<th>Derivative:</th>
<th>m.p.:</th>
</tr>
</thead>
<tbody>
<tr>
<td>-HgCl</td>
<td>76.0-77.0°C</td>
</tr>
<tr>
<td>-HgBr</td>
<td>94.0-95.0°C</td>
</tr>
<tr>
<td>-HgI</td>
<td>99.5-100.5°C</td>
</tr>
</tbody>
</table>

Anal. Calcd. for C$_8$H$_{15}$OBrHg: C, 23.57; H, 3.71.
Found: C, 23.55, 23.68; H, 3.58, 3.72.

3. **Solvent Studies**

1,1-Dimethylallene was oxymercurated in isopropyl and in t-butyl alcohol. The products were worked up in the usual manner and then converted to the iodomercuri and simple iodo derivatives by reactions described above. Nmr spectra of all these derivatives were taken and used to support the structures of the three products of each reaction (see table 2).

The side reaction with water was confirmed when an equimolar amount of H$_2$O was added to the mercuric acetate-alcohol solution before the addition of the allene. In the case of isopropyl alcohol as solvent, the percentage of β-hydroxyalkylmercuric product rose from 28 to 53% after an addition of water.
4. **Allene vs. Simple Olefin Rate Studies**

Solutions (0.240 M in methanol) were prepared of tetramethylethylene and tetramethylallene. Equal volumes of the two solutions were placed in separate nmr tubes and mixed with an identical volume of methanol. The methyl singlet in each case was recorded and integrated, this value being used as the "zero time" concentration for the two separate oxymercuration reactions.

The tubes were emptied, dried, and again filled with equal volumes of the two solutions. An equal volume of 0.240M solutions of mercuric acetate in methanol was added to each, the solutions quickly mixed and the resulting nmr spectra taken with identical probe temperatures (43°C) and spinning rates. The methyl peak of each of the organic reactants was repeatedly integrated over a period of one hour.

- $\frac{1}{2}$ life ($\supset$) = 20 min.
- $\frac{1}{2}$ life ($\succsim$) < 5 sec. (a)

Another run was made after diluting all solutions by a factor of 5.

- $\frac{1}{2}$ life ($\supset$) = 45 min.
- $\frac{1}{2}$ life ($\succsim$) < 5 sec. (a)

(a) The reaction with tetramethylallene could not be slowed to an observable rate by the dilution technique and still be followed using nmr spectroscopy. Moreover, lowering the temperature of the reaction medium was not practical due to the decreased solubility of mercuric acetate in methanol below room temperature.
Using the latter data:

@ 43°C., \(1/2\) life \((\text{gem})\) = 40(60) = \(2400\) sec.

@ 20°C., \((a)\) \(1/2\) life \((\text{gem})\) < 5 sec.

\[2400/5 \times 4(\text{temp. factor}) = 2000/1\]

5. The Reversibility of Allene Oxymercuration

The chloromercuri derivative of compound VI (adduct of tetramethylallene) (0.8g.) was dissolved in 0.5 ml. of methanol and the nmr spectrum recorded. Next, one drop of perchloric acid was added to the nmr tube with shaking. The new spectrum showed loss of the \text{gem}-dimethyl singlet but also appearance of many unassignable peaks. A bright orange precipitate also formed upon addition of the acid.

A heterogeneous reaction was then tried using benzene and dilute hydrochloric acid. Eight tenths gram of the aforementioned compound was dissolved in 0.5 ml. of benzene and placed in the nmr tube. Hydrochloric acid (1 drop 6 M) was added, which quickly settled to the bottom of the tube. The resultant nmr spectrum showed a rapid disappearance of adduct and formation of tetramethylallene with no agitation of the system other than the spinning motion in the probe. After five minutes no other peaks except the methyl singlet of the allene could be detected.

The benzene solution of tetramethylallene was then separated, washed with a dilute sodium carbonate solution, dried, and poured into methanol. An equimolar amount of

\((a)\) Solution was not in probe long enough to warm to 43°C.
mercuric acetate was added and, following the usual work-up, a product identical in all respects to VI was isolated.

B. NMR Investigation of Long-Range $^{199}\text{Hg}^{-1}\text{H}^1$ Spin-Spin Coupling

1. Preparation of Pertinent Olefins

(a) **Propylene, cis-2-butene, and trans-2-butene** were all obtained commercially (C.P. grade, 99.0% min.) from the Matheson Company, Inc. All were analyzed by vpc and nmr and found to be quite pure.

(b) **Isobutylene** was prepared by heating a solution of 0.5g. p-toluenesulfonic acid in t-butanol (50 ml.) under reflux. The gaseous olefin (b.p. -6°C.) was passed through a U-tube filled with calcium chloride before use.

(c) **2-Methyl-2-butene** was prepared by the method of L. F. Fieser. Sixty grams (0.68 moles) of 5-amyl alcohol yielded 37.9g. (0.54 moles) of the olefin (b.p. 38-39°C.) when distilled from a solution of 36 ml. of conc. sulfuric acid in 70 ml. of water. Vpc analysis showed less than 1% contamination by 2-methyl-1-butene (b.p. 31°C.).

(d) **Tetramethylethylene** was isolated as one of the dehydration products of pinacolyl alcohol. Pinacolone (62g., 0.62 mole) was reduced to pinacolyl alcohol (33.1g., 0.324 mole, 52.5%) by reaction with LAH. The alcohol was then distilled into a 2' x 1" column of 4-8 mesh alumina heated to 350°C. The olefin mixture afforded 10.3g. (0.122 mole, 37.6%) of tetramethylethylene (b.p. 73°C.) when purified by vpc (20' x 3/8" silicon column).
(e) **2,3-Dimethyl-1-butene** was isolated as another product of the dehydration of pinacolyl alcohol above. Preparative vpc (same column as above) yielded 5.1g. (0.006 mole, 18.5%) of the terminal olefin (b.p. 56°C).

(f) **t-Butylethylene** was isolated as the third product of the dehydration above. Vpc gave 3.0g. (0.036 mole, 11.1%) of this olefin (b.p. 41.2°C).

(g) **2,3,3-Trimethyl-1-butene** was obtained commercially ("puriss. grade") from Aldrich Chemical Company, Inc. Vpc and nmr analysis showed no other compounds to be present.

(h) **2-Methyl-1-butene** was isolated as the minor product in the sulfuric acid-catalyzed dehydration of t-amyl alcohol (see above). The distillation of olefin mixture from this reaction was stopped at 35°C. for this product. The distillate analyzed (vpc) for about an equal amount of both olefins. 2-Methyl-1-butene (b.p. 31°C.) was separated from its higher boiling partner on the silicon preparative column.

(i) **Methallyl chloride** (2-methyl-3-chloropropene) was obtained commercially (tech. grade) from the Shell Chemical Corporation. The reagent, only about 50% methallyl chloride, was purified by fractional distillation (b.p. 71.5-72.5°C).

(j) **Methallyl bromide** (b.p. 92-94°C.) was prepared in 90% yield from methallyl chloride by refluxing the latter with an excess of aqueous potassium bromide.
(k) Methallylbenzene, p-methallylanisole, methallylmesitylene, and 2,4,4-trimethyl-1-pentene were graciously donated by R. Sato, (a) J. Carter, (b) and P. Yano. (b) The compounds were all prepared by Grignard coupling reactions of methallyl chloride with the appropriate alkyl magnesium halides.

(l) N,N-Dimethylmethallylamine was donated by R. Sato who isolated it from the reaction of methallyl chloride and dimethylamine.

(m) 1-Methylcyclohexene was prepared by zinc debromination of 1-methyl-1,2-dibromocyclohexane, which was the major product from photobromination of methylcyclohexane.

