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The Reaction of Chlorine With Cis- And Trans-Cyclodecenes.

Dewitt Boyd Stone Jr

Louisiana State University and Agricultural & Mechanical College

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CYCLODECENES.

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THE REACTION OF CHLORINE
WITH cis- AND trans-CYCLODECENES

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in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in
The Department of Chemistry

by
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ABSTRACT

Convenient syntheses of cis-cyclodecene and trans-cyclodecene have been developed. These syntheses involve radical chlorination of cyclodecane followed by dehydrochlorination. The stereo-selective nature of each dehydrohalogenation was due to a fortuitous combination of ring geometry, solvent, and base to favor either syn or anti elimination. Product distribution data were obtained for the free radical and ionic additions of Cl₂ from molecular chlorine and from iodobenzene dichloride to both cis- and trans-cyclodecene. The addition of molecular chlorine with cis-cyclodecene in CCl₄ under both ionic and radical conditions yields the expected trans-1,2-dichlorocyclodecane. However, trans-cyclodecene reacts under both ionic and radical conditions to give only transannular rearrangement products. Indirect chlorination of cis-cyclodecene with iodobenzene dichloride yields a mixture of 1,2- and 1,6-dichlorides under ionic conditions, but yields only transannular products under radical conditions. The reaction of trans-cyclodecene under both radical and ionic conditions yields only trans-1,6-dichlorocyclodecane. In all cases the allylic product, 3-chlorocyclodecene, is produced.

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Monocyclic aliphatic compounds are classified for convenience as small, common, medium, or large rings. Small rings include the three- and four-membered rings and are so highly strained from bond angle deformation that they readily undergo ring-enlargement or ring cleavage reactions. Rings having five-, six-, or seven-members are widely found in nature, are readily synthesized from acyclic aliphatic compounds or by hydrogenation of aromatic compounds, and are denoted as common rings. Common rings are relatively free of angle strain and generally undergo the same reactions as acyclic compounds except that their cyclic structures restrict the normal rotation about sigma bond axes and thus facilitate stereochemical studies of reaction mechanisms. Large rings contain twelve or more carbon atoms, are only slightly strained and behave chemically similar to the acyclic aliphatic compounds.

The medium-ring classification includes eight-, nine-, ten-, and eleven-membered ring compounds.\textsuperscript{1} Thermochemical combustion measurements indicate that these rings are highly strained. Angle strain (deformation of the C-C-C bond angle) and Pitzer-strain (steric repulsions between bonds and groups on adjacent carbon atoms) account for some of the strain energy, but a major source is steric repulsion between hydrogen atoms bonded to carbon atoms on opposite sides of the ring but compressed together near the center of the ring.
This type of interaction, called transannular ("across-the-ring") strain is responsible for several unusual chemical consequences, including rearrangement reactions. The present investigation has been concerned with the occurrence of rearrangements during the radical and ionic additions of chlorine to cyclodecenes.

These transannular interactions are responsible for the low yields obtained from the classical cyclization reactions when the synthesis of a medium-ring is attempted. For example in the acyloin condensation cyclization:

\[
\begin{array}{c}
\text{COOR} \\
(CH_2)_n \\
\text{COOR}
\end{array} \xrightarrow{\text{Na}} \begin{array}{c}
\text{C=O} \\
(CH_2)_n \\
\text{CH-OH}
\end{array}
\]

and in the Ziegler nitrile cyclization:

\[
\begin{array}{c}
\text{CN} \\
(CH_2)_n \\
\text{CN}
\end{array} \xrightarrow{\text{LiN-Et}} \begin{array}{c}
\text{C=NH} \\
(CH_2)_{n-1} \\
\text{CH-CN}
\end{array}
\]

the yields\(^2\) drop appreciably for medium-ring syntheses:

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Transannular strain is partially relieved by the introduction of one or more trigonal or trivalent atoms into the ring, as evidenced by increased cyclization yields of I over II and III over IV by the acyloin condensation process: 3, 4

![Chemical structures](image)

The degree of transannular strain is reduced by the inclusion of a triple bond in the ring, but the adverse geometric effect (angle strain) of having four atoms in linear arrangement causes the acyloin condensation with alkyne derivatives to fail for eleven-membered and smaller rings.

The study of the chemistry of medium ring compounds has been hindered by the low efficiency of the classical syntheses. Recently, however, a reaction has been developed 5 which produces medium-ring hydrocarbons from 1,3-butadiene and ethylene with nickel biscyclooctadiene as a catalyst:

2 \[\text{\(\text{CH}_2\)} \quad + \quad \text{\(\text{CH}_2\)} \quad \rightarrow \quad \text{\(\text{CH}_2\)}

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Cyclooctane and cyclodecane and various alkenes are now produced commercially with this process followed by catalytic hydrogenation.

The chemical reactions of medium-ring compounds are of interest because the reaction intermediates often undergo transannular rearrangements. If a carbonium ion center is formed adjacent to an electron-withdrawing group, X, the transannular migration of a hydride ion allows the formation of a new, more-stable carbonium ion:

\[
\begin{align*}
&\text{HC-H} + \text{CH} \\
&\text{HC-X} \\
&\rightarrow \\
&\text{HC+} \\
&\text{HCH} \\
&\text{HC-X}
\end{align*}
\]

Thus the acetylation of cis- or trans-1,2-cyclooctanediol ditosylate gives a high percentage of rearranged products, with all products apparently arising from the rearranged intermediate, VI:
The acetolysis of cis-1,4-cyclooctanediol ditosylate yields a mixture of these same products. Thus the rearrangement of V to VI is rapid and irreversible. The destabilizing effect of the para-toluene sulfonate group on an adjacent carbonium ion center has been reported previously. Other reported medium ring reactions involving trans-annular hydride shifts include acid-catalyzed hydrolysis of epoxides and deamination of amines.

Free radical reactions involving the transannular rearrangement of a hydrogen atom are also known. One interesting example involves the reaction of longifolene, a terpene, with bromotrichloromethane:

An example of transannular hydrogen atom transfer recently studied in this research group involves the addition of carbon tetrachloride to cis-cyclooctene:
Yields of up to 73% were obtained of a mixture of cis- and trans-1-chloro-4-trichloromethylcyclooctane.

Other transannular rearrangement reactions involving bond shifts rather than hydrogen or hydride shifts have been reported. The reaction of cis, cis-1,5-cyclooctadiene with carbon tetrachloride under free radical conditions is an example:

A few transannular rearrangement reactions involving carbenes, nitrenes, or other intermediates have been reported. The $\beta$-elimination reactions of medium ring compounds are of particular interest because of the ability of eight-membered and larger ring systems to contain trans as well as cis double bonds. A part of the present work involved the development of stereoselective syntheses of cis- and trans-cyclodecenes from chlorocyclodecane.
using $\beta$-elimination reactions.

The classical bimolecular elimination (E2) reaction involves anti elimination of H and X from adjacent carbon atoms:

$$\text{A} \quad \text{B} \\
\text{Y} \quad \text{Z} \quad \text{C}$$

\[ \text{-HX} \]

\[ \text{Y} \quad \text{Z} \quad \text{C} \]

\[ \quad \text{A} \quad \text{B} \]

\[ \equiv \]

to give a product having the geometry shown. If the conformation having H and X at $180^\circ$ is precluded by bulky A, B, Y or Z groups or by the geometrical requirements of a cyclic system, the activation energy for the elimination rises sharply. For example the dehydrochlorination of the $\beta$-isomer of benzenehexachloride (the only one

\[ \text{C1} \quad \text{C1} \quad \text{C1} \]

\[ \text{C1} \quad \text{C1} \quad \text{C1} \]

\[ \text{C1} \quad \text{C1} \quad \text{C1} \]

of the eight possible stereoisomers which has no hydrogen and chlorine pair situated anti) proceeds at $10^{-4}$ of the average rate of the four other isomers studied.\(^{14}\)

In a recent study,\(^{15}\) DePuy suggests that coplanar transition states, whether anti or syn, are vastly preferable to non-coplanar ones. Thus syn-eliminations are feasible, but are rare due to the infrequent incidence of suitable molecular geometry. One reported example involved the following reaction:
The syn-elimination proceeds through a planar transition state and is faster than the anti-elimination, which must proceed through a non-planar transition state.

