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Effects of Ring Size on Addition Reactions of Methylene cycloalkanes.

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Louisiana State University and Agricultural & Mechanical College

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EFFECTS OF RING SIZE ON ADDITION REACTIONS
OF METHYLENECYCLOALKANES.

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by

Octavius Santos Pascual
B.S. in Chem., University of the Philippines, 1951
M.S. in Chem., Louisiana State University, 1954
August, 1956
TO

MY FATHER AND MOTHER,

with Love, Respect and Affection.

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ACKNOWLEDGMENT

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ABSTRACT

Brown, Brewster and Shechter (J. Am. Chem. Soc., 76, 467 (1954)) emphasized the importance of ring strain in cyclic systems. They suggested that a change in the coordination number of a ring carbon atom from $sp^3$ to $sp^2$ may either increase or decrease the number and degree of unfavorable conformations in the system. Reactions involving this change will be sterically hindered in the 4- and 6-membered ring systems and sterically facilitated in the 5- and 7-membered ring systems. Although the above generalization can account for numerous previously unexplained phenomena such as the equilibria involving exo- and endo-double bond isomers and the direction of olefin formation in terpenes, some studies (Dreiding and Hartman, J. Am. Chem. Soc., 76, 1216 (1956)) suggest the desirability of further experimental study to test its general utility and applicability.

The following addition reactions to a series of methylenecycloalkanes (methylenecyclobutane, methylenecyclopentane, methylenecyclohexane and methylenecycloheptane) were selected for investigation:

1. The ionic and free radical additions of hydrogen bromide.
2. The addition of hypochlorous acid.
3. The addition of hypobromous acid.
4. The addition of chlorine in the presence and in the absence of extraneous anions.

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A related problem (Part 5) involving the reaction of hydrobromic acid with the corresponding methylenecycloalkane oxides (except methylenecyclobutane oxide) was also investigated. The identities of the products (except in parts 4 and 5) were established by comparison of the physical constants and infrared spectra of the addition products with authentic samples prepared by independent methods. In reactions where mixtures were obtained, the ratio of the products was determined by comparison of the quantitative infrared spectra of various mixtures of the pure compounds with the infrared spectrum of the reaction mixture.

The ionic and radical additions of hydrogen bromide were all found to proceed normally, with ionic additions leading to tertiary bromides and radical additions to primary bromides. Apparently, the destabilizing energy due to the formation of intermediates or transition states with a trigonal ring carbon in 4- and 6-membered rings is not sufficient to cause abnormal orientations. Some rearranged products were isolated from the ionic addition of hydrogen bromide to methylenecyclobutane but the isomeric bromomethylcyclobutane was not detected. The side reaction products were attributed to transannular participation within the cyclobutyl ring (Applequist and Roberts, J. Am. Chem. Soc., 78, 874 (1956)).

Both isomeric chlorohydrins were obtained in the
addition of hypochlorous acid to methylenecycloalkanes. The composition of the product is in agreement with that predicted by the I-strain theory developed by Brown, Brewster and Shechter; i.e., the 4- and 6-membered ring systems led predominantly to 1-chloro-1-hydroxymethylcycloalkanes while the 5- and 7-membered ring systems led mostly to 1-chloromethylcycloalkanols. Obviously, the relief of ring strain is an important factor in determining the orientation of hypochlorous acid addition.

The additions of hypobromous acid to methylenecycloalkanes gave mostly 1-bromo-1-hydroxymethylcycloalkanes (90-99%) with some cycloalkanecarboxaldehyde (except with methylenecyclopentane which gave methylenecyclopentane oxide instead of the aldehyde). Evidences were obtained to show that the side-reaction product came from the bromohydrin rather than vice versa. The exclusive formation of the non-Markownikoff product may be attributed to the great tendency of bromine to participate in neighboring group displacement reactions, to the preference of $S_N2$ attack at the least substituted carbon and to repulsion between non-bonded atoms in the transition state due in part to the steric requirements of the cycloalkane ring.

The addition of chlorine to methylenecyclobutane yielded the dichloride in addition to some rearranged products attributed to transannular participation. The addition to the other methylenecycloalkanes gave mainly chloromethylcycloalkenes probably by way of a transient
ring intermediate (Lee, **Diss. Abstr.**, XV, 39 (1955)). The products formed in the presence of extraneous anions were attributed either to mass effect or I-strain.

The addition of hydrobromic acid to methylenecycloalkane oxides gave 1-bromo-1-hydroxymethylcycloalkanes and cycloalkanecarboxaldehydes regardless of ring size. The varying amount of aldehyde formed was attributed to I-strain effects in the transition state.
"The wayfarer, perceiving the pathway to truth, was
struck to find it so thickly overgrown with weeds.
'Ah,' he said, 'I see that no one has passed this way
in a long time.'
"But, discovering that each blade of grass was a
singular knife,
Turning back, he muttered,
'Doubtless, there are other ways.'"
I. INTRODUCTION

The mechanism of addition reactions of olefins is probably far from being fully elucidated at present. Various competing polar and steric factors complicate the problem. Although the classical carbonium ion theory does not explain the observed trans-addition to olefins, the suggestion of a cyclic carbonium ion intermediate to overcome this deficiency is not fully satisfactory since it does not explain the following:

1. Why do olefins react only with positive ions? The carbon-carbon double bond is symmetrical and hence should equally well add negative ions, e.g.,

\[ \text{\(y^+ + \text{C=C} \rightarrow \text{C}=\text{C}^-\)} \]

\[ \text{\(y^- + \text{C=C} \rightarrow \text{C}^-\text{C}^-\)} \]

2. Since the addition product is presumably formed by an S\(_{N2}\) attack on the cyclic carbonium ion intermediate, the product that can be expected to predominate will be the one wherein

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the anion or potential anion is attached to
the least substituted ethylenic carbon atom\(^4\).

The following reactions\(^5\) show otherwise:

\[
\begin{align*}
\text{CH}_3\text{CHCH}_2 & + \text{Br}_2 \rightarrow \text{CH}_3\text{CHCH}_2\text{Br} + \text{CH}_3\text{CHBrCH}_2\text{Cl} \\
\text{CH}_3\text{CH} = \text{CH}_2 & + \text{ICl} \rightarrow \text{CH}_3\text{CHCICH}_2\text{I} + \text{CH}_3\text{CHICH}_2\text{Cl} \\
\phi\text{-CH} = \text{CH}_2 & + \text{ICl} \rightarrow \phi\text{-CHCICH}_2\text{I} + \phi\text{-CHICH}_2\text{Cl}
\end{align*}
\]

Wheland\(^5\) attributes the above orientation to the
greater ease of bond-breaking of a secondary C-X bond
compared to that of a primary C-X bond. He bases this
collection on the observation that a radical reagent
preferentially attacks the least substituted end of an
olefin, suggesting that the terminal atom of such a system
forms a stronger bond than the central one. Hine\(^6\) expressed
a similar opinion and considers the ease of bond-breaking
as the most important factor in determining where the S\(_{\text{N}2}\)
attack will occur. However, Hazeldine and Steele\(^7\) have

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\(^4\) Second order displacement type reactions take
place preferentially at the least substituted carbon atom,
Hughes, Trans. Faraday Soc., **37**, 612 (1941). It is also
the position favored on steric grounds.

\(^5\) Wheland, "Resonance in Organic Chemistry,"


\(^7\) Hazeldine and Steele, J. Chem. Soc., 3005
(1955).
shown that the orientation in free radical addition is probably governed not by the availability of the terminal position but by the relative stability of the intermediate radical that may be formed in the system. An interesting example is the following reaction:

\[ \text{CF}_3\text{CH} = \text{CF}_2 + \text{CF}_3\text{H} \xrightarrow{hv} \left[ \text{CF}_3\text{CH} - \text{CF}_2 \right] \xrightarrow{\text{CF}_3\text{H} - \text{CF}_2} \]

in which the radical attack is not on the terminal carbon which is more susceptible sterically but on the carbon atom which gives the more stable intermediate (through hyperconjugation).

To overcome some of the above mentioned criticisms of the carbonium ion theory of addition to olefins, Dewar suggested that the cation combines with the olefin to form a pi-complex. The pi-complex which is formed by the overlap of the occupied pi-orbital of the olefin with the empty orbital of the cation is then attacked by the anion at the carbon atom with a lower pi-electron density. This is the one carrying the most alkyl substituents. Unfortunately, this theory cannot account for the difference in the orientation observed in the following reactions:

(For example, the pi-complex theory can explain why anions do not add to olefins. Approximate molecular orbital treatment shows that only one of the molecular orbitals in the system is bonding so that only a pair of electrons can be accommodated and the extra electron or pair of electrons (from an anion) would be forced into a high energy anti-bonding orbital. Hence, simple anions would be too unstable to exist.)
Insipite of the inability of existing theories to account for the various orientations observed in the addition to olefins, it is generally accepted that the first step consists of an electrophilic attack by the adding reagent or by one of its components. Extraneous ions compete with the anion or potential anion of the adding reagent in completing the reaction. Hence, the ionic addition to olefins is often represented as:

\[
\begin{align*}
\text{C} &= \text{C} + X-Y \\
\text{C}^+ &= \text{C}^- + Y^- \quad \text{and} \quad \text{C}^+ + Z^- \rightarrow \text{C}^- + Z^-
\end{align*}
\]

The following observations give us some clues about the nature of the attacking cation in hypohalous acid additions:

a. The kinetics of hypochlorous acid addition to various mono-olefins has been found by Chung and Israel to be complex. In each reaction, the

term \((\text{HOCl})^2\) appeared in the kinetic equation. It was surmised that this term represents the rate of formation of \(\text{Cl}_2\text{O}\) from \(\text{HOCl}\). The \(\text{Cl}_2\text{O}\) was then suspected of giving rise to the chloronium ion.

\[
\begin{align*}
2 \text{HOCl} & \rightarrow \text{Cl}_2\text{O} + \text{H}_2\text{O} \\
\text{Cl}_2\text{O} & \rightarrow \text{Cl}^+ + \text{OCl}^-
\end{align*}
\]

The potential ease of separation of \(\text{Cl}^+\) from \(\text{Cl}_2\text{O}\) has been calculated\(^{11}\) to be \(10^6\) times greater than that from \(\text{HOCl}\).

b.\(^{(1)}\) For the chlorination of reactive aromatic compounds with hypochlorous acid\(^{12}\) in the presence of perchloric acid and silver perchlorate\(^{13}\), the velocity coefficient is dependent on the acidity and is independent of the concentration of the aromatic compound. Hence, the aromatic compound is not involved in the rate-determining step of the reaction.

It was concluded that the measured rate is that


\(^{13}\) The perchloric acid was used to reduce the acid dissociation constant of \(\text{HOCl}\) and therefore to decrease the concentration of the \(\text{OCl}^-\) ion thus eliminating completely the reaction route through \(\text{Cl}_2\text{O}\). The silver perchlorate was used to prevent the intervention of chlorine through the reaction: \(\text{HOCl} + \text{H}^+ + \text{Cl}^- \rightarrow \text{Cl}_2 + \text{H}_2\text{O}\).
of the formation of a more active halogenating agent than HOCl which may be Cl⁺ or H₂OCl⁺.

\[
\text{HOCl} + H^+ \rightleftharpoons H_2OCl^+
\]

\[
H_2OCl^+ \rightleftharpoons H_2O + Cl^+
\]

(2). With less reactive aromatic compounds the halogenation becomes second order since the aromatic compound is not sufficiently reactive to combine with the halogenating agent as fast as it is formed.

\[
\frac{-d (\text{HOCl})}{dt} = k (\text{ArH}) (\text{HOCl})
\]

(3). With more reactive compounds (certain olefins), the addition is also second order since the olefin is reactive enough to react with the conjugate acid of HOCl so that it need not wait for the formation of Cl⁺, i.e.,

\[
\begin{align*}
\text{CH}_2=\text{CH}_2 + H_2OCl^+ & \overset{\text{slow}}{\longrightarrow} H_2O + \text{CH}_3\text{CH}=\text{CH}_2 \\
\text{CH}_2=\text{CH}_2 + H_2O & \overset{\text{fast}}{\longrightarrow} \text{CH}_2=\text{CH}_2\text{OH}
\end{align*}
\]

Ingold suggested that there should be an energy barrier between Cl⁺ and H₂OCl⁺ in

\[
\]
aqueous solution despite the fact that one is merely the hydrate of the other. de la Mare\textsuperscript{12} suggested that the formation of Cl\textsuperscript{+} rather than that of H\textsubscript{2}OCl\textsuperscript{+} is the rate-controlling step in the first-order reaction since proton donation from oxygen to oxygen would be too rapid to measure. However, Hine\textsuperscript{15} doubts whether we can make such an unequivocal statement about proton transfer to a very weak base.

Swain and Ketley\textsuperscript{16} resolved the above question in a very simple but elegant manner by a study of the hypochlorous acid halogenation of methyl p-tolyl ether in a strong solution of perchloric acid. The original rate equation reduced to:

\[
- \frac{d (\text{HOCl})}{dt} = k' (\text{H}^+) (\text{HOCl})
\]

If the above terms represent a rate-determining proton transfer to form H\textsubscript{2}OCl\textsuperscript{+} as an intermediate, the rate should be faster in light than in heavy water because of the difference in zero point energies\textsuperscript{17} of H\textsubscript{3}O\textsuperscript{+} and D\textsubscript{3}O\textsuperscript{+}, i.e., \( k_1 \) \( k_2 \).

\[
\begin{align*}
\text{H}_3\text{O}^+ + \text{HOCl} & \xrightarrow{k_1} \text{H}_2\text{OCl}^+ + \text{H}_2\text{O} \\
\text{D}_3\text{O}^+ + \text{DOCl} & \xrightarrow{k_2} \text{D}_2\text{OCl}^+ + \text{D}_2\text{O}
\end{align*}
\]

\( (15) \) Reference 6, pages 194 and 343.