In the first step, 50g. (0.51 mole) of methylcyclohexane (Eastman Kodak Co., reagent grade) and 39g. (0.244 mole) of bromine were irradiated for three hours with a G.E. sunlamp (375 watts) at a distance of 20 cm. The mixture was stirred magnetically and cooled by a running-water bath. Distillation yielded 12.30g. of 1-methyl-1,2-dibromocyclohexane (b.p. 113-115°C./25mm; 40% yield based on bromine).

Seven and eight tents grams (0.03 mole) of the dibromo compound was added a slurry of zinc dust (5g., 0.083 g-atom), stirred magnetically in 20 ml. of 95% ethanol. After a 0.5 hour reflux, the mixture was decanted into aqueous

(a) N.S.F. Undergraduate Research Participant in Chemistry
(b) N.S.F. Secondary Science Trainee
acid, separated and the crude olefin, washed with H₂O and
dried over anhydrous K₂CO₃. Analysis by vpc and nmr showed
about 96% purity (2.33g., 80%).

(n) 1,2-Dimethylcyclohexene was prepared by dehydra-
tion of 1,2-dimethylcyclohexanol prepared from methyl mag-
nesium bromide and 2-methycyclohexanone (Eastman Kodak Co.).
The starting ketone was analyzed by vpc and nmr, revealing
that it contained about 25% of 2-methycyclohexanol. This
mixture was oxidized with chromic acid using the technique
of H. C. Brown²⁴ to give a product which was no longer
contaminated by the alcohol.

Methylmagnesium bromide (0.5 mole, supplied by
Arapahoe Chemicals, Inc. as a 3M solution in ether) was
added to the ketone (56g., 0.5 mole) and worked up in the
normal fashion using a saturated ammonium chloride solution
for hydrolysis. After evaporating most of the ether from
the dried solution, a few crystals of iodine were added²⁵
and the dehydration product distilled, the fraction of b.p.
120-140°C. being collected. Total yield of all isomeric
olefins was 90%, and the product distribution (ca. by vpc)
was the same as that obtained by Hammond.²⁵ 1,2-Dimethyl-
cyclohexene (b.p. reported²⁵ 136.2°C.) was separated in 60%
yield on the 20' x 3/8" silicon preparatory column from
2,3-dimethylcyclohexene (b.p. reported²⁵ 130.5°C., 30% yield)
and 1-methyl-2-methylenecyclohexane (b.p. 124.8°C., trace).
(o) **1,2-Dimethylcyclobutene** was synthesized photochemically following the method of Crowley.\(^2\) 2,3-Dimethyl-1,3-butadiene (8.0 g., 0.0975 mole) in 320 ml. of dry ether was irradiated 47 hours with a 550 watt type 673A Hanovia lamp in a water-cooled Vycor immersion well. The vessel was also water-cooled externally. The ether was then fractionally distilled through a 10" x 1/2" column packed with metal halices and the product collected at 68-69\(^\circ\)C. (b.p. reported\(^2\) 61\(^\circ\)C or\(^2\) 68\(^\circ\)C.). Analysis by vpc and nmr showed no contamination of the cyclic olefin by the starting diene (b.p. 69\(^\circ\)C.). The yield was 4.8 g. (61%).

2. **Oxymercuration of the Olefins**

The liquid olefins of the preceding list were oxymercurated in a manner similar to that described for the substituted allenes described previously.

Mercuric acetate was added to the gaseous olefins by bubbling the latter through methanolic solutions of mercuric acetate (usually 0.8 g. in 25 ml. of methanol) until the test for free mercuric ion with sodium carbonate proved negative.

After the usual work-up of all the products, the acetoxy derivative was analyzed by nmr spectroscopy and then divided into two portions, the first of which was used to prepare the chloromercuric derivative by the standard procedure (page 19). This derivative constantly gave larger long-range \(J_{\text{Hg}199-\text{H}1}\) coupling values than the original adduct,
and was therefore useful in cases where coupling was very small.

The second portion of acetoxy compound was used to prepare the iodomercuri derivative, the nmr spectrum of which showed approximately the same chemical shifts for all protons but with an extreme broadening of all the mercury satellite peaks. The comparison of this spectrum with that of the original acetoxymercuri or chloromercuri derivatives permitted positive identification of the Hg$^{199}$ satellites in the latter spectra.

Finally, by replacement of the iodomercuri group with iodine (see page 17), a large chemical shift in the nmr spectrum was noted for most protons of the compounds investigated. This final derivative usually cleared up any remaining structural uncertainty caused by overlapping of peaks, etc. The nmr spectrum of the iodides also confirmed the identity of the originally mercury-coupled protons, since these peaks now regained the 17% area which they had lost by Hg$^{199}$-H$^1$ spin coupling.
III. RESULTS

A. Oxymercuration of Allenes

1. Products

(a) Allene

The addition of a mercuric acetate/methanol solution to allene rapidly precipitated a single compound in 95% yield (Fig. 16). Reverse and low temperature additions did not seem to produce any side products.

The structure of cpd. I, 1,3-bis-(acetoxymercuri)-2-propanone, was determined by IR and nmr spectra, elemental analysis, and chemical degradation to 1,3-diiodoacetone. A mixed melting point of this diiodo compound with an authentic sample was not depressed.

The nmr spectrum of I, as with those of the other oxymercuration products, proved to be the most powerful method of structural determination. The existence of two separate sets of satellites(a) for the equivalent methylene groups proves not only that these protons are coupled to two different mercury-199 atoms, but also the exact position of each mercury atom. A comparison of the coupling constants \( J_{Hg^{199}-H1} \) with those of known brommercuriacetone (Table 1) amply confirms the structure of I.

A later investigation\(^2\) of the long-range coupling \( J_Y \), Table 1) found in I, showed that mercury-199 quite

---

(a) These satellites were found when integration data (Table 1) indicated a greater loss of methylene area than coupling with one mercury atom would predict.
OXYMERCURATION OF ALLENE

\[
\text{CH}_2=\text{C}==\text{CH}_2 + \text{Hg} (\text{OAc})_2 \xrightarrow{\text{CH}_3\text{OH}} \text{CH}_2\text{C}==\text{C}==\text{CH}_2
\]

\[
\text{AcOHg} \quad \text{OCH}_3 \quad \text{HgOAc}
\]

\[
\text{CH}_2==\text{C}==\text{CH}_2 \rightarrow \text{CH}_2\text{C}==\text{C}==\text{CH}_2
\]

95%

\[
\text{AcOHg} \quad \text{HgOAc}
\]

Fig. 16.
**N.M.R. DATA**

\[\text{AcOHg—CH}_2—\text{C—CH}_2—\text{HgOAc}\]

*in D}_2\text{O}*

- \(J \propto \text{Hg}^{199} \text{H'} = 338 \text{ cps}\)
- \(J \gamma \text{Hg}^{199} \text{H'} = 20 \text{ cps}\)

\[
\frac{\text{AREA (OAc)}}{\text{AREA (CH}_2\text{)}} = \frac{6.0}{2.8}
\]

\[
\begin{bmatrix}
0.83(0.83) = 0.69 \\
0.69(4.00) = 2.76
\end{bmatrix}
\]

\[\text{Br Hg—CH}_2—\text{C—CH}_3\]

*in CCl}_4*

- \(J \propto \text{Hg}^{199} \text{H'} = 297 \text{ cps}\)
- \(J \gamma \text{Hg}^{199} \text{H'} = 12 \text{ cps}\)

\[
\frac{\text{AREA (CH}_3\text{)}}{\text{AREA (CH}_2\text{)}} = \frac{3.0}{2.0}
\]

Table 1. NMR Constants of 1,3-Bis-(acetoxy-mercuri)-2-propanone and 1-Bromomercuri-2-propanone
often interacts with protons four sigma bonds distant to produce J constants of 6 to 48 c.p.s., depending on the molecule involved. Thus, in Compound I, the smaller of the J values (20 c.p.s.) proves one mercury atom must be at the opposite end of the acetone molecule relative to a given methylene group. The other coupling constant (333 c.p.s.), although rather large for alpha Hg-H coupling,11,12,13 requires that the second mercury atom be directly attached to the same methylene carbon.