Sicher and co-workers have extensively studied $\beta$-elimination reactions in cyclic systems having various leaving groups, using various bases and solvents. In these studies data from kinetics, kinetic isotope effects and isotopic labeling showed that both anti and syn mechanisms operate.

The dehydrobrominations of a series of cycloalkyl bromides (cyclopentyl through cyclooctadecyl) have been studied kinetically for the following base-solvent systems:

- Potassium tert-butoxide in tert-butyl alcohol at $82.5^\circ$ (system A),
- Potassium tert-butoxide in benzene at $100^\circ$ (system B),
- Potassium ethoxide in ethanol at $58.5^\circ$ (system C), and
- Lithium tert-butoxide in dimethylformamide at $40^\circ$ (system D). The rate profiles (dependence of rate constant of cis- and trans-olefin formation on ring size) are shown below:
In systems A and B the reaction leading to the \textit{trans} olefin exhibits a rate maximum in the medium ring region. This is the same type of rate profile that has been shown to be characteristic of the \textit{syn}-eliminations of cycloalkyl`onium salts. A free energy graph of the rates of the system A or system B reactions versus either the rates of cycloalkene formation from cycloalkyldimethylamine oxides or from cycloalkyltrimethylammonium chlorides gives a good linear plot. Thus the reaction which produces \textit{trans}-cycloalkene from cycloalkyl
bromides and potassium tert-butoxide in tert-butyl alcohol or benzene is predominately if not exclusively a syn-elimination process. If the Dunitz conformation of the cyclodecyl ring is assumed, the transition state would resemble

with some lessening of the angle $\phi$ due to steric repulsions of the transannular hydrogen atoms, $H_\phi$. The rate profiles for the production of cis-cycloalkenes in systems A and B indicate that these are predominately anti-elimination processes. This situation wherein a given substrate under a given set of conditions may react by either of these stereoselective mechanisms has been referred to as the "syn-anti elimination dichotomy".

In systems C and D, the rate profiles for dehydrobromination of cycloalkyl bromides indicate that anti-elimination mechanisms lead to both the cis- and trans-cycloalkene products. The explanation for the presence of syn-elimination in systems A and B and the lack of it in systems C and D involves the different capacity of the solvents to support ion-pair formation. The expected order of ion-pair supporting ability is benzene (B) $\gg$ tert-butyl alcohol (A) $\gg$ ethanol (C) $\gg$ dimethylformamide (D). This order corresponds to the amount of syn-elimination found in these four systems. For cyclodecyl bromide, relative amounts of syn-elimination product in

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The transition state likely involves both ions of the base,

and a necessary condition for this mechanism appears to be a solvent in which at least some of the base may exist as an undissociated ion-pair.

The major part of the present work involved the addition of chlorine, from molecular chlorine and from iodobenzene dichloride, to cis- and trans-cyclodecene. The ionic and the free radical additions were studied for both cases.

The electrophilic addition of chlorine to an unsaturated system in a hydroxylic solvent seems to proceed through this mechanism:\textsuperscript{20}

A similar mechanism likely applies in chloroform or carbon tetrachloride, but non-reproducible results in these solvents have
hindered kinetic studies\textsuperscript{21} so that mechanistic details are not definitely known. If the substrate is a medium-ring cycloalkene, the intermediate ion, \textit{III}, will likely undergo transannular rearrangement to a more stable carbonium ion which does not have the adjacent destabilizing chlorine substituent. This type of rearrangement has been reported\textsuperscript{1} for the ionic brominations of \textit{cis}- and \textit{trans}-cyclodecenes. The addition of bromine to \textit{cis}-cyclodecene in carbon tetrachloride at \(-10^\circ\text{C}\) gave \textit{cis}-1,6-dibromocyclodecane. During the reaction HBr was evolved, probably due to the loss of a proton vicinal to the carbonium ion center:

\[
\begin{align*}
\text{Cyclodecene} & \quad + \text{Br}_2 & \quad \rightarrow & \quad \text{cis-1,6-dibromocyclodecane}
\end{align*}
\]

The allylic product was not actually isolated. In the original work the presence or absence of the "normal" \textit{trans}-1,2-dibromocyclodecane was not proved. This compound was recently synthesized\textsuperscript{22} by an ingeneous route which is not complicated by transannular rearrangement.
The trans stereochemistry of the product was confirmed by its reaction with silver acetate to give the known trans-diacetate. Reexamination of the product from the bromination of cis-cyclodecene by preparative chromatography on silica gel showed that 10% of trans-1,2-dibromocyclodecane and 40% of cis-1,6-dibromocyclodecane were formed in this reaction. The relative yields of these two products did not change when the reaction temperature was varied from -10°C to -80°C. The reaction of bromine with trans-cyclodecene under the same reaction conditions yielded a 25% yield of trans-1,6-dibromocyclodecane plus other unidentified products.

The only other reported ionic additions of halogen to a medium-ring olefin are the additions of chlorine\(^{23}\) and bromine\(^{24}\) to cis-cyclooctene to give the normal trans-1,2-dihalocyclooctanes.

The free radical addition of molecular chlorine to alkenes generally proceeds through the following mechanism:

\[
\begin{align*}
\text{Cl}_2 + \text{energy} & \rightarrow 2\text{Cl}^* \\
\text{Cl}^* + \text{C} &= \text{C} \rightarrow \text{C-Cl} \\
\text{C-Cl} + \text{Cl}_2 & \rightarrow \text{C-Cl} + \text{Cl}^* \\
\text{C}^* + \text{Cl}_2 & \rightarrow \text{C-Cl} + \text{Cl}^* \\
\end{align*}
\]

etc.
Recent studies have shown, however, that in some cases initiation does not require external energy but can occur even in the dark at $-70^\circ C$ by a process known as "induced homolysis".  

\[
\begin{align*}
\text{Cl}_2 + \text{C} &= \text{Cl}_2^+ + \text{C} \\
\text{Cl}_2^+ + \text{C} &= 2\text{C-Cl} \\
\text{C-Cl} + \text{Cl}_2 &= \text{C-Cl} + \text{Cl}_2^+
\end{align*}
\]

(a complex)

In a chain process such as these, many molecules of product may be produced by only a few initiation reactions.

Iodobenzene dichloride (IBD) can be used as a "halogen carrier" in both ionic and free radical chlorine addition reactions. In a definitive study recently reported the following ionic mechanism was given for the reaction of IBD with norbornene:
It is not certain that this reaction was completely free of a radical mechanism component. However, the use of molecular oxygen as an inhibitor and low reaction temperatures gave a product mixture which indicated that the ionic process was dominant (65-92%). In a typical reaction, carried out in carbon tetrachloride at 40° for 222 hours with oxygen present to inhibit the free-radical process, the yields were 43% I, 13% II, 38% III, and 6% IV. In every reaction reported, I was produced in greater yield than II, thus raising serious question about a previously proposed cis-five-center mechanism.

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The fact that no V was produced is possible evidence against this mechanism, although the exclusive production of II could be due to a great preference for exo addition.

The radical addition of chlorine to norbornene by use of IBD is much faster than the ionic reaction and will predominate if not inhibited. The following chain-reaction mechanism has been proposed:

\[
\begin{align*}
\text{(initiation)} & : & \phi \text{ICl}_2 \xrightarrow{\text{heat or light}} \phi \text{ICl} + \text{Cl}^- \\
\text{(propagation)} & : & \text{Cl}^- + \begin{array}{c}
\text{Cl}^- + \\
\phi \text{ICl}_2
\end{array} \rightarrow \begin{array}{c}
\text{Cl}^- + \\
\phi \text{ICl}
\end{array} \\
\phi \text{ICl} & \rightarrow \phi \text{I} + \text{Cl}^- 
\end{align*}
\]

Neither of the ionic products III or IV was produced at any temperature between -20° C and 78° C when oxygen was excluded from the reaction. Hydrogen abstraction reactions did not appear to be important in these reactions.
CHAPTER II
RESULTS AND DISCUSSION

Convenient syntheses of cis-cyclodecene and trans-cyclodecene have been developed. These syntheses involve radical chlorination of cyclodecane followed by dehydrochlorination. The stereo-selective nature of each dehydrohalogenation was due to a fortuitous combination of ring geometry, solvent, and base to favor either syn or anti elimination. Product distribution data were obtained for the free radical and ionic additions of \( \text{Cl}_2 \) from molecular chlorine and from iodobenzene dichloride to both cis- and trans-cyclodecene. The addition of molecular chlorine with cis-cyclodecene in CCl\(_4\) under both ionic and radical conditions yields the expected trans-1,2-dichlorocyclooctadecane. However, trans-cyclodecene reacts under both ionic and radical conditions to give only transannular rearrangement products. Indirect chlorination of cis-cyclodecene with iodobenzene dichloride yields a mixture of 1,2- and 1,6-dichlorides under ionic conditions, but yields only transannular products under radical conditions. The reaction of trans-cyclodecene under both radical and ionic conditions yields only trans-1,6-dichlorocyclooctadecane. In all cases the allylic product, 3-chlorocyclooctadecene, is produced.

