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Bromination Of 1,2-Cyclononadiene And 1,3-Dimethylallene

Edward Benny Samuel

University of the Pacific

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BROMINATION OF 1,2-CYCLONONADIENE
AND
1,3-DIMETHYLALLENE

A Dissertation
Presented to
The Faculty of the Graduate School
University of the Pacific

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy

by
Edward Benny Samuel
May 1971
This dissertation, written and submitted by

Edward B. Samuel

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Graduate Council, University of the Pacific.

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Dated May 14, 1971
BROMINATION OF 1,2-CYCLONONADIENE AND 1,3-DIMETHYLALLYLENE

ABSTRACT OF DISSERTATION

1,2-Cyclononadiene and 1,3-dimethylallene were brominated using molecular bromine and N-bromosuccinimide in carbon tetrachloride and various reactive polar solvents.

Bromination of 1,2-cyclononadiene using molecular bromine in carbon tetrachloride yielded cis-2,3-dibromocyclononene and cis-1,4-dibromocyclononene in the ratio of 40:60. Bromination of 1,2-cyclononadiene using NBS and molecular bromine in methanol yielded cis-2-bromo-3-methoxycyclononene and cis-1-bromo-4-methoxy-cyclononene in the ratio of 40:60. Similarly, the bromination of 1,2-cyclononadiene in aqueous acetone and glacial acetic acid yielded the corresponding cis-2,3 and cis-1,4 substituted isomers. The structure determination was made using spectral and chemical methods. Solvolysis of the dibromo adducts to yield the corresponding oxy-products was used both for structural proof and synthetic purposes. The bromomethoxy isomers were reduced by lithium metal to provide further structural information.

The bromination of 1,3-dimethylallene in carbon tetrachloride yielded almost exclusively trans-3,4-dibromo-2-pentene (97% and about 3% of the cis isomer). The brom-
inination of 1,3-dimethylallene in methanol produced
trans and cis-3-bromo-4-methoxy-2-pentene in the ratio
of 90:10. Mutual structural verification was provided
by the methanolysis of the dibromopentene products to
yield the corresponding bromomethoxy products.

The possible mechanisms for the brominations
of the allenes have been analyzed. The most favorable
trans addition transition state for 1,3-dimethylallene
predicts preferential formation of trans-3,4-isomers.
This is in accord with the experimental results. In
contrast, models show that one side of each of the π-bonds
is sterically protected by the methylene bridge in 1,2-
cyclononadiene. Taking this into account an analysis of
possible transition states leads to the tentative con-
clusion, substantiated by the experimental results,
that the cis-configuration should be preferentially
produced. The rearranged product is produced as a
result of a 1,5-hydride shift.
DEDICATED

to my wife Stella
ACKNOWLEDGEMENTS

It is a pleasure to thank Dr. Donald K. Wedegaertner for his help and inspiration, and acknowledge his personal interest in making this dissertation possible.

A special thanks is due to Dr. Charles Matuszak for his constructive criticism of this thesis and for being my research advisor during the absence of Dr. Wedegaertner. I also wish to thank Dr. Richard Dodge, Dr. John Tyndall and Dr. David Yoder for their comments in the preparation of this dissertation, and Virginia Gall for typing it.
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CHAPTER I
INTRODUCTION

Electrophilic additions to allenes have been studied rather extensively, although by no means completely, during the last decade. Several comprehensive reviews\textsuperscript{15,17,23,32,36} have been written on the subject.

Much information has been obtained on the orientation of unsymmetrical reagents about substituted allenes. Although hydrogen halide addition to 1,2-propadiene yields 2-halopropenes,\textsuperscript{20,31} it has been amply demonstrated, at least in the case of halogenation and oxymercuration of the 1,3-alkyl substituted allenes, that the attacking electrophile ends up in the product attached to the central carbon of the original allenic system.\textsuperscript{20,22,31,34,38,39,40} Using optically active 1,3-dimethylallene(15) it has been shown that the bromination and oxymercuration of 15 is stereospecific.\textsuperscript{22,39} Knowledge of the absolute configurations of the optically active addition products have made it possible to propose a plausible mechanism for the reactions (eq 1).
EQUATION 1

The suggested mechanism involves the formation of a dissymmetrically $\sigma$-bridged halonium or mercurinium ion, with subsequent attack of the incoming nucleophile trans to the bridge to form the 3,4-substituted-2-pentene products. Recently, convincing spectral evidence has been presented for the presence of bridged halonium ions produced as the result of the initial attack of an electrophilic halide on the allenic system.\textsuperscript{6}

Work done in this laboratory, included in this thesis, and work done by Caserio and coworkers on open chain allenes,\textsuperscript{22,39} have for the first time been concerned with the stereochemical orientation about the unreacted double bond of the allenic monoadduct. Wedegaertner and Millam\textsuperscript{40} were the first to call attention
to the importance of such a study. We have found, as confirmed by Caserio and coworkers, that the addition of bromine, for example, to \textit{15} in methanol, produced \textit{trans}-3-bromo-4-methoxy-2-pentene(\textit{17}) predominantly (83-98\%, the \textit{cis} isomer made up the minor product).

Ethoxymercuration of 1,2-cyclononadiene(\textit{1}) with mercuric chloride in ethanol as reported by Gardner and coworkers\textsuperscript{34}, gave \textit{cis}-2-chloromercury-3-ethoxycyclononene. More recently optically active \textit{1} has been oxymercurated to give optically active \textit{cis} adducts.\textsuperscript{1} Addition of 2,4-dinitrobenzenesulpheny1 chloride also gave a \textit{cis} adduct.\textsuperscript{21} However, the addition of bromine to \textit{1} in carbon tetrachloride, as investigated by Wedegaertner and Millam,\textsuperscript{40} gave two isomeric products, whose elemental analysis was consistent with a dibromocyclononene. They characterized them as a 60:40 mixture of \textit{trans} and \textit{cis}-2,3-dibromocyclononene, respectively. Although the structure assignment of one of the isomers has been shown to be incorrect, the conclusion was significant in that it focused attention on the stereochemical orientation about the remaining double bond of the monoadduct. The initial purpose of this research was to explore the mechanistic implications of the observations made by Wedegaertner and Millam.

1,2-Cyclononadiene(\textit{1}) was brominated in methanol and a 40:60 mixture of two products corresponding to
isomeric bromomethoxycyclononenes was obtained. Preliminary, chemical and spectral evidence indicated that the isomeric mixture definitely did not consist of cis-trans geometrical isomers. The primary objective of the research then became the identification of the isomeric bromination products of 1,2-cyclononadiene (1) in various reactive solvents. The results are discussed with reference to the intermediates that may be involved in these reactions.
CHAPTER II
RESULTS

A. BROMINATION OF 1,2-CYCLONONADIENE (1)
IN METHANOL

cis-2-Bromo-3-methoxycyclononene(2) and cis-1-
bromo-4-methoxycyclononene(3). The bromination of 1 in
anhydrous methanol was accomplished by the gradual addi-
tion of N-bromosuccinimide (NBS)* to a stirred solution
of 1 in methanol at 0°. The reaction was exothermic.
The product was extracted from an aqueous solution of the
reaction mixture and was concentrated before analysis by
vapor phase chromatography (vpc). Three groups of peaks
were observed (VPC-2).

The second of the three groups consisted of two
peaks in the ratio 40:60 and accounted for 70% of the
total product. The two peaks were readily separable
by vpc, unlike the difficulty encountered during the
separation of dibromocyclononenes obtained by the brom-
ination of 1 in carbon tetrachloride.14 The first of
the two peaks was identified as cis-2-bromo-3-methoxy-

*NBS when used with polar solvents gives results
similar to those obtained when molecular bromine is used.
This is not surprising as the brominating agent when NBS
is used is, indeed, molecular bromine in small concen-
trations.18 Use of NBS is much more convenient than mole-
cular bromine, due to its ease of handling. There has
been no evidence of NBS producing any side reactions.
Even when it was used with water-acetone, no evidence of
oxidation of the bromohydrin to the corresponding bromo-
ketone14 was observed under the conditions like those
described in the experimental section.
cyclononene(2). Elemental analysis was consistent with the empirical formula C_{10}H_{17}BrO. The spectral data* was consistent with the proposed structure: nmr (NMR-4) 
\[ \gamma 3.69 (t, 1, J = 8.5 \text{Hz}, -\text{CH}=\text{CBr}^-), ~5.58 (m, 1, -\text{CH}_2-\text{OH}), ~6.72 (s, 3, -\text{COCH}_3), ~7.5-8.0 (m, 2, -\text{CH}_2-\text{C}=\text{C}), ~8.0-9.0 ~\text{(m, 10, } -(\text{CH}_2)_5^-) \] (The interpretation of the nmr spectrum is completely analogous to the interpretation of the nmr spectrum of cis-2,3-dibromocyclononene as reported by Wedegaertner and Millam.\(^{40}\)); mass spectrum (MS-1) m/e (rel intensity) 234(35) 232(38) (P, C_{10}H_{17}BrO), 202(6) 200(5) (C_9H_{13}Br^+, P - \text{CH}_4O), 164(51) 162(51) (C_5H_7BrO^+, P - C_5H_{10}), 153(56) (C_{10}H_{17}O^+, P - \text{Br}), 121(87) (C_9H_{13}^+, P - \text{CH}_4\text{BrO}), 96(74) (C_7H_{12}^+, P - C_3H_5\text{BrO}), 71(100) (base peak). The ultra-violet (uv) absorption at \( \lambda \text{max 208 } \text{m}\mu \) (\( \varepsilon \approx 7000 \)) arises from the vinyl bromide system -\text{CH}=\text{CBr}-. This conclusion was reached after discovering that compounds with known structures whose only common structural features was that they were cyclic, and had the vinyl bromide system also displayed maximum absorption very close to \( \lambda \text{max 208} \). Two such compounds, cis-2,3-dibromocyclononene\(^{40}\) and 2-bromo-3-hydroxycyclooctene\(^{7}\) displayed absorption at \( \lambda \text{max 210 and 208 } \text{m}\mu \) respectively (\( \varepsilon \approx 7000 \) for both).