Addition of an equimolar amount of water during the reaction quickly completed the precipitation of I, supporting the assumption that the ketone is formed via rapid hydrolysis of the initially-formed dimethyl ketal (Fig. 15) by atmospheric moisture. Attempts at isolating the ketal intermediate failed. Its temporary existence, however, was at least verified by nmr observations (see page 16).

(b) Methylallene

Oxymercurcation of methylallene yielded two compounds (Fig. 17).

Compound IIA, 2-acetoxymercuri-3-butene, was isolated in 60% yield. The structure of this compound was conclusively proven when the measured mercury 199-proton spin-spin coupling constants were compared with those in the literature(a)(Page 7).

(a) The size of the coupling constants for the R2Hg compounds must be multiplied by a factor = 2.4 to compare with those of RHgX compounds (see Wells and Kitching, ref. 11). However, the relative (alpha vs. beta) values are constant.
OXYMERCURICATION OF METHYLALLYLENE

\[
\text{CH}_3\text{C}═\text{C}═\text{C}═\text{CH} \quad \text{Hg}(\text{OAc})_2 \quad \text{CH}_3\text{OH}
\]

\[
\text{HgOAc} \quad \text{CH}_3\text{C}═\text{C}═\text{C}═\text{CH} \quad \text{HgOAc}
\]

\[
\text{CH}_3\text{C}═\text{C}═\text{C}═\text{CH} \quad \text{H}\quad \text{AcO} \quad \text{HgOAc}
\]

\[
\begin{align*}
\text{H} & \quad \text{OCH}_3 \\
\text{CH}_3 & \quad \text{H} \\
60\% &
\end{align*}
\]

\[
\begin{align*}
\text{J}_\alpha \text{Hg}^{199} \text{CH}_3 & \leq 2 \text{ cps} \\
\text{J}_\beta \text{Hg}^{199} \text{cis H} & = 290 \text{ cps} \\
\text{J}_\beta \text{Hg}^{199} \text{trans H} & = 585 \text{ cps}
\end{align*}
\]

Fig. 17.
Compound IIB, 1,3-bis-(acetoxymercuri)-2-butanone, was isolated in 35% yield. The probable ketal precursor of this ketone was apparently more stable than that of I, and could be easily analyzed by nmr before much solid had precipitated from the solution. As in the case of unsubstituted allene addition, the full yield of IIB could be realized quickly if an equimolar amount of H₂O was added immediately after mixing the two reagents in methanol. Addition of water did not change the ratio of IIA to IIB.

The carbonyl absorption at 1616 cm⁻¹ (identical to that of the allene adduct) and elemental analysis are also supporting evidence for the proposed structure of IIB.

(c) 1,1-Dimethylallene

Oxymercuration of 1,1-dimethylallene produced only one compound (Fig. 18) in 84% yield. The structure of compound III, (a) 2-acetoxymercuri-3-methoxy-3-methyl-1-butene, was proven conclusively, again by nmr coupling constants. By comparing the values of Moy, Emerson, and Oliver (page 7) with those observed for compound III, no doubt is left as to the position of mercury with respect to the two vinyl hydrogens, which are themselves identified by the chemical shift data.

(a) This compound like all the other monoadducts in the allene series, would not add another mole of mercuric acetate. Equimolar amounts of III and mercuric acetate yielded only starting material after stirring in methanol for 24 hours.
OXYMERCURATION OF 1,1-DIMETHYLALLENENE

\[
\begin{align*}
\text{CH}_3 & \quad \begin{array}{c}
\text{C} \equiv \text{C} \equiv \text{C} \equiv \text{CH}_2 \\
\text{CH}_3 \\
\end{array} \quad \begin{array}{c}
\text{HgOAc} \\
\text{CH}_3 \text{OH} \\
\end{array} \\
\text{CH}_3 & \quad \begin{array}{c}
\text{C} \equiv \text{C} \equiv \text{C} \equiv \text{CH}_2 \\
\text{CH}_3 \\
\end{array} \quad \begin{array}{c}
\text{Hg}^{199} \quad \text{CH}_3 \quad 6 \text{ cps} \\
\text{cis H} \quad 315 \text{ cps} \\
\text{trans H} \quad 620 \text{ cps} \\
\end{array}
\end{align*}
\]

Fig. 18.
The additional observation of Hg$^{199}$-H$^1$ coupling through four sigma bonds is added support of structure III. The aforementioned investigation into this type of coupling dictates that mercury must be beta to the methyl groups and joined by only sigma bonds to them. These facts in combination allow only the one structure proposed for compound III.

(d) 1,3-Dimethylallene

The addition of 1,3-dimethylallene to mercuric acetate in methanol gave two compounds (Fig. 19). Compound IVA, 3-acetoxymercuri-4-methoxy-2-pentene, was formed in 75% yield. The structure of this compound was confirmed when mercury-199 coupling constants with the cis methyl and trans hydrogen were compared both to the literature values for these systems (page 7) and to the measured constants of the other allene adducts.

The unexpected absence (a) of long-range mercury-proton coupling through sigma bonds, although disheartening,

(a) Several olefins investigated also failed to exhibit any long-range coupling ($J \leq 2$ c.p.s.). The fact could be related to the degree of rotational freedom which the methyl group (in the models studied) may have about the mercury atom. Hence, compounds like IVA probably have very little preference for any one conformation.
OXYMERCURATION OF 1,3-DIMETHYLALLLENE

Fig. 19.
at least proves that mercury can not be any closer to the saturated methyl groups than is proposed.

Compound IVB, the geometrical isomer of IVA, was isolated in 18% yield. The structure of this compound was also proven conclusively by comparing the mercury 199-proton J value with the literature (page 7).

Additional proof of the structures for IVA and IVB is found when the long-range H¹-H¹ allylic coupling of these two compounds is compared. No rotation of bonds in IVA can place the two lone protons in the preferred "M arrangement," whereas structure IVB quite nicely fits this criterion. It is especially comforting, therefore, that JH¹-H¹ (allylic) in IVA = 1.0 c.p.s. and in IVB = 1.5 c.p.s.

(e) Trimethylallene

Oxymercuration of trimethylallene in methanol gave two products, the structures of which represent addition of the mercury salt across the two different double bonds (Fig. 20). Although these compounds were not separated, positive identification was made by the size of the JHg¹⁹⁹-H¹ constants in the case of VA and chemical shift data for VB (see page 34).

Compound VA, 3-acetoxymercuri-4-methyl-4-methoxy-2-pentene, was formed in approximately 72% yield. The Hg¹⁹⁹ coupling with the trans-hydrogen and cis-methyl group correlate with that obtained for IVA, the olefinic portion of
OXYMERCURATION OF TRIMETHYLLALLENE

\[
\begin{align*}
\text{CH}_3 & \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{H} \\
\text{CH}_3 & \quad \text{Hg(OAc)}_2 \\
\text{CH}_3 & \quad \text{OH} \\
\text{HgOAc} & \\
\text{CH}_3 & \quad \text{OCH}_3
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3 & \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{CH}_3 \\
\text{HgOAc} & \\
\text{CH}_3 & \quad \text{OCH}_3
\end{align*}
\]

72% 

\[
\begin{align*}
J_\gamma & \text{Hg}^{199} \quad \text{CH}_3 = 5 \text{ cps} \\
J_\gamma & \text{Hg}^{199} \quad \text{cis CH}_3 = 40 \text{ cps} \\
J_\beta & \text{Hg}^{199} \quad \text{trans H} = 566 \text{ cps}
\end{align*}
\]

18%

Fig. 20.
which is identical. Moreover, the small but significant long-range coupling to the gem-dimethyl protons (5 c.p.s.) is extra support of structure VA for reasons previously discussed (page 53).