The structures of the products from the above reactions were established by infrared and nuclear magnetic resonance spectroscopy (NMR), and by comparison with authentic samples synthesized by alternate methods. Retention times from vapor phase chromatography and \( R_f \)
values from thin layer chromatography were also utilized in product identification.

A. Synthesis of cyclodecenes

Although both cis- and trans-cyclodecene have been prepared by several different routes, none of the published routes is truly convenient in the sense of requiring few steps from cheap starting materials. Cyclodecane is now available and we find that it is easily chlorinated by a free radical substitution reaction:

\[ \text{Cl}_2 \xrightarrow{h\nu} 2\text{Cl}^- \]

\[ \text{H} + \text{Cl}^- \rightarrow \text{HCl} \]

\[ \text{H} + \text{Cl}_2 \rightarrow \text{Cl}^- + \text{Cl}^- \]

An unfrosted 150-watt light bulb provides the necessary energy for the initiation reaction. No solvent is required in this reaction, but an excess of cyclodecane is used to statistically minimize the formation of polychlorocyclodecanes. A convenient reaction involved the use of 3.0 moles of cyclodecane and 1.0 mole of chlorine. This mixture gave a 64% yield (based on chlorine) of chlorocyclodecane and only 13% of mixed dichlorocyclodecanes. The small residue of heavier polychlorocyclodecanes could not be fractionated at 0.2 mm without decomposition.

Various procedures for the dehydrochlorination of chlorocyclodecane were investigated. The classical KOH/CH₃OH system

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proved to be ineffective. Only 4% of the chlorocyclodecane had reacted after 40 hours at reflux. The use of a higher boiling alcoholic solvent to speed this reaction is hindered by the decomposition of chlorocyclodecane at higher temperatures. Dehydrochlorination with the stronger base system C₂H₅ONa/C₂H₅OH was more successful, giving a 34% yield of 88% cis- and 12% trans-cyclodecene after 40 hours of reflux. The system tert-C₄H₉OK/dimethyl sulfoxide gave complete dehydrochlorination after 3 hours at room temperature. The product isomer ratio was 94% cis/6% trans.

The order of base strength is tert-C₄H₉O° > C₂H₅O° > OH°, but the use of a non-alcoholic solvent with tert-butoxide introduces the possibility that the increased reactivity of this system may be due to a solvent effect rather than to base strength. All three solvents have very strong ion pair dissociating properties, and the elimination process likely proceeds predominately through the anti mechanism:

This is consistent with the reported mechanism of dehydrobromination of bromocyclodecane using similar base systems.¹⁸ The cis/trans product ratios are comparable:
<table>
<thead>
<tr>
<th>Halocyclodecane</th>
<th>Base System</th>
<th>% of cis product</th>
<th>ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>bromo</td>
<td>EtOK/EtOH</td>
<td>85</td>
<td>18</td>
</tr>
<tr>
<td>chloro</td>
<td>EtONa/EtOH</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td>bromo</td>
<td>tBuOLi/DMF</td>
<td>88</td>
<td></td>
</tr>
<tr>
<td>chloro</td>
<td>tBuOK/DMSO</td>
<td>94</td>
<td></td>
</tr>
</tbody>
</table>

Sicher has shown using rate profile diagrams that the small amount (<15%) of trans-cyclodecene is formed chiefly through an anti-elimination mechanism.

If dehydrohalogenation is carried out in the cyclodecane system with a solvent which supports ion-pair formation, rather than ion-pair dissociation, the syn-elimination mechanism will predominate. Thus the system lithium dicyclohexylamide/ether gives a 7% cis-93% trans-cyclodecene product mixture. This result is similar to the reported reaction of lithium di-sec-butylamide with bromocyclodecane to give 85-94% trans-cyclodecene. Eastham and coworkers have reported that lithiumalkyls can form coordination complexes with ethers or amines in a 1:2 base:lithium ratio.

B. Ionic Chlorine Additions

The ionic addition of molecular chlorine to cis-cyclodecene, with oxygen gas being used to inhibit the competing radical process, gives an 8.5% yield of 3-chlorocyclodecene, and a 73% yield of trans-1,2-dichlorocyclodecane. The NMR spectrum of the dichloride product indicates that the chlorine atoms are bonded to adjacent carbon atoms, but does not establish whether the 1,2-dichlorocyclodecane produced is cis or trans or a mixture. The possibility that this product is a cis/trans mixture was ruled out by examining the NMR spectrum of the unreacted dichloride remaining after partial reactions with two different reagents. Partial dehalogenation with
zinc dust/ethanol left unreacted dichloride with the same 100MHz NMR absorption pattern for the H-C-Cl protons as the starting material. The isomeric cis- and trans-1,2-dichlorocyclodecanes in a mixture should undergo dehalogenation at different rates, so that the mixture of unreacted dichlorides would have a composition different from that of the starting material. Partial dehydrochlorination of a second sample of the 1,2-dichlorodecane product with tBuOK/DMSO again yielded unreacted starting material with an unchanged NMR spectrum. The product of this reaction was the vinyl chloride, 1-chlorocyclo-
decene (73% yield based on tBuOK). Attempts to synthesize trans-
1,2-dichlorocyclodecane from trans-1,2-cyclodecanediol by a stereo-
chemically reliable route using thionyl chloride in dioxane were unsuccess-
ful. However, the other possible isomer, cis-1,2-chloro-
cyclodecane, was synthesized from cis-1,2-cyclodecanediol by this method. The cis isomer is a colorless crystalline solid (m.p. 84°-
86°C) which can be purified by vacuum sublimation. Thus the liquid dichloride product from the ionic addition of chlorine to cis-
cyclodecene must be trans-1,2-dichlorocyclodecane.

This conclusion is in contrast to a reported23 tentative identification of this product as cis-1,2-dichlorocyclodecane. That cis assignment was based on the fact that dechlorination of the dichlorocyclodecane with zinc dust/ethanol gives 78% trans-cyclo-
decene. This elimination has been shown32 to occur in other systems by an anti mechanism. However, a more recent study33 involving medium ring systems reports that debromination of trans-
1,2-dibromocyclodecane with zinc dust/methanol primarily proceeds.
through a syn-elimination mechanism to give 87% trans-cyclodecene.

The production of a single unrearranged addition product in the ionic reaction of chlorine with cis-cyclodecene is in contrast to the addition of bromine to this alkene to give 80% of the rearranged cis-1, 6-dibromocyclodecane and only 20% of the expected trans-1, 2-dibromocyclodecane. The stereospecific nature of the chlorine and bromine addition reactions can be explained either by an open carbonium ion mechanism in which molecular geometry dictates the direction of attack on the carbonium ion, or by a bridged carbonium ion mechanism. A possible bridged-ion mechanism is shown below:

\[ \text{trans-1, 2} \]

\[ \text{cis-1, 6} \]

If X is chlorine, the reaction of the intermediate with chloride ion to form the trans-1, 2-product requires sufficiently less energy of activation than a transannular hydride shift so that no transannular products are formed. If X is bromine transannular as well as vicinal products are formed. The formation of the cis-1, 6-dibromocyclodecane product can be explained by the concerted bromide attack-hydride...
shift mechanism shown above (with or without bridging in the initially formed ion) or by a hydride shift followed by stereospecific reaction of bromide ion with the 6-bromocyclodecyl carbonium ion.