The second peak of the second group of products

*The form and abbreviations used in presenting the spectral data were those recommended for authors by the editors of the Journal of Organic Chemistry.\(^{29}\)
was identified as cis-1-bromo-4-methoxycyclononene (3). The elemental analyses and mass spectroscopy established 3 to be an isomer of 2. Attempts were made to isomerize either isomer to the other. Dilute solutions of each compound and iodine crystals dissolved in dry pentane were irradiated with a 60 watt incandescent light bulb from one hour to several days. Vpc analyses at various times showed no evidence of isomerization. The experiment was based upon a successful isomerization reaction discussed by Noyes and coworkers.\textsuperscript{30} Lack of isomerization coupled with the fact that the mass spectrum of 3 (MS-2) was markedly different from the mass spectrum of 2 (MS-1), cast serious doubt as to the possibility that the isomer in question was trans-2. It is generally accepted that geometrically isomeric alkenes produce identical mass spectra.

The lack of reaction of 3 (and 2) with dilute and concentrated hydrochloric acid or cold alcoholic silver nitrate eliminated the possibility that the structure of 3 might be 2-methoxy-3-bromocyclononene. If 3 were of the above structure, hydrochloric acid should have easily hydrolyzed the enol ether, and silver ions should have reacted with the allylic bromide ions.

The spectral data available was in good conformity with the proposed structure for 3. The uv absorption of 3 at $\lambda_{\text{max}}$ 208 mp ({$\epsilon$} 7000) indicated the presence of the
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vinyl bromide system as in 2. The nuclear magnetic resonance (nmr) of 3 (NMR-5) was consistent with its proposed structure, although not unambiguously so without using double irradiation. The triplet at \( \tau 4.08 \) represents the vinyl proton on C-2 (-CBr=CH-) split by the two methylene protons on C-3 (\( J = 9.0 \) Hz). The methine proton (-CH-OCH\(_3\)) on C-4 absorbs at \( \tau 6.77 \). Interestingly enough, its chemical shift coincides with that of the methoxy protons (C-OCH\(_3\)), absorbing, also, at \( \tau 6.77 \) as a singlet. The chemical shift of the C-4 methine proton as compared with the methyl protons of the methoxy group is higher field than expected.\(^{34a}\) The multiplet centered at \( \tau 7.4 \) is due to the methylene protons (=CBr-CH\(_2\)-) on C-9. The other allylic methylene protons on C-3 (-CHOCH\(_3\)-CH\(_2\)-CH=C) appear as a doubly split doublet, at \( \tau 7.68 \) split by the methine proton on C-4 (\( J = 6.0 \) Hz) and the vinyl proton on C-2 (\( J = 9.0 \) Hz). All ambiguity in the interpretation of the nmr was removed when spin-spin decoupling was used. Irradiation at \( \tau 7.68 \), the allylic region where the methylene protons on C-3 absorb, caused the triplet at \( \tau 4.08 \), the vinyl proton at C-2, to collapse to a singlet. In turn, irradiation at \( \tau 4.08 \) collapsed the double doublet at \( \tau 7.68 \) to a doublet. Irradiation of the methine proton region at \( \tau 6.77 \) also collapsed the allylic protons at \( \tau 7.68 \) to a doublet. The mass spectrum (MS-2) of 3 was sig-
nificantly different from that of 2: m/e (rel intensity)
234(2) 232(2) (P,C_{10}H_{17}Br0), 153(96) (C_{10}H_{17}O^+, P - Br),
121(98) (C_{9}H_{13}^+, P - CH_2Br0), 79(42), 71(100) (base peak),
67(38).

Bromination of 1 in anhydrous methanol using
molecular bromine also produced 2 and 3 in roughly the
same ratio, together with the other two sets of peaks
produced in the bromination reaction using NBS.

Reactions of lithium with cis-2-bromo-3-methoxy-
cyclononene (2) and cis-1-bromo-4-methoxycyclononene (3).
Further substantiation for the assigned structures for 2
and 3 was provided by the reduction of 2 and 3 by lithium
metal (Scheme 1).

Reaction of 2 with lithium metal in tetrahydrofuran
gave after aqueous work-up the elimination product 1,2-
cyclononadiene (1) and cis-3-methoxycyclononene (7). 2
The alkenyllithium intermediate 5 was presumably the
precursor to both. The nmr of 1 was consistent with
the proposed structure: (NMR-7) \( \tau \) 4.50 (m,2,-HC=CH-),
5.82 (m,1,-CH -OCH_3), 6.72 (s,3,(C-OCH_3), 7.6-8.2
(m,2,-CH_2-C=C), 8.2-8.9 (m,10,-(CH_2)_5-).

The reaction of lithium with 3 in all probability
produced the alkenyllithium compound 6 which upon hydro-
lysis yielded cis-4-methoxycyclononene (8). The nmr was
in accord with the proposed structure for 8: (NMR-8)
\( \tau \) 4.45 (m,2,-HC=CH-), 6.69 (m,4,-CH-OCH_3), 7.35-8.05
(m,4,CH_2-C=C-CH_2), 8.05-8.80 (m,8,-(CH_2)_4-). Although
the nmr is consistent with the structure assignment for 
8 it does not exclude the possibility of the methoxy 
group being located on other carbons in the ring besides 
C-3 and C-4. The only other positions available are 
C-5 and C-6. Placing the methoxy group on C-6 would make 
the molecule symmetrical thereby making the vinyl protons 
equivalent. C-6 can be excluded on the basis that there 
are at least two sets of triplets at the vinyl region 
instead of a clean triplet. C-5 cannot be excluded on 
nmr arguments alone. Nevertheless, the fact that the Li 
reduction of 3 did not produce 1 considered along with 
the nmr evidence suggests that the methoxy group is 
definitely not located on C-3.

The lack of absorption at 965 cm\(^{-1}\) in the infra-
red (ir) spectra of 7 and 8 and the presence of a medium 
absorption at 740 and 735 cm\(^{-1}\), respectively, indicates 
that the configuration about the double bond is \textit{cis}.\textsuperscript{27} 

Normant,\textsuperscript{28} in his review article on alkenylmagne-
nesium halides, citing several references points out 
that it has been proved that both the formation of the 
alkenylmagnesium halide and its subsequent reactions 
proceed without any stereochemical change. Similar 
conclusions had been reached for the lithium alkenyls.\textsuperscript{11} 
Applying this to the lithium reduction of 2 and 3 would 
imply that the stereochemical orientation about the 
double bonds in 2 and 3 are also \textit{cis}.
Elimination and High-boiling products of the bromination of 1,2-cyclononadiene (1). The first group of peaks (mainly two, 4a and 4b, VPC-2) that appear upon the vpc analysis of the product mixture of the bromination of 1 in methanol are generally studied as a mixture. These peaks represent isomers with the empirical formula C₉H₁₃Br. The structures of 4a and 4b are not completely determined. The nmr showed that the proton distribution was three in the vinyl region and ten protons in the allylic and methylene region, indicating that 4a and 4b are vinyl bromocyclononadienes.

Both 4a and 4b display uv absorption at $\lambda_{\text{max}}$ 210 μm (ε 8000) indicating the presence of the vinyl bromo system. Whether or not the dienes are conjugated is still in question. It has been reported by Baird and Reese³ that 2-bromo-1,3-cyclononadiene has a $\lambda_{\text{max}}$ (shoulder) at 260 μm (ε 825).³ Unsubstituted cis-trans-1,3-cyclononadiene¹² absorbs at $\lambda_{\text{max}}$ 220 μm (ε 2500) and cis-trans-1,3-cyclodecadiene⁵ absorbs at $\lambda_{\text{max}}$ 222 μm (ε 7250). However, cis-cis-1,3-cyclodecadiene shows no maximum absorption in the 215-230 μm region.⁵ In the ten membered dienes the cis-cis isomer seems to be sufficiently "rigid" that its two double bonds are unable to assume a coplanar arrangement. Consequently, 4a and 4b might very well be cis-cis-1,3-cyclononadienes, displaying absence of evidence for resonance due to conjugation.
Framework molecular models (Prentice-Hall) of cis-cis-1-bromo-1,3-cyclononadiene and cis-cis-2-bromo-1,3-cyclononadiene clearly show that resonance due to conjugation is difficult if not impossible. The structure of the compound reported by Reese would, then, have to be cis-trans or trans-cis-2-bromo-1,3-cyclononadiene.

The high boiling products observed in varying ratios were not identified. Vpc retention times of authentic samples of 2,3-dibromocyclonene (9) and 1,4-dibromocyclonene (10) crudely overlapped this unknown set of products. However, the presence of at least five well defined peaks indicated that there are other products besides 9 and 10 if, indeed, two of the five peaks are 9 and 10.

B. BROMO ADDUCTS OF 1,2-CYCLONONADIENE (1)

cis-2,3-Dibromocyclonene (9) and cis-1,4-dibromocyclonene (10). The bromination of 1 with molecular bromine in carbon tetrachloride was carried out exactly as described by Wedegaertner and Millam. The major products have been identified as cis-2,3-dibromocyclonene (9) and cis-1,4-dibromocyclonene (10) in a 4:6 ratio respectively (Scheme II). The identification of 9 was originally made by Wedegaertner and Millam. However, it was Reese and Shaw that, correctly, determined the structure of 10.
SCHEME II
The vpc analysis of the bromination product produced evidence that \(14\%\) of the product corresponded to \(4\).