If they represent instead a rate-determining fission of \( \text{H}_2\text{OCl}^+ \) to form \( \text{Cl}^+ \) as intermediate, the rate should be slower in light than in heavy water \((k_4 \gg k_3)\) since the

\[
\begin{align*}
\text{H}_2\text{OCl}^+ & \xrightarrow{k_3} \text{H}_2\text{O} + \text{Cl}^+ \\
\text{D}_2\text{OCl}^+ & \xrightarrow{k_4} \text{D}_2\text{O} + \text{Cl}^+
\end{align*}
\]

acid dissociation constants of protium-protonated compounds like \( \text{H}_2\text{OCl}^+ \) are generally higher than those of deuterium-protonated compounds such as \( \text{D}_2\text{OCl}^+ \) so that the hypochlorous acidium ion would be lower in concentration in the lighter solvent. It was found that the rate in light water was only 52% that in heavy water. This result requires the interpretation with the chloronium ion as an intermediate.

de la Mare and Pritchard\(^\text{18}\) have shown in connection with the addition of \( \text{HOC1} \) to allyl chloride that the same general pattern (as in aromatic substitution) is followed. Both \( \text{Cl}^+ \) and \( \text{H}_2\text{OCl}^+ \) were found to contribute in the initiation of the addition. Similar observations\(^\text{19}\) have been made for aromatic halogenations with hypobromous and hypiodous acids.

The evidences presented above and other numerous observations\(^\text{20}\) characteristic of olefin addition reactions

\[\text{eqn} \]


make it quite reasonable to assume that the first step in the addition of hypohalous acids to olefins may involve the formation of a halonium ion, i.e.,

\[
\begin{align*}
\text{I} & \quad \text{II} \quad \text{III} \quad \text{IV} \\
\text{C} & \text{C} + \text{X}^+ \quad \rightarrow \quad \text{C}^- \text{C}^- \quad \equiv \quad \text{C}^- \text{C}^- \quad \equiv \quad \text{C}^- \text{C}^- \\
\end{align*}
\]

in which (II) and (IV) do not necessarily have to be resonance forms of (III). Little is known concerning their energy relationships and it is not known whether (III) can be of sufficient life to be classified as an intermediate rather than as a transition state separating the other two possible intermediate carbonium ions (II) and (IV). However, when \(X\) is bromine, (II) and (IV) may be resonance forms of (III) so that the two C-X bonds in (III) may be equivalent. This is favored by the great tendency of bromine to exert a neighboring group effect. The equivalence of the two C-X bonds in (III) is also supported by the investigations of Kwart and Weisfeld in which the acid-catalyzed isomerization of 5-alpha-6-beta-dibromocholestan (VI) was interpreted

\[
\begin{align*}
\text{V} & \quad \text{VI} \quad \text{VII} \quad \text{VIII} \\
\end{align*}
\]


as going through a bromonium-bromide ion pair intermediate (VII). However, the above isomerization process shows characteristics different from those observed in the normal addition of halogens to olefins; e.g.,

(1). There is no common ion effect or any significant effect of neutral salt or added nucleophilic reagent.

(2). The amount of solvolytic side reaction attending the mutarotation is negligible.

(3). The rate in hexane (medium of low polarity and low ion solvating power) is very fast compared to the rate in much higher dielectric solvents.

(4). The position of equilibrium indicates that the intermediate bromonium-bromide ion pair (VII) is transformed more rapidly into (VIII) than into (VI).

The above characteristics suggest that (VII) may not be the intermediate in the original bromine addition.

Brown, Brewster and Shechter have emphasized the importance of ring strain in cyclic systems. A change in the coordination number of a ring carbon atom from 4 to 3

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(i.e., from sp$^3$ to sp$^2$ hybridization) increases the number and degree of unfavorable conformations when the atom is part of a 6-membered ring system. Such a change has the opposite effect when it is part of a 5-membered ring system. Hence, reactions involving this change are sterically hindered in cyclohexane derivatives and are sterically facilitated in cyclopentane derivatives. Similarly, an exo-double bond in a 5-membered ring results in a less strained conformation than one in a 6-membered ring system. These considerations, plus the assumption (justified on the basis of thermochemical data) that the difference in stability between exo-double bonds in the 5- and 6-membered rings is larger than the difference in stability between endo-double bonds in these systems, led Brown, Brewster and Shechter to the generalization that "reactions will proceed in such a manner as to favor the formation or retention of an exo-double bond in the 5-membered ring and to avoid the formation or retention of the exo-double bond in the 6-ring systems."

The above generalization accounts for the equilibria involving exo- and endo-double bond isomers, the direction


of olefin formation in monocyclic terpenes and related compounds, the relative ease of ring-opening reactions of cyclic esters, lactones and related substances and the preference for pyranose and furanose structures in the sugars and sugar acids respectively. It has been applied successfully to the rearrangement of some terpene alcohols containing cyclopentane and cyclohexane rings. It can account for the isomerization of Vitamin D$_2$ to isotachysterin and also for the rates of acetolysis of the cycloalkyl p-toluene- and p-bromobenzenesulfonates. However, the rearrangement of some substituted allyl alcohols to their isomeric ketones and the base-catalyzed rearrangement of l-cyclohexenylmethyl diphenylacetate yielded products which are not in accord with the above predictions. Hence, more experimental study is desirable to test the general utility and applicability of the proposed generalization.

The present investigation is an attempt to test and


if possible to extend the generalization to addition reactions of *exo*-cyclic olefins. With the proper choice of ring system, either (IX) or (X) may be predicted to be the type of intermediate favored by relief of ring strain in that system.

\[ \text{(IX)} \quad \text{(X)} \]

The following addition reactions to methylenecyclobutane, methylenecyclopentane, methylenecyclohexane and methylenecycloheptane were selected for study:

1. The ionic and radical additions of hydrogen bromide.
2. The addition of hypochlorous acid.
3. The addition of hypobromous acid.
4. The addition of chlorine in the presence and in the absence of extraneous anions.

A related problem (Part 5) involving the reaction of hydrobromic acid with the corresponding methylenecycloalkane oxides (except methylenecyclobutane oxide) was also investigated.
II. EXPERIMENTAL

A. THE PREPARATION OF METHYLENECYCLOALKANES.

1. The Preparation of Methylenecyclobutane.
   
a. Pentaerythrityl tetrabromide.  
   
Pentaerythritol (107 g, 0.79 mole) was placed in a 500-ml., one-neck round bottom flask provided with a condenser bearing at its upper end a dropping funnel and a gas-outlet tube connected to a trap for absorbing the large quantity of gas (HBr) which was evolved. The flask was heated by an oil bath which was kept at 90-100°. Freshly-distilled phosphorus tribromide (132 g., 1.60 moles) was added very cautiously from the dropping funnel. After the addition was complete, the temperature of the oil bath was raised very gradually to 170-180° where it was kept for 24 hours. Cold water (100 ml.) was added from the dropping funnel to destroy any unreacted phosphorus tribromide. The orange-red precipitate was filtered with

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(34) The PBr₃ was prepared by adding Br₂ to a stirred suspension of red phosphorus in CCl₄. The yield is 90%.

(35) The gradual rise in temperature avoids the formation of phosphorus hydrides which spontaneously ignites and destroys the preparation.
suction. It was washed several times with hot water and then with two 150-ml. portions of cold ethyl alcohol to remove any bromohydrin. The precipitate was extracted exhaustively with ethyl alcohol in a Soxhlet extractor. The pentaerythrityl tetrabromide, which precipitated from the chilled extract, was filtered with suction and recrystallized from ethyl alcohol. A 72% yield (220 g.) was obtained; m.p. 162-163°. (Reported\(^{33}\): m.p. 163°).

b. \textit{Methylenecyclobutane}\(^{36}\).

A solution of 11.6 g. of zinc bromide and 35 ml. of ethanol in 800-ml. of water was placed in a 3-liter, 3-neck flask equipped in the middle neck with a Hershberg stirrer and a thermometer which extended into the solution. Another neck was fitted with a Claisen head which was connected to a West and a Friedrichs condenser in series. The receiver at the end of the latter condenser was immersed in a Dry Ice-acetone bath. Stirring was begun and 552 g. (8.45 g. atoms) of zinc dust was added. The contents of the flask were heated to 90° and 785 g. (2.14 moles) of pentaerythrityl tetrabromide was added by means of a rubber tube\(^{37}\) through the third neck in portions as rapidly as was permitted by the foaming of the mixture.


The temperature was maintained at 90° during the addition and afterwards for half an hour. The hydrocarbon which steam distilled during this time was washed with cold water and dried with anhydrous magnesium sulfate. Fractionation through a Vigreaux air-condenser gave 75.5 g. (52%) of methylenecyclobutane; b.p. 41-42°, d^20_4 0.7409, n^20_D 1.4204. (Reported: b.p. 42°36°38, 40°39, d^20_4 0.7401, d^15_4 0.742539; n^20_D 1.4208738, n^15_D 1.423539.)

2. The Preparation of Methylenecyclopentane.
   a. Cyclopentanone. 40

   Adipic acid (975 g., 6.56 moles) and 77.1 g. (0.67 mole) of mangancus carbonate were placed in a 2-liter flask fitted with a thermometer which reached nearly to the bottom and with an 8-inch Vigreaux distilling column. The flask was heated slowly and after the mixture had entirely melted, the heat was increased until the thermometer registered 280°, at which temperature decomposition took place. The temperature was maintained at 280-290° until a dense fog was evolved which signified the end of


the reaction\(^{41}\). Sufficient potassium carbonate was added
to the two-phase distillate to saturate the aqueous phase.
The cyclopentanone layer was washed with saturated potassium
carbonate solution and dried with anhydrous potassium
carbonate. On distillation, 362.3 g. (65%) of cyclopentanone
was obtained; b.p. 129-130°, d\(^{20}\)\(_{4}\) 0.9445, n\(^{20}\)\(_{D}\) 1.4365.
(Reported: b.p. 129°(756 mm.)\(^{42}\), 129\(^{043}\); d\(^{20}\)\(_{4}\) 0.9450\(^{42}\),
0.9502\(^{43}\); n\(^{20}\)\(_{D}\) 1.43680\(^{42}\), 1.4370\(^{43}\).)

b. 1-Methylcyclopentanol\(^{44}\).

Cyclopentanone (252 g., 3.0 moles), methyl iodide\(^{45}\)
(426 g., 3.0 moles) and magnesium turnings (72 g., 3.0 g.
atoms) gave 1-methylcyclopentanol (174 g., 58%), b.p.
135-136°, d\(^{20}\)\(_{4}\) 0.9109, n\(^{20}\)\(_{D}\) 1.4445. (Reported\(^{46}\): b.p.
135-136°, d\(^{23.5}\)\(_{4}\) 0.9044, n\(^{23.5}\)\(_{D}\) 1.4429.)

c. 1-Methylcyclopentyl acetate\(^{44}\).

1-Methylcyclopentanol (172 g., 1.72 moles), pyridine
(140 g., slightly more than 1.72 moles) and acetyl chloride

\(^{41}\) The residue in the flask is hard to remove.
Let the flask stand overnight with some alcoholic KOH.


\(^{43}\) Noller and Adams, J. Am. Chem. Soc., 48,
1080 (1926).

\(^{44}\) For details, see procedure for the preparation
of the cyclohexyl analog.

\(^{45}\) CH\(_3\)Br gave a higher yield, 71 and 86% yields
of 1-methylcyclopentanol and 1-methylcyclohexanol respectively.

\(^{46}\) Zelinsky and Moser, Ber., 35, 2685 (1902).
(145 g., slightly more than 1.72 moles) were used in the preparation of 1-methylocyclopentyl acetate. Some alcohol (13 g., 8%) was recovered and 170 g. (75%, based on unrecovered alcohol) of the ester was collected; b.p. 155-156°, d²⁰ 0.9462, n₂₀ 1.4320.

d. Methylenecyclopentane.

1-Methylocyclopentyl acetate (125 g., 0.78 mole) was pyrolysed at 450°. Some ester (32.1 g., 25%) was recovered and some methylenecyclopentane (37 g., 69%) was collected; b.p. 75-76°, d²⁰ 0.7777, n₂₀ 1.4310. (Reported: b.p. 75-76°², 75.7°², d²⁰ 0.7787², 0.7806²; n₂₀ 1.13078², 1.435547.)

3. The Preparation of Methylenecyclohexane.

a. 1-Methylocyclohexanol.

Magnesium turnings (67.5 g., 2.78 g. atoms) were placed in a 3-liter, 3-neck flask fitted with a dropping funnel, a Hershberg stirrer and a Friedrichs condenser. A nitrogen inlet-tube leading to a mercury valve was attached to the dropping funnel and a drying tube filled with Drierite and soda lime was connected to the outlet of the condenser. Anhydrous ether (200 ml.) was added to cover the magnesium. A few ml. of the methyl iodide solution (395 g., 2.78 moles, in 400 ml. of anhydrous ether) was added to start

the reaction. After the reaction had subsided, the remainder of the methyl iodide solution was added fast enough to maintain gentle refluxing. After all the methyl iodide had been added, the mixture was refluxed for an hour then cooled to room temperature.

Freshly-distilled cyclohexanone\(^{48}\) (272 g., 2.78 moles) in anhydrous ether (400 ml.) was added dropwise to the Grignard reagent. After approximately half of the cyclohexanone solution had been added, a precipitate started forming which made the mixture hard to stir\(^{49}\). The stirring was continued by hand until all the cyclohexanone solution had been added. Cracked ice (600 g.) was added all at once to the solidified mass to avoid local superheating and thus prevent the mixture from foaming out of the flask. The mixture was rapidly agitated until the decomposition of the Grignard complex was complete. The ether layer was decanted and the precipitate was extracted twice with ether. The combined organic material was steam distilled\(^{50}\). The ether layer separated and the aqueous layer was salted out with sodium chloride. The combined organic portion was dried

(48) A lower yield was always obtained if the ketone was not freshly distilled.

(49) The heavy precipitate, which was not formed when CH\(_3\)MgBr is used, causes inadequate mixing and was probably responsible in part for the lower yield when CH\(_3\)I is used.

(50) Steam distillation at this point minimizes dehydration to 1-methylcycloalkene during purification of the alcohol.
with anhydrous potassium carbonate and distilled. A 75% yield (236 g.) of 1-methylcyclohexanol was obtained; b.p. 155-156°, \(d_{20}^0 0.9290\), \(n_{20}^D 1.4610\). (Reported: b.p. 70° (25 mm.), 51, 53-54° (7 mm.), 52; \(d_{20}^2 0.9325\); \(n_{20}^D 1.4546\), 1.4610.52.)

b. 1-Methylcyclohexyl acetate.

Procedure A53.