The ionic addition of molecular chlorine to trans-cyclodecene gave a 39% yield of 3-chlorocyclodecene and 5% of trans-1,6-dichlorocyclodecane. An additional 13% yield of unidentified dichlorocyclodecane(s) and a small amount of solid polymeric material was also produced. Examination of a molecular model of trans-cyclodecene indicates that one olefinic carbon atom is accessible to attack by Cl⁻ and the other is buried within the molecule. Thus the initially formed carbonium ion intermediate is sterically hindered from reaction with Cl⁻ and undergoes loss of H⁺ to form an olefin, or undergoes transannular rearrangement. Approximately 4.5 times as much 3-chlorocyclodecene is formed in this case as in the case of cis-cyclodecene. A 1,5-hydride shift leads to the trans-1,6 product. The NMR spectrum of the 13% yield of unidentified dichlorocyclodecane(s) is not consistent with 1,2- or 1,3-isomers. Previous workers have noted that both 1,5- and 1,6-hydride shifts commonly occur in cyclodecane systems. Thus the 13% of product likely contains a mixture of 1,5- and/or 1,6-dichlorocyclodecanes. The low total yield (18%) of transannular products indicates that a transannular hydride shift requires a high energy of activation compared to the other reactions of the carbonium ion intermediate. The polymeric product was insoluble in carbon tetrachloride but was soluble in methanol, indicating a relatively low molecular weight. The elemental analysis (65.00% C, 11.05% H) is not consistent
with any simple molecular formula. Attempts to add chlorine or hydrogen chloride to 3-chlorocyclodecene under these reaction conditions failed, indicating that none of the products from cis- or trans-cyclodecene are formed in this manner.

C. Radical Chlorine Additions

The radical addition of molecular chlorine to cis-cyclodecene gives the following products:

\[
\text{cis-Cyclodecane} + Cl_2 \xrightarrow{N_2, uv, CCl_4} \text{cis-Allylic Chloride} + \text{trans-Allylic Chloride}
\]

In this reaction the allylic chloride is produced by abstraction of the reactive allylic hydrogen by a chlorine atom:

\[
\text{cis-Cyclodecane} + Cl^- \xrightarrow{?} \text{cis-Allylic Chloride} \xrightarrow{?} \text{trans-Cyclodecane} + Cl^-.
\]

\[
\text{cis-Cyclodecane} + Cl_2 \xrightarrow{?} \text{cis-Allylic Chloride} + Cl^-.
\]

In the addition process, the transannular migration of a hydrogen atom does not compete with the reaction of the radical intermediate with a chlorine molecule.
The stereospecific production of the trans-1,2 product may be due to a sterically shielded intermediate radical (I), a bridged radical\(^{34}\) (II), or a molecular complex\(^{25}\) (III) which reacts with a chlorine molecule from the upper side to give the trans product.

The radical addition of molecular chlorine to \textit{trans}-cyclododecene gives the following products:
Here, as in the case of the ionic addition of chlorine to the trans-alkene, one olefinic carbon atom is accessible to attack by Cl· and the other is buried within the molecule. Thus the geometry of the molecule causes the radical intermediate to undergo transannular hydrogen atom shift rather than to abstract a chlorine atom from a chlorine molecule. Unlike the ionic intermediate, the radical intermediate does not eliminate hydrogen to give the allylic product. The relatively low yield of dichloride products is partly due to the reactivity of the double bond being halved by the inaccessibility of one of the two olefinic carbon atoms. The orientation factor\(^{35}\) favors allylic substitution rather than addition to the double bond.

D. Ionic Chlorinations involving Iodobenzene Dichloride

The ionic reaction of IBD with cis-cyclodecene gave the following products:
The production of transannular dichloride products is in contrast to the ionic reaction involving molecular chlorine. This may be due to the production of an intermediate such as IV which is of higher energy than the initially formed 2-chlorocyclodecyl carbonium ion in the reaction with molecular chlorine.
It is unlikely that the -Cl-Cl-I- \( \Phi \) group exerts as great a destabilizing effect on the adjacent carbonium ion center as would -Cl. The relatively low energy of ion V may be due to bridging, as shown. Steric shielding of the carbonium ion center in IV by the large adjacent \( \Phi IC_2^- \) group may hinder the reaction which leads to the vicinal product. Another possibility is that the effective concentration of chloride ion is reduced due to complexing with iodobenzene. This would allow the rearrangement process to compete more favorably with the reaction of chloride ion with the 2-chlorocyclodecyl carbonium ion. The dichlorocyclodecane products were identified as 25% vicinal and 75% transannular (1,4-, 1,5-, or 1,6-) by NMR. Attempts to separate or further analyze them were unsuccessful.

The ionic reaction of IBD with trans-cyclodecene gave the following products:

\[
\text{trans-Cyclodecene} + \Phi IC_2^- \xrightarrow{\text{O}_2, \text{CCl}_4} \xrightarrow{46\%} \text{Cl} + \xrightarrow{10\%} \text{Cl}
\]

The relatively large amount of allylic product and the production of only rearranged dichloride products are analogous to the ionic reaction of molecular chlorine with this alkene.

E. Radical Chlorinations involving Iodobenzene Dichloride

The radical reactions of IBD with cis- and trans-cyclodecene were much more rapid than the corresponding ionic reactions. The radical reaction of IBD with cis-cyclodecene gave the following products:
The small amount of allylic chloride formed is in keeping with the small amount of hydrogen abstraction reported\textsuperscript{26} in the radical reaction of IBD with norbornene. NMR analysis of the dichloride product(s) indicates that little if any vicinal dichloride is formed. This result could be due to iodobenzene being involved in an intermediate such as VI

![Image](image.png)

which is of higher energy than the initially formed 2-chlorocyclodecyl radical in the reaction with molecular chlorine.

![Image](image.png)

Reaction Progress

As in the case of the ionic intermediates IV and V above, the relative stability of VII may be due to bridging, as shown. Again, the size of
the \( \Phi \text{ICl}_2 \)- group may hinder the reaction which leads to the vicinal product. Another possible explanation for the lack of vicinal products is that a chlorine atom may be abstracted more slowly from \( \Phi \text{ICl}_2 \) than from \( \text{Cl}_2 \). This favors the irreversible hydride shift which leads to transannular products. Attempts to further separate or identify the dichloride products were not successful.

The radical reaction of IBD with trans-cyclodecene gave 31\% of 3-chlorocyclodecene and 32\% of a mixture of transannular dichlorocyclodecanes. As in the other chlorinations of trans-cyclodecene, there was no vicinal dichloride product.

F. Summary of Chlorine Additions Studied

In summary, the following products were obtained in the additions of chlorine to cyclodecenes

\[
\begin{align*}
\text{cis} & : \text{Cl}_2 & \text{ionic} & & \text{VIII} & & 8\frac{1}{2} & & 73 & \text{IX} & & 22 & & 29 & \text{X} & & 39 & & 5 & & 13 & \text{XI} & & 43 & & 9 & & 9 & \text{XII} \\
\text{trans} & : \text{Cl}_2 & \text{ionic} & & 39 & & 5 & & 13 & \text{cis} & : \text{ICl}_2 & \text{ionic} & & 10 & & 8 & & 24 & \text{cis} & : \text{ICl}_2 & \text{radical} & & 6 & & 45 & & 9 & & 9 & \text{trans} & : \text{ICl}_2 & \text{ionic} & & 46 & & 10 & & 32 & \text{trans} & : \text{ICl}_2 & \text{radical} & & 31 & & 32 & & 9 & & 9 &
\end{align*}
\]

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For each of the four reaction types the trans olefin gave a larger percentage of allylic product than did the cis olefin. The reaction of molecular chlorine with cis-cyclodecene under both ionic and radical conditions yielded the expected trans-1,2-dichlorocyclodecane. Trans-cyclodecene reacts under both ionic and radical conditions to give transannular products, including trans-1,6-dichlorocyclodecane. Indirect chlorination of cis-cyclodecene with iodobenzene dichloride yields a mixture of vicinal and transannular dichlorides under ionic conditions, but yields only transannular dichlorides under radical conditions. The reaction of trans-cyclodecene with iodobenzene dichloride under both radical and ionic conditions yields only transannular products, including trans-1,6-dichlorocyclodecane.