The methanolysis of cis-2,3-dibromocyclononene (9) and cis-1,4-dibromocyclononene (10). A 40:60 mixture of 9 and 10 dissolved in methanol was stirred for 6 days at room temperature. The vpc analysis (VPC-6) indicated that about 60\% of the dibromides 9 and 10 had reacted to produce 2 and 3 in the ratio of 40:60.

Silver ion assisted methanolysis of a mixture of 9 and 10 in the same ratio as above, showed evidence of complete reaction. The vpc analysis (VPC-5) of the worked up reaction product after 10 min. stirring of a dilute methanolic solution of 9 and 10 with a slight excess of silver nitrate, showed that the starting material had completely disappeared and 2 and 3 had been produced. The bromoethers 2 and 3 in the ratio of 20:80 represented 50\% of the total peak area. Ten per cent of the products corresponded to 4. The remaining 40\% appeared in two peaks in the ratio of 70:30 at very long retention times compared with those of 2 and 3. It is suggested that these two peaks represent cis-2-bromo-3-hydroxycyclononene (11) and cis-1-bromo-4-hydroxycyclononene (12) produced as a result of the hydrolysis of the corresponding nitrate esters. This possibility has not been confirmed.

It is most reasonable that 9 produced 2 and 10.
produced 3. This is based chiefly on the fact that in the silver unassisted methanolysis the ratio of the starting materials was the same as the ratio of the products. Although it is conceivable, it is chemically unlikely that there will be a large amount of scrambling of the correspondence of products to starting materials.

cis-2-Bromo-3-hydroxycyclononene (11) and cis-1-bromo-4-hydroxycyclononene (12). The bromination of 1 using NBS in an aqueous acetone solvent system produced a 50:50 mixture of cis-2-bromo-3-hydroxycyclononene (11) and cis-1-bromo-4-hydroxycyclononene (12), together with small amounts of 4 and high boiling products crudely possessing the same retention times as 9 and 10. The main proof of the structure is provided by the nmr spectra. The interpretation of the nmr spectra of 11 and 12 was identical to those of 2 and 3: nmr of 11 (NMR-9) \( \tau \) 3.88 (t, J = 9 Hz, -CH-CBr-), 5.38 (t, J = 7 Hz, -CH-OH), 7.5-8.0 (m, 3*-CH=C=C, C-OH (7.88)), 8.0-9.0 (m, 10-(CH_2)_5-); nmr for 12 (NMR-10) \( \tau \) 4.07 (t, J = 9.0 Hz, -CH=CBr), 6.0-6.5 (m, 1,-CH-OH), 7.0 (s, 1, C-OH), 7.15-7.5 (m, 2, C=CBr-CH_2-), 7.65 (dd, 2, J = 5.0, 9.0 Hz, HOC-CH_2-CH=).

Silver ion assisted hydrolysis of a 40:60 mixture of 9 and 10 left no starting material in producing 11 and 12 in the ratio of 34:65 together accounting for 85% of the product. The remaining 15% of the product is made up of 4. The fact that the hydrolysis of the
structurally established 9 and 10 produced 11 and 12 provides additional proof for the structures of 11 and 12.

The bromination of 1,2-cyclononadiene (1) in acetic acid. The bromination of 1 in glacial acetic acid produced cis-2-bromo-3-acetoxycyclononene (13) and an isomer 14 in the ratio of 34:66 together making up 60% of the product. The other 40% is made up of the products corresponding to 4. The ir of 13 is identical to the ir of an authentic sample. The comparison of the vpc retention times by coinjection with an authentic sample indicated that 14 is not trans-2-bromo-3-acetoxycyclononene. The mass spectrum was consistent with the proposed structure for 13: (MS-4) m/e (rel intensity) 262(1) 260(1) (P, C_{11}H_{17}BrO_2^+), 181(86) (C_{11}H_{17}O_2^+, P - Br), 139(100) (base peak), 121(44) (C_9H_{13}^+, P - C_2H_4BrO_2), 43(38) (C_2H_3O^+, P - C_9H_{14}BrO). The mass spectrum of 14 was significantly different from that of 13: (MS-5) m/e (rel intensity) 262(1) 260(1) (P, C_{11}H_{17}BrO_2^+), 202(26) 200(26) (C_{9}H_{13}Br^+, P - C_2H_4O_2), 181(31) (C_{11}H_{17}O_2^+, P - Br), 121(100) (C_9H_{13}^+, P - C_2H_4BrO_2), 43(98) (C_2H_3O^+, P - C_9H_{14}BrO). Based upon the pattern set by the reactions of bromine with 1 in reactive solvents and the information available it is suggested that the structure of 14 is cis-1-bromo-4-acetoxycyclononene.

The mass spectrum of a mixture of the large
amount of elimination products \( \text{4} \), obtained in the reaction of NBS with \( \text{1} \) in acetic acid, provided additional information pertaining to their structure: (MS-3) \( \text{m/e} \) (rel intensity) 202(14) 200(14) \((\text{P}, \text{C}_{9}\text{H}_{13}\text{Br}^{+})\), 121(100) \((\text{C}_{9}\text{H}_{13}^{+}, \text{P} - \text{Br})\), 93(35), 79(49), 67(27).

C. BRMO ADDUCTS OF 1,3-DIMETHYLLALLENE (15)

Bromination of 1,3-dimethylallene (15) in carbon tetrachloride. The reaction of 1,3-dimethylallene with bromine in carbon tetrachloride gave 97% trans-3,4-dibromo-2-pentent (16) and 3% of cis-16 (Scheme III). The nmr spectrum \( [\delta 3.86 \text{ (qrt, 1, J = h.5 Hz, C=CH), 5.26 (qrt, 1, J = 6.5 Hz, CHBr-CBr=0), 8.18 (d, 3, J = 6.5 Hz, CH}_{3}-\text{CHBr})] \) corresponds closely to that reported for the same compound by Waters, Linn and Caserio. Repetition of the addition reaction at different temperatures did not produce anywhere near the 17% cis product reported by Caserio and coworkers. However, close observation of the nmr spectrum when compared with the assigned values for the cis product reported, indicates the presence of about 3% of the cis isomer.

Bromination of 1,3-dimethylallene (15) in methanol. Bromination of 15 in anhydrous methanol or NBS gave a 90:10 (determined by vpc and nmr) mixture of trans and cis-3-bromo-4-methoxy-2-pentene (17). The nmr of trans-17 is in perfect agreement with the nmr spectrum of trans-3 reported by other workers: \(\text{NMR-6} \ (\delta 4.03)\).
(qrt, 1, J = 6.5 Hz, BrC=CH), 6.32 (qrt, 1, J = 6.5 Hz, CH-OCH₃), 6.85 (s, 3, C-OCH₃) 8.23 (d, 3, J = 6.5 Hz, C=C-CH₃), 8.76 (d, 3, J = 6.5 Hz, CH₃-COCH₃). The nmr of cis-17 evident as minor peaks on the nmr spectrum of the mixture is also consistent with the values given.

Bromination of 15 in methanol produced less than 2% of 16. However, bromination (with Br₂) in a saturated solution of sodium bromide in methanol produced 30% of 16 along with an 85:15 mixture of trans and cis-17, respectively.

Mutual substantiation of structure assignments for 16 and 17 are provided by the silver assisted and unassisted methanolyis of 16 to give 17 with no apparent stereochemical change. The conversion was carried out at room temperature.

![Scheme III](image-url)
CHAPTER III
DISCUSSION

As has been suggested in the introduction, the bromination of 1,3-dimethylallene (15) probably occurs in two steps. First, the bromonium ion intermediates 18 and 19 are formed by bromine reacting with the double bonds of the allenic system. Second, attack of the nucleophile opens the bromonium ion bridge. This results in a trans addition, with the nucleophile becoming attached to the allylic carbon to give the 3-bromo-4-substituted-2-pentene products. The experimental results show that the bromination of 15 stereoselectively produces the trans isomer.

If the first step were the slow step, and also the product determining step, it would imply that the formation of the bromonium ion is stereoselective. Electrophilic attack by bromine to form the bromonium ion 19 (eq 2) would ultimately give the cis product. Bromine attack on the other side of the -bond would give ion 18 which would lead to the formation of the trans product. However, examination of a molecular model (Prentice-Hall) of 15, as illustrated by 15 in eq 2, shows that all the -clouds are relatively open for reaction with bromine. If there were a difference in the transition state energies that would favor the formation of one or the other bromonium ion, that will
subsequently open up to give the products, the transition state that leads to 19 should be favored. The transition state (T-19) that produces the intermediate 19 involves bromine approaching the π-cloud cis to the hydrogen on the double bond not undergoing reaction, whereas the transition state (T-18) that produces 18 involves the bromine approaching the π-cloud cis to the methyl group of the double bond not undergoing reaction. If all sides of the allenic system were equally available, and the rate determining step was the first step, the product should be equally distributed between the cis and trans isomers. However, if the above steric factors were significant, then the majority of the products should be cis. The results show that 83 to 97% of the products are trans. Therefore, it is apparent, that the first step is not the rate determining step. The results can be more readily explained by assuming that the first step is reversible and that 18 and 19 are in equilibrium with each other, because 18 and 19 are in equilibrium with 15.

The second step is the rate determining step. The second step involves the opening of the bromonium bridges of 18 and 19 with the attack of the nucleophile in a direction trans to the bridge. The attack occurs at the allylic carbon, opening up the ring to send the bridging bromine atom to the vinyl position. The
transition states that are involved in the slow step, are probably approximated by 20 and 21. The transition state 20 leads to the trans isomer and 21 to the cis isomer. The trans to cis product ratio would be controlled by the difference in free energies of the transition states 20 and 21.\textsuperscript{11a} The difference in energy is due to the cis vinyl, 1,2-CH\textsubscript{3},Br and 1,3-N,H interactions and the cis vinyl, 1,2-H,Br and 1,3-N,CH\textsubscript{3} interactions, in 20 and 21 respectively. The 1,2,3,-methyl substituted allylic cations 22 and 23 serve as useful models for transition states 20 and 21, respectively.