1-Methylcyclohexanol (37 g., 0.32 mole) and finely-powdered magnesium (7.8 g., 0.32 g. atom) were placed in a 250-ml., 3-neck flask fitted with a stirrer, a condenser and a dropping funnel. A few ml. of acetic anhydride was added and the flask was heated on a steam bath to start the reaction. After the reaction had started, the steam bath was removed and acetic anhydride (35 g. total, slightly more than 0.32 mole) was added slowly. Ice (75 g.) was added and the mixture was extracted with petroleum ether. The petroleum ether extract was washed successively with water, with dilute sodium carbonate solution and finally with water. The extract was dried with anhydrous potassium carbonate and distilled. Some alcohol (1816 g., 50%) was recovered and 13.5 g. (54%, based on unrecovered alcohol)

of ester was collected; b.p. 178-179°, d$_{20}^4$ 0.9572, n$_{20}^D$ 1.4380.

**Procedure B.**

1-Methylcyclohexanol (403 g., 3.54 moles) and pyridine (385 g., slightly more than 3.54 moles) were placed in a 1-liter, 3-neck flask which was immersed in an ice-bath and was equipped with a stirrer, a condenser and a dropping funnel. Slightly more than 3.54 moles (280 g.) of acetyl chloride were added slowly. After all the acetyl chloride had been added and the reaction mixture had subsided, the ice-bath was removed and the mixture was heated on a water bath (approximately 60°) for 3 hours. Ice (200 g.) was added and the mixture was extracted with 200 ml. of petroleum ether. The extract was washed with water, with dilute sodium carbonate solution and with water. It was dried with anhydrous potassium carbonate and distilled. Some alcohol (58 g., 14%) was recovered and 381.5 g. (74%) of ester was collected; b.p. 178-179°, d$_{20}^4$ 0.9568, n$_{20}^D$ 1.4375. (Reported$^53$: 177-178°, d$_{25}^{25}$ 0.9545, n$_{25}^{25}$ 1.4355.)

c. Methylene cyclohexane$^53$.

The *exo*-olefin was prepared by pyrolysis of the tertiary acetate.

The apparatus for pyrolysis consisted of a Pyrex glass tube, 9 mm. in diameter and 45 cm. in length, 25 cm. of which was packed with 1/8-inch Pyrex helices. The tube was inserted in a Sargent Carius Combustion Apparatus,
arranged vertically, which was kept at 450°, and was continually swept out with dry nitrogen gas. The lower end of the pyrolysis tube was connected to a condenser which led to a distilling flask receiver immersed in a chloroform-Dry Ice bath.

1-Methylcyclohexyl acetate (109.7 g., 0.70 mole) was pyrolysed at the rate of 3 ml. per minute (one drop per second). The slow stream of nitrogen maintained a non-oxidizing condition within the tube and also forced the pyrolysate vapor into the receiver. Care was taken so that minimum carbonization occurred in the tube. This was done by adjusting the rate and the temperature of the pyrolysis. The optimum condition was obtained when only 60-70% of the acetic acid was cracked out.53

The pyrolysate was extracted with petroleum ether (b.p. 30-38°) and the extract was washed with water, with dilute sodium carbonate solution and with water. It was dried with anhydrous potassium carbonate and fractionated through a Vigreux air-condenser. Some ester (35 g., 33%) was recovered and 38 g. (84%, based on unrecovered ester) of methylenecyclohexane was collected; b.p. 108-109°, d204 0.8038, h20D 1.4508. (Reported: b.p. 102-103° (764 mm.) 42,

Identity of Methylenehexane Sample.

Due to the great diversity in the physical constants reported in the Literature for methylenehexane, it is desirable to authenticate the identity of the pyrolysis product. Since 1-methylcyclohexene is the most probable side-reaction product, it was synthesized in an independent way. The physical constants and infrared spectra of the two olefins were determined and are compared in Tables I and II.

**TABLE I**

<table>
<thead>
<tr>
<th></th>
<th>B.p.</th>
<th>$d_{20}^\circ$</th>
<th>$n_{20}^D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methylenehexane</td>
<td>108-109°</td>
<td>0.8038</td>
<td>1.4508</td>
</tr>
<tr>
<td>1-Methylcyclohexene$^a$</td>
<td>110-111°</td>
<td>0.8097</td>
<td>1.4502</td>
</tr>
</tbody>
</table>

$^a$Reported: b.p. 110° (769 mm.), 106-107°$^5$, 109.5°$^5$, d$^\circ_{20}$ 0.8127$^42$, 0.799$^5$, 0.8117$^57$; n$^D_{20}$ 1.45067$^42$, 1.44324$^54$, 1.4505$^57$.


(56) Synthesized by dehydration of 1-methylcyclohexanol with hot concentrated phosphoric acid in 85% yield.

(57) Reference 55, p.326.
### TABLE II

Comparison of Spectrum of Olefins.

<p>| Methylene- | 1-Methyl- | Methylene- | 1-Methyl- |</p>
<table>
<thead>
<tr>
<th>cyclohexane.</th>
<th>cyclohexene.</th>
<th>cyclohexane.</th>
<th>cyclohexene.</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.33 μ (w) -- 2.39 μ (w)</td>
<td>9.18 μ (m) -- 9.21 μ (s)</td>
<td>9.78 (w) -- 9.79 (m)</td>
<td></td>
</tr>
<tr>
<td>5.76 (w) -- 5.80 (m)</td>
<td>10.15 (w) -- absent</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6.02 (m) -- 5.97 (w)</td>
<td>10.34 (w) -- 10.35 (m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.24 (m) -- 7.28 (s)</td>
<td>10.90 (m) -- 10.92 (s)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.44 (w) -- 7.47 (w)</td>
<td>11.27 (s) -- 11.20 (m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.64 (w) -- 7.66 (w)</td>
<td>11.69 (m) -- 11.64 (m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>7.87 (w) -- 7.90 (m)</td>
<td>12.19 (w) -- 12.21 (m)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8.65 (w) -- 8.67 (m)</td>
<td>13.16 (m) -- 13.17 (s)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The methylenecyclohexane was converted to the glycol (52% yield) with peroxyformic acid; m.p. 76-77°C (Reported: 76-77°C). The 1-methylcyclohexene glycol is reported to melt at 84°C.

To test further the authenticity of the methylenecyclohexene sample, the glycol was heated with concentrated hydrobromic acid solution. It gave an 81% yield of cyclohexanecarboxaldehyde; b.p. 49.5°C (10 mm.), d²⁰ 0.9303, n²⁰ D 1.4490 (Reported: b.p. 61-63°C (24 mm.))

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n18D 1.450359); m.p. of 2,4-dinitrophenylhydrazone, 172-173° (Reported59: 172°).

No explanation for the difference in b.p. between the sample of methylenecyclohexane prepared here and those previously described is apparent.

4. The Preparation of Methylenecycloheptane.

a. Cycloheptanone.

Procedure A.

(1) Ethyl N-methylcarbamate61.

Ethyl chlorocarbonate (217 g., 2.0 moles), a 25% aqueous solution of methylamine (24.8 g., 2.0 moles) and sodium hydroxide (80 g., 2.0 moles) gave a 92% yield (188.14 g.) of ethyl N-methylcarbamate; b.p. 86.5-87.5° (38 mm.), d20 1.0145, n20D 1.4195. (Reported61: b.p. 55-56°(12 mm.)

(2) N-Nitrosomethyleneurethane62.

Ethyl N-methylcarbamate (155 g., 1.5 moles), sodium nitrite (435 g., 6.0 moles) and a 35% nitric acid solution (800 ml., 4.5 moles) gave an 84% yield (166 g.) of N-nitrosomethyleneurethane; b.p. 51-52°(7.3 mm.), d20 1.335, n20D 1.4389. (Reported62: b.p. 59-61°(10 mm.), d20 1.133.)


(62) Hartman and Philipps, reference 61, p. 464. Extreme caution must be exercised throughout this preparation since the urethane is very irritating, corrosive, toxic and explosive.

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(3) Cycloheptanone\(^{63}\).

Freshly-distilled cyclohexanone (125 ml., 118 g; 1.21 moles) and N-nitrosomethylurethane (150 g., 1.14 moles) gave 12% (15 g.) of recovered cyclohexanone, 8% (9.8 g.) of methylencyclohexane oxide and 57% (71.8 g.) of cycloheptanone; b.p. 76-81°(33 mm.), d\(^{20}\) 0.9484, n\(^{20}\)D 1.4594.

Procedure B.

(1) Cyclohexanone cyanohydrin\(^{64}\).

Cyclohexanone (210 g., 2.14 moles) was added with shaking to a saturated solution of sodium bisulfite, prepared by dissolving 400 g. (2.40 moles) of sodium metabisulfite in 600 ml. of water, decanting the solution and adding 200 ml. of ethanol. The bisulfite addition product was filtered with suction and was washed with ethanol and with ether.

The bisulfite addition product was placed in a 2-liter, 3-neck flask fitted with a stirrer and condenser and cooled with an ice-bath. A solution of 159 g. (2.45 moles) of potassium cyanide in 300 ml. of water was added. After half an hour, the ice-bath was removed and the stirring was continued for 2 hours. The cyanohydrin was separated


and the aqueous layer was extracted with ether. The extract was washed with water, dried with anhydrous magnesium sulfate and distilled. A 70% yield (180 g.) of the cyano­hydrin was obtained; b.p. 105-106°(6 mm.), d₂⁰ 1.0135, n₂⁰ 1.4645. (Reported⁵: b.p. 91-95°(2 mm.), n₂⁰ 1.4643.)

(2) Cycloheptanone⁶⁶.

Lithium aluminum hydride (76 g., 2.0 moles) was placed in a 3-liter, 3-neck flask equipped with a stirrer, a dropping funnel and a Friedrichs condenser fitted with a drying tube. Anhydrous ether (1.2 l.) was added from the dropping funnel and the mixture was refluxed for several hours (approximately 5 hours) until the suspended solid no longer diminished in quantity.

The slurry was cooled and a solution of 125 g.(1.0 mole) of cyclohexanone cyanohydrin in 200 ml. of anhydrous ether was added slowly. The mixture was refluxed for 5 hours and the stirring was continued for 24 hours at room temperature. With an ice-bath surrounding the flask, the addition complex was decomposed by adding successively, dropwise, 50 ml. of water, 40 ml. of 20% sodium hydroxide and 150 ml. of water. The precipitated alumina was extracted with 200 ml. of benzene in a Soxhlet extractor.

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The 1-aminomethylcyclohexanol was extracted from the combined organic portions with a cold solution of acetic acid (180 ml. of glacial acetic acid diluted with 1-liter of water). The aqueous extract was placed in a 3-liter, 3-neck flask equipped with a stirrer and a dropping funnel. A cold solution of 116 g. (1.68 moles) of sodium nitrite in 300 ml. of water was added dropwise to the solution whose temperature was maintained near -5°. The mixture was stirred an hour longer and then allowed to come to room temperature overnight as the ice in the cooling bath melted. Small portions of solid sodium bicarbonate were added to the reaction mixture to neutralize the acetic acid. The neutral solution was steam distilled. The oily layer in the distillate was separated and the aqueous layer was salted out. The combined organic material was dried with anhydrous magnesium sulfate and distilled. A 45% yield (51 g.) of cycloheptanone was collected; b.p. 85-86°(37 mm.), 179-180°; d_20^\text{D} 0.9500, n_20^\text{D} 1.4610. (Reported: b.p. 180°(760 mm.)^42, 66-70°(16 mm.)^67; d_20^\text{D} 0.9491^42, 0.9490^67; n_20^\text{D} 1.45976^42, 1.460867.)

b. 1-Methylcycloheptanol

Cycloheptanone (42 g., 0.37 mole) methyl iodide (57 g., 0.40 mole) and magnesium turnings (9.6 g., 0.40 g. atom) were used in the synthesis of 1-methylcycloheptanol.

A 63% yield (30 g.) of the alcohol was collected; b.p. 93-94° (40 mm.), d²₀ 0.9332, n²₀ 1.4690. (Reported⁶⁸: b.p. 183-185°, d²₂ 0.9285, n²₂ 1.4677.)

c. 1-Methylcycloheptyl acetate⁴⁴.

1-Methylcycloheptanol (53 g., 0.41 mole), pyridine (37 g., slightly more than 0.41 mole) and acetyl chloride (36 g., slightly more than 0.41 mole) were used in the preparation of the ester. Some alcohol (12 g., 23%) was recovered and 32 g. (58%, based on unrecovered alcohol) of ester was collected; b.p. 110-111° (40 mm.), d²₀ 1.0332, n²₀ 1.528.

d. Methylene cycloheptane⁴⁴.

1-Methylcycloheptyl acetate (29.0 g., 0.17 mole) was pyrolysed at 450°. Some of the ester (8.7 g., 30%) was recovered and 9.3 g. (72%, based on unrecovered ester) of methylene cycloheptane was obtained; b.p. 138-139°, d²₀ 0.8231, n²₀ 1.4609. (Reported: b.p. 138-139°⁵⁴, 138-140°⁶⁹; d²₀ 0.8241⁵⁴, 0.824⁶⁹; n²₀ 1.4611⁵⁴, ⁶⁹.)

B. THE ADDITION OF HYDROGEN BROMIDE TO METHYLENE CYCLOALKANES⁷⁰.

⁶⁸ Wallach, Ann., 345, 139 (1906).

⁶⁹ Reference 39, p. 599.

⁷⁰ Except for the cyclobutane derivatives, the identity of the products were established by comparison of the physical constants and infrared spectra of the addition product and of the authentic sample prepared by independent methods. In each case the infrared spectrum of the synthesized product and the corresponding addition product were identical. The infrared spectra were taken with a Perkin Elmer Model 21 double-beam recording infrared spectrophotometer.
Ionic Addition.

A solution of approximately 0.1 mole of methylene-cycloalkane in 50 ml. of glacial acetic acid was placed in a 200-ml., 3-neck flask which was cooled with an ice-bath. The flask was equipped with a gas-inlet tube, a stirrer and a gas-outlet tube connected to a 
CCl₄-valve. Slightly more than 0.1 mole of anhydrous hydrogen bromide was passed into the solution. The temperature of the mixture was kept at 5-10° for 8 hours. The reaction mixture was poured into 100 ml. of water. The product was taken up in petroleum ether (b.p. 30-38°), was washed with dilute sodium bicarbonate solution and with water. It was dried with anhydrous sodium sulfate. The dried extract was fractionated and the portion which distilled at a narrow and constant range was collected.

Free Radical Addition.

The radical addition was promoted by ultraviolet irradiation. A 250-watt General Electric type H Mercury vapor lamp was used as the source of ultraviolet light.