The comparable ionic and radical reactions seem to be mechanistically similar. The intermediate 2-chlorocyclodecyl cation or radical reacts without rearrangement if the reactive site is not sterically shielded and if the appropriate chloride or chlorine atom donor is available. The allylic and rearranged products formed from the trans olefin are likely due to steric shielding of the reaction intermediate. The rearranged products formed from the reactions of the cis olefin with iodobenzene dichloride may be due to the lessened availability of the chloride ion or chlorine atom for the final step of the reaction.
CHAPTER III
EXPERIMENTAL

General

Elemental analyses were performed by Mr. R. Seab of these laboratories and are given as the average of three determinations. Vapor phase chromatography (VPC) was performed on a Beckman model GC-5 instrument equipped with a thermal conductivity detector and a 12 foot by 1/8 inch column packed with 5% Carbowax 20M on 60/80 mesh Chromasorb P. Temperatures for specific analyses are given as injector temperature/column temperature/detector temperature. Sixty megaHertz nuclear magnetic resonance (NMR) spectra were obtained by the author on a Varian model A-60A instrument, and 100 MHz spectra were obtained by Mr. W. Wegner on a Varian model HA/HR-100 instrument. NMR data are given in parts per million (ppm) downfield from the tetramethylsilane (TMS) reference signal. All spin-spin decoupling spectra were obtained on the HA/HR-100 instrument. Infrared (IR) spectra were obtained on a Perkin-Elmer model 137 instrument. Many of the IR spectra show the 6.238 micron polystyrene absorption as a reference. Melting points were obtained with a Thomas-Hoover capillary melting point apparatus and are uncorrected.

Cis-cyclooctene, cyclodecane, and cis, trans-1,5-cyclodecadiene were generously supplied by Columbian Carbon Company, Lake Charles, Louisiana.
A. **Preparation of chlorocyclodecane**

A 1-l. three-neck Pyrex flask equipped with a condenser, stirrer, and gas dispersion tube was charged with cyclodecane (420 g, 3.0 moles) and irradiated with a 150-w light bulb in a reflector about 4 in. from the flask. Chlorine gas (71 g, 1.0 mole) was passed through a trap containing concentrated sulfuric acid, through an empty trap, and into the stirred cyclodecane for 4 hours. Irradiation was continued for 35 min longer, and air was then bubbled through the mixture for 30 min to sweep out chlorine and hydrogen chloride. Distillation of the mixture at reduced pressure gave the following three well-separated fractions:

Recovered cyclodecane amounted to 286 g (2.04 moles), bp 72-73.5° (12mm), n\(^{25}\)D 1.4697.

Chlorocyclodecane was obtained in 64% yield (based on Cl\(_2\)) (111.4 g), bp 109-110.5° (12mm), n\(^{25}\)D 1.4923. **Anal.** Calcd for C\(_{10}\)H\(_{19}\)Cl: C, 68.74; H, 10.96. Found: C, 68.55; H, 10.75.

Dichlorocyclodecane was formed in small amount (14.1 g, 13.5%), bp 135-137° (12mm), n\(^{25}\)D 1.5078. **Anal.** Calcd for C\(_{10}\)H\(_{18}\)Cl\(_2\): C, 57.42; H, 8.67. Found: C, 58.00; H, 8.92. The 60MHz NMR spectrum (appendix, page 64) is consistent with the reported spectrum.

B. **Dehydrochlorination of chlorocyclodecane**

1. **Potassium tert-butoxide in dimethyl sulfoxide (DMSO)**

A solution of chlorocyclodecane (105 g, 0.60 mole), dimethyl sulfoxide (500ml), and potassium tert-butoxide (100.8 g, 0.90 mole) was stirred for 3 hr. The mixture was diluted with water (750 ml.)...
and extracted with four 200-ml portions of petroleum ether (bp 60-70°). The combined organic material was dried with Drierite and concentrated by rotary evaporation. Distillation of the residue gave cis-cyclodecene (66.0 g, 80%), bp 44-45° (2mm). Analysis by VPC at 115°/115°/200° indicated that the sample contained 94% cis- and 6% trans-cyclodecene.

The infrared spectrum of the product (appendix, page 56) shows the C-H out-of-plane deformation absorption at 14.10 microns, which is characteristic of the cis double bond. The C=C stretching absorption at 5.92 microns is weak. The 60MHz NMR spectrum (appendix, page 65) is consistent with the assigned structure.

2. Lithium dicyclohexylamide in hexane-ethyl ether

A solution of butyllithium in hexane (400 ml, 1.6M) was added to a solution of dicyclohexylamine (124 g, 0.68 mole) in anhydrous ethyl ether (200 ml) contained in a 2-l. flask fitted with a condenser, magnetic stirrer, and nitrogen atmosphere. To the resulting mixture was added a solution of chlorocyclodecane (105 g, 0.60 mole) in hexane (200 ml). The mixture was refluxed for 24 hr, allowed to cool, washed with four 50-ml portions of water, and dried with Drierite. Removal of solvent by rotary evaporation and distillation of the residue gave trans-cyclodecene (58.0 g, 70%), bp 53-55° (4mm). Analysis by VPC at 115°/115°/200° indicated that the sample contained 93% trans- and 7% cis-cyclodecene. Dicyclohexylamine was recovered in good yield by continuing the distillation. Dicyclohexylammonium chloride is sparingly soluble in water. When attempts were made to remove the amine (as its salt) from the organic layer...
by washing with aqueous acid, a heavy, white precipitate formed and made subsequent work-up difficult.

The infrared spectrum of the product (appendix, page 57) shows the C-H out-of-plane deformation adsorption at 10.20 microns, which is characteristic of the trans double bond. The C=C stretching absorption at 5.95 microns is weak. The 60MHz NMR spectrum (appendix, page 66) is consistent with the assigned structure.

3. **Potassium hydroxide in methanol**

Chlorocyclodecane (1.75 g, 0.01 mole) and potassium hydroxide (0.84 g, 0.015 mole) were dissolved in 50 ml of methanol, and the solution was refluxed for 40 hours. VPC analysis of the reaction mixture showed 96% chlorocyclodecane and approximately 2% each of cis- and trans-cyclodecenes.

4. **Sodium ethoxide in ethanol**

Chlorocyclodecane (1.75 g, 0.01 mole) was dissolved in 50 ml of ethanol. Sodium (0.35 g, 0.015 mole) was added in order to generate sodium ethoxide, and the solution was refluxed for 40 hours. VPC analysis of the reaction mixture showed 66% chlorocyclodecane, 30% cis-cyclodecene, and 4% trans-cyclodecene.

5. **Silver nitrate in dimethyl sulfoxide (DMSO)**

Chlorocyclodecane (1.75 g, 0.01 mole) was dissolved in 25 ml of DMSO and added to a solution of silver nitrate (2.55 g, 0.015 mole) in 25 ml of DMSO. The reaction mixture was heated on the steam bath. A precipitate appeared after about 10 minutes, and heating was continued one hour longer. The reaction was then cooled, diluted with 50 ml of water and extracted with two 40-ml portions of
petroleum ether. The petroleum ether solution was washed with water, dried over anhydrous MgSO₄, and analyzed by VPC. Analysis showed 92% cis-cyclodecene and 8% trans-cyclodecene.

6. Pyrolysis of chlorocyclodecane

Chlorocyclodecane is unstable at temperatures above approximately 90° C. Thus VPC of chlorocyclodecane with the flash heater temperature at 150° and the column temperature at 85° resulted in a chromatogram with a single peak having the same retention time as cis-cyclodecene. This pyrolysis product was not further analyzed.

C. Preparation of cis-cyclodecene from cis, trans-1, 5-cyclodecadiene

cis, trans-1, 5-Cyclodecadiene (68 g, 0.50 mole) and 85% hydrazine hydrate (147 g, 2.5 moles) were dissolved in 700 ml of 95% ethanol in a 2-l. three-neck flask equipped with a condenser and a gas dispersion tube. The flask was placed in a room temperature water bath. One gram of finely powdered copper sulfate pentahydrate catalyst was added. Air was vigorously bubbled through the reaction mixture and the reaction progress was followed by VPC. After twelve hours no diene remained in the mixture. The air was stopped, 600 ml of water was added to the reaction mixture, and the resulting solution was extracted with six 125-ml portions of petroleum ether. The extracts were washed with 100 ml of 10% HCl, washed with water, dried over MgSO₄, and concentrated on a rotary evaporator. Distillation gave cis-cyclodecene (37.7 g, 0.27 mole, 54% yield), bp 45.5-47° at 2.5mm. Infrared analysis showed strong absorption at 14.24 microns (cis double bond) but no absorption at
10.29 microns (trans double bond). VPC analysis showed a trace of cyclodecane present.