Compound VB, 2-methyl-3-acetoxymercuri-4-methoxy-2-pentene, was formed in approximately 18% yield. Although the concentration of VB was not great enough to permit observation of the mercury 199 satellites for this compound, assignment of the main peaks (page 34) was possible since they were chemically shifted from those of VA. The chemical shifts of these protons allow only the one plausible structure for VB (Fig. 19).

(f) Tetramethylallene

Oxymercuration of tetramethylallene in methanol gave one product (Fig. 21). Compound VI, 2,4-dimethyl-3-acetoxymercuri-4-methoxy-2-pentene, was formed in 90% yield. Again nmr spectroscopy conclusively settled any ambiguity of structure. The cis and trans Hg199-CH3 coupling constants (page 37) are directly comparable with those of compounds IV and V. The long-range coupling is also of the same order as in the preceding examples.

2. Solvent Effects

In order to discover what type of products would be formed if the oxymercuration of allenes were to take place in more hindered (and therefore less reactive) alcohols, 1,1-dimethylallene was added to mercuric acetate in isopropanol
OXYMERCURATION OF TETRAMETHYLALLLENE

\[
\begin{align*}
\text{CH}_3 & \quad \text{C} = \text{C} \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{C} = \text{C} \quad \text{CH}_3
\end{align*}
\]

\[
\text{Hg(OAc)}_2 \quad \xrightarrow{\text{CH}_3\text{OH}} \quad \text{CH}_3 \quad \text{C} = \text{C} \quad \text{CH}_3
\]

\[
\begin{align*}
J_{\gamma \text{Hg}^{199}} \quad \text{CCH}_3 & = 8 \text{ cps} \\
J_{\gamma \text{Hg}^{199}} \quad \text{trans CH}_3 & = 25 \text{ cps} \\
J_{\gamma \text{Hg}^{199}} \quad \text{cis CH}_3 & = 39 \text{ cps}
\end{align*}
\]

Fig. 21.
and tertiary butanol. The products of these reactions (Table 2) were determined by careful analysis of the nmr spectra of the mixtures obtained in each case.

1,1-Dimethylallene gave only one product in methanol, whereas in isopropyl and t-butyl alcohols a mixture of three adducts resulted. The product percentages show that oxymercuration in bulky alcohols is accompanied by increasingly competitive reactions involving water (the solvents were not dried) and the solvated acetate ion which accompanies the mercurinium ion intermediate (page 3).

\[
\begin{align*}
\text{CH}_3\text{OH} & \quad \begin{cases}
\text{HgOAc} & \\
\text{OAc} & \\
\text{H}_2\text{O} &
\end{cases} \\
\text{OCH}_3 & \\
\text{C} & \\
\text{C} & \\
\text{CH}_2 & \\
\end{align*}
\]

In the secondary alcohol, the reaction produced 56% of the isopropyl ether and a total of 44% of the other two products shown above. Results in the tertiary alcohol emphasize the competition reactions to an even greater extent. Only 10% of the product in this case was the t-butyl ether, the remaining 90% being the hydroxy and acetoxy derivatives.

3. Rate of Allene vs. Olefin Addition

In order to determine the relative rates of addition of mercuric acetate to an allene and a simple olefin, the
EFFECT OF SOLVENT CHANGES ON OXYMERCURICATION OF 1,1-DIMETHYLLALLENE

<table>
<thead>
<tr>
<th>%</th>
<th>-OR</th>
<th>-OH</th>
<th>-OAc</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALCOHOLS</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CH₃OH</td>
<td>100</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>CH₂CH₂OH</td>
<td>56</td>
<td>28</td>
<td>14</td>
</tr>
<tr>
<td>CH₃C₂OH</td>
<td>10</td>
<td>60</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 2.
reactions of tetramethylallene and tetramethylethylene were followed quantitatively by nmr spectroscopy.

The reaction of mercuric acetate with the allene in methanol was so fast at the experimentally necessary temperature and concentration conditions that its rate could not be measured by this technique. However, since the substituted ethylene reaction was much slower, the allene addition at least divulged a minimum rate with which a comparison might be made.

Using the half-lifes of the two reactions and taking into account that the allene reaction was completed at 20°C. before warming to probe temperature (43°C.), a minimum relative rate ratio of 2000/1 (TMA/TME) was obtained. By how much this ratio is actually exceeded, however, could only be solved by using a different experimental procedure than was employed here.

4. Reversibility of Reaction

The mono-oxymercuration of allenes was shown to be a reversible reaction when tetramethylallene was regenerated from the chloromercuri derivative of VI, by shaking with dilute aqueous HCl. This reaction gave back only the allene, a surprising fact in view of the great ease with which tetramethylallene isomerizes to a conjugated diene.

B. Long-Range Hg\textsuperscript{199}-H\textsuperscript{1} Spin-Spin Coupling Constants

In order to explain the appearance of certain extraneous peaks in the nmr spectra of some of the organomercurials
above, an investigation of possible long-range Hg$^{199}$-H coupling was undertaken.

This type of coupling was first suspected when the nmr spectrum of compound III (Fig. 10) displayed two sharp peaks symmetrically disposed about the gem-dimethyl singlet. Upon integration it was found that the two smaller areas totaled to about 17% of the area of the large (six hydrogen) singlet plus the two satellites. Since spin-spin coupling with mercury-199 through two or three sigma bonds was known$^{10,11,12,13}$ to produce similar satellite peaks, but with much larger J values, it was probable that the same type of interaction over four sigma bonds was happening in this case.

Twenty model olefins were used for the study of long-range coupling. All had the following general structure, where either $R_2$ or $R_3$ (or both) was a hydrogen atom to insure Markovnikov addition to the double bond, thus placing the mercury atom on $C_2$, four sigma bonds distant from the methyl protons in the resulting adduct. In addition $R_1$ was varied in both size and electron donating ability in order to discover what factors might influence the magnitude of the long-range coupling.
The derivative chosen for comparison of $J_{4\sigma}(J_{\text{Hg-199}}$ C-C-CH$_3$) values was the chloromercuiri compound because of its ease of purification (page 21) and larger long-range coupling values (page 21) relative to the original adduct. Table 3 shows the long-range mercury-199-proton coupling constants of all these chloromercuiri derivatives.
Table 3. Long-Range Hg$^{199}$-H$^1$ Spin-Spin Coupling Constants

![Diagram of chemical structure](OCH_3\text{C}_1\text{C}_2\text{HgCl})