A solution of approximately 0.1 mole of methylene-cycloalkane in 50 ml. of purified petroleum ether (b.p. 35-40°) was placed in a quartz reaction flask equipped with

(71) Anhydrous HBr was prepared by dropping Br₂ into hot tetralin and was freed from Br₂ by bubbling it through a solution of phenol in CCl₄ or a suspension of red phosphorus in CCl₄ and into a column of copper turnings. The gas was dried by passing it through a column of Drierite.
a gas-inlet tube and a thermometer. Anhydrous HBr was passed for 2 hours into the solution which was maintained at -20 to -25° by means of a Dry Ice-CCl₄ bath. The reaction mixture was poured into 100 ml. of water and was washed successively with dilute ferrous sulfate solution, with dilute sodium bicarbonate solution and finally with water. The organic material was dried with anhydrous sodium sulfate. The dried extract was fractionated.

1. Methylenecyclobutane.
   a. Ionic Addition.

   The reaction product from 6.0 g. (0.09 mole) of methylenecyclobutane gave 8.0 g. (61.0%) of the suspected 1-bromo-1-methylcyclobutane; b.p. 111-112°, d₂⁰ 1.3187, n₂⁰D 1.4695. (Reported²a: b.p. 55-57° (100 mm.); d₂⁰ 1.3179, n₂⁰D 1.4698.) Side reaction products were also isolated: I, an unidentified fraction containing bromine with b.p. 76-77°, d₂⁰ 1.5630, n₂⁰D 1.4582; Anal.²b, C, 8.76, 8.90%; H, 0.60, 0.42%; and II, 1,2-dibromo-2-methylbutane, b.p. 83-84° (40 mm.), d₂⁰ 1.6701, n₂⁰D 1.5090. (Reported⁷⁻: b.p. 47-48° (9 mm.), d₂⁰ 1.6711, n₂⁰D 1.5088.)

   Treatment of 10.0 g. (0.15 mole) of methylenecyclobutane with an excess of hydrogen bromide yielded 8.4 g. of the

unidentified fraction (b.p. 76-77°, n²⁰D 1.4587), 7.8 g. (35.8%) of 1-bromo-1-methylcyclobutane (b.p. 110-111°, n²⁰D 1.4690) and 9.5 g. (26.1%) of 1,2-dibromo-2-methylbutane (b.p. 82-83°(37 mm.), n²⁰D 1.5085).

Isomerization of 6.2 g. (0.04 mole) of 1-bromo-1-methylcyclobutane under the same conditions as the addition reaction yielded 1.5 g. of the unidentified fraction (b.p. 76-77°, n²⁰D 1.4583), 0.5 g. (8%) of the starting material and 3.5 g. (37%) of 1,2-dibromo-2-methylbutane (b.p. 80-81°(34 mm.), n²⁰D 1.5080).

b. Free Radical Addition.

The radical addition of hydrogen bromide to 6.0 g. (0.09 mole) of methylenecyclobutane gave 7.8 g. (59.3%) of the suspected bromomethylcyclobutane; b.p. 122-123°, d¹⁵ 1.3259, d²⁰ 1.3183, n²⁰ 1.4726, n²⁵ 1.4707. (Reported: b.p. 121-123°(710 mm.), 81-83°(125 mm.)75, 137-139°76; d¹⁵ 1.36075, d¹⁹ 1.40076; n²⁵ 1.470474, n¹⁹ 1.487876.)

Infrared analysis of various fractions of the reaction mixture suggests the absence of any side-reaction product.

2. Methylenecyclopentane.

a. Ionic Addition.

The ionic addition of hydrogen bromide to 6.5 g.


(76) Demjanow, Ber., 40, 4959 (1907).
(0.08 mole) of methylenecyclopentane gave 6.8 g. (52.6%) of the suspected 1-bromo-1-methylcyclopentane; b.p. 56-57° (37 mm.), $d^{20}_{4} = 1.2993$, $n^{20D} = 1.4817$. (Authentic 1-bromo-1-methylcyclopentane: b.p. 55-56° (36 mm.), $d^{20}_{4} = 1.2984$, $n^{20D} = 1.4815$.)

b. Free Radical Addition.

The radical addition of hydrogen bromide to 5.0 g. (0.06 mole) of methylenecyclopentane gave 6.0 g. (60.4%) of the suspected bromomethylcyclopentane; b.p. 71-72° (37 mm.), $d^{20}_{4} = 1.2722$, $n^{20D} = 1.4832$. (Authentic bromomethylcyclopentane: b.p. 72-73° (38 mm.), $d^{20}_{4} = 1.2713$, $n^{20D} = 1.4831$.)

3. Methylenecyclohexane.

a. Ionic Addition.

Ionic addition of hydrogen bromide to 14.0 g. (0.14 mole) of methylenecyclohexane yielded 16.7 g. (64.7%) of the suspected 1-bromo-1-methylcyclohexane; b.p. 77-78° (38 mm.), $d^{20}_{4} = 1.2495$, $n^{20D} = 1.4866$. (Authentic 1-bromo-1-methylcyclohexane: b.p. 77-78° (38 mm.), $d^{20}_{4} = 1.2506$, $n^{20D} = 1.4866$.)

b. Free Radical Addition.

Radical addition of hydrogen bromide to 5.0 g. (0.05 mole) of methylenecyclohexane yielded 6.5 g. (67.3%) of the suspected bromomethylcyclohexane; b.p. 92-93° (37 mm.); $d^{20}_{4} = 1.2832$, $d^{25}_{4} = 1.2760$, $n^{20D} = 1.4928$, $n^{25D} = 1.4905$. (Authentic bromomethylcyclohexane: b.p. 93-94° (38 mm.), $d^{25}_{4} = 1.2760$, $n^{25D} = 1.4906$.)
   a. Ionic Addition.

   Ionic addition of hydrogen bromide to 2.0 g. (0.02 mole) of methylene cycloheptane gave 2.2 g. (63.4%) of the suspected 1-bromo-1-methylcycloheptane; b.p. 101-102° (38 mm.), d$_{20}^{4}$ 1.2353, n$_{D}^{20}$ 1.4962. (Authentic 1-bromo-1-methylcycloheptane: b.p. 102-103° (39 mm.), d$_{20}^{4}$ 1.2363, n$_{D}^{20}$ 1.4966.)

   b. Free Radical Addition.

   Radical addition of hydrogen bromide to 2.0 g. (0.02 mole) of methylene cycloheptane gave 2.1 g. (60.5%) of the suspected bromomethylcycloheptane; b.p. 107-108° (38 mm.), d$_{20}^{4}$ 1.253, n$_{D}^{20}$ 1.4989. (Authentic bromomethylcycloheptane: b.p. 106-107° (38 mm.), d$_{20}^{4}$ 1.254, n$_{D}^{20}$ 1.4987.)

THE SYNTHESSES OF THE ADDITION PRODUCTS FROM HYDROGEN BROMIDE AND METHYLENE CYCLOALKANES.

a. 1-Bromo-1-methylcyclopentane

1-Methylcyclopentanol (50 g., 0.50 mole) (see p. 17) and 48% hydrobromic acid (220 g., 1.30 moles) gave 36 g. (47%) of 1-bromo-1-methylcyclopentane; b.p. 55-56° (36 mm.), d$_{20}^{4}$ 1.2984, n$_{D}^{20}$ 1.4815. (Reported: b.p. 74-76° (82 mm.), d$_{13}^{4}$ 1.3004, n$_{D}^{13}$ 1.4823.)

b. Bromomethylcyclopentane.

(1) Chlorocyclopentane\textsuperscript{78}.

Cyclopentanol (138 g., 1.60 moles) and a solution of anhydrous zinc chloride (470 g., 3.48 moles) in concentrated hydrochloric acid (328 g., 3.94 moles) gave a 68\% yield (112 g.) of chlorocyclopentane; b.p. 114-115\(^\circ\), \(d_{20}^\circ 1.0045\), \(n_{20}^\circ 1.4515\). (Reported\textsuperscript{79}: b.p. 114.5-115\(^\circ\) (777 mm.), \(d_{20}^\circ 1.0053\), \(n_{20}^\circ 1.45127\).)

(2) Cyclopentylcarbinol\textsuperscript{114}.

Chlorocyclopentane (104 g., 1.0 mole), magnesium turnings (24 g., 1.0 g. atom) and paraformaldehyde (30 g., 0.33 mole) gave 65 g. (65\%) of cyclopentylcarbinol; b.p. 162-163\(^\circ\), \(d_{20}^\circ 0.9305\), \(n_{20}^\circ 1.4576\). (Reported\textsuperscript{80}: b.p. 162-162.5\(^\circ\), \(d_{20}^\circ 0.9313\), \(n_{20}^\circ 1.4579\).)

(3) Bromomethylcyclopentane\textsuperscript{114}.

Cyclopentylcarbinol (25 g., 0.40 mole) and phosphorus tribromide (38 g., slightly more than 0.14 mole) gave a 47\% yield (20 g.) of bromomethylcyclopentane; b.p. 73-74\(^\circ\) (38 mm.), \(d_{20}^\circ 1.2713\), \(n_{20}^\circ 1.4831\). (Reported\textsuperscript{79}: b.p. 56-57\(^\circ\) (17 mm.).

c. 1-Bromo-1-methylcyclohexane.

1-Methylcyclohexanol (25 g., 0.22 mole) (see p.18) was placed in a 250-ml., 3-neck flask equipped with a stirrer, and a dropping funnel. The alcohol was cooled and 48\%
hydrobromic acid (110 g., 0.65 mole) was added slowly. The stirring was continued for an hour after all the alcohol had been added. The mixture was extracted with 75 ml. of petroleum ether. The extract was washed with dilute sodium bicarbonate solution and with water. It was dried with anhydrous calcium chloride and distilled. Collected were 20 g. (52%) of 1-bromo-1-methylcyclohexane; b.p. 78-79° (38 mm.), \( \delta_{20}^\text{D} 1.2506, n_{20}^\text{D} 1.4866 \). (Reported\(^{81}\): b.p. 66-66.5° (22 mm.), \( n_{25}^\text{D} 1.4468 \).)

**d. Bromomethylcyclohexane.**

(1) Cyclohexylcarbinol\(^{83}\).

Magnesium turnings (36 g., 1.5 g. atoms), anhydrous ether (200 ml.) and a crystal of iodine were placed in a 2-liter, 3-neck flask fitted with a dropping funnel, a Hershberg stirrer and a Friedrichs condenser stoppered by a drying tube. A few ml. of a cyclohexyl bromide solution (245 g., 1.50 moles of cyclohexyl bromide in 300 ml. of anhydrous ether) was added. Heat was applied to start the reaction. When the color of the iodine had disappeared and the reaction had subsided, the heat was removed and the remainder of the cyclohexyl bromide solution was added

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\(^{82}\) This may be a misprint since the values for \( n_{20}^\text{D} \) for the lower and higher homologous 1-bromo-1-methylcycloalkanes are 1.4815 and 1.4966 respectively.

at such a rate that gentle refluxing was maintained. The mixture was refluxed for an hour after all the halide had been added and was then cooled to room temperature.

The dropping funnel was replaced by a wide glass tube (approximately 12 mm. inside diameter) which reached almost to, but not below, the surface of the liquid. The wide tube was connected to a 500-ml. flask which contained 45 g. (0.5 mole) of paraformaldehyde and an inlet-tube for admitting nitrogen. The paraformaldehyde had been dried previously for 2 days in a vacuum desiccator over phosphorus pentoxide. The paraformaldehyde was heated at 180-200° and the formaldehyde formed was carried over to the Grignard reagent by the slow stream of nitrogen. After the reaction was complete, 400 g. of cracked ice was added all at once, followed by 500-ml. of 30% sulfuric acid. The mixture was steam distilled. The 2-phase distillate was saturated with sodium chloride and extracted with ether. The combined extract was dried with anhydrous potassium carbonate and distilled. A 62% yield (107 g.) of cyclohexylcarbinol was obtained; b.p. 69-70° (5 mm.), d₂₀ 0.9272, n₂₀ 1.4650. (Reported: b.p. 91° (18 mm.), d₂₀ 0.9280, n₂₀ 1.4649.)

(2) Bromomethylcyclohexane.

Cyclohexylcarbinol (38 g., 0.33 mole) was placed in a 125-ml., 3-neck flask equipped with a stirrer and a

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dropping funnel. The alcohol was cooled and redistilled phosphorus tribromide (33 g., slightly more than 0.11 mole) was added slowly so that the temperature of the mixture did not rise above 0°. The temperature was allowed to rise gradually to room temperature after the addition was complete. Ice was added and the product was extracted with petroleum ether. The extract was washed with dilute sodium carbonate solution and with water, dried with anhydrous calcium chloride and steam distilled. A 53% yield (31.1 g.) of bromomethylcyclohexane was obtained; b.p. 94-95° (38 mm.), d^25_4 1.2760, n^25_D 1.4906. (Reported^85: b.p. 82-83° (26 mm.), d^25_4 1.2763, n^25_D 1.4906.)

e. 1-Bromo-1-methylcycloheptane^44.

1-Methylcycloheptanol (20.0 g., 0.16 mole) (see p.28) and 48% hydrobromic acid (79 g., 0.47 mole) gave a 52% yield (15.5 g.) of 1-bromo-1-methylcycloheptane; b.p. 102-103° (39 mm.), d^20_4 1.2363, n^20_D 1.4966.

f. Bromomethylcycloheptane.

(1) Cycloheptanol^86.

Lithium aluminum hydride (5.0 g., 0.13 mole) and anhydrous ether (200 ml.) were placed in a 1-liter, 3-neck flask and refluxed for 5 hours to make the slurry (see p.27). To a cold slurry was added slowly a solution of


30 g. (0.27 mole) of cycloheptanone in 50 ml. of anhydrous ether. The mixture was refluxed for an hour and then cooled. Cold water (30 ml.) was added slowly, followed by 250 ml. of 3 M sulfuric acid. The product was extracted with petroleum ether and processed in the usual manner. An 87% yield (26.5 g.) of cycloheptanol was obtained; b.p. 185-186°, d^{20}_{4} 0.9475, n^{20}_{D} 1.4750. (Reported^{42}: b.p. 185°(761 mm.), d^{20}_{4} 0.9478, n^{20}_{D} 1.47470.)

(2) Bromocycloheptane^{44}.

Cycloheptanol (15 g., 0.13 mole) and phosphorus tribromide (13 g., 0.04 mole) gave a 65% yield (15 g.) of bromocycloheptane; b.p. 100-101°(38 mm.), d^{20}_{4} 1.3193, n^{20}_{D} 1.5009. (Reported^{87}: b.p. 101.5°(40 mm.), d^{18}_{15} 1.299, n^{22}_{D} 1.4996.)

(3) Cycloheptylcarbinol^{44}.