The energy difference between 23 and 22 is estimated to be 6.0 kcal/mol.\textsuperscript{6} Assuming that the incoming nucleophile would encounter as much steric hindrance as a methyl group would, it could be argued that the energy difference between the transition states 21 and 20 is
about 6 kcal/mol. As it is apparent in the case of the models 22 and 23 the cis vinyl 1,2 interactions are not as important as the 1,3 interactions. This implies that transition state 20 will be of lower energy than transition state 21 and that the predominant product will be the trans-isomer. This is in accord with experiment.

In summary, the suggested mechanism involves the initial formation of 18 and 19 by the electrophilic addition to the allenic system. The intermediates 18 and 19 are in rapid equilibrium with the starting material, consequently are in equilibrium with each other. The product determining slow step is the trans addition of the nucleophile to produce the products, proceeding via two transition states at different energy levels, corresponding to 20 and 21. The stereoselectivity is attributed to the reaction proceeding preferentially via the transition state 20 which has the lower free energy value.

In contrast to the situation with 15 the bromination of 1 produces exclusively the cis isomer. This is true also with oxymercuration and other electrophilic addition reactions. This difference in the orientation about the unreacted double bond of the allenic systems of the open chain allene 15 and 1 is primarily due to the unique geometry of 1. Unlike in 15, only one side of each of the double bonds of the allenic systems of
1 is exposed or unprotected by the methylene bridge.

Bromination of 1 in carbon tetrachloride and reactive polar solvents yielded the cis-2-bromo-3-substituted cyclononene products analogous to the oxymercuration products. However, a significant difference discovered with the bromination of 1 was that the major products were the 1-bromo-4-substituted cyclononenes. These rearranged products result from a 1,5 transannular hydride shift.

Bach has observed that the mechanism for the oxymercuration of 1 is basically the same as that observed for the two step mechanism for the oxymercuration of 15. In turn, the mechanism for the oxymercuration of 15 is analogous to the bromination of 15. Therefore, it is logical to assume that the bromination of 1 also proceeds via a two step mechanism, namely, the initial formation of the bromonium ion intermediate and the subsequent bridge opening by the nucleophile to produce the products.

The mechanism of the bromination reaction of 1 can be analyzed in terms of the possible transition states, as was done in the case of 15. It is reasonable
that the initial step is the formation of the bridged bromonium ions 24 or 25.

\[
\begin{align*}
&\text{(CH}_2\text{)}_6\text{C} \equiv \text{C} \equiv \text{C} \\
&\text{H} \quad \text{H} \quad \text{Br} \\
&\text{C----Br} \quad \text{C} \equiv \text{C} \\
&\text{C----H} \quad \text{C} \equiv \text{C} \\
&\text{24} \quad \text{25}
\end{align*}
\]

The highly strained 25 is produced by the electrophilic bromine coming from the inside of the ring to combine with the side of the allenic double bond that is protected by the methylene bridge. Consequently, the transition state (T-25) corresponding to the production of 25 is probably very high in energy. The sterically crowded 25 in turn can react with the nucleophile to produce the trans products. It is not clear, as to which of the two transition states T-25 or the transition state corresponding to the second step, the production of the trans product (T-trans) would be higher in free energy. Nevertheless, the pathway involving 25 represents a high energy process where the free energy value of T-25 or T-trans is the high point of the pathway.

On the other hand, the formation of 24 goes through a transition state (T-24) lower in energy than T-25. This is due to the fact that the electrophile
combines with the $\pi$-clouds of the allenic system that are protruding away from the ring. The intermediate $2^4$ does not have the bromonium ion sticking into the middle of an already crowded ring, as is the case with $2^5$. Consequently, T-$2^4$ and $2^4$ are probably considerably lower in energy than T-$2^5$ and $2^5$, respectively. The geometry of the intermediate $2^4$ apparently is responsible for the deviation from the reaction pattern set by the open chain allene. As has been illustrated in the drawing of $2^4$, and can be verified by examining models (Prentice-Hall), the methylene bridge is wrapped around in such a way as to make the addition of the nucleophile in a direction trans to the bromonium ion bridge difficult. Although trans opening of the bromonium bridge is stereoelectronically preferred, it is suggested that the nucleophile combines with C-3 of $2^4$ and opens up the ring in a cis direction. The second step, in other words, involves a cis addition of the nucleophile to $2^4$. In support of this proposition is the fact that the major reaction $2^4$ undergoes is the 1,5-hydride shift, which occurs in a direction trans to the bromonium ion bridge. The energy of the transition state corresponding to trans addition to $2^4$ would probably be close to T-trans. Therefore, trans addition to $2^4$ would involve energetically unfavorable interactions similar to those predicted in T-trans. This implies that trans addition to $2^4$ will be of too high an energy to be a significant
Correlating the pathway that produces the cis products with that of the pathways involved in the open chain allene it is possible to estimate, roughly, the relative energy values of the transition states involved. The energy value for T-24 is probably about the same as for the transition state involved in producing 19. The transition state T-cis corresponding to the production of the cis-2,3-product however, is probably higher than 21. The product ratio of 2,3-isomers to 1,4-isomers indicates that T-cis and the transition state (T-hyd) corresponding to the production of 26 are of about the same energy level.

The fact that the energy high-point on the pathway leading to the trans products is probably, considerably higher, forces the reaction to proceed via the lower energy pathway that leads to the cis products. The results indicate that the preference for the cis over the trans pathway is 100% within experimental error.

It would now be logical to theorize that the elimination products 4 are cis-cis-2-bromo-1,3-cyclononadiene arising from 24 and cis-cis-1-bromo-1,3-cyclononadiene arising from the rearranged carbonium ion 26 after the transannular 1,5-hydride shift.

The recent work by Bach provides an interesting comparison. He reacted optically active 1 with various mercuric salts in ethanol to produce the organomercury
compounds which were in turn (in situ) reduced by boron trifluoride etherate to 3-ethoxycyclononene. The optical activity of the resulting cis-3-ethoxycyclononenes was measured and tabulated corresponding to the salts used. The production of optically active cis-3-ethoxycyclononene from its corresponding organomercury compound provides convincing evidence for the presence of the bridged mercurinium ion. The optical purity of the product, however, varied due to racemization caused by the formation of an allylic carbonium ion in equilibrium with the mercurinium ion, racemization increasing with increasing electrophilicity of the substituent on the mercury atom.

The absolute configuration of the cis-3-ethoxycyclononene is not known, but if established it would permit one to decide whether the stereochemistry of the addition in this case was cis or trans, inasmuch as the absolute configuration of the optically active starting material 1 was known.\textsuperscript{10}

The above work might raise the question of whether or not resonance stabilized allylic ions such as 27 and 28 might also participate in the bromination reactions.
of 1. The possibility of forming the rearranged product by a 1,5-hydride shift from 27 and 28 seems to be unlikely for several good reasons. (1) Models of 27 and 28 indicate that hydride transfer from 5 or 5' to 1 or 1' is physically impossible. (2) The process of forming a secondary carbonium ion on C-5 or C-5' is thermodynamically an "uphill" process. (3) Acetolysis of 9,9-dibromobicyclo(6.1.0)nonane which goes through a resonance stabilized allylic ion does not produce any rearrangement. However, it is conceivable that intermediate 24 produces all the rearranged product but 27 (with attack at C-1 only) or 28 arising from 24 produces the cis normal addition products. The possibility of the allylic carbonium such as 28 participating in the formation of the cis-2,3-disubstituted cyclononenes cannot be completely ruled out. However, it would seem more likely that the cis-2,3-disubstituted cyclononenes and 26 both arise directly from 24.

Scheme IV summarizes the most reasonable overall picture of the bromination of 1. The initial reaction involves the formation of an intermediate 24 produced by the reaction of bromine with the exposed sides of the allenic system. Similar to the situation in the bromination of 15, 24 probably is in equilibrium with 1. However, for prohibitive energy considerations, 25 and the pathway it represents is excluded. The intermediate
SCHEME IV

\[ \text{Br, } \text{H} \]

\[ \text{Br} \]

\[ \text{X} \text{or} \text{HX} \]

\[ \text{X} = \text{OCH}_3 \ (2, 3) \]
\[ = \text{Br} \ (9, 10) \]
\[ = \text{OH} \ (11, 12) \]
\[ = \text{OC}_2\text{H}_3 \ (13, 14) \]

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24, in turn, undergoes one of three reactions, (1) eliminates a proton to produce cis-cis-2-bromo-1,3-cyclononadiene (4), (2) undergoes ring opening as a result of a cis addition by the nucleophile to produce the cis-2-bromo-3-substituted cyclononene products, and (3) undergoes a 1,5-hydride shift to produce the rearranged carbonium ion 26. Simultaneously with its production or subsequently 26 either eliminates to give cis-cis-1-bromo-1,3-cyclononadiene or reacts with a nucleophile to give the cis-1-bromo-4-substituted products.

The fact that the bromination of 1 produced transannular hydride transfer and the addition to 1 with other electrophiles reported earlier, did not, certainly implies that the alkenyl bromonium ion is different from the bridged mercurinium ion, for example. The nature of this bromonium ion deserves more study.