<table>
<thead>
<tr>
<th>Compound</th>
<th>R$_1$</th>
<th>R$_2$</th>
<th>R$_3$</th>
<th>$J_{^{199}\text{Hg}-\text{CH}_3}$, c.p.s.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H</td>
<td>H</td>
<td>H</td>
<td>0</td>
</tr>
<tr>
<td>2(a)</td>
<td>H</td>
<td>H</td>
<td>CH$_3$</td>
<td>7</td>
</tr>
<tr>
<td>3(a)</td>
<td>H</td>
<td>CH$_3$</td>
<td>H</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>CH$_3$</td>
<td>H</td>
<td>H</td>
<td>22</td>
</tr>
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<td>CH$_3$</td>
<td>CH$_3$</td>
<td>H</td>
<td>22</td>
</tr>
<tr>
<td>6</td>
<td>CH$_3$</td>
<td>CH$_3$</td>
<td>CH$_3$</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>C$_2$H$_5$</td>
<td>H</td>
<td>H</td>
<td>20</td>
</tr>
<tr>
<td>8</td>
<td>i-C$_3$H$_7$</td>
<td>H</td>
<td>H</td>
<td>17</td>
</tr>
<tr>
<td>9</td>
<td>-C$_4$H$_9$</td>
<td>H</td>
<td>H</td>
<td>27</td>
</tr>
<tr>
<td>10</td>
<td>CH$_2$- -C$_4$H$_9$</td>
<td>H</td>
<td>H</td>
<td>16</td>
</tr>
<tr>
<td>11</td>
<td>p-C$_6$H$_4$OCH$_3$</td>
<td>H</td>
<td>H</td>
<td>20</td>
</tr>
<tr>
<td>12</td>
<td>CH$_2$Cl</td>
<td>H</td>
<td>H</td>
<td>30</td>
</tr>
<tr>
<td>13</td>
<td>CH$_2$Br</td>
<td>H</td>
<td>H</td>
<td>33</td>
</tr>
<tr>
<td>14</td>
<td>CH$_2$C$_6$H$_5$</td>
<td>H</td>
<td>H</td>
<td>39</td>
</tr>
<tr>
<td>15</td>
<td>p-CH$_2$C$_6$H$_4$OCH$_3$</td>
<td>H</td>
<td>H</td>
<td>44</td>
</tr>
<tr>
<td>16</td>
<td>CH$_2$-N(CH$_3$)$_2$</td>
<td>H</td>
<td>H</td>
<td>46</td>
</tr>
<tr>
<td>17</td>
<td>2,4,6-CH$_2$-C$_6$H$_2$(CH$_3$)$_3$</td>
<td>H</td>
<td>H</td>
<td>48</td>
</tr>
</tbody>
</table>

(a) Compound 2, prepared from trans-2-butene, should be the erythro isomer; compound 3, from cis-2-butene, the threo.
Table 3 Continued

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \text{J}_{4\text{c}}, \text{ c.p.s.} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>18(a)</td>
<td>![Compound 18(a) diagram]</td>
</tr>
<tr>
<td>19(a)</td>
<td>![Compound 19(a) diagram]</td>
</tr>
<tr>
<td>20(b)</td>
<td>![Compound 20(b) diagram]</td>
</tr>
</tbody>
</table>

(a) Oxymercuration of cyclohexene proceeds via a trans mechanism.\(^{30}\)

(b) Oxymercuration of a cyclobutene may proceed via a cis mechanism if analogous to the reaction of norbornene.\(^{30}\)
IV. DISCUSSION

A. Oxymercuration

1. Aspects of Addition

Oxymercuration of allene and its five methyl-substituted derivatives have produced a variety of mono and diadducts. Certain aspects of these additions are prominent and may be analyzed individually.

Allene and to a certain extent methylallene both react with mercuric acetate in a manner such that the electrophilic mercuric ion attacks the terminal carbon of the allenic system. This fact indicates an apparent polarization of the carbon-carbon double bond in the ground state of allene:

\[
\begin{align*}
\text{H} & \quad \text{C} = \text{C} = \text{C} & \quad \text{H} \\
\text{H} & \quad \text{C} = \text{C} = \text{C} & \quad \text{H}
\end{align*}
\]

This dipole might then produce some type of unsymmetrical mercurium ion\(^{(a)}\) intermediate.

\[
\begin{align*}
\begin{array}{c}
\text{C} \quad \text{C} = \text{C} = \text{C} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H}
\end{array}
\quad \underset{\text{Hg(OAc)}_2}{\rightleftharpoons}
\begin{array}{c}
\text{C} \quad \text{C} = \text{C} = \text{C} \\
\text{H} & \quad \text{H} & \quad \text{H} & \quad \text{H}
\end{array}
\end{align*}
\]

The longer of the mercury-carbon bonds, being the weaker, could then easily open as nucleophilic methanol approached from the opposite side.

\(\text{(a) See page 70 for a more detailed discussion of this ion.}\)
A second aspect of allene oxymercuration, illustrated by the reactions of allene and methylallene, is that once a molecule of mercuric acetate has added to an allene producing the terminal mercury species, the remaining double bond without exception adds a second molecule of mercury salt in a similar manner, even in the presence of excess allene. This fact implies that the addition of the second molecule of Hg(OAc)\(_2\) is much faster than the first.

\[
\begin{align*}
\text{H}_2\text{C} & \quad \text{C} \quad \text{H} \\
\text{H} & \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \ quad
A third generalization of allene oxymercuration is that all the monoadducts of the unsymmetrical allenes are the thermodynamically less stable products of the two possible allylic isomers. Methylallene, 1,1-dimethylallene and trimethylallene all add mercuric acetate to the "wrong" double bond, if thermodynamic considerations are of the greatest importance. The major product in each case is the more hindered ether with the less substituted double bond.

\[
\begin{align*}
\text{CH}_3&\text{C}\text{C}\text{C}\text{CH}_2\text{HgOAc} \\
\text{CH}_3&\text{OCH}_3
\end{align*}
\quad \text{vs.} \quad
\begin{align*}
\text{CH}_3&\text{C}\text{C}\text{CH}_2\text{OCH}_3 \\
\text{CH}_3&\text{HgOAc}
\end{align*}
\]

Hence, these reactions must be overall kinetically controlled.

Since the primary complexation step is thought to be rapid and reversible, (a) both pi-bonds should be initially coordinated with mercury to some extent. However either the more substituted complex is more stable and therefore present in much larger amount, or the attack by methanol on this complex is more favorable.

(a) This premise is based on deoxymercuration results in which loss of the protonated methoxy group with simultaneous formation of the cyclic mercurinium ion is thought to be the rate controlling step of the reaction.
Trimethylallene

Where,

Either: \( K_1 \gg K_2 \)

Or: \( K_1 \not\approx K_2 \) but \( k_3 \gg k_4 \)

Either explanation seems feasible, since the geminal groups should exert a greater activating effect on both the pi-bond (toward initial electrophilic attack) and on the mercurinium ion (by giving the terminal carbon atom more carbonium ion character).

Another generalization of these reactions is that in all the monoadducts obtained, mercury is found on the center carbon of the allenic system. This preference for Markovnikov addition, if such a term may be applied to the allenes, is quite common to oxymercuration reactions.\(^1\) However, these additions are extremely specific compared to other polar reagents in that no "backward addition" products are ever detected.
The intermediate pi-complex (page 3) must therefore involve some type of structure which places more positive charge at the carbon with that greater number of alkyl groups. At the same time this intermediate must also retain the appearance of a complex to explain the stereospecific trans addition common to most oxymercuration reactions. Therefore Traylor's structure\textsuperscript{30} (Fig. 22), or some modification of it\textsuperscript{31} must play an important role in this reaction.

![Fig. 22. Unsymmetrical Mercurinium Ion](image)

The relative shortness of the Hg-C\textsubscript{2} bond indicates the greater electron density between those atoms compared to the Hg-C\textsubscript{1} bond. Although the actual position of mercury is not an important factor, it is natural to assume if C\textsubscript{1} is more positively charged than C\textsubscript{2} in the intermediate complex, then it must be further removed from mercury than the latter.

One more conclusion about these oxymercuration reactions can be drawn if the products of 1,3-dimethylallene and trimethylallene addition are compared. In both cases the major adducts contain mercury cis to the olefinic methyl.
The product percentages of the di-substituted allene (75%: Hg cis to CH₃; 18%: Hg trans to CH₃) is a measurement of this preference for the cis compound.

This phenomenon might be explained if one considers the two possible intermediate π-complexes (a) for trimethylallene as shown below.

In the case of intermediate A, the approach of methanol is somewhat restricted by the olefinic methyl group, whereas structure B has only hydrogen to partially block the attack of the nucleophile. However, the difference between these two intermediates should not entirely prohibit the formation of the less favorable product. In support of this argument an 18% yield of that minor product was obtained in the 1,3-dimethylallene addition. Such a 4:1 preference in that reaction would predict a 15% yield of the Hg-trans-to-CH₃ product from the oxymercuration of trimethylallene, were it not for the competing addition to that double bond (18%) in the latter case.