D. Ionic addition of molecular chlorine to cis-cyclodecene

A solution of cis-cyclodecene (7.0 g, 0.05 mole) in 100 ml of carbon tetrachloride was placed in a 38 mm by 200 mm test tube. Oxygen was vigorously bubbled through the solution for 10 minutes through a sintered gas-dispersion tube. The oxygen flow was maintained while chlorine gas (Matheson 99.5% purity), which had been dried by passing it through concentrated sulfuric acid, was bubbled through the solution. During the reaction a colorless gas was evolved which gave a silver chloride precipitate with aqueous silver nitrate solution, turned wet blue litmus paper red, but did not affect wet starch-iodide test paper. This gas was presumed to be hydrogen chloride. The chlorine flow was discontinued when the solution exhibited the yellow color characteristic of excess chlorine, and the oxygen flow was then continued for an additional 30 minutes to sweep out any remaining HCl or Cl₂ gas.

The CCl₄ was removed from the mixture by rotary evaporation and the residue was distilled at reduced pressure to give the following fractions:

I  0.73 g  bp 51-55° (0.15 mm)
II 7.64 g  bp 71-83° (0.15 mm)

1. Identification of fraction I

The carbon-hydrogen analysis of I (69.42% C, 10.02% H) is in good agreement with the calculated values (69.55% C, 9.92% H) for C₁₀H₁₇Cl. The IR spectrum of I (appendix, page 58) yields
little information. The 60 MHz NMR spectrum of I (appendix, page 67) showed the following absorptions: -5.50 ppm (2 vinyl protons), -4.21 ppm (1 proton, Cl-C-H), -2.05 ppm (ca. 4 protons, allylic protons and CH₂-C-Cl) and -1.43 ppm (ca. 10 protons, CH₂-CH₂-CH₂).

The elemental analysis and NMR spectrum are consistent with either of the allylic chloride structures:

Fraction I represents a 8.5% yield of 3-chlorocyclodecene based on the starting cis-cyclodecene.

2. **Identification of fraction II**

The carbon-hydrogen analysis of II (57.77% C, 8.81% H) is in good agreement with the calculated values (57.42% C, 8.67% H) for C₁₀H₁₈Cl₂. The IR spectrum of II (appendix, page 59) yields little information. The 100 MHz NMR spectrum (appendix, page 68) of II showed the following absorptions: -4.36 ppm (2 protons, Cl-C-H), -2.08 ppm (4 protons, Cl-C-C-H), and -1.57 ppm (12 protons, CH₂-CH₂-CH₂). The above data indicate that fraction II is cis-and/or trans-1,2-dichlorocyclodecane. The absorption at -4.36 ppm is a broad complex band with no discernable splitting pattern, most probably due to the non-rigid and non-free-rotating nature of the -CH₂-CHCl-CHCl-CH₂- unit in the ten-membered ring. The 100 MHz NMR spectrum shows this absorption to contain at least 20 peaks.

Spin-spin decoupling was accomplished at 100 MHz by irradiating the

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Cl-C-C-H protons at -1.77 ppm. The Cl-C-H pattern changed to a singlet-like band, 8 cps wide, at -5.51 ppm. The width of this band indicates that it is likely made up of a number of unresolved peaks. Examination of molecular models does not indicate a clear correlation between the NMR data and either cis- or trans-1,2-dichlorocyclodecane. Subsequent work (section E) proved that fraction II was not a mixture of isomers and fraction II was confirmed as the trans isomer by the stereoselective synthesis of cis-1,2-dichlorocyclodecane (section G).

E. Dehalogenation of Chlorine Addition Product

A solution of fraction II (1.31 g, 0.0063 mole) from the previous reaction in 15 ml of absolute ethanol was treated with zinc dust (0.205 g, 0.0031 mole) and one drop of concentrated hydrochloric acid was added to generate ZnCl₂ for a catalyst. The reaction mixture was heated at reflux for eight days. The reaction mixture was then cooled and poured into 100 ml of ethyl ether. This solution was washed three times with 50 ml portions of water to remove the ethanol, dried over anhydrous MgSO₄, and concentrated by rotary evaporation. Analysis of the residue by NMR showed that approximately 15% of the dichloride had been converted to olefin. Analysis of the olefin mixture by VPC at 115⁰/115⁰/145⁰ showed 78% trans- and 22% cis-cyclodecene. These percentages are corrected to allow for the 2.35 times greater response of the VPC detector to the cis isomer. An enlarged 100 MHz NMR spectrum of the unreacted dichloride showed no change in the absorption pattern for the H-C-Cl protons, indicating that the dichloride is not a
mixture of isomers, except in the unlikely case that both isomers react at the same rate in this reaction.

F. Dehydrohalogenation of Chlorine Addition Product

A solution of potassium tert-butoxide (1.68 g, 0.015 mole) in 60 ml of reagent grade DMSO was added over thirty minutes to a stirred solution of fraction II from reaction D above (3.13 g, 0.015 mole) in 25 ml of DMSO. The reaction mixture was then stirred for 18 hours at room temperature. The reaction mixture was diluted with 250 ml of water, and the organic products were extracted into four 100-ml portions of petroleum ether. The combined extracts were washed with four 50 ml portions of water and then dried sequentially over anhydrous MgSO$_4$ and CaSO$_4$. After the petroleum ether had been removed by rotary evaporation, distillation of the residue gave the following fractions:

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Amount</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>few drops</td>
<td>35-52 (0.6 mm)</td>
</tr>
<tr>
<td>II</td>
<td>1.88 g</td>
<td>52-58 (0.6 mm)</td>
</tr>
<tr>
<td>III</td>
<td>0.63 g</td>
<td>85-87 (0.6 mm)</td>
</tr>
</tbody>
</table>

Fraction I was not investigated. Fraction II was identified as the vinyl chloride, 1-chlorocyclodecene, by NMR (appendix, page 69). The vinyl proton absorption at -5.67 ppm is split into a clean triplet ($J = 7.6$ Hz) indicating that the allylic protons at position three are equivalent with respect to the vinyl proton. The IR spectrum (appendix, page 60) shows a sharp C=C stretching absorption at 6.05 microns. The available data are not sufficient to indicate the geometry of the double bond. Fraction II represents a 7.3% yield.

Fraction III was identified by its NMR and IR spectra as starting...
material. An enlarged 100 MHz NMR spectrum of this unreacted di-
chloride showed no change in the absorption pattern for the H-C-Cl
protons. This result indicates that the dichloride is not a mixture of
isomers, except in the unlikely event that the isomers react at
the same rate in this reaction.

A previous attempt to accomplish the above dehydrochlorina-
tion using KOH in a solvent mixture of 20 DMSO/5 CH₃OH/5 HOH yielded starting material as the only product.

G. Synthesis of cis-1, 2-dichlorocyclodecane

1. cis-1, 2-cyclodecanediol

A cold (0° C) solution of potassium permanganate (23.2 g, 0.147 mole) and sodium hydroxide (5 g, 0.125 mole) in 600 ml of
water was added rapidly to a cold (0° C) stirred solution of cis-
cyclodecene (13.8 g, 0.10 mole), 750 ml of tert-butyl alcohol and
750 ml of water. Reaction occurred rapidly, producing a large
amount of MnO₂ precipitate and causing a slight temperature rise.
The reaction mixture was stirred for two hours and then filtered
through a bed of glass wool, Celite filter aid, and filter paper in a
large Buchner funnel to remove the manganese dioxide. The solution
was concentrated to 300 ml on the rotary evaporator and extracted
with five 100-ml portions of ether. The combined extracts were
washed with water and dried over anhydrous magnesium sulfate. Eva-
poration of the ether gave cis-1, 2-cyclodecanediol (4.43 g, 47% yield). The crude diol was used without further purification in the
following synthesis.
2. **cis-1,2-dichlorocyclooctane**

Thionyl chloride (3.57 g, 0.030 mole) was added dropwise to a stirred solution of cis-1,2-cycloctanediol (1.72 g, 0.010 mole) in 60 ml of dioxane. The resulting mixture was heated at reflux for 4 hours, and the solvent and unreacted SOCl₂ were removed on the rotary evaporator. The crude residue was allowed to stand undisturbed for 4 weeks, during which time a few large, flat, parallelogram-shaped crystals formed and grew. These crystals were purified by vacuum sublimation at ca. 90° (0.1 mm) to give 0.88 g of colorless prisms of m.p. 84½-86½. The IR spectrum (appendix, page 61) shows no OH stretching absorption near 2.8 microns and no C=C stretching absorption near 6.0 microns. The 60 MHz NMR spectrum (appendix, page 70) is consistent with structure of cis-1,2-dichlorocyclooctane, the expected product from this previously reported stereospecific reaction. The yield was 42%.