When the work reported in this thesis was nearly complete it was learned that two groups of workers headed by Reese 4 in Cambridge, England, and Caserio 8 at UC Irvine have brominated 1 and have confirmed much of the results presented here. By using optically active 1, Caserio and coworkers have shown that both the normal addition and transannular hydride shift are at least in part stereospecific.
CHAPTER IV
EXPERIMENTAL

An Aerograph P-90 (Varian Aerograph Inc.) gas chromatograph fitted with a 5 ft. x 1/4 in. or 10 ft. x 1/4 in. pyrex glass column was used. The columns were packed with 10% carbowax 20M (polyethylene glycol) on Aeropack-30 or varopack, 80/100 mesh (both from Varian Aerograph), or hexamethyldisilane (HMDS) treated 80/100 mesh Chromosorb P (Johns Manville). All gas chromatographic (VPC) analyses and preparative gas chromatography were made using the above columns, except when otherwise noted. All analyses were made isothermally at suitable temperatures and each new analysis was continued from two to three times the time required for the last component to appear. In most cases, only column temperatures (°C) are reported. The injector temperature is generally about 30° above the column temperature and the detector temperature is, in turn, about 30° above the injector temperature. The presence of a large peak soon after injection in the chromatograms is due to solvent present because the sample is a concentrated, crude, reaction product, or the solvent had been intentionally added to facilitate better separation. Pure components of a mixture of reaction products are isolated by preparative vpc. The collecting device consists of a
bent glass tubing, one end of which fits into the exit port of the gas chromatograph and the other end leads through a 2-holed stopper to the bottom of a centrifuge tube. The other hole of the stopper is also fitted with a bent glass tubing that barely reaches below the stopper. A length of rubber tubing is used to close the device immediately after collection by fitting over the open ends of both glass tubings. Generally the receiving tube is cooled in an icebath.

The infrared spectra (ir) were obtained using either a Perkin-Elmer sodium chloride prism model 137 spectrophotometer or a Perkin-Elmer model 337 grating spectrophotometer. All samples were run "neat" between KBr or NaCl plates and/or liquid cells. All absorptions are reported in cm\(^{-1}\).

Refractive indexes were obtained on a Bausch and Lomb Abbe-3L refractometer.

All boiling points are reported in degrees centigrade. The distillation pressure was measured by a McLeod guage.

The ultraviolet (uv) spectra were obtained using a Perkin-Elmer visible-ultraviolet Model 202 spectrophotometer with silica cells (1.0 cm path length). 95% ethanol was used as the solvent for all runs.

Melting points were determined with a Thomas-Hoover Uni-Melt capillary melting point apparatus.
Elemental analyses were carried out by Alfred Bernhardt, Mikroanalytisches Laboratorium, 5251 Elbach über Engelskirchen, Fritz-Pregl-Strasse 14-16, West Germany.

The author is grateful to Dr. G. E. Pollard at the Shell Development Company in Modesto, California, and Dr. A. T. Bottini and his students, Mr. Ken Frost and Mr. Ross Fitzgerald, at the University of California at Davis, for determining the nmr spectra. In each case a Varian A-60 (60 MHz) instrument was used using carbon tetrachloride as the solvent and tetramethylsilane (TMS) as an internal standard. The nmr spectra with double irradiation were obtained on Joelco MH 100 (100 MHz) spectrometer. Chemical shift values are reported in $\gamma$ units relative to TMS. The author is also indebted to the Chemistry Department at the University of Rochester, Rochester, New York, for the mass spectra.

The essential chemicals used are listed below with a brief description of its purity.

Acetic acid (Baker-Adamson, glacial) was used as received. It was observed to be pure by vpc.

Acetic anhydride (Matheson, Coleman and Bell, practical) was used as received.

Acetone (J. T. Baker, reagent) was used as received. It was vpc pure.
Bromine (Merck and Co. and Mallinckrodt Chemical Works, analytical reagent grade) was used as received.

Bromoform (Matheson, Coleman and Bell) was distilled (colorless fraction 144-145°) before use.

N-Bromosuccinimide (NBS) (Arapahoe Chemicals, Inc., mp 179-180°) was used without purification.

cis and trans-2-Butene (Matheson, Coleman and Bell) was used as received.

Carbon tetrachloride (Eastman Organic Chemicals, spectrophotometric grade) was used as received.

Cyclohexane (J. T. Baker, analyzed) was re-distilled (bp 81.5°).

Cyclooctene (Aldrich) was distilled (bp 143-145°) before use.

1,2-Dibromoethane (Eastman Chemical, white label) was used as received.

Diethyl ether (Merck, anhydrous ether) was generally used as received. However, when used as a solvent in reactions it was distilled from lithium aluminium hydride or calcium hydride and stored over Dri-Na (J. T. Baker, sodium-lead alloy).

Lithium (Foote Mineral Co., high purity, covered with petrolatum) was used soon after the petrolatum was
washed off with diethyl ether. Transferring and subsequent reaction was generally carried out under dry nitrogen gas.

Methanol (J. T. Baker, laboratory grade) was purified by the procedure of Feiser\textsuperscript{13} (bp 66\degree).

Methyl iodide (Fischer, certified reagent grade) was used directly. The chemical was only slightly discolored.

The methyllithium used for the syntheses of the various allenes was initially prepared by the method of Gilman, \textit{et al.}\textsuperscript{16}, however, in subsequent syntheses, methyllithium supplied as an ethereal solution by Foote Mineral Co. was used as supplied. Unused methyllithium solution, after the factory seal was broken, was stored under dry nitrogen in the refrigerator.

Pentane (Eastman Chemical, oleum and permanganate washed, practical) was used as received as the solvent for carrying out reactions. The pentane used in the first few reactions was prepared by the procedure of Millam\textsuperscript{24} (bp 40-50\degree).

Petroleum ether (J. T. Baker, reagent) was used as received. It is stored over a drying agent such as Dri-Na.

Potassium \textit{t}-butoxide (K and K Laboratories) was used as received. It was always dispensed, used and stored under dry nitrogen.
Tetrahydrofuran (J. T. Baker, analyzed reagent) was treated with potassium hydroxide and redistilled from sodium metal (bp 65.5°C).

Many of the reactions produce several products and in all cases the product ratios are determined by gas chromatography (vpc). Most of the compounds corresponding to the peaks of the chromatograms have been, at least partially, determined. In most cases where a variety of products resulted from a reaction, no attempt has been made to obtain yield data.

The product ratios are presented as percentages and are calculated from the integration patterns obtained with the use of the Disc integrator fitted to the Leeds Northrop Speedmax W recorder that is attached to the chromatograph. The ratios are uncorrected for differences in thermal response and are generally of the crude reaction mixture soon after the reaction has been quenched, washed, extracted and dried, and sometimes concentrated.

The physical properties, spectral and other data are presented, basically, in the form recommended for authors by the editors of the Journal of Organic Chemistry.29

9,9-Dibromobicyclo (6.1.0) nonane. The 9,9-dibromobicyclo (6.1.0) nonane was prepared by the method of von Doering and Hoffman37 and adapted from the des-
cription of the above method by Millam. The vpc (5 ft.-col. 185°, He 200 ml/min, 6 min) after vacuum distillation showed that the product was over 99% pure: bp 90° (0.6mm); n^25_D 1.5519 (lit. 35 bp 80-82° (0.1mm); n^20_D 1.5520; ir (IR-1) 2950, 2900 (C-H) (lit. 24 identical).

1,1-Dibromo-2,3-dimethylcyclopropane. The experimental procedure was similar to that used in the preparation of 9,9-dibromobicyclo (6.1.0) nonane.

To a 1-l. three-neck round-bottom flask was fitted a mechanical stirrer, and a dry ice condensor filled with a methanol-dry ice mixture (-30°). Potassium-t-butoxide (100g, 0.895 mol) and 350 ml of dry pentane were stirred to a slurry at 0°. By means of a tube inserted through the third neck of the flask 40.0g (0.714 mol) of 2-butene was added slowly to the slurry, making sure the end of the tube was at all times below the surface of the stirring reaction mixture. The weight of the 2-butene gas was determined by monitoring the weight of the lecture flask that contained the gas while the addition was being made. To facilitate the proper transportation of the often condensed 2-butene gas, a flow of dry nitrogen gas was added to the 2-butene gas flow by means of a T-tube. The entire reaction was carried out under dry nitrogen atmosphere.
After the 2-butene was added 156 g (0.600 mol) of bromoform dissolved in 100 ml of pentane was added dropwise over a period of 9 hr at 0°. The reaction mixture was stirred for an additional 12 hr at 0°, after which it was washed with 500 ml of water. The reaction flask was washed with 500 ml of water and 500 ml of low boiling petroleum ether. The combined organic solutions were washed with water until neutral and dried (MgSO₄). The pentane and petroleum ether was removed by flash distillation. After two fractional distillations, using a vigreux column, 89.4 g (65.5%) of the product was obtained. The vpc (5 ft.-col 155°, He 9 ml/min) peak at 6 min was over 97% of the total peak area: bp 59-61° (24mm); \( \mu_{24.5}^D \) 1,5105; ir (IR-2) 2900, 2860 (C-H).

Anal. calcd for C₅H₈Br₂: C, 26.36; H, 3.54; Br, 70.19. Found C, 26.41; H, 3.67; Br, 70.19.

1,2-Cyclononadiene (1). The 1,2-cyclononadiene was prepared by the method of Moore and Ward²⁵ as described by Millam.

The 1,2-cyclononadiene prepared as described from the reaction of methyl lithium with 9,9-dibromo-bicyclo(6.1.0)nonane was 99% pure by vpc analysis (5 ft.-col 210°, He 7 ml/min): bp 45° (3mm); \( \mu_{23}^D \) 1,5046; (lit. bp 58° (6mm); \( \mu_{22}^D \) 1.5061); ir (IR-3) 1960 (C=C=C); ir (IR-3) 960 (C=C=C) (lit.²⁴ identical).
1,3-Dimethylallene (15). The experimental procedure for the synthesis of the allene was the same as that used for the synthesis of 1,2-cyclononadiene, with a few minor adaptations.