(a) These mercurinium ions are probably "bent" as shown since C₂ now has much sp² character.
2. **Mechanism**

Taking into account the aforementioned aspects of these addition reactions, the probable mechanism by which an allenic system is oxymercurated can now be described.

The primary step is assumed to be a rapid and reversible (a) mercurinium complex formation.\(^{33-45}\) This complex can be formed on either side of either double bond, producing a total of four possible intermediate ions.

With the possible exception of methylallene, these four intermediates are also unsymmetrical, the mercury atom being further from the carbon atom better able to support a positive charge (Fig. 22). Also, the more highly alkyl-substituted mercurinium ions will be more stable than the others and hence present in larger concentration.

\[\text{Fig. 22: Structures of possible intermediate ions.}\]

(a) Although this has not been specifically demonstrated for allenes, the results do not rule out such an equilibrium and the other obvious similarities of this reaction to oxymercuration of simple olefins would seem to justify such an assumption.
The second step of the reaction, deduced by deoxygenation studies of olefin adducts to be the rate determining step, involves a probable trans attack by the nucleophilic methanol on this intermediate mercurinium ion. The alcohol attacks only the carbon more distant from mercury and in cases where cis and trans isomers can result, prefers the sterically less hindered (to a trans approach) mercurinium ion.

The entire scheme is summarized by the diagram of the oxymercuration of trimethylallene (Fig. 23).

3. Rate of Oxymercuration

A discussion about the rate of this reaction must also be considered when a comparison with olefin addition is made. The fact that tetramethylallene adds mercuric acetate at least 2,000 times faster than tetramethylethylene must mean that either allenes give a very stable intermediate complex or the complex from allenes allow a more facile approach of methanol. Another possibility is that the double bonds of allenes are particularly activated towards electrophilic attack by mercury when compared to their olefin counterparts.

A look at the two mercurinium ions involved suggests that methanol should not be seriously restricted in its approach to either molecule. Even if the latter were true, the complex form tetramethylallene should be the more crowded
Where: $K_1, K_2 > K_3, K_4$ and $k_2 > k_1$, but $k_3 = k_4$

Fig. 23. Mechanism of Trimethylallene Oxymercuration
due to the olefinic methyl group (since methanol attacks a gem-dimethyl carbon in both A and B). The answer to this rate difference must lie in the ability of the second double bond of the allenic system to either stabilize the mercurinium ion (preventing reformation of the allene) or activate the second double bond of the ground state allene for a more rapid electrophilic attack by mercuric acetate. Since it has been suggested that pi-delocalization of the second double bond does not occur in allene addition reactions, these interactions must be primarily inductive ones.

4. Comparison with Hydrohalogenation

As noted on pages 4-6, some investigation into hydrohalogenation products of allenes has been made. Since this type of addition as well as oxymercuration may be termed electrophilic in nature, a comparison of the adducts of the two types should be profitable.

(a) T. L. Jacobs claims that the perpendicular $\pi$-cloud probably does not achieve coplanarity (and thus resonance) with the terminal carbonium ion during HX addition to such a system.
Unfortunately, the hydrogen halide adducts of only three of the six allenes used in the present research have been studied to any extent.\textsuperscript{2,4-7} The discussion shall therefore be limited to a comparison of these three reactions.

Allene, according to Griesbaum,\textsuperscript{2} adds hydrogen halide to give four different products in varying amounts (page 5). Table 4 compares his results at ambient temperature\textsuperscript{(a)} with those obtained for oxymercuration of the same compound. In both cases the electrophilic agent adds solely to terminal methylene carbons. It is interesting to note that mercuric acetate, like hydrogen iodide, produces predominantly the diadduct species.

The fact that no cyclic products were detected in the oxymercuration reaction merely supports the existence of a bridged mercurinium ion (mercury pi-complex) as a product-determining intermediate and illustrates the relative absence of positive charge on carbon in this species.\textsuperscript{3} The complete lack of monoadduct is probably related to some electronic activating effect of the methoxy group;\textsuperscript{46} similar results were obtained by Griesbaum in hydrogen iodide addition.\textsuperscript{2}

The hydrohalogeneration of methylallene and 1,1-dimethylallene has been studied by several workers (pages 5-6).\textsuperscript{4-7} However, only Jacobs' results with hydrogen chloride\textsuperscript{4} have been reported in any detail and for that reason constitute the data in Table 5.

\textsuperscript{(a)} At low temperatures up to 40% cyclic dimers were isolated\textsuperscript{2}
Table 4. Comparison of Hydrohalogenation and Oxymercuration of Allene

Table 5. Comparison of Hydrochlorination and Oxymercuration of Methylallene and 1,1-Dimethylallene
During hydrochlorination, methylallene adds hydrogen ion to the terminal methylene group but apparently does not form the diadduct.\(^{(a)}\) The same orientation is observed to some extent in mercuric acetate addition, but the monoadduct quickly adds one more mole of the mercury salt. Both these reactions are quite analogous to the allene case, the production of diadduct again probably caused by electron enrichment of the remaining double bond by the methoxy group.\(^{46}\)

The major product of oxymercuration of methylallene, however, is that in which mercury is attached to the central carbon of the allenic system and methoxy to the more substituted of the terminal carbon atoms. An explanation for this different behavior must represent the dissimilar mechanisms by which oxymercuration and hydrochlorination occur.

The formation of both oxymercuration products can be accounted for if one assumes that when the first mole of mercuric acetate adds to the unsubstituted pi-bond, a terminal mercury species is produced, which in turn quickly adds another mole of mercuric acetate and forms the 1,3-dimercuri compound as in the case of allene itself.

Addition of mercuric acetate to a monomethyl or dimethyl-substituted allene double bond, however, places mercury on the central carbon of the allenic system, forming a stable monoadduct.

\(^{(a)}\) It may be remembered that Hennion and Sheehan\(^{7}\) did get some diadduct in their addition of HCl to methylallene (page 6).
In contrast, the ionic addition of hydrogen chloride to this allene probably does not proceed by a bridged-ion intermediate\(^{(a)}\) but by protonation of a terminal carbon atom, producing a localized positive charge on its neighbor. The preferential protonation of the terminal methylene can only\(^{(b)}\) be explained (as in the allene case) by a form of Markovnikov's Rule, assuming that the vinyl moiety, like an alkyl group, stabilizes a positive charge better than hydrogen. Although the reason for attack of that particular double bond is not clear, the fact that another molecule of hydrogen chloride does not then add to the second pi-bond is explained by the deactivating effect of the electro-negative chlorine atom as in the case of vinyl chloride.\(^{47}\)

Both oxymercuration and hydrochlorination of 1,1-dimethylallene result in electrophilic attack on the central carbon of the allene systems. However, the nucleophile in the former case then becomes attached to the gem-dimethyl carbon, while in the latter case, the primary carbon atom is attacked by chloride.\(^{(c)}\)

\(^{(a)}\) The existence of a bridged protonium ion has been proven in certain special cases.\(^{48}\) However such a 3-centered bond is undoubtedly much weaker than the mercurinium complex and must therefore play a less important part in the outcome of these reactions.

\(^{(b)}\) The reaction cannot be thermodynamically controlled since it is not reversible under these conditions.\(^{32-44}\)

\(^{(c)}\) Jacobs claims this may be the only product and not just the major one\(^{4}\) (see page 6).
These results are peculiar since again hydrogen halide has preferred to add to the less substituted bond whereas mercuric acetate has done the opposite. Moreover, the position of hydrogen has now switched to the central atom of the allenic system which is opposite to the results of the less-substituted allenes.

A brief review of these two electrophilic reactions can now be made. Hydrochlorination of unsymmetrical allenes to produce monoadducts occurs across the less substituted double bond, the opposite being true for oxymercuration. Although hydrogen chloride adds a proton to the terminal methylene of allene and monosubstituted allenes, the presence of two or more alkyl groups results in a centrally protonated product.