Bromocycloheptane (14 g., 0.08 mole), magnesium turnings (1.9 g., 0.08 g. atom) and paraformaldehyde (3.0 g., 0.03 mole) gave a 46% yield (7.0 g.) of cycloheptylcarbinol; b.p. 114-115°(40 mm.), d^{20}_{4} 0.9315, n^{20}_{D} 1.4678. (Reported^{88}: b.p. 204-206°(749 mm.), d^{20}_{4} 0.9315, n^{20}_{D} 1.4685.)

(5) Bromomethylcycloheptane^{44}.

Cycloheptylcarbinol (6.0 g., 0.05 mole) and phosphorus tribromide (6.0 g., 0.02 mole) gave a 36% yield (3.0 g.) of bromomethylcycloheptane; b.p. 106-107°(38 mm.) d^{20}_{4}

(87) Markownikoff, Ann., 327, 59 (1903).

1.254, n^20_D 1.4678. (Reported^{88}: b.p. 80-82^\circ(15 \text{ mm}).)

C. THE ADDITION OF HYPOCHLOROUS ACID TO METHYLENECYCLOALKANES.

Mercuric oxide (217 g., 1 mole)^{10} and water (500 ml.) were placed in a 2-liter, 3-neck flask equipped with a stirrer, a gas-dispersion tube and a gas outlet tube. The flask was cooled and when the temperature of the mixture had reached approximately 5^\circ, chlorine gas was passed until the red precipitate of the oxide turned pale yellow. The precipitate was filtered, washed with 100 ml. of water and distilled at reduced pressure in the dark with a water bath (about 35^\circ).

The concentration of the hypochlorous acid distillate was determined by adding 1 ml. of it to an excess of acidified potassium iodide solution. The iodine liberated was titrated with standard sodium thiosulfate solution. The amount of hypochlorous acid solution necessary for the addition reaction was calculated. This amount was diluted to 500 ml. before it was used^{89}.

In a 2-liter, 3-neck flask equipped with a stirrer and a thermometer were placed 200 ml. of water and approximately 0.12 mole of methylenecycloalkane. About 1/5 of slightly

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(89) The use of concentrated HOC1 solution may lead to side reaction products especially with methylenecyclobutane where a high boiling compound (b.p. 59-61^\circ(2 \text{ mm}), d^{20}_H 1.3051, n^{20}_D 1.4850) became the major product. It was not obtained from dilute solutions.
more than the calculated amount of the cold hypochlorous acid was added. The mixture was kept below 15° and was stirred vigorously until it gave no blue color with starch-iodide paper moistened with glacial acetic acid. A second portion of hypochlorous acid was added and the process was repeated until the required amount of hypochlorous acid solution had been added. The mixture was stirred an hour longer, washed with dilute potassium iodide solution and saturated with sodium chloride. The lower layer was separated, washed with dilute sodium carbonate solution and with water and dried with anhydrous magnesium sulfate. The infrared spectrum and refractive index were taken. The combined washings and the aqueous layer were extracted with ether to recover the remainder of the product. The product was fractionated and the components were identified by comparison of the physical constants and infrared spectra with authentic samples synthesized by independent methods. The ratio of the chlorohydrins were determined by comparison of the quantitative infrared spectra of various mixtures of the pure compounds with the infrared spectrum of the reaction mixture. The infrared band at approximately 7.26 μ which is characteristic of a tertiary hydroxyl group was useful in the above determinations.

1. Methylene cyclobutane.

The addition of hypochlorous acid to 8.0 g. (0.01 mole) of methylene cyclobutane gave 10.5 g. (71.8%) of product which consisted of 60% 1-chloro-1-hydroxymethylcyclobutane.

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(b.p. 69-71° (20 mm.), d$_{20}^0$ 1.153, n$_{20}^0$ 1.4765) and 40% of 1-chloromethylcyclobutanol (b.p. 59-60° (20 mm.), d$_{20}^0$ 1.135, n$_{20}^0$ 1.4688; reported$^{90}$: b.p. 64.5° (20 mm.), d$_{15}^0$ 1.1502, n$_{15}^0$ 1.4657). No products other than chlorohydrins could be detected spectroscopically in the reaction mixture.

The suspected 1-chloro-1-hydroxymethylcyclobutane formed a precipitate instantaneously with an alcoholic solution of silver nitrate and gave negative tests with the Lucas reagent and with sodium iodide in acetone. Examination of the infrared spectrum shows that the band at 7.24 μ which is present in the spectrum of the isomeric 1-chloromethylcyclobutanol and is characteristic of tertiary alcohols, is absent.

Treatment of the suspected 1-chloro-1-hydroxymethylcyclobutane with 50% aqueous potassium hydroxide yielded a hydrocarbon (b.p. 58-60°, n$_{20}^0$ 1.3756) while 1-chloromethylcyclobutanol gave methylenecyclobutane oxide (b.p. 90-91°, n$_{20}^0$ 1.4255; reported$^{90}$: b.p. 89-92° (754 mm.), n$_{15}^0$ 1.4230.)

2. Methylenecyclopentane.

Addition of hypochlorous acid to 10.0 g. (0.12 mole) of methylenecyclopentane gave 10.5 g. (64.4%) of product which consisted of 41% 1-chloro-1-hydroxymethylenecyclopentane (b.p. 62-64° (2.7 mm.), d$_{20}^0$ 1.183, n$_{20}^0$ 1.5038) and 58% of 1-chloromethylenecyclopentanol (b.p. 57-59° (6 mm.), d$_{20}^0$ 1.144, n$_{20}^0$ 1.4834). A trace of cyclopentanecarboxaldehyde could be detected spectroscopically in the reaction mixture.

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(90) Demjanow and Dojarenko, Ber., 55B, 2730 (1922).
The suspected 1-chloro-1-hydroxymethylcyclopentane reduced neutral permanganate solution, failed to react with a solution of bromine in carbon tetrachloride and formed a precipitate instantaneously with an alcoholic solution of silver nitrate. It gave negative tests with the Lucas reagent and with sodium iodide in acetone. Acid hydrolysis (see p. 51) gave a 65% yield of cyclopentanecarboxaldehyde. All the above characteristics support the assignment of structure to the fraction mentioned.

The suspected 1-chloromethylcyclopentanol reduced neutral permanganate solution, liberated HBr when treated with a solution of bromine in carbon tetrachloride and formed a precipitate with a solution of sodium iodide in acetone. It slowly formed a precipitate with an alcoholic solution of silver nitrate and gave a positive Lucas test. Examination of the infrared spectrum shows a band at 7.27 μ which is characteristic of tertiary alcohols. This band is absent in the spectrum of the suspected 1-chloro-1-hydroxymethylcyclopentane.


The addition of hypochlorous acid to 10.0 g. (0.10 mole) of methylene cyclohexane gave 14.1 g. (91.5%) of product which consisted of 67% 1-chloro-1-hydroxymethylcyclohexane (b.p. 53-55°(2.4 mm.), d^20_4 1.113, n^20_D 1.4910) and 32% of 1-chloromethylcyclohexanol (b.p. 54-56°(4 mm.), d^20_4 1.128, n^20_D 1.5030). A trace of cyclohexanecarboxaldehyde could be detected spectroscopically in the reaction mixture.

The suspected 1-chloromethylcyclohexanol gave the same chemical tests as the analogous cyclopentane derivative.
The infrared spectrum has an absorption band at 7.25 μ which was ascribed to a tertiary hydroxyl group.

The addition of hypochlorous acid to methylenecyclohexane has been reported\textsuperscript{91} to give exclusively 1-chloro-1-hydroxymethylcyclohexane; b.p. 90-93°(16 mm.).

4. Methylenecycloheptane.

Addition of hypochlorous acid to 9.5 g. (0.09 mole) of methylenecycloheptane gave 12.0 g. (85.7\%) of product which consisted of 35\% 1-chloro-1-hydroxymethylcycloheptane (b.p. 71-73°(2.5 mm.), d\textsuperscript{20} 1.127, n\textsuperscript{20} 1.5110) and 64\% of 1-chloromethylcycloheptanol (b.p. 57-59°(2.3 mm.), d\textsuperscript{20} 1.119, n\textsuperscript{20} 1.4990). A trace of cycloheptanecarboxaldehyde could be detected in the reaction mixture.

The suspected 1-chloro-1-hydroxymethylcycloheptane and the suspected 1-chloromethylcycloheptanol gave the same chemical tests as the analogous cyclopentane derivatives. The infrared band at 7.27 μ is present in the spectrum of 1-chloromethylcycloheptanol and is absent in the spectrum of 1-chloro-1-hydroxymethylcycloheptane.

THE SYNTHESSES OF THE ADDITION PRODUCTS FROM HYPOCHLOROUS ACID AND METHYLENECYCLOALKANES.

a. 1-Chloro-1-hydroxymethylcyclobutane.

(1) Methyleneclcyclobutane oxide\textsuperscript{90}.

1-Chloromethylyclobutanol\textsuperscript{90} (6.6 g., 0.06 mole)

\textsuperscript{91} Tiffeneau, Weill and Tchoubar, Compt. rend., 205, 144 (1937).
and a 50% aqueous solution of potassium hydroxide (15 g.,
0.18 mole in 15 ml. water) gave a 17% yield (0.8 g.) of
methylenecyclobutane oxide; b.p. 90-92°, n^20_D 1.4207
(Reported^90: b.p. 89-92°(754 mm.), n^15_D 1.4230.).

(2) l-Chloro-l-hydroxymethylenecyclobutane^14.

Methylenecyclobutane oxide (0.6 g., 0.07 mole) and
concentrated hydrochloric acid (10 ml.) gave 0.2 g. (25%)
of a chlorohydrin with b.p. 69-70°(20 mm.), d^20_4 1.154,
n^20_D 1.4760, MR_exp. 29.3, MR_calc. 29.9.

Examination of the infrared spectrum and the physical
constants show that it is identical with the suspected l-chlo-
ro-l-hydroxymethylenecyclobutane obtained from the addition
of hypochlorous acid to methylenecyclobutane.

b. l-Chloro-l-hydroxymethylenecyclopentane^14.

Methylenecyclopentane oxide (3.5 g., 0.36 mole) (see p. 52)
and 5 M hydrochloric acid (20 ml.) gave a 15% yield (0.7 g.)
of a chlorohydrin with b.p. 62-63°(2.7 mm.), d^20_4 1.182,
n^20_D 1.5036, MR_exp. 33.6, MR_calc. 34.1.

Comparison of the physical constants and infrared spectrum
with the suspected l-chloro-l-hydroxymethylenecyclopentane
obtained from the addition of hypochlorous acid to methylen-
cyclopentane suggests that they are identical.

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(92) Atomic refractions used in the calculation
of all molecular refractions reported herein came from
Glasstone "Textbook of Physical Chemistry," D. Van Nostrand
c. 1-Chloromethylcyclopentanol.  

1-Chloro-1-chloromethylcyclopentane (2.8 g., 0.18 mole) (see p. 57) was hydrolyzed with an aqueous suspension of calcium carbonate. A 32% yield (0.8 g.) of a chlorohydrin was collected; b.p. 57-58° (6 mm.), d^20_4 1.143, n^20_D 1.4841, MR_{exp} 33.7, MR_{calc} 34.1. 

Examination of the infrared spectrum and physical constants suggest that it is identical with the suspected 1-chloromethylcyclopentanol isolated from the addition of hypochlorous acid to methylenecyclopentane.

d. 1-Chloro-1-hydroxymethylcyclohexane.  

Methylenecyclohexane oxide (7.0 g., 0.06 mole) (see p. 26) was added dropwise to concentrated hydrochloric acid (20 ml.). The reaction temperature was maintained below 5° during the addition and afterwards for an hour. The mixture was poured on to ice and processed in the usual manner. A 54% yield (5.0 g.) of 1-chloro-1-hydroxymethylcyclohexane was obtained; b.p. 53-54° (2.4 mm.), d^20_4 1.126, n^20_D 1.4905, MR_{exp} 38.2, MR_{calc} 38.7 (Reported: b.p. 90-93° (16 mm.)).

e. 1-Chloromethylcyclohexanol.  

1-Chloro-1-chloromethylcyclohexane (10.0 g., 0.06 mole) (see p. 59), calcium carbonate (4 g.) and water (500 ml.) were refluxed for 6 hours. Most of the dichloride was recovered (6.0 g., 60%) but a 28% yield (1.0 g.) of a chlorohydrin was obtained; 

b.p. 54-55° (4 mm.), d₂₀ 1.127, n₂₀ D 1.5024, MRₜₐₓ 38.9, MRₜₐₒ₋ₚ 38.7.

Comparison of the physical constants and infrared spectrum with the suspected 1-chloromethylcyclohexanol obtained by the addition of hypochlorous acid to methylenecyclohexane suggests that they are identical.

f. 1-Chloro-l-hydroxymethycycloheptane

(1) Methylene cycloheptane oxide.

The 1-chloromethylcycloheptanol (4.8 g., 0.03 mole) obtained in the addition of HOCl to methylenecycloheptane and 10.0 g. (0.18 mole) of potassium hydroxide gave 2.0 g. (42%) of recovered chlorohydrin and 1.4 g. (70%) of a compound assumed to be methylenecycloheptane oxide; b.p. 84-85° (40 mm.), d₂₀ 0.938, n₂₀ D 1.4552, MRₜₐₓ 36.4, MRₜₐₒ₋ₚ 36.4.

(2) 1-Chloro-l-hydroxymethycycloheptane.

Methylene cycloheptane oxide (1.5 g., 0.12 mole) and concentrated hydrochloric acid (15 ml.) gave 0.5 g. (26%) of a chlorohydrin with b.p. 70-71° (2 mm.), d₂₀ 1.128, n₂₀ D 1.5114, MRₜₐₓ 42.5, MRₜₐₒ₋ₚ 43.3.

Examination of the physical constants and infrared spectrum of the above chlorohydrin and that of the suspected 1-chloro-l-hydroxymethycycloheptane isolated from the addition of HOCl to methylenecycloheptane suggests that they are identical.

g. 1-Chloromethylcycloheptanol

Hydrolysis of 2.0 g. (0.01 mole) of 1-chloro-l-chloro-
methylcycloheptane (see p. 61) with an aqueous suspension of calcium carbonate gave 0.7 g. (39%) of a chlorohydrin with b.p. 56-58° (2 mm.), d²⁰ 1.118, n²⁰ 1.4997, M R exp. 42.6, M R calc. 43.3.