Vapor phase chromatography using a 5 ft. x 1/4 in. aluminum column packed with 10% SE-30 on hexamethyldisilane treated 80/100 mesh chromosorb P (Johns Manville), showed that petroleum ether, the solvent that is used for extraction and washing purposes in the synthesis of 1, is completely unsatisfactory for vpc analysis. The allene appears as one of the peaks among the several peaks corresponding to the several component compounds of petroleum ether. The column, treated with 10% carbowax that is generally used, was unable to separate the components of petroleum ether, much less the allene from the petroleum ether.

A fairly good yield of allene was obtained using anhydrous diethyl ether throughout the synthetic procedure, both as a reaction solvent and for extraction. The ether was distilled off using a 3 ft. spinning band column (Nester Faust) and the allene, upon simple distillation of the concentrated product, was obtained in three fractions of varying degrees of purity, the only contaminant being diethyl ether. The third fraction was greater than 98% pure, determined by vpc analysis (the above SE-30 column 25° (rt), He 100 ml/min,
3-5 min). The physical properties were observed with respect to this the third and most pure fraction: bp 48°; n\textsuperscript{25}D 1.4191; ir (IR-4) 1970 (C=C=C).

The bromination of 1,2-cyclononadiene in carbon tetrachloride. To a stirred solution of 6.34 g (0.052 mol) of 1,2-cyclononadiene (1) in 25 ml of carbon tetrachloride, under dry nitrogen at -20° a solution of 9.0 g (0.056 mol) of bromine in 30 ml of carbon tetrachloride was added dropwise over a period of about 0.5 hr. The addition was stopped as soon as the brown color of the bromine persisted. The reaction mixture was allowed to stir under the above conditions for an additional five minutes. 2-Butene gas was bubbled through to remove excess bromine. The reaction mixture was then washed with water (4 x 25 ml) and dried (MgSO\textsubscript{4}) and concentrated by flash distillation under reduced pressure (water aspirator). A single distillation product was obtained by fractional distillation through a small vigreaux column. VPC with a fresh column (VPC-1, 5 ft.-col. 160°, inj. 200°, det. 230°, He-flow 300 ml/min) of an approximately 10% (V/V) of the above dibromide product in pentane analyzed at the maximum attenuation provided on the chromatograph yielded the following results: the large solvent peak was followed by a set of three small peaks in the ratios of 1:3:8 appearing at 1.3, 1.6 and 2.0 min respectively. These peaks
corresponded to peaks representing (4) and together account for 14% of the total peak area. The two large peaks identified as dibromocyclononenes by VPC analysis with an authentic sample prepared by Millam,\textsuperscript{24} appeared in the ratio 35:65 at retention times, 11.9 and 13.3 min respectively. The two peaks together, comprised 78% of the total peak area.

The first one corresponds to cis 2,3-dibromo-cyclononene (9) and the second to 1,4-dibromocyclononene (10). The unidentified products (8%) appeared in equal amounts at 9.2 and 14.7 min. A few physical properties obtained on the dibromocyclononene mixture compared favorably to those obtained on a similar mixture by Millam: bp 85° (0.2 mm); \( \eta^2_28 \equiv 1.5605 \) (lit.\textsuperscript{40} bp 84° (0.2 mm); \( \eta^2_{23} \equiv 1.5671 \)); uv max (95% EtOH) 210 mpl (\( \varepsilon \) appr. 7000); its IR (IR-5) spectrum is identical to that obtained by Millam.

The bromination of 1,3-dimethylallene (15) in carbon tetrachloride. The procedure followed was similar to that used for the bromination of 1,2-cyclononadiene (1).

To a stirred solution of 1.09 g (0.016 mol) of 15 in 10 ml of carbon tetrachloride, a solution of 0.77 ml (0.015 mol) of bromine in 10 ml of carbon tetrachloride was added dropwise over a period of 20-30 min. The reaction mixture was stirred for an additional 5 min. The reaction mixture was honey colored, and the color

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did not disappear upon several washings with deionized water. Towards the end of the washing the color turned pink and persisted. The pink color was ascribed to free iodine. The source of the iodine impurity was not conclusively determined, however, it is suggested that it was introduced during the washings and admitted as iodide and oxidized by the free bromine present. The color was removed by titrating with a dilute solution of sodium thiosulfate. After several more washings the clear, colorless solution was dried (MgSO₄) and analyzed by vpc (5 ft.-col 145⁰, He-flow 75 ml/min, 5 min). One component, trans-3,4-dibromo-2-pentene (16), other than the solvent was observed: bp 46⁰ (0.3mm); n D 1.5304; ir (IR-6) 3020 (–CH–); nmr (NMR-1, CCl₄) r 3.86 (qrt, 1, J = 6.5 Hz, C=CH), 5.26 (qrt, 1, J = 6.5 Hz, CHBr–CBr=C), 8.18 (d, 3, J = 6.5 Hz, CH₃–CH=C), 8.22 (d, 3, J = 6.5 Hz, CH₃–CHBr) (lit. 39 r 3.78, 5.21, 8.16, 8.20, respectively). Careful observance of the nmr spectrum (NMR-1) indicates the presence of the cis-isomer. Applying the chemical shift values given by Caserio and coworkers 39 to the additional peaks of the methine and vinyl protons and the shouldering of the methyl protons would indicate that there is a small amount of cis-3,4-dibromo-2-pentene.
The reaction of 1,2-cyclononadiene (1) with N-bromosuccinimide in methanol. The experimental procedure for the reaction of 1,2-cyclononadiene (1) with N-bromosuccinimide was adapted from a reaction described by Winstead and Henderson. 41

To a magnetically stirred solution of 14.8 g (0.121 mol) of 1 in 50 ml of anhydrous methanol at 0°, 20.6 g (0.116 mol) of N-bromosuccinimide (NBS) was added in small amounts through a powder funnel, through a claisen head connected to the 250 ml round bottom reaction flask. A water-cooled reflux condenser was fitted to the arm of the claisen head, and the system was flooded with dry nitrogen introduced through the open end of the condenser. The reaction was immediate and exothermic. The reaction mixture was allowed to stir for 4 hr (other times the reaction mixture has been allowed to stir overnight). Undissolved succinimide crystals could be filtered from the reaction mixture, but due to its lack of solubility in ether it was generally left in during the subsequent work-up. 200 ml of ice water and 50 ml of ether were added to the reaction vessel and the ether fraction removed. The aqueous solution was extracted (3 x 50 ml) with ether. The combined ether solution was washed (4 x 50 ml) with water and dried (K₂CO₃). The vpc analysis (VPC-2, 5 ft. col 165°, inj 225°, det 280°, He-flow 29 ml/min) of the
crude concentrated product produced the following results: the solvent and unreacted allene peaks appeared at 0-1.7 min. A group of peaks were observed at 2.5-5.5 min. This group was dominated by two major peaks at 2.9 and 3.6 min in the ratio of 40:60. There are other minor peaks evident, one of these is at 4.7 min. The combined peaks from 2.5-5.5 min comprise 30% of the total product peak areas. The other 70% of the product is made up of two peaks at 11.4 and 13.2 min in the ratio of 40:60 respectively. Starting at 20.5 min the chromatogram indicated the presence of a series of, possibly, highboiling products such as dibromocyclononenes. The total area or the identity of these products was not determined, consequently they were largely ignored.

No reaction nor significant change in product ratio was observed upon treating a product mixture with both dilute and concentrated HCl.

The combined 2.5-5.5 min products 4 were obtained by preparative vpc: $\frac{n^2}{D} = 1.5370$; uv max (95\% EtOH) vpc 2.9 min, 210 μu (ɛ 8000), vpc 3.6 min 210 μu (ɛ 7000); ir (IR7a,b) 3000 (=CH-), 1700, 1600 (C=C); vpc 2.5-5.5 min mixture (NMR-2), vpc 2.9 min (NMR-3);

**Anal. calcd. for C_{9}H_{13}Br: C, 53.65; H, 6.47; Br, 79.91. Found: C, 53.87, 53.83; H, 6.66, 6.58; Br, (39.47), 39.73.**

The 11.4 min vpc fraction 2 was obtained by
preparative vpc: \( n^{26} D = 1.5159 \); uv max (95% EtOH) 208 
mu ( \( \lambda \) 7000); ir (IR-8) 1640 \((C=C)\), 1200 \((C-O-C)\); nmr 
(NMR-4, CDCl3) \( \tau \) 3.69 \((t, 1, J = 8.5 \text{ Hz}, -CH=CBr-)\), 
5.58 \((m, 1, -CH-OCH3)\), 6.72 \((s, 3, C-OCH3)\), 7.5-8.0 
\((m, 2, -CH2-C=C)\), 8.0-9.0 \((m, 10, -(CH2)5-)\); mass spec-
trum (MS-1, 75eV) \( m/e \) (rel intensity) 235(5), 234(35), 
233(5), 232(38), 202(6), 200(5), 177(36), 175(39), 164(51), 
162(51), 153(56), 149(30), 121(87), 96(74), 93(33), 
79(44), 71(100), 67(33), 41(36), 28(45).

**Anal. calcd. for C10H17BrO:** C, 51.52; H 7.35; 
Br, 34.27; 0 6.86. Found: C, 51.39; H, 7.15; Br, 
34.29; 0, 6.89.

The 13.2 min vpc fraction 3 was obtained by 
preparative vpc: vpc analyses with a 10 ft. column 
at 150° produced a shoulder on this peak indicating 
the presence of an additional compound, possibly a geo-
metrical isomer of (9): \( n^{26} D = 1.5185 \); uv max (95% 
EtOH) 208 mu ( \( \lambda \) 7000); ir (IR-9) 1650 \((C=C)\), 1200 
\((C-O-C)\); nmr (NMR-5, CCl4) \( \tau \) 4.08 \((t, 1, J = 9.0 \text{ Hz}, 
-CBr=CH-)\), 6.77 \((m, 4, -CH-OCH3)\), centered around 7.4 
\((m, 2, (=CBr-CH2-)\), 7.68 \((dd, 2, J = 6.0 \text{ and } 9.0 \text{ Hz}, 
-0-CH-CH2-CH=)=, 8.0-9.0 \((m, 8, -(CH2)4-)\); mass spec-
trum (MS-2, 75 eV) \( m/e \) (rel intensity) 234(2), 232(2) 
\((P, C_{10}H_{17}BrO)\), 214(1), 212(2), 210(1), 153(96), 121(98), 
79(42), 71(100), 67(38), 28(174).