Oxymercuration, while showing similar preference for terminal vs. central carbons in the case of allene, changes from the former to the latter with one alkyl substituent.

Looking over these generalizations it is not immediately evident whether or not the mechanism of oxymercuration parallels that of hydrohalogenation in all cases. However, the reactions of 1,1-dimethylallene appear to represent two distinct types of electrophilic addition.

Jacobs' results with hydrogen chloride can only be explained by a classical carbonium ion intermediate (see Fig. 24). His conclusion that the entire product of hydrochlorination of 1,1-dimethylallene is probably the primary
Cilkz

CH3 - CH = CH2

Where: \( K_1 > K_2 \), but \( k_2 \gg k_1 \), and \( k_3 \gg k_1 \)

Fig. 24. Probable Mechanism for the Hydrochlorination of 1,1-Dimethylallene
allylic chloride must be due to the fact that the primary carbonium ion (unstabilized by resonance) is much more reactive than its tertiary isomer (Fig. 24), and that addition of chloride to this ion is the product-controlling step of the reaction.

If a bridged-ion did exist and were similar to the mercurinium ion, the same products should be formed by both reactions since the central allenic carbon receives the electrophile in each case. Thus, either the cyclic protonium ion does not exist, or it reverts to a classical carbonium ion prior to the product-determining step.

In conclusion, a comparison of the two reactions must be brief since only after more investigation into the initial products of HX addition can such statements be justified. More detailed statements regarding the oxymercuration mechanism could be made only if detailed kinetic studies were made in order to establish the rate-determining step, and sterochemical studies requiring the preparation of optically active allenes.

B. Long-Range Hg^{199}-H\textsuperscript{1} Spin-Spin Coupling

From the range of observed $J_{\text{Hg}^{199}\text{-CH}_3}$ values in Table 3 (page 64), it can be seen that mercury-proton spin-spin coupling through four sigma bonds can vary between 6 and 48 c.p.s. To explain the variety of coupling magnitudes one must first discuss the probable mechanism of this long-range interaction.
1. **Mechanism of Long-Range Spin-Spin Coupling**

   Of the possible mechanisms for transmission of H1-H1 spin-spin coupling, the major contribution in the great majority of cases has been shown to arise from a Fermi contact potential term,\(^49,50\) in which a nuclear spin moment is transmitted from one nucleus to another through bonding orbitals between the coupled atoms. The theory predicts a rapidly decreasing J value with increasing interatomic distances such that coupling through more than three sigma bonds should be negligible. Substantial coupling over four sigma bonds has been noted in certain compounds,\(^29\) which according to Wiberg\(^50\) and others cannot be explained by a normal Fermi contact mechanism. In such cases a "through-space" mechanism has been claimed to account for this observed coupling.

   The "through-space" theory of spin-spin coupling assumes that if the "through-bond" distance between two interacting nuclei predicts too small coupling from Fermi contact potential calculations, some other type of closer overlap involving other orbitals must exist. For protons separated by four sigma bonds, the ideal arrangement for this type of interaction appears to be the "M" configuration\(^49\) in Fig. 25.

---

![Fig. 25. The "M" Arrangement](image_url)
The transmission of nuclear spin from $H_1$ to $H_2$ is accomplished by overlap of the small $sp^3$ posterior lobes of the $H_1C_1$ and $H_2C_3$ bonds. Various investigators have also noted that as $\theta$ decreases, $J_{H_1-H_2}$ ($J_{4\sigma}$) also decreases.\(^2\)

Because mercury-$^{199}$ is another nucleus capable of magnetic resonance under a given field and radio frequency, such long-range interactions should also hold for Hg-$^{199}$-Hg-$^{199}$ and Hg-$^{199}$-$^1$H systems. Thus any organomercurial in which a proton can be held in such an "M" configuration with mercury might likewise be expected to exhibit this type of coupling.

In all of the compounds involved in the study of this long-range coupling a beta-methyl group was taken as the locus of observable protons four sigma bonds removed from mercury ($\gamma$-protons). Such an arrangement is pictured in Fig. 26 (A) with its Newman projection along the $C_2-C_3$ axis in Fig. 26 (B). It is obvious that free rotation exists.

---

**Fig. 26.** The "M" - Arrangement in Organomercurials
about the C₁-C₂ and C₂-C₃ bonds in this molecule. While the chemical environment of the three methyl hydrogens will be time-averaged, thereby reducing the overall coupling to Ha, such coupling will exist with all three methyl protons because of free rotation. However, rotation about C₂-C₃ will diminish the coupling by a factor proportional to the amount of time the molecule spends in the other rotational conformations.

In light of this "M" arrangement it is possible to divide the compounds of Table 3 (page 64) into three main groups. Compounds 1-10 are those in which non-bonded steric factors appear to govern whether or not the structure of Fig. 26 (B) is a stable rotamer for the given organomercurial. In compounds 11-17, the desired coplanarity of Fig. 26 (B) is attained by an electronic attraction between R₁ and the mercury atom. The final three compounds constitute a group in which there is a rather rigid spacial relationship between the mercury atom and the methyl group.

2. Dependence on Steric Effects

To explain the appearance (or non-appearance) of long-range mercury satellite peaks in the nmr spectra of the first group of compounds (1-10) it is necessary to consider the nonbonded steric interactions between R₁, R₂, R₃, and CH₃ of Fig. 26 (A). Of this group, cpds. 1, 3, and 6 fail to show any long-range coupling.
Compound 6, the organomercurial from tetramethyl-ethylene, clearly must prefer only one rotamer due to serious beta-methyl interactions. This structure, of course, eliminates any possibility for a mercury-methyl 'M' arrangement.

\[
\begin{array}{ccc}
  \text{CH}_3 & \text{OCH}_3 & \text{CH}_3 \\
  \text{CH}_3 & \text{HgX} & \text{CH}_3 \\
\end{array}
\]

The prerequisite for this assumption is that the mercury atom is less bulky towards beta substituents than is a methyl group. The fact is not novel since the long carbon-mercury bond (2.23\,\text{Å}) \textsuperscript{51} causes mercury to behave in much the same manner on the cyclohexane ring, preferring neither an axial nor equatorial conformation. \textsuperscript{52} Thus while the mercury atom itself is large (r=1.44\,\text{Å}) \textsuperscript{53} it is effectively removed from many neighboring interactions.

Compound 3, derived from cis-2-butene also exhibits no long-range coupling, while its isomer (2), from trans-2-butene, has a $J_{4\sigma}$ value of 7 c.p.s.

To explain this surprising difference one further complication must be introduced at this point. It appears that while steric factors may play an important role in the population of each staggered conformer, a mercury-methoxy attraction also exists. \textsuperscript{54} In the cases under present
consideration the *threo* isomer (below) clearly has one stable conformation(a) in which the methyl-methyl interaction is minimized and mercury is **gauche** to methoxy.

![Threo](image)

It is easy to see how such a structure prohibits long-range coupling if the 'M' arrangement is a necessary geometry for this type of interaction.

The *erythro* isomer, on the other hand, has two sterically equivalent conformers with the methoxy group **gauche** to the mercury atom.

![Erythro](image)

---

(a) Kreevoy, Schaleger, and Ware reached the same conclusions based on their deoxymercuration studies.54
The existence of long-range coupling (7 c.p.s.) for this compound demonstrates that while A may not be the only stable rotamer, it certainly must exist to some extent.