Comparison of the physical constants and infrared spectrum of the above chlorohydrin with that of the suspected 1-chloromethylcycloheptanol obtained from the addition of HCl to methylenecycloheptane suggests that they are identical.

D. THE ADDITION OF HYPOBROMOUS ACID⁹⁴ TO METHYLENECYCLOALKANES.

Procedure A⁹⁵.

Approximately 0.12 mole of methylenecycloalkane and 100 ml. of water were placed in a 1-liter, 3-neck flask equipped with a stirrer and a thermometer. N-Bromosuccinimide (23 g., 0.12 mole; 95% purity) was added in small portions. The mixture was stirred vigorously while the temperature was maintained at 10-20°⁹⁶. The disappearance of the N-bromosuccinimide is a criterion of the progress of the reaction. The mixture was allowed to stand half an hour after all the N-bromosuccinimide had been added. The

(⁹⁴) The ratio of the addition products was found to be the same whether pure HOBr solution or N-bromosuccinimide was used.


(⁹⁶) With methylenecyclopentane the temperature was maintained at 0-5° since the products are unstable.
lower layer was separated, washed with dilute sodium carbonate solution and with water and was dried with anhydrous magnesium sulfate. The refractive index and the infrared spectrum of the product were taken. The washings and the aqueous layer were combined and extracted with ether to recover the remainder of the product. The ether was removed with the aspirator and the residue was fractionated. The components of the product were identified by comparison of the physical constants and infrared spectra with authentic samples synthesized by independent methods.

Procedure

Silver sulfate (153 g., 0.75 mole) and water (400 ml.) were placed in a 2-liter, 3-neck flask equipped with a stirrer and a dropping funnel. The flask was cooled with an ice-bath to approximately 5° and 125 g. (0.69 mole) of bromine was added dropwise. The precipitate was filtered and washed with 100 ml. of water. The hypobromous acid solution was distilled in the dark under reduced pressure with a water bath at 40-50°.

The concentration of the hypobromous acid was determined with potassium iodide and thiosulfate solutions. Slightly more than the theoretical amount of hypobromous

(97) Purification of the product at this point by steam distillation produced a large amount of cycloalkane-carboxaldehyde except for that from methylenecyclobutane which produced an unidentified hydrocarbon.

acid was added in portions to approximately 0.12 mole of methylenecycloalkane. The details are similar to that of the addition of HOC\textsubscript{1} to methylenecycloalkanes (p. 40).

1. Isobutylene.

The addition of hypobromous acid to 8.9 g (0.16 mole) of isobutylene gave 18.8 g (77.4\%) of product which consisted of 97\% 1-bromo-2-methyl-2-propanol (b.p. 62-62.5\°(31 mm.), d\textsuperscript{20}\textsubscript{4} 1.4510, n\textsuperscript{20}_D 1.4722; reported\textsuperscript{99}: b.p. 61-62\°(31 mm.), d\textsuperscript{25}\textsubscript{4} 1.437, n\textsuperscript{25}_D 1.4710) and 3\% of an unidentified fraction which was thought to be 2-bromo-2-methyl-1-propanol. The unidentified fraction had infrared bands at 6.10 and 12.58 \(\mu\). Oxidation with CrO\textsubscript{3} gave a product with an absorption band at 5.69 \(\mu\).

2. Methylenecyclobutane.

Addition of hypobromous acid to 7.0 g (0.10 mole) of methylenecyclobutane gave 13.2 g (78.1\%) of product which consisted of 99\% 1-bromo-1-hydroxymethylcyclobutane (b.p. 63-56\°(10 mm.), d\textsuperscript{20}\textsubscript{4} 1.5057, n\textsuperscript{20}_D 1.5036) and 1\% of an unidentified material which has an absorption band attributable to a carbonyl group.

The suspected 1-bromo-1-hydroxymethylcyclobutane yielded a hydrocarbon (b.p. 58-60\°, d\textsuperscript{20}\textsubscript{4} 0.671, n\textsuperscript{20}_D 1.3758; Anal. 72\% C, 83.32, 83.56\%; H, 16.51, 14.34\%) on treatment with 50\% aqueous potassium hydroxide solution. The hydrocarbon obtained is the same as that obtained from the analogous chlorohydrin. Their infrared spectra are identical. The above bromohydrin

also formed a precipitate instantly with an alcoholic solution of silver nitrate and gave negative tests with the Lucas reagent and with sodium iodide in acetone.


The addition of hypobromous acid to 10.0 g. (0.12 mole) of methylene cyclopentane gave 13.0 g. (66.9%) of product which consisted of 91% 1-bromo-1-hydroxymethylene cyclopentane (b.p. 45-46° (2 mm.), d^20_4 1.463, n^20_D 1.5126) and 9% of methylene cyclopentane oxide (b.p. 43-44° (61.4 mm.), d^20_4 0.9224, n^20_D 1.4288).

The suspected 1-bromo-1-hydroxymethylene cyclopentane formed a precipitate instantly with an alcoholic solution of silver nitrate and gave negative tests with the Lucas reagent and with sodium iodide in acetone. Acid hydrolysis with 5 M hydrochloric acid (refluxed for 5 hours) gave a 70% yield of cyclopentanecarboxaldehyde; b.p. 54-55° (35.5 mm.), d^20_4 0.919, n^20_D 1.4346; reported\(^\text{100}\): b.p. 135°.


Addition of hypobromous acid to 10.0 g. (0.10 mole) of methylene cyclohexane gave 18.0 g. (89.4%) of product which consisted of 98% 1-bromo-1-hydroxymethylene cyclohexane (b.p. 55-56° (2 mm.), m.p. 82-83°; reported\(^\text{91}\): m.p. 82°) and 2% of cyclohexanecarboxaldehyde (b.p. 51-52° (11 mm.), d^20_4 0.931, n^20_D 1.4492; reported\(^\text{59}\): 61-63° (24 mm.), n^18_D 1.4503).

5. Methylenecycloheptane.

The addition of hypobromous acid to 8.7 g. (0.08 mole) of methylenecycloheptane gave 13.5 g. (87.3%) of product which consisted of 87% of 1-bromo-1-hydroxymethylcycloheptane (b.p. 73-75° (3 mm.), d²₀ 1.340, n²₀ 1.5225) and 13% of cycloheptanecarboxaldehyde (b.p. 46-47° (4 mm.), n²₀ 1.4625).

The bromohydrin isolated above gave the same chemical tests as the analogous cyclopentane derivative. Acid hydrolysis (p. 51) with 5 M hydrochloric acid gave a 60% yield of cycloheptanecarboxaldehyde; b.p. 45-47° (4 mm.), n²₀ 1.4628.

THE SYNTHESES OF THE ADDITION PRODUCTS FROM HYPOBROMOUS ACID AND METHYLENECYCLOALKANES.

a. 1-Bromo-1-hydroxymethylocyclobutane

Methylenecyclobutane oxide (0.5 g., 0.06 mole) (p. 44) and concentrated hydrobromic acid (15 ml., 48%) gave 0.2 g. (21%) of a bromohydrin; b.p. 64-65° (10 mm.), d²₀ 1.5061, n²₀ 1.5041.

Comparison of the physical constants and infrared spectrum with the suspected 1-bromo-1-hydroxymethylocyclobutane obtained from the addition of hypobromous acid to methylenecyclobutane suggests that they are identical.

b. Methylenecyclopentane oxide.

Potassium hydroxide (15 g., 0.27 mole) and water (15 ml.) were placed in a 100-ml., 3-neck flask equipped with a stirrer and a dropping funnel. With the temperature being maintained at 0-5°, 1.0 g. (0.08 mole) of 1-bromo-1-
hydroxymethylcyclopentane was added slowly. Half an hour
after all the bromohydrin had been added, the ice-bath was
removed and the stirring was continued an hour longer. The
oxide was extracted with ether, dried with anhydrous magnesium
sulfate and distilled. Some of the bromohydrin was recovered
(3.0 g., 21%) and 4.0 g. (73%, based on unrecovered bromo-
hydrin) of methylenecyclopentane oxide was collected; b.p.
43-44°C (61.4 mm.), d²⁰ 0.9226, n²⁰ D 1.4290, MRexp 27.3,
MRcalc 27.5.

The suspected methylenecyclopentane oxide was refluxed
(6 hours) with a suspension of anhydrous magnesium bromide in
anhydrous ether. A 50% yield of cyclopentanecarboxalde-
hyde was obtained; b.p. 55-56°C (36 mm.), n²⁰ D 1.4345.
(Authentic sample of cyclopentanecarboxaldehyde: b.p. 54-
54.5°C (35.5 mm.), n²⁰ D 1.4343.)

c. 1-Bromo-1-hydroxymethylcyclopentane

Methylenecyclopentane oxide (4.0 g., 0.05 mole) and
concentrated hydrobromic acid (20 ml., 48%) gave a 19%
yield (1.4 g.) of a bromohydrin with b.p. 45-46°C (2 mm.),
d²⁰ 1.463, n²⁰ D 1.5126, MRexp 36.9, MRcalc 37.0, and
0.5 g. of cyclopentanecarboxaldehyde; b.p. 55-56°C (36 mm.),
n²⁰ D 1.4348.

Comparison of the physical constants and infrared
spectrum with the suspected 1-bromo-1-hydroxymethylcyclo-
pentane obtained from the addition of hypobromous acid to
methylenecyclopentane suggests that they are identical.
d. Cyclopentanecarboxaldehyde.

Methylenecyclopentane glycol\(^{101}\) (8.0 g., 0.07 mole) and concentrated hydrobromic acid (20 ml., 48%) were heated for 3 hours. Ice was added to the mixture and solid sodium carbonate was added to neutralize the acid. The aldehyde was extracted with ether and processed in the usual way. On distillation, 2.0 g. (30%) of cyclopentanecarboxaldehyde was collected; b.p. 54-54.5\(^\circ\) (35.5 mm.), \(d^{20}D\) 0.9195, \(n^{20}D\) 1.4343, \(MR_{\text{exp}}\) 27.8, \(MR_{\text{calc}}\) 27.6; semicarbazone, m.p. 123-124\(^\circ\). (Reported\(^{100}\): b.p. 135\(^\circ\); semicarbazone, m.p. 123\(^\circ\).)

e. Cyclohexanecarboxaldehyde.

This preparation is described on page 24.

f. 1-Bromo-1-hydroxymethylcyclohexane\(^{102}\).

Methylenecyclohexane oxide (8.9 g., 0.08 mole) (p.26) and concentrated hydrobromic acid (20 ml., 48%) gave a 59% yield (9.0 g.) of 1-bromo-1-hydroxymethylcyclohexane; b.p. 55-56\(^\circ\) (2 mm.), m.p. 82-83\(^\circ\). (Reported\(^{91}\): m.p. 82\(^\circ\).)

Acid hydrolysis (5 M hydrochloric acid) of 1-bromo-1-hydroxymethylcyclohexane (refluxed for 5 hours) gave an 83% yield of cyclohexanecarboxaldehyde; b.p. 51-52\(^\circ\) (11 mm.), \(n^{20}D\) 1.4492.

(101) Prepared from methylenecyclopentane and peroxyformic acid\(^{36}\) in 58% yield.

g. 1-Bromo-1-hydroxymethylcycloheptane and Cycloheptane-carboxaldehyde.

(1) Methylenecycloheptane oxide.

1-Chloromethylcycloheptanol (4.8 g., 0.03 mole) and a 50% aqueous solution of potassium hydroxide (20 g.) were heated for 3 hours. On distillation, 2.0 g. (42%) of the chlorohydrin was recovered and 1.4 g. (70%) of methylenecycloheptane oxide was collected; b.p. 84-85°(40 mm.), d^20_4 0.938, n^20_D 1.4552, MR_{exp.} 36.4, MR_{calc.} 36.7.

(2) 1-Bromo-1-hydroxymethylcycloheptane and Cycloheptane-carboxaldehyde.

The suspected methylenecycloheptane oxide (2.0 g., 0.02 mole) was added to concentrated hydrobromic acid (15 ml., 48%). A 40% yield (1.3 g.) of a bromohydrin (b.p. 73-74°(3 mm.), d^20_4 1.339, n^20_D 1.5232, MR_{exp.} 46.1, MR_{calc.} 46.2) and a 20% yield (0.4 g.) of cycloheptane-carboxaldehyde (b.p. 45.5-46°(4.1 mm.), n^20_D 1.4621; semicarbazone, m.p. 154-155°.) (Reported^103: b.p. 60-62°(8 mm.); semicarbazone, m.p. 155-156°.)

Examination of the physical constants and infrared spectrum of the above mentioned bromohydrin and that of the suspected 1-bromo-1-hydroxymethylcycloheptane suggests that they are identical. Acid hydrolysis (5 M hydrochloric acid) of the above mentioned bromohydrin gave a 50% yield of cycloheptane-carboxaldehyde; b.p. 46-47°(4.5 mm.), n^20_D 1.4625.

E. THE ADDITION OF CHLORINE$^{104}$ TO METHYLENECYCLOALKANES.

In the Absence of Extraneous Anions.

Approximately 0.12 mole of methylenecycloalkane and 100 ml. of carbon tetrachloride were placed in a 200-ml., 3-neck flask equipped with a stirrer, a gas-dispersing tube and a gas-outlet tube. With the temperature being maintained at 0° to -5°, chlorine gas was passed into the solution for approximately 3 hours. The mixture was washed with water, with dilute sodium carbonate solution and with water. It was dried with anhydrous calcium chloride, the solvent was removed with the aspirator and the residue was fractionated.

In the Presence of Extraneous Anions.

The chlorination of approximately 0.12 mole of methylenecycloalkane was carried out in the presence of a saturated solution of either sodium chloride (35 g. in 100 ml. of water) or sodium nitrite (72 g. in 100 ml. of water). The product was extracted with ether, washed, dried and fractionated.

(104) The addition of chlorine is quite peculiar. The addition of bromine to methylenecyclopentane and to methylenecyclohexane gave the expected dibromides in fairly good yields; 47% of 1-bromo-1-bromomethylcyclopentane, b.p. 33-34°(2 mm.), d$^{20}$ 1.7330, n$^{20}$D 1.393; and 55% of the cyclohexane analog, b.p. 62-63°(3 mm.), d$^{20}$ 1.6590, n$^{20}$P 1.5432 (reported$^{105}$: b.p. 112°(16 mm.), n$^{20}$P 1.5442$^*$.)