**Anal. calcd. for C10H17BrO:** C, 51.52; H, 7.35;
Br, 34.27; O, 6.86. Found: C, 51.43; H, 7.16; Br, 34.36; O, 6.76.

Further evidence for the structure was obtained by double irradiation of the nmr. Double irradiation at \( \tau \) 7.68 caused the triplet at \( \tau' \) 4.08 to collapse to a singlet, conversely, irradiation at \( \tau' \) 4.08 collapsed the double doublet at \( \tau \) 7.68 to a doublet. Irradiation at \( \tau \) 6.77 also collapsed the double doublet to a doublet at \( \tau' \) 7.68. The change of multiplicity of the multiplet at \( \tau' \) 6.77 was not observed due to the overlapping of two peaks at the same region.

The reaction of 1,3-dimethylallene (15) with N-bromosuccinimide in methanol. The procedure was identical to that employed in the reaction of 1,2-cyclononadiene (1) with NBS in methanol. The vpc analysis (VPC-3, 5 ft., col 120°, He-flow 46 ml/min) of the concentrated product yielded three peaks at 1.1, 2.3, 3.0 min, with the peak area in the ratio of 89:9:2, respectively. The physical and spectral data presented include the minor products along with the major product, trans-17 obtained by preparative vpc: \( \nu \) 24 \( \text{D} \) 1.4645; ir (IR-10) 3020 (=CH), 1670 (C=C), 1110 (C-O-); nmr (NMR-6, CCl\(_4\)) \( \tau' \) 4.03 (qrt, 1, \( J = 6.5 \) Hz, BrC=CH), 6.32 (qrt, 1, \( J = 6.5 \) Hz, CH-OCH\(_3\)), 6.85 (s, 3, C-OCH\(_3\)), 8.23 (d, 3, \( J = 6.5 \) Hz, C=C-CH\(_3\)), 8.76 (d, 3, \( J = 6.5 \) Hz, CH\(_3\)-COCH\(_3\)).
Bromination of 1,2-cyclononadiene (1) in methanol.

A solution of 2.40 g (0.015 mol) of bromine in 25 ml of anhydrous methanol was slowly added to 1.61 g (0.013 mol) of 1,2-cyclononadiene (1) in 50 ml anhydrous methanol. The reaction was relatively slow. After 2 hr of stirring about 200 ml of water was added to the reaction mixture and extracted with pentane, dried (MgSO₄) and analyzed by vpc (VPC-4, 10 ft.-col 182°, inj 205°, det 250°, He-flow rate 110 ml/min); Two peaks corresponding to 4a and 4b in the ratio of 1:1-2 at retention times 1.9 and 2.3 min, making up 21% of the total peak areas were the first set of compounds to be observed other than the solvent. The next set of peaks 2 and 3 in the ratio of 34:66 appearing at 5.1 and 6.2 min, respectively, accounted for 53% of the product peak areas. The remaining 26% of the products is made up of an unknown series of peaks at 13.1, 14.1, and 15.5-16.0 min in the ratio of 75:23:2.

Bromination of 1,3-dimethylallene (15) in methanol.

To a solution of 0.50 g (0.0072 mol) of 1,3-dimethylallene (15) in 30 ml of anhydrous methanol, chilled in an ice bath, a bromine solution (1.0 g in 25 ml MeOH) was added slowly until the rapid decolorization of the bromine solution stopped and the honey color of a dilute bromine solution persisted. About 200 ml of water was added to the reaction mixture after five min reaction and extracted
with ether (3x). The combined ether extracts were washed (4x) and dried (K₂CO₃). An 88:12 mixture of trans and cis-17 was observed upon vpc analysis (5 ft.-col 120°) making up 99% of the products with less than 1% of high boiling products.

A repetition of the above reaction, but with the reaction now conducted in the presence of bromide ions (the reaction solution being saturated with NaBr), yielded in addition to trans and cis-17 a significant amount of 16 in the ratio of 62:11:28, respectively.

The silver ion assisted methanolysis of cis-2,3-dibromocyclononene (9) and cis-1,4-dibromocyclononene (10). To a stirred solution of 0.36 g (1.3 mmol) of 9 and 10 (40:60 mixture) in 25 ml of anhydrous methanol, 25 ml of a methanolic silver nitrate solution (2.0 mmol in 25 ml MeOH) was added gradually. Reaction was immediate. After 10 min of stirring 0.12 g (10 mmol) of Na₂CO₃ was added and the stirring continued for an additional five min. The reaction was filtered and concentrated. The product was removed from an aqueous solution of the concentrated methanolic solution by extraction with pentane (3x). The combined pentane solution was washed (3x) and dried (MgSO₄). The concentrated pentane solution was vpc analysed (VPC-5, 10 ft.-col 185°, inj 233°, det 282°, He-flow rate 60 ml/min). The product appeared
roughly in three groups except for a lone unidentified peak at 1.9 min making up 7.5% of the total peak area. The first group of peaks is made up of three peaks at 2.8, 3.5 and 3.9 min, in the ratio of 1:3.6:1.8 making up 10.5% of the total correspond to 4. Three more peaks in which the second and third peaks were 2 and 3 appeared in the ratio of 6:17:77 accounting for 45% of the total, at 6.2, 7.3 and 8.8 min, respectively. The last two peaks are 2 and 3. The final two high boiling peaks, making up 37% of the total were divided in the ratio of 71:29 and appeared at 21.4 and 31.0 min respectively. The uv absorbance of the reaction mixture (in 95% EtOH) was at \( \lambda \text{max } 209 \text{ mu.} \)

The methanlysis of cis-2,3-dibromocyclononene (9) and cis-1,4-dibromocyclononene (10). A dilute solution of a 60:40 mixture of 9 and 10 in anhydrous methanol was refluxed for six days. A portion of the reaction mixture was removed after three days of reaction. The reaction mixtures were worked up in the same way as the silver assisted methanlysis. The vpc analysis (VPC-6, 10 ft.-col 182°, inj 205°, det 250°, He-flow rate 110 ml/min) of a concentrated solution of the three-day reaction mixture showed that a 40:60 mixture of 2 and 3 were produced along with 4 and a large amount of the unreacted starting material 9 and 10. The ratio of the combined yield of bromo ethers to the unreacted dibromides,
obtained by vpc peak areas, was 0.52. The vpc analysis (same conditions as above) of the six-day reaction mixture showed the presence of an unknown peak at 1.3 min and accounted for 15% of the total peak area. Three peaks at 2.0, 2.4 and 2.7 min in the ratio 1:3.5:3.5 together made up 7% of the total peak area and represented the peaks of 4. The bromoether peaks 2 and 3 appeared at 5.1 and 6.1 min, respectively, along with an unidentified peak at 4.3 min. The three peaks in the ratio of 4:38:58, respectively, in their chronological order, together made up 78% of the total. The ratio of 2 to 3 was 40:60 and the ratio of the bromoethers to unreacted dibromides was 1.40.

Attempted isomerization of cis-2-bromo-3-methoxy-cyclononene (2) and cis-1-bromo-4-methoxycyclononene (3) using iodine. The procedure followed was adapted from that described by Noyes and coworkers.\textsuperscript{30} Dilute (less than 5%) solutions of the compounds to be isomerized and iodine in pentane sealed in 6 in. x \( \frac{1}{2} \) in. glass tubing were irradiated with a 60 watt incandescent lamp at about a distance of 8 in. for various time periods. The solutions with iodine were irradiated along with similar solutions without iodine. Vpc analyses at time periods of 1 hr. to 7 days showed no change in ratios of mixtures and production of new peaks when pure samples of 2 and 3 were used.
Methanolation of trans-3,4-dibromopentene (16). A dilute solution of 16 in anhydrous methanol was allowed to sit at room temperature for a week. A vpc analysis of the reaction mixture showed that 16 had completely disappeared and the only product was trans-17.

The reduction of cis-2-bromo-3-methoxycyclononene (2) and cis-1-bromo-4-methoxycyclononene (3) with lithium. About 1.3 g (0.19 mol) of lithium ribbon (15 cm in length) was cut up into large 3 cm pieces, after the protective petrolatum was washed away with ether. The 3 cm pieces were scratched and small notches and holes cut into them before adding them to the reaction solution of 1.9 g (8.0 mmol) of a 40:60 mixture of 2 and 3 in 100 ml of pentane in a 250 ml three-neck flask fitted with a water cooled condensor closed with a drying tube. The stirring of the reaction mixture was regulated such that the large pieces of lithium metal rubbed against each other. After 40 hr of reaction (at room temperature), the lithium metal pieces were well dissolved exposing the shiny metal. The cloudy reaction mixture was rapidly filtered in a drybox through a wad of glass wool. The crudely filtered reaction mixture was hydrolyzed with 10% H₂SO₄ until the vigorous reaction ceased and the solution turned clear. About 100 ml of water was added and the product extracted into pentane (3 x 50 ml). The
combined pentane extract was washed (3x) with water and dried (MgSO\(_4\)) and concentrated. The vpc analysis (VPC-8, 5 ft.-col 160\(^\circ\), inj 190\(^\circ\), det 225\(^\circ\), He-flow rate 80 ml/min) showed that the starting materials 2 and 3 completely reacted to give the products, including 1,2-cyclononadiene (1) at 4.6 min which accounted for 21% of the total product. The other 79% of the product was made up of cis-3-methoxycyclononene (7) and cis-4-methoxycyclononene (8) in the ratio 28:51 appearing at 9.0 and 10.5 min, respectively. The ir of the fraction at 4.6 min was identical to that of an authentic sample of 1,2-cyclononadiene (1).