The third organomercurial in which no coupling was found (a) was compound 1, the adduct of propylene. In this case there being no alpha methyl group, (b) the primary factor governing conformational stability must be the mercury-methoxy attraction. Moreover, an eclipsed conformation (below) should not be unfavorable since the proton-methyl interaction is very small.55

That cpd. 1 does indeed show a strong conformational preference of some kind is suggested by the large non-equivalence (Δν'=18 c.p.s.) of the methylene protons on the alpha carbon.57

The remaining six compounds of this first group all exhibit long-range coupling of 16-27 c.p.s. It should be

(a) Klose56 was unable to detect any long-range Hg199 satellites about the methyl triplet of di-n-propylmercury.

(b) It should be remembered that the adducts of both methylallene and 1,3-dimethylallene also failed to show long-range coupling. These systems having only one methyl on the reactive double bond are analogous to the propylene case.
noted that in none of these cases does a steric interaction prohibit the rotamer in which mercury is \textit{trans} to a methyl group. Although it is interesting to speculate about the size of this coupling with relation to varying steric factors, such a study does not seem to produce any consistent results. However one generality does seem to prevail throughout the list. Whenever $R_1$ (Fig. 26) is an alkyl group, substantial coupling ($J \geq 16$ c.p.s.) is observed. This last phenomenon is probably due to increased conformational stability of the "$M"$ arrangement in these beta-dialkyl compounds.

3. Dependence on Interelectronic Attraction

Compounds 11-17 were prepared to see if instead of sterically "pushing" the organomercurial into the "$M"$ arrangement, the molecule could be held in that configuration by a strong electron donor-mercury chelate bond.

A meaningful quantitative relationship is noticed in this series if it is assumed that when the chelate bond between $R_1$ and mercury is strongest, the best "$M"$ arrangement will exist, resulting in the largest long-range coupling. Hence $J_{4\sigma}$ of cpd. 13 is larger than that of cpd. 12 (Table 3, page 64). Likewise the order of ring electron density from cpds. 14 to 15 to 17 parallels the increase in $J_{4\sigma}$ for these compounds.
The large difference in coupling between compounds 11 and 15 suggests that a methylene group between C₁ and the electron-rich substituent places the latter closer to the mercury atom, thereby making a tighter bond.

Additional conformational proof for compounds such as cpd. 15 is based on the fact that the protons of both methylene groups are extremely non-equivalent. By using magnetic anisotropic data calculated for benzene substituents, the exact positions of these protons are unambiguously defined.

The metal chelate bond is itself demonstrated by measuring the nmr spectra of these organomercurials in solvents of varying basisity. As the solvent base strength
increases, the mercury atom becomes coordinated with solvent and less tightly held to R₁, resulting in decreased long-range coupling as well as coalescence of both methylene quartets.

4. Coupling in Rigid Molecules

Compounds 18, 19, and 20 were prepared to study the effect of a rigid geometry between mercury and a methyl group on the long-range coupling. Although the methyl group in such molecules enjoys free rotation around its own C-C axis, the C₂-C₃ bond of Fig. 26 (A) is relatively frozen to rotation.

The methyl group of cpd. 18 should lie almost entirely in the equatorial position. The dihedral angle between mercury (no axial-equatorial preference) and methyl will be approximately 65-75°. The observed Hg¹⁹⁹-CH₃ coupling of 7 c.p.s. for this molecule necessarily indicates therefore that Hg¹⁹⁹-H₁ coupling through four sigma bonds does not require a fixed trans-coplanar relationship. The size of this coupling, however, does show what effect a lack of the "M" arrangement has on the magnitude of the coupling.

The long-range spin-spin coupling (7 c.p.s.) in cpd. 19 (page 65) was predicted to be similar to that observed for cpd. 18, since both methyl groups may simultaneously occupy equatorial positions, thereby fixing the geometry even more tightly than in the previous case. In a rigid chair formation of this type the mercury-methyl dihedral
angle will be about 70°. In addition the mercury and methoxy groups will lie trans and exactly coplanar to one another. This latter hypothesis is born out by an unprecedented(a) $J_{\text{Hg}^{199}-\text{H}^1}$ value of 6.5 c.p.s. through five sigma bonds to the methoxy group.

If oxymercuration of 1,2-dimethycyclobutene takes place via a cis-addition mechanism, as may be expected from Traylor's results, the dihedral angle between the mercury atom and the methyl group should be 90-120°, depending on the degree of puckering of the four-membered ring. (b) On the other hand, a trans mechanism would leave a mercury-methyl dihedral angle of 0-30°. The mercury-methoxy angle in each case would, of course, be the same as the mercury-methyl in the opposite isomer. The fact that $J_4$ in cpd. 20 is 9 c.p.s. and $J_{\text{Hg}-\text{OCH}_3} \leq 2$ c.p.s. does not indicate which product was formed but does show that mercury is not coplanar with either beta group.

(a) To this author's knowledge spin-spin coupling with the hydrogens of a methoxy group of an ether over any number of bonds in a saturated compound is unknown.

(b) Cyclobutane itself is puckered by 180°.60
V. SUMMARY AND CONCLUSIONS

A. Oxymercuration of Allenes

The addition of mercuric acetate to allene, and its five methyl-substituted derivatives is quite rapid in methanol at room temperature.

Allene itself adds mercury onto its terminal carbons. The original monoadduct, its double bond activated by the centrally situated methoxy group, quickly adds a second mole of mercuric acetate, yielding a ketal which then is hydrolyzed to the ketone by atmospheric moisture. The formation of the methanol-insoluble ketone is favored due to the ability of a β-mercury substituent to stabilize the transition state for hydrolysis of methoxy groups.

Methylallene yields an analogous ketone, but in minor yield. The major product is a monoadduct in which mercury has added to the center carbon of the allenic system. The other methyl-substituted allenes give one or two similar monoadducts which, once dissolved in benzene, can be deoxymercurocurated with aqueous HCl to give back the pure allene.

A mechanism which successfully predicts the addition products of all these reactions includes an intermediate mercurinium pi-complex similar to that proposed for normal olefin additions. In all substituted allenes this pi-complex if formed preferentially across the double bond of greater substitution. The actual shape of the mercurinium ion must
be non-symmetrical to allow more positive charge on the carbon of greatest substitution. The latter is then exclusively attacked by the nucleophilic methanol.

A comparison of the oxymercuration and hydrohalogenation products of allenes suggests that there are two distinctly different mechanisms for these electrophilic addition reactions. The formation of primary chloride upon hydrochlorination of 1,1-dimethylallene indicates an "open" terminal carbonium ion which is more reactive toward chloride ion than its tertiary isomer. In contrast, the production of a tertiary methoxy organomercurial supports a "non-carbonium ion" mechanism, i.e., the cyclic mercurinium ion in which most of the positive charge is on the mercury atom.

B. Long-Range $^{199}\text{Hg} - H^1$ Spin-Spin Coupling

Long-range $^{199}\text{Hg} - H^1$ spin-spin coupling can occur over four sigma bonds in acyclic as well as cyclic organomercurials. Although not as large as geminal or vicinal coupling, the $J_{4\sigma}$ values do attain a size of 50 c.p.s., depending on the compound in question. The dominant feature of this spin-spin coupling is its increased magnitude in a trans-coplanar geometry.

Factors controlling the size of the coupling are three-fold. In mercury-olefin adducts having little restriction to internal rotation, the mercury-methoxy attraction increases the energy of the "$M$" configuration, resulting in zero or small $J_{4\sigma}$ values. In molecules where these non-bonded
repulsions are much larger, some long-range coupling will be observed if these steric effects do not also prevent the "M" arrangement. Finally, in molecules with a very strong interelectronic chelate bond holding the organomercurial in the preferred geometry, the long-range coupling constants are quite large and increase with increasing chelation strength.

The observation of Hg\(^{199}\) satellite peaks in the nmr spectra of three cyclic organomercurials suggests that long-range mercury-199-proton coupling, like vicinal H\(^1\)-H\(^1\) coupling, can occur at many dihedral angles, but probably reaches a maximum in coplanar geometries.
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