The addition of bromine to methylenecyclobutane also gave predominantly the expected dibromide.$^{106}$


1. **Methylenecyclobutane.**

   a. **In the Absence of Extraneous Anions.**

      Addition of chlorine to 10.5 g. (0.15 mole) of methylenecyclobutane gave 14.8 g. of product which was fractionated. The following fractions were collected: (a) 4.0 g. (19%) of 1-chloro-1-chloromethylcyclobutane; b.p. 49-50° (14 mm.), d$_{20}$^4 1.175, n$_{20}^D$ 1.4777, MR$_{exp.}$ 33.25, MR$_{calc.}$ 33.30 (reported: 67-69° (36 mm.), d$_{15}$^4 1.172, n$_{15}^D$ 1.4756); (b) 2.8 g. (13%) of 1,1-bis(chloromethyl)cyclopropane; b.p. 56-57° (14 mm.), d$_{20}$^4 1.180, n$_{20}^D$ 1.4832, MR$_{exp.}$ 33.45, MR$_{calc.}$ 33.53; (c) 3.2 g. (10%) of 1,2,4-trichloro-2-chloromethylbutane; b.p. 55-56° (6.3 mm.), d$_{20}$^4 1.305, n$_{20}^D$ 1.4945, MR$_{exp.}$ 44.95, MR$_{calc.}$ 44.76.

      The structures assigned to fractions (b) and (c) were based on the behavior of methylenecyclobutane to bromine.$^{106}$ Both fractions were saturated to permanganate, gave precipitates with sodium iodide in acetone and showed no double-bond infrared absorptions.

2. **Methylenecyclopentane.**

   a. **In the Absence of Extraneous Anions.**

      The addition of chlorine to 11.7 g. (0.14 mole) of methylenecyclopentane gave 17.3 g. of product which consisted mainly of polymeric material. Two fractions were isolated: (d) 2.0 g. (12%) of the suspected 1-chloromethylcyclopentene; b.p. 69-71° (42 mm.), d$_{20}$^4 1.021, n$_{20}^D$ 1.4732, MR$_{exp.}$ 32.48, MR$_{calc.}$ 32.11; (e) and 2.5 g. (14%) of the suspected 1-chloro-1-chloromethylcyclopentane; b.p.
55-56° (7 mm.), d^20_4 1.191, n^20_D 1.4982, MR_{exp} 37.39, 
MR_{calc} 37.44.

The suspected 1-chloromethylcyclopentene was unsaturated to permanganate and bromine in carbon tetrachloride, gave precipitates with alcoholic silver nitrate and sodium iodide in acetone, and showed double-bond infrared absorptions.

The suspected 1-chloro-1-chloromethylcyclopentane was saturated to permanganate and bromine in carbon tetrachloride, gave precipitates with alcoholic silver nitrate and sodium iodide in acetone, and showed no double-bond infrared absorptions.

b. In the Presence of Sodium Chloride.

The addition of chlorine to 10.0 g. (0.12 mole) of methylenecyclopentane in the presence of sodium chloride gave 14.4 g. of product which consisted mainly of polymeric materials. Some of the suspected 1-chloromethylcyclopentene (3.0 g., 21%) (b.p. 69-71° (42 mm.), n^20_D 1.4735) and 2.0 g. (11%) of the suspected 1-chloro-1-chloromethylcyclopentane (b.p. 59-60° (8.5 mm.), n^20_D 1.4985) were collected.

c. In the Presence of Sodium Nitrite.

The chlorination of 10.5 g. (0.13 mole) of methylenecyclopentane in the presence of sodium nitrite gave 13.5 g. of product which was very unstable. The decomposition was fast even at room temperature. Fractionation of the product gave, besides tar, 2.5 g. (17%) of the suspected 1-chloromethylenecyclopentene (b.p. 69-71° (42 mm.), n^20_D 1.4736); 1.5 g. (13%) of the suspected 1-chloromethyl-1-nitrito-
cyclopentane (b.p. 52-53° (3.2 mm.), d^20_4 1.232, n^20_D 1.4980, MR_{exp} 38.53, MR_{calc} 38.92) and 2.0 g. of an unidentified fraction (b.p. 55-56° (57.2 mm.), d^20_4 0.979, n^20_D 1.4565).

The unidentified fraction gave a positive test with alcoholic silver nitrate, liberated HBr with bromine in CCl_4, readily reduced neutral permanganate, gave no infrared absorption bands between 6.1-6.8 μ (covalent nitrite) and decomposed on standing.

The suspected 1-chloromethyl-1-nitritocyclopentane gave a positive test with sodium iodide in acetone, showed infrared absorption bands attributable to a covalent nitrite (6.08 and 6.44 μ) and also showed absorption bands similar to the suspected 1-chloromethylcyclopentene at a region attributable to a primary chloride (12.0 to 14.7 μ.).


a. In the Absence of Extraneous Anions.

The addition of chlorine to 15.0 g. (0.16 mole) of methylene cyclohexane gave 11.0 g. of product which was fractionated. The fractions collected were: 8.0 g. (39%) of 1-chloromethylcyclohexene (b.p. 54-56° (16 mm.), d^20_4 1.010, n^20_D 1.4930, MR_{exp} 37.32, MR_{calc} 36.73; reported^{105}: b.p. 78° (32 mm.), n^25_D 1.4912) and 1.5 g. (6%) of 1-chloro-1-chloromethylcyclohexane (b.p. 85-87° (15 mm.), d^20_4 1.169, n^20_D 1.4915, MR_{exp} 41.7, MR_{calc} 42.1; reported^{105}: b.p. 97° (32 mm.), n^20_D 1.4910).
b. In the Presence of Sodium Chloride.

The addition of chlorine to 13.2 g. (0.14 mole) of methylenecyclohexane in the presence of sodium chloride gave 16.5 g. of product which was fractionated. Besides a high boiling material, the following fractions were collected: 1.5 g. (8%) of 1-chloromethylcyclohexene (b.p. 54-56°(16 mm.), n\textsuperscript{20}D 1.4925) and 6.5 g. (29%) of 1-chloro-1-chloromethylcyclohexane (b.p. 85-87°(15 mm.), n\textsuperscript{20}D 1.4918).

c. In the Presence of Sodium Nitrite.

The addition of chlorine to 16.0 g. (0.17 mole) of methylenecyclohexane in the presence of sodium nitrite gave 16.0 g. of product which was fractionated. The fractions collected were: 4.0 g. (19%) of 1-chloromethylcyclohexene (b.p. 54-56°(16 mm.), n\textsuperscript{20}D 1.4932), 0.2 g. (1%) of 1-chloro-1-chloromethylcyclohexane (b.p. 85-87°(15 mm.), n\textsuperscript{20}D 1.4917), 2.0 g. (7%) of the suspected 1-chloromethyl-1-nitritocyclohexane (b.p. 35-37°(2.7 mm.), d\textsuperscript{20} 1.141, n\textsuperscript{20}D 1.4829, MR\textsubscript{exp} 44.20, MR\textsubscript{calc} 43.53) and 4.0 g. (14%) of the suspected 1-chloro-1-nitritomethylcyclohexane (b.p. 45-47°(1.5 mm.), d\textsuperscript{20} 1.160, n\textsuperscript{20}D 1.4929, MR\textsubscript{exp} 44.55, MR\textsubscript{calc} 43.53).

The suspected 1-chloromethyl-1-nitritocyclohexane had infrared bands at 5.77, 5.96, 6.14 and 6.46 μ (covalent nitrite), gave a positive test with sodium iodide in acetone and showed absorption bands similar to the suspected...
l-chloromethylcyclohexene at a region attributable to a primary chloride (12.0 to 14.7 \( \mu \)).

The suspected 1-chloro-1-nitritomethylcyclohexane had infrared absorption bands at 5.77, 6.02, 6.14 and a broad band at 6.38-6.36 \( \mu \) (covalent nitrite), gave a negative test with sodium iodide in acetone and reacted instantly with an alcoholic solution of silver nitrate. It also decomposed on standing.


a. In the Absence of Extraneous Anions.

The addition of chlorine to 4.3 g. (0.04 mole) of methylenecycloheptane gave 5.0 g. of product which was fractionated. Some of the suspected 1-chloromethylcycloheptene (2.0 g., 36\%) (b.p. 47-48\(^\circ\) (5.3 mm.), \( d^2_4 \) 1.001, \( n^2_0D \) 1.4825, \( M_{\text{exp}} \) 41.10, \( M_{\text{calc}} \) 41.10) and 0.9 g. (14\%) of the suspected 1-chloro-1-chloromethylenecycloheptane (b.p. 61-62\(^\circ\) (3.3 mm.), \( d^2_4 \) 1.045, \( n^2_0D \) 1.4910, \( M_{\text{exp}} \) 48.69, \( M_{\text{calc}} \) 48.88) were collected.

The suspected 1-chloromethylenecycloheptane was unsaturated to permanganate and to bromine in carbon tetrachloride, gave precipitates with alcoholic silver nitrate and sodium iodide.

The suspected 1-chloro-1-chloromethylenecycloheptane was saturated to permanganate and to bromine in carbon tetrachloride, gave precipitates with alcoholic silver nitrate and sodium iodide in acetone, and showed no double-bond infrared absorptions.
F. THE REACTION OF HYDROBROMIC ACID WITH METHYLENECYCLOALKANE OXIDES.

Approximately 0.1 mole of methylene cycloalkane oxide was added slowly to 20 ml. of concentrated hydrobromic acid (48%). The mixture was maintained at 0-5°. After all the oxide had been added, the mixture was stirred for an hour longer. Solid sodium carbonate was added to neutralize the excess acid. The mixture was extracted with ether and the extract was processed in the usual way. The ether was removed, the infrared spectrum was taken and the ratio of the products was checked by fractional distillation of the reaction products.

Since the physical constants of the products obtained in this series of reactions are reported at appropriate places in this Dissertation (preparation of 1-bromo-1-hydroxymethylcycloalkanes), they will not be repeated here. The various evidences for the structure of the products obtained in each reaction are also presented therein.

1. Methylenecyclopentane Oxide.

The addition of hydrobromic acid to 4.0 g. (0.04 mole) of methylenecyclopentane oxide gave 2.5 g. (45%) of product consisting of 65% 1-bromo-1-hydroxymethylcyclopentane and 35% of cyclopentanecarboxaldehyde.

2. Methylenecyclohexane Oxide.

The addition of hydrobromic acid to 8.9 g. (0.08 mole) of methylenecyclohexane oxide yielded 10.0 g. (68%) of
product consisting of 95% 1-bromo-1-hydroxymethylcyclo-
hexane and 5% of cyclohexanecarboxaldehyde.

3. Methylene cycloheptane Oxide.

The addition of hydrobromic acid to 2.0 g. (0.02 mole) of methylene cycloheptane oxide gave 2.1 g. (87%) of product consisting of 68% 1-bromo-1-hydroxymethylcycloheptane and 32% cycloheptanecarboxaldehyde.

A summary of the principal products in additions to methylene cycloalkanes is presented in Table III.
TABLE III

Principal Products in Additions to \((\text{CH}_2)_n \rightarrow \text{CH}_3\) \((\text{C} = \text{CH}_2)\).

<table>
<thead>
<tr>
<th>n</th>
<th>HBr, ionic</th>
<th>HBr, radical</th>
<th>HOCl</th>
<th>HOBBr</th>
<th>Cl_2</th>
<th>Cl_2 + NO_2^-</th>
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<td>![H]</td>
<td>![Cl]</td>
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<td> </td>
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<td>Caloro nitrites and polymer</td>
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</table>
III. INTERPRETATION OF RESULTS

"It isn't simple at all... It's desperately complicated. But at the end there's light."

Steinbeck

Ionic additions to exo-cyclic olefins may be considered to go through the following steps:

Applying the generalization developed by Brown, Brewster and Shechter, we may expect (X) to be the favored transition state for the 4- and 6-membered ring systems and (IX) for the 5- and 7-membered ring methylenecycloalkanes. Consequently, the composition of the product may be predicted

(107) There are 3 sources of steric strain: (a) the compression of van der Waals radii, (b) the distortion of bond angles, more correctly, poor orbital overlap, and (c) bond opposition forces. For small rings (3 and 4), the internal strain arises primarily from poor orbital overlap while in the 5-membered and larger rings, the strain is attributed mainly to repulsion terms arising from unfavorable conformations. For medium rings (8-12-membered) both bond opposition and compression of van der Waals radii may be involved.

(108) Barring rearrangements.

by considering which transition state can be sterically accomodated with the least strain by the various ring systems.

**HYDROGEN BROMIDE ADDITIONS**

When the affinity of the electrophilic group is relatively weak (e.g., a proton), the original electron distribution of the double bond may be only mildly disturbed so that a \( \pi \)-complex rather than a carbonium ion may be initially formed\(^{110}\). Hence, the addition of hydrogen halides to olefins may involve the formation of a \( \pi \)-complex which then isomerizes to a carbonium ion. This is suggested by studies on olefin hydration. Taft\(^{111}\) has presented evidence that the transition state in the hydration of isobutene must be a conjugate acid of the olefin which is not firmly bound to any water molecule since the rate follows Hammett's acidity function \( (H_\alpha) \) rather than the hydrogen ion concentration \( (pH) \). The transition state was interpreted as involving a unimolecular isomerization from one unstable intermediate to another. The \( \pi \)-complex and the carbonium ion fit the needs of the two required intermediates. Theoretical

\(^{110}\) The \( \pi \)-complex is of such nature that the stereochemistry of the olefin is preserved in the fast reversible step. The positive charge is probably nearly equally shared by the two carbon atoms, while in the carbonium ion, one of the two carbon atoms bears a greater portion of the charge and the preservation of the stereochemistry of the positive carbon depends on the nature of \( X \).

analysis by Dewar\textsuperscript{21} suggests that the relative stability of the $\pi$-complex with respect to the carbonium ion may make the conversion of the former to the latter the rate determining step. This suggestion is supported by the studies of Kwart and Weisfeld\textsuperscript{112} concerning the hydration of optically active 3-$\text{E}$-menthene. They excluded the mechanism which requires the carbonium ion to be formed rapidly and reversibly in a non-rate determining step. They concluded that the rate-determining step of the reaction (in agreement with the mechanism proposed by Taft) is the transition from a $\pi$-complex to a carbonium ion with little or no return from the carbonium ion. Dewar\textsuperscript{3} also indicated that there are theoretical reasons for believing that the above process requires activation.