The 9.0 min vpc fraction 7 was collected by preparative vpc: ir (IR-11) 3030 (=CH-), 1660 (C=C), 1110 (C-O), 740 (C=C); nmr (NMR-7, CDCl\(_3\)) \(\gamma\) 4.50 (m, 2, -HC=CH-), 5.82 (m, 1, -CH-OCH), 6.72 (s, 3, -OCH\(_3\)), 7.6-8.2 (m, 2, -CH\(_2\)-C=C), 8.2-8.9 (m, 10, -(CH\(_2\))\(_5\)).

\textbf{Anal. calcd. for C\(_{10}\)H\(_{18}\)O: C, 77.79; H, 11.69.}

\textbf{Found: C, 77.68; H, 11.76.}

The 10.5 min fraction 8 was collected by preparative vpc: ir (IR-12) 3030 (=CH-), 1110 (C-O), 734 (C=C); nmr (NMR-8, CDCl\(_3\)) \(\gamma\) 4.45 (m, 2 HC=CH-), 6.69 (m, 1, -CH-OCH\(_3\)), 6.69 (s, 3, C-OCH\(_3\)), 7.35-8.05 (m, 4, CH\(_2\)-C=CH\(_2\)), 8.05-8.80 (m, 8, -(CH\(_2\))\(_4\)).

\textbf{Anal. calcd. for C\(_{10}\)H\(_{18}\)O: C, 77.79; H, 11.69.}

\textbf{Found: C, 77.24; H, 11.52.}

A small quantity of vpc collected 2 was reacted
with lithium and worked up as above. The vpc analysis (5 ft.-col 160°, He-flow rate 80 ml/min) of the reaction mixture showed that product consisted of 1 at retention time 4.5 min and a new peak at retention time 3.7 min.

Similarly, a quantity of 2 was reacted and the results upon vpc analysis under the same conditions as above showed that the only product was 8.

The reaction of 1,2-cyclononadiene (1) with N-bromosuccinimide in acetic acid. A 0° solution of 3.03 g (25 mmol) of 1,2-cyclononadiene (1) and 4 ml of acetic anhydride in 25 ml of glacial acetic acid was magnetically stirred under dry nitrogen. To this solution, 4.42 g (25 mmol) of N-bromosuccinimide (NBS) was added, in small amounts, through a powder funnel. The reaction was immediate and exothermic. After 2.5 hrs of reaction, enough 10% NaHCO₃ solution was added to neutralize the acid and about 10 ml of excess bicarbonate solution was added. The product was extracted with petroleum ether (3 x 30 ml). The combined ether solution was washed with 10% NaHCO₃ (2 x 50 ml) and water (3 x 50 ml) and dried (MgSO₄). The concentrated reaction mixture was vpc analyzed (VPC-9, 10 ft.-col 160°, inj 190°, det 230°, He-flow rate 140 ml/min). The first set of peaks were the elimination peaks corresponding to 4 the first and last of the set of four peaks were at 1.4 and 2.2 min respectively, together making up 40% of the total product. Analyses of other reaction products and expanded
chromatograms of the above reaction mixture indicate the presence of isomers or other compounds along with 13 and 14 and also the presence of an additional set of two products which appear soon after 13. The retention times of the minor products crudely overlap with the retention times for 9 and 10. However, reaction with methaholic AgNO₃ does not destroy them completely. The other 60% of the product is made up of cis-2-bromo-3-acetoxycyclononene (13) and cis-1-bromo-4-acetoxycyclononene (14) in the ratio of 34:66 appearing at 9 and 14 min respectively.

The 1.4-2.2 min fraction 4 was collected by preparative vpc: ir(IR-13) 3050 (=CH), 1730, 1630 (-C=C-); mass spectrum (MS-3, 20 eV) m/e(rel intensity) 202(14), 200(14), 121(100), 93(35), 79(49), 67(27), 55(11), 43(9), 28(10).

The 9 min vpc fraction 13 was collected by preparative vpc: ir (IR-14) 3030 (=CH-), 1740 (-CO-0-) (lit.⁷ identical); mass spectrum (MS-4, 20 eV) m/e(rel intensity) 262(1), 260(1), 181(86), 139(100), 121(44), 93(16), 79(20), 43(37).

The 14 min vpc fraction 14 was collected by preparative vpc: ir (IR-15) 1740 (-CO-0-); mass spectrum (MS-5, 20 eV) m/e(rel intensity) 262(1), 260(1), 202(26), 200(26), 181(31), 139(14), 121(100), 93(14), 79(15), 67(11), 43(98).
The reaction of 1,2-cyclononadiene (1) with N-bromosuccinimide in aqueous acetone. To a stirred solution of 20 ml of water and 10.0 g (82 mmol) of 1,2-cyclononadiene (1) in 100 ml of acetone 15 g (84 mmol) of N-bromosuccinimide was added cautiously. Vigorous reaction followed with acetone refluxing. After 15 min of stirring, an excess of water was added and the products were extracted with cyclohexane (3 x 50 ml). The combined organic solution was washed (3 x 50 ml) and dried (MgSO₄) and concentrated. The vpc analysis (VPC-10a, 5 ft.-col 180°, inj 220°, det 270°, He-flow rate 160 ml/min) of the reaction mixture showed that apart from 4 and some new peaks in the same area the major products were cis-2-bromo-3-hydroxy-cyclononene (11) and cis-1-bromo-4-hydroxycyclononene (12). However, the peak representing 11 was closely preceded by a set of two peaks appearing in a stepwise manner and they crudely coincided with the retention times for 9 and 10. Treatment with aqueous AgNO₃ removed most of the two peaks. The AgNO₃ created product (VPC-10b) was made up of 11 and 12 appearing at 8.3 and 12.1 min in the ratio of 50:50 with a small amount of the above mentioned impurity at 5-7 min. The nmr spectra are in agreement with those reported for 11 and 12 in the literature. 4

The 8.3 min vpc fraction 11 was collected by preparative vpc: nmr (NMR-9, CCl₄) 7 3.88 (t, 1, J =
9 Hz, -CH=CBr-), 5.38 (t, 1, J = 7 Hz, -CH-OH) 7.5-8.0 (m, 3, -CH₂=C=, -OH(7.88)), 8.0-9.0 (m, 10, -(CH₂)₅-).

The 12.1 min vpc fraction 12 was collected by preparative vpc: nmr (NMR-10, CCl₄) 7.07 (t, 1, J = 9, -CH=CBr), 6.0-6.5 (m, 1, -CH-OH), 7.0 (s, 1, C-OH), 7.15-7.5 (m, 2, =CBr-CH₂-) 7.65 (dd, 2, J = 5, 9 Hz, HOC-CH₂CH=).

Silver ion assisted hydrolysis of cis-2,3-dibromocyclononene (9) and cis-1,4-dibromocyclononene (10). A dilute solution of (2.29, 8 mmol) 40:60 mixture of 9 and 10 in 20 ml of a 90:10 acetone-water solvent was magnetically stirred with a slow addition of an excess of an aqueous AgNO₃ solution (saturated) until precipitation stopped. Additional water was added and the product extracted with cyclohexane (3 x 20 ml). The combined cyclohexane mixture was washed (3 x 30 ml), and dried (MgSO₄). The vpc analysis (5 ft.-col 160°) showed that 15% of the product was 4 and 85% of the product was 11 and 12 in the ratio of 35:65.
BIBLIOGRAPHY


APPENDIX A

GAS CHROMATOGRAMS
VPC-1

The products of the Bromination of 1,2-clononadiene in CCl$_4$
VPC-2

The products of the bromination of 1,2-cyclononadiene (1) in methanol using NBS
The products of the bromination of 1,3-dimethylallene (15) in methanol
The products of the bromination of 1,2-cyclononadiene (1) in methanol using bromine.

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The silver ion assisted methanolysis products of cis-2,3-dibromocyclononene (9) and cis-1,4-dibromocyclononene (10).
VPC-6
The methanolysis products of cis-2,3-dibromocyclononene (9) and cis-1,4-dibromocyclononene (10)
VPC-8
The products of the reduction of cis-2-bromo-3-methoxycyclononene (2) and cis-1-bromo-4-methoxycyclononene (3) with lithium.
The products of the reaction of 1,2-cyclononadiene (1) with NBS in acetic acid.
The products of the reaction of 1,2-cyclononadiene (1) with NBS in aqueous acetone.
The products of the reaction of 1,2-cyclononadiene with NBS in aqueous acetone after treatment with AgNO₃.
APPENDIX B

INFRARED SPECTRA
IR-2

1,1-Dibromo-2,3-dimethylcyclopropane
IR-3
1,2-Cyclononadiene (1)
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IR-7a
Elimination products CnH13Br (4)
IR-9

cis-1-Bromo-4-methoxycyclononene (3)
IR-10

trans-3-Bromo-4-methoxy-2-pentene (17)
IR-11

cis-3-methoxycyclonene (1)
IR-13

Elimination products C₉H₁₃Br (4)
NMR-1

trans-3,4-dibromo-2-pentene (16)
Isomers of C₉H₈Br₃ (4)

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NMR-3

One Isomer of C₉H₁₃Br (4a)
cis-3-methoxycyclononene (7)
cis-4-methoxycyclonene (8)
NMR-9

cis-2-Bromo-3-hydroxycyclononene (III)
MS-1

cis-2-Bromo-3-methoxycyclononene (2)
MS-2

cis-1-Bromo-4-methoxycyclononene (3)