H. **Ionic Addition of Molecular Chlorine to trans-cyclooctene**

This reaction was carried out in the same manner as described above for the addition of Cl₂ to cis-cyclooctene. Hydrogen chloride gas was evolved and in addition about 0.5 g of a flocculent solid separated during the reaction. After the reaction was completed, this solid was filtered off and recrystallized from chloroform-methanol to give colorless needles with a melting point above 330° C. Carbon-hydrogen analysis gave 65.00% C and 11.05% H which corresponds to \((\text{C}_8\text{H}_{16}\text{Cl}_{1.00})_x\) if the remaining 23.95% is assumed to be chlorine. This solid was insoluble in benzene, carbon tetrachloride, and chloroform and was assumed to be a low molecular
weight polymer. The CCl₄ was removed from the reaction mixture by rotary evaporation and the residue was distilled to give the following fractions:

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Weight</th>
<th>Boiling Point</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>3.40 g</td>
<td>bp 35-38° (0.10mm)</td>
</tr>
<tr>
<td>II</td>
<td>few drops</td>
<td>intermediate cut</td>
</tr>
<tr>
<td>III</td>
<td>2.00 g</td>
<td>bp 63-66° (0.10mm)</td>
</tr>
</tbody>
</table>

1. **Identification of fraction I**

The carbon-hydrogen analysis of I (69.28% C, 10.16% H) is in good agreement with the calculated values (69.55% C, 9.92% H) for C₁₀H₁₇Cl. The IR and NMR spectra agree closely with the spectra of 3-chlorocyclooctadecene as described above. Fraction I represents a 39% yield of this product.

Fraction II was not examined.

2. **Identification of fraction III**

Fraction III partially crystallized on standing. Separation yielded 0.56 g of solid (III S) and 1.44 g of liquid (III L).

The solid was recrystallized from hexane and dried under vacuum to give colorless crystals of mp 101-3°. The carbon-hydrogen analysis of III S (57.46% C, 8.85% H) is in good agreement with the calculated values (57.42% C, 8.67% H) for C₁₀H₁₈Cl₂. The IR spectrum of III S in CCl₄ (appendix, page 62) yields little information. The 100 MHz NMR spectrum of III S in CDCl₃ (appendix, page 71) shows an A:B:X-proton ratio of 8:8:2. This is consistent with a 1,4-, 1,5- or 1,6-dichlorocyclooctadecane structure. The trans-1,6-dichlorocyclooctadecane structure was considered to be the most likely by analogy to the reported¹ addition of bromine to
trans-cyclodecene. An attempt to prepare the known trans-1,6-bis-phenylthiocyclodecane from IIIS by the method of Sicher\(^1\) failed. A second attempt in which the reaction time was extended from the specified 5 hours to 72 hours yielded a crystalline derivative which had a melting point of 101-3\(^{0}\), identical to the reported\(^1\) value for trans-1,6-bis-phenylthiocyclodecane. A mixture of this derivative and the starting material had a melting point below 93\(^{0}\). Thus, IIIS represents a 5.4% yield of trans-1,6-dichlorocyclodecane.

The liquid, IIII, gave an NMR spectrum with an A:B:X-proton ratio of 8:8:2, indicative of transannular products, and virtually identical with that of IIIS. Fraction IIII could not be analyzed by VPC because temperatures sufficiently high to allow these high molecular weight molecules to move through the packed column caused their decomposition. Column chromatography on Merck acid-washed alumina gave no separation of components. Thin-layer chromatography on silica gel plates which were activated at 120\(^{0}\) immediately prior to use and with reagent hexane as the solvent indicated that IIII contained two components in approximately 90:10 ratio. It was assumed that the 10\% represents trans-1,2-dichlorocyclodecane formed from the 7\% cis-cyclodecene impurity in the starting material, and that IIII is primarily trans-1,6-dichlorocyclodecane. The overall yield of this product is then about 18%.

I. Free Radical Addition of Molecular Chlorine to cis-cyclodecene

A solution of cis-cyclodecene (6.9 g, 0.05 mole) in 100 ml of carbon tetrachloride was placed in a 38 x 200 mm test tube and irradiated with a clear 150 watt light placed 4 inches away.
Nitrogen was vigorously bubbled through the solution for 10 minutes through a sintered-glass gas-dispersion tube. The nitrogen flow was maintained while dry chlorine gas (3.55 g, 0.05 mole) was bubbled through the solution. Hydrogen chloride gas was evolved during the reaction. The nitrogen flow was continued for 30 minutes after the chlorine had been added to sweep out residual gases. The solvent was removed by rotary evaporation and the residue was distilled to give the following:

1.93 g (22% yield) of 3-chlorocyclodecene, bp 41-4° (0.17 mm). This product was identified by its IR and 60 MHz NMR spectra and by its carbon-hydrogen analysis (Calc. for C_{10}H_{17}Cl: 69.55% C, 9.92% H. Found: 69.57% C, 10.10% H).

3.02 g (29% yield) of trans-1,2-dichlorocyclodecane, bp 68-72° (0.17 mm). This product was also identified by its IR and 60 MHz NMR spectra and by its carbon-hydrogen analysis (Calc. for C_{10}H_{18}Cl: 57.42% C, 8.67% H. Found: 57.88% C, 8.74% H).

J. Free Radical Addition of Molecular Chlorine to trans-cyclodecene

This reaction was carried out in the same manner as described above for radical addition of Cl₂ to cis-cyclodecene. Hydrogen chloride gas was evolved during the reaction, and 0.15 g of flocculent solid separated during the reaction. After the reaction was completed, this solid was filtered off and examined. It contained 64.34% C and 11.26% H, did not melt at 300° C, and was assumed to be polymeric. The reaction mixture was concentrated and distilled to give the following:

3.70 g (43% yield) of 3-chlorocyclodecene, bp 49-52° (0.32
This product was identified by its IR and 60 MHz NMR spectra and by its carbon-hydrogen analysis (Calc. for $\text{C}_{10}\text{H}_{17}\text{Cl}$: 69.55% C, 9.92% H. Found: 69.14% C, 10.05% H). 1.87 g (18% yield) of transannular dichlorocyclodecanes. On standing this distillation fraction partially crystallized to give 0.95 g of trans-1,6-dichlorocyclodecane which was identified by its IR and NMR spectra and by a mixed melting point with an authentic sample. The NMR of the remaining 0.92 g of liquid was consistent with trans-1,6-dichlorocyclodecane contaminated to the extent of about 10% with trans-1,2-dichlorocyclodecane, probably arising from the 7% cis-olefin impurity in the starting material.

K. Ionic Reaction of Iodobenzene Dichloride with cis-cyclodecene

A solution of cis-cyclodecene (6.90 g, 0.05 mole) in 30 ml of carbon tetrachloride was placed in a 38 x 200 mm test tube protected from the light. Oxygen gas was bubbled through this solution for 10 minutes, then iodobenzene dichloride (13.74 g, 0.05 mole) was added, and the oxygen flow was continued. Thirty-six hours were required for the completion of the reaction, which was signified by the disappearance of the insoluble IBD. Hydrogen chloride gas was evolved during the course of the reaction. Rotary evaporation of the solvent and distillation of the crude product mixture gave the following fractions:

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Weight</th>
<th>Boiling Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>6.77 g</td>
<td>bp 44.5-45.5° (4mm)</td>
</tr>
<tr>
<td>II</td>
<td>1.26 g</td>
<td>bp 51-55° (0.15 mm)</td>
</tr>
<tr>
<td>III</td>
<td>3.34 g</td>
<td>bp 78-84° (0.20 mm)</td>
</tr>
</tbody>
</table>

Analysis of I by NMR showed it to be a mixture of cis-cyclodecene.
and iodobenzene.