The experimental data show that in the ionic addition of hydrogen bromide to the methylenecycloalkanes, 1-bromo-1-methylcycloalkanes were the only products isolated\textsuperscript{113}. This suggests that the tendency to form the most stable carbonium ion (type IX) outweighs any influence ring size may exert in the conversion of the $\pi$-complex to the carbonium ion. Using the stabilization energies quoted by

\begin{quote}
\textsuperscript{(112)} Kwart and Weisfeld, Abstract of Papers, 128th A.C.S. Meeting at Minneapolis, Minn., p. 55-0, 1955.
\textsuperscript{(113)} Except in the case of methylenecyclobutane which is very susceptible to rearrangement. However, the isomeric bromomethylcyclobutane was not detected.
\end{quote}
Baker\textsuperscript{114}, the difference in stabilization energies between a tertiary (with 7 alpha-hydrogens) and a primary (with 1 alpha-hydrogen) carbonium ion may be estimated and amounts to approximately 16 kcal/mole. The experimental data then suggest that the destabilizing effect of ring strain in (X) is less than 16 kcal/mole. The mechanism of ionic addition of hydrogen bromide to methylenecycloalkanes may be represented as:

\begin{align*}
\text{CH}_2\text{CH}_2\text{CH}_2\text{C} = \text{CH}_2 & \xrightarrow{H^+} \left[ \text{CH}_3\text{CH}_2\text{C} = \text{CH}_2 \right]^{+} \xrightarrow{\text{S}L\text{OW}} \text{CH}_3\text{CH}_2\text{C} = \text{CH}_2 \xrightarrow{H^+} \text{CH}_3\text{CH}_2\text{C} = \text{CH}_2 \xrightarrow{\text{B}_n} \text{CH}_3\text{CH}_2\text{C} = \text{CH}_2 \\
\text{CH}_2\text{CH}_2\text{CH}_2\text{C} = \text{CH}_2 & \xrightarrow{H^+} \left[ \text{CH}_3\text{CH}_2\text{C} = \text{CH}_2 \right]^{+} \xrightarrow{\text{S}L\text{OW}} \text{CH}_3\text{CH}_2\text{C} = \text{CH}_2 \xrightarrow{H^+} \text{CH}_3\text{CH}_2\text{C} = \text{CH}_2 \xrightarrow{\text{B}_n} \text{CH}_3\text{CH}_2\text{C} = \text{CH}_2 \\
\end{align*}

The hydrogen bromide probably dissociates first since the covalent acid as such cannot protonate the olefin\textsuperscript{115}. In the case of methylenecyclobutane, transannular participation in the cyclobutane ring\textsuperscript{106} may be responsible for the formation of the side reaction products.

\begin{align*}
\text{H}^+ & \xrightarrow{H^+} \text{CH}_3 \xrightarrow{\text{HBr}} \text{CH}_3 \xrightarrow{\text{HBr}} \text{CH}_3 \xrightarrow{\text{HBr}} \text{CH}_3 \xrightarrow{\text{HBr}} \text{CH}_3
\end{align*}


\textsuperscript{(115)} This is the conclusion reached by de la Mare, Hughes, Ingold and Pocker (J. Chem. Soc., 2930 (1954)) to explain the kinetic effect exerted by Br\textsuperscript{-} and Cl\textsuperscript{-} in the addition of HBr and HCl to isobutylene in nitromethane.
The experimental data on the radical addition of hydrogen bromide to methylenecycloalkanes also indicate that the effect of ring strain, if any, is less than the stabilizing energy gained by forming the free radical with the least free energy. With the help of the stabilization energies quoted by Baker\textsuperscript{114}, the difference in stabilizing energies between a tertiary free radical (with 7 alpha-hydrogens) and a primary free radical (with 1 alpha-hydrogen) is estimated to be about 5-7 kcal./mole. It seems that the destabilizing energy due to ring strain in the free radical\textsuperscript{118} is less than the above value.

Examination of the physical constants reported for bromomethylocyclobutane shows that the radical addition product obtained here and the one reported by Krug, Smith and Fry\textsuperscript{74} are probably identical but that they are different from the material described by two other groups of investigators\textsuperscript{75,76}. The infrared spectrum of the addition product has an absorption band at 7.26 $\mu$ which may be ascribed to a methyl group. However, the nuclear magnetic resonance spectrum\textsuperscript{119} suggests the following tentative conclusions,

\textsuperscript{(116)} Similar to (IX) or (X) in which the ring carbon is an sp\textsuperscript{2} hybrid with the odd electron in a perpendicular $p$-orbital.

\textsuperscript{(119)} The author is indebted to Dr. Homer Hix and Dr. J. R. Zimmerman, of the Magnolia Petroleum Company, Dallas, Texas, for the nuclear magnetic resonance spectrum and interpretation.
quoted from the report by Dr. Zimmerman:

"(a) on the basis of the two models suggested (bromomethylcyclobutane and 1-methyl-1-bromo-methylcyclopropane) there is evidence only for the structural model

(b) There are at least four distinct hydrogen groups (groups having different electronic environments) associated with this molecule. (c) There is one sharp spectral line which appears to have no relation to the molecule studied. It is presumed that it probably arises from a cyclic compound (cyclopentane or one of higher molecular weight) which is present as an impurity with a concentration of about 1% molecular ratio. (d) There is strong evidence of the existence of a single hydrogen in one of the chemical groups, presumably at the 1C position. (e) The electron coupling between the hydrogens and the bromine nuclei in the 5C group is unusually strong. To a lesser extent there is an interaction between the 1C hydrogen and the 5C group. There is some suggestion that a "bridge" type electronic bond exists between the bromine and the 1C hydrogen. (f) There is no evidence of the second chemical model."

Kuivila and Masterton\(^{120}\) attempted to synthesize bromomethylcyclobutane by treating cyclobutylcarbinol with phosphorus tribromide in an effort to minimize the possibility of a rearrangement observed when concentrated hydrobromic acid was used\(^{76}\). They obtained a product whose physical constants\(^{121}\) are very close to those reported by

\(^{120}\)Kuivila and Masterton, J. Am. Chem. Soc., 74, 4953 (1952).

\(^{121}\)B.p. 135-136°, d\(^{27}\) 1.366, n\(^{25}\)\(^D\) 1.4825.
the two groups of investigators\textsuperscript{75, 76} previously mentioned. Kinetic analysis by Kuivila and Masterton\textsuperscript{120} indicated that their product was a mixture of bromomethylcyclobutane (44\%) and bromocyclopentane (56\%). Infrared analysis of various fractions of the radical addition product suggests the presence of only one compound and rules out the possibility of the formation of more than one product.

It is interesting to consider the hybrid radical intermediate suggested by Goering, Abell and Aycock\textsuperscript{122} to account for the stereochemistry of radical addition to cyclic olefins since approximate molecular orbital treatment\textsuperscript{3} requires the intermediate to be open chain rather than cyclic or pi-complex in nature. The following observations also rule out the possibility of the formation of hybrid radical intermediates.

1. Bromine and iodine atom-induced exchange and isomerization of dibromo- and didiodoethylenes\textsuperscript{123} indicate the existence of rotational isomers of structure $\text{CHXCH}_2\text{X}$ and a barrier greater than 3 kcal./mole opposing the interconversion of these isomers by rotation about the carbon-carbon double bond.


2. The addition of thioacetic acid\(^{124}\) to cyclic olefins produced both diasteriomeric thioacetates.

3. The radical addition of bromotrichloromethane to cis- and trans-2-butenes\(^{125}\) produced identical product mixtures suggesting that the same mixture of diastereomeric radicals were produced.

Incidentally, the observed trans-addition to 1-substituted-cyclohexenes may be explained\(^{126}\) by consideration of the steric requirements of the cyclohexane ring.

**HYPOHALOUS ACID ADDITIONS**

In the addition of hypochlorous acid the transition state may be depicted as (IX) or (X) in which X is chlorine.

![Diagram](attachment:diagram.png)

Probably (XII) does not play an important part in the reaction since chlorine exhibits very little tendency to

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\(^{124}\) Bordwell and Hewett, Abstract of Papers, 126th A.C.S. Meeting at New York, N.Y., 1954, p. 6-0.


participate in neighboring group displacement reactions. It is noteworthy that the non-Markownikoff addition of hypochlorous acid to allyl chloride was attributed to the migration of the chlorine from the 1- to the 2-position rather than to an $S_{N2}$ attack on the cyclic chloronium ion similar to (XII). Examination of the experimental data shows that the predominating product is the one predicted by the $I$-strain theory developed by Brown, Brewster and Shechter. This may imply that in the addition of hypochlorous acid, the stabilizing energy of a tertiary carbonium ion relative to a primary carbonium ion is less than the destabilizing energy of a sterically favorable but hyper-conjugatively unfavorable transition state. Since this conclusion is opposite to that reached in the addition of hydrogen bromide, the size of the attacking cation must have an important role in determining whether hyperconjugation or ring strain will be the predominating factor in the addition. As to why this is so is a subject for speculation. The addition of hypochlorous acid to methylenecycloalkanes may be represented as:

The experimental data in the addition of hypobromous acid show that it is quite different from the additions of hydrogen bromide and hypochlorous acid. The orientation of the addition is exactly the opposite of that of hydrogen bromide. The exclusive formation of the non-Markownikoff product suggests that the cyclic bromonium ion (type XII) may be the most favorable transition state regardless of the ring size. Since the addition of hypochlorous acid suggests that ring strain is the predominating factor in additions to methylenecycloalkanes involving cations of approximately the same size as the chloronium ion, some other factors must be operating in the system aside from ring strain and hyperconjugation which leads to the exclusive formation of the non-Markownikoff product. The following may be responsible for the observed orientation:
a. The great tendency of bromine to participate in neighboring group displacement reactions favors the formation of the cyclic bromonium ion as the intermediate or transition state regardless of ring size. Analogy of the opening of the cyclic bromonium ion with that of cycloalkane oxides will lead to the observed products.

b. The preference of $S_N2$ type displacement reactions at the least substituted carbon atom in bromonium ions would also lead to the non-Markownikoff product.

c. The fact that isobutylene reacts normally (i.e., gives almost exclusively (97%) 1-bromo-2-methyl-2-propanol) indicates that the presence of the cycloalkane ring has an effect on the orientation of the addition. It is possible that the geometry of the transition state involving the attack of the solvent or anion in the final phase of the reaction is such that repulsion between non-bonded atoms is much less when there is no ring present. Hence, the possibility of large repulsion forces between non-bonded atoms in the transition state (XV) due in part to the non-flexibility of the cycloalkane ring may make the primary carbon atom more sterically susceptible to attack by the anion or solvent in the concluding step of the addition.
The addition of hypobromous acid to methylenecycloalkanes may be depicted as:

The formation of cycloalkanecarboxaldehyde when \( n \) is 6 or 7 may be due to a pinacol-type rearrangement of the bromohydrin.

The methylenecyclopentane oxide which was isolated when \( n \) is 5 probably came from the bromohydrin and not vice versa. This is suggested by the fact that distillation of the decomposition product of the bromohydrin gave, besides tar, some oxide. The products obtained in the addition of hydrogen bromide to methylene cyclopentane oxide are in agreement with this conclusion. The formation of methylenecyclopentane oxide
instead of cyclopentanecarboxaldehyde may be due to less strain in the oxide compared to the aldehyde.

Long and Pritchard\textsuperscript{129} investigated the hydrolysis of substituted ethylene oxides in oxygen-18 labeled water under acidic, basic and neutral conditions. They concluded that the basic reaction goes by an $S_N2$ mechanism and that the acid-catalyzed reaction involves a carbonium ion mechanism. Hence, the addition of hydrobromic acid may involve an $S_{N1}$ mechanism. According to the I-strain theory, the transition state (XXI) is more stable when $n$ is 5 and 7. This relative stability may facilitate rearrangement to the less strained aldehyde in these systems. Examination of the experimental data reveals a higher yield of cyclopentanecarboxaldehyde and cycloheptanecarboxaldehyde, in agreement with theory.

\begin{itemize}
  \item [(XIX)] \begin{align*}
  \text{(CH}_2\text{)}_{n-3} & \text{C} - \text{CH}_2 \\
  & \text{CH}_2 \\
  \text{O} \\
  \end{align*}
  \begin{array}{c}
  \text{FAST} \\
  \end{array}
  \begin{array}{c}
  \text{H}^+ \\
  \end{array}

  \begin{itemize}
    \item [(XI)] \begin{align*}
      \text{(CH}_2\text{)}_{n-3} & \text{C} + \text{CH}_2 \\
      & \text{OH} \\
    \end{align*}
    \end{itemize}

  \item [(XXI)] \begin{align*}
      \text{(CH}_2\text{)}_{n-3} & \text{C} + \text{CH}_2 \\
      & \text{OH} \\
    \end{align*}
  \begin{array}{c}
    \text{SLOW} \\
    \end{array}

  \item [(XVIII)] \begin{align*}
      \text{(CH}_2\text{)}_{n-3} & \text{C} - \text{CH}_2 \text{OH} \\
      & \text{Br}^- \\
    \end{align*}

  \end{itemize}


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CHLORINE ADDITIONS

The addition of chlorine to methylenecyclobutane is complicated by the ease with which cyclobutyl carbonium ion rearranges. The mechanism\textsuperscript{106} which can account for the products isolated may be formulated as follows:

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 & \xrightarrow{\text{Cl}_2} \text{CH}_2\text{CH}_2\text{CH}^+_1\text{CH}_2 \xrightarrow{\text{Cl}_2^-} \text{CH}_2\text{CH}_2\text{Cl}^-\text{CH}_2 \quad (19\%)
\end{align*}
\]

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2 & \xrightarrow{\text{Cl}_2} \text{CH}_2\text{CH}_2\text{CH}_2\text{Cl}^-\text{CH}_2 \quad (13\%)
\end{align*}
\]

In the chlorination of the other methylenecycloalkanes, with \( n = 5, 6 \) and 7, the formation of chloromethylcycloalkenes may be due to a one-step process involving a transient cyclic intermediate\textsuperscript{130}. Arnold and Lee\textsuperscript{105} also obtained mostly 1-chloromethylcyclohexene in the chlorination of methylenecyclohexanes. The higher yield of 1-chloromethylcyclohexene may be due to the greater ease with which the endo-cyclic

\(\text{(130) }\text{Lee, } \text{Diss. Abstr.}, \text{ XV, 39 (1955)}.\)
double bond is accommodated by the cyclohexane ring. The large amount of polymeric material formed with methylene-cyclopentane may be due to the resistance of the molecule to tolerate the endo-double bond while the relative absence of polymeric material formed with methylenecycloheptane may be attributed to the greater steric requirements of the latter.

The increase in the yield of the dichloride in the chlorination of methylenecyclohexane in the