Analysis of II by NMR showed it to be a mixture of 3-chlorocyclodecene and isomeric chloroiodobenzenes which have been previously reported\textsuperscript{55} as by-products in ionic chlorinations involving IBD. Integration of the NMR spectrum of II shows the percentage of allylic chloride to be about 75 mole % or 69 weight % (corresponding to 0.87 g, 0.0050 mole, 10% yield).

Analysis of III by NMR indicated that it contained a mixture of dichlorocyclodecanes. The integration of this spectrum shows an A:B:X-proton ratio of 51.3:38.9:9.8. This is consistent with a mixture containing 25% 1,2-dichlorocyclodecane and 75% transannular (1,4-, 1,5-, and/or 1,6-) dichlorocyclodecanes as shown on the graph below:

![Graph showing the relationship between percentage of 1,2-isomer in the mixture and A:B proton ratio.](image-url)
The points on this graph were calculated from the 12:4:2 and 8:8:2 ratios of A:B:X protons in vicinal and transannular dichlorocyclodecanes, respectively. The IR spectrum of III was not significantly different from that of trans-1,2-dichlorocyclodecane or that of trans-1,6-dichlorocyclodecane. No further separation or analysis of III could be achieved.

L. Ionic Reaction of Iodobenzene Dichloride with trans-cyclodecene.

This reaction was carried out in the same manner as described above for cis-cyclodecene. Hydrogen chloride gas was evolved during the reaction. When the reaction was completed, 1.08 g of white flocculant solid was removed by filtration, the solvent was removed by rotary evaporation, and the crude product was distilled to give the following fractions:

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Weight (g)</th>
<th>Boiling Point (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>7.92</td>
<td>50-2° (5.0 mm)</td>
</tr>
<tr>
<td>II</td>
<td>6.05</td>
<td>50-80° (0.4 mm)</td>
</tr>
<tr>
<td>III</td>
<td>1.67</td>
<td>80-93° (0.4 mm)</td>
</tr>
</tbody>
</table>

Analysis of I by NMR showed it to be a mixture of trans-cyclodecene and iodobenzene.

Analysis of II by NMR showed it to be a mixture of 3-chlorocyclodecene, iodobenzene and chloroiodobenzenes. NMR integration showed that II contained 68 mole % or 60 weight % of 3-chlorocyclodecene (3.63 g, 0.021 mole, 42% yield).

Fractions II and III were difficult to separate and were discolored with free iodine, presumably from thermal decomposition of the aromatic iodides. NMR analysis of III indicated that 0.002 mole of 3-chlorocyclodecene was present in this fraction, bringing the
total yield of allylic chloride to 46%. Inspection of the A:B proton ratio in the NMR spectrum showed that the remainder of III consisted of one or more transannular (1,4-, 1,5-, and/or 1,6-) dichlorocyclodecanes (1.31 g, 0.0063 mole, 13% yield).

M. **Free Radical Reaction of Iodobenzene Dichloride with cis-cyclodecene**

A solution of cis-cyclodecene (6.90 g, 0.05 mole) in 30 ml of carbon tetrachloride was placed in a 100 ml round-bottom flask. Iodobenzene dichloride (13.74 g, 0.05 mole) was added and the mixture was degassed by the freeze-thaw method to eliminate molecular oxygen from the reaction. The mixture in the sealed flask was then stirred with a magnetic stirrer and allowed to warm to room temperature. Five hours was required for the disappearance of the solid IBD. A large quantity of HCl was evolved when the flask was opened. The solvent was removed by rotary evaporation, and the crude product mixture was distilled to give the following fractions:

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Weight (g)</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>6.65</td>
<td>bp 61-40 (10 mm)</td>
</tr>
<tr>
<td>II</td>
<td>2.02</td>
<td>bp 57-61 (1 mm)</td>
</tr>
<tr>
<td>III</td>
<td>4.67</td>
<td>bp 81-90 (0.25 mm)</td>
</tr>
</tbody>
</table>

Analysis of I by NMR showed it to be a mixture of cis-cyclodecene and iodobenzene.

Analysis of II by NMR showed it contained 3-chlorocyclodecene (0.49 g, 0.0028 mole, 6% yield) mixed with isomeric chloroiiodobenzenes.

The NMR spectrum of III shows an A:B:X-proton ratio of 1:1:4.2, which is consistent with one or a mixture of transannular (1,4-, 1,5-, and/or 1,6-) dichlorocyclodecanes (4.67 g, 0.022 mole,
45% yield).

N. Free Radical Reaction of Iodobenzene Dichloride with cis-cyclodecene

This reaction was carried out in the same manner as described above for cis-cyclodecene. Hydrogen chloride gas was evolved during the reaction. When the reaction was completed, 1.33 g of white floculant solid was filtered off. This solid was recrystallized from chloroform-methanol to give needles of mp above 330° C. The solvent was removed by rotary evaporation, and the crude product was distilled to give the following fractions:

<table>
<thead>
<tr>
<th>Fraction</th>
<th>Weight (g)</th>
<th>BP (°C) (mmHg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>6.70</td>
<td>52-4 (6 mm)</td>
</tr>
<tr>
<td>II</td>
<td>4.07</td>
<td>56-65 (1 mm)</td>
</tr>
<tr>
<td>III</td>
<td>3.33</td>
<td>80-92 (0.35 mm)</td>
</tr>
</tbody>
</table>

Fraction III was discolored by I₂ and was purified by dissolving it in diethyl ether, washing this solution with 20% sodium thiosulfate and redistilling. NMR analysis of these fractions showed:

I  trans-cyclodecene
   iodobenzene

II 65 weight % 3-chlorocyclodecene (31% yield)
   35 weight % isomeric chloriodobenzenes

III transannular (1,4-, 1,5-, and 1,6-) dichlorocyclodecenes (32% yield)
REFERENCES


39 Reference 23, p. 42.


41 P. M. Greene, M.S. Thesis, Louisiana State University, 1959.


SELECTED BIBLIOGRAPHY


APPENDIX I
Infrared Spectra

All IR spectra were obtained with a Perkin-Elmer Model 137
Infrared Spectrophotometer.
INFRARED SPECTRUM: \( \text{trans-1,2-Dichlorocyclohexane (neat)} \)

WAVELNGTH (MICRONS)
INFRARED SPECTRUM: 1-Chlorocyclohexene (neat)
APPENDIX II

Nuclear Magnetic Resonance Spectra

These spectra were obtained on the instruments described in chapter three. In every case the sweep width was 500 Hz, the sweep time was 500 seconds, and the temperature was 37°C. None of these compounds showed any absorption downfield from -6.5 ppm.
$60\text{ MHz NMR SPECTRUM: cis-Cyclooctene (in CDCl}_3\text{)}$
60 MHz NMR SPECTRUM: 3-Chlorocyclooctene (in CDCl₃)
100 MHz NMR SPECTRUM: trans-1,2-Dichlorocyclohexane (in CDCl₃)
Sweep offset 50 Hz
VITA

DeWitt Boyd Stone, Jr. was born in Rahway, New Jersey, on October 23, 1939. He attended public school in Knoxville, Tennessee, and was graduated from Young High School in May of 1957. He entered The University of Tennessee in September of 1957 and was awarded a Bachelor of Science in Chemical Engineering degree in March of 1962. He enrolled in the Graduate School of the University of Tennessee in September of 1962, being supported as a teaching assistant by funds from the Chemistry Department. He was married in August, 1963 to Carolyn Ruth Varner. In August of 1964 he received a Master of Science degree under the direction of Dr. Jerome F. Eastham. He enrolled in the Graduate School of Louisiana State University in September, 1964 as a National Aeronautics and Space Administration trainee. In September of 1966 he accepted a position as Assistant Professor of Chemistry at the University of Tennessee at Martin. His daughter, Anne Carol, was born on March 12, 1967.

He is a member of Tau Beta Pi, Sigma Xi, and the American Chemical Society. He is presently a candidate for the degree of Doctor of Philosophy at Louisiana State University.
EXAMINATION AND THESIS REPORT

Candidate: DeWitt Boyd Stone, Junior

Major Field: Chemistry

Title of Thesis: "The Reaction of Chlorine with cis- and trans-Cyclodecenes"

Approved:

[Signature]
Major Professor and Chairman

[Signature]
Dean of the Graduate School

EXAMINING COMMITTEE:

[Signature]

[Signature]

[Signature]

Date of Examination:

January 10, 1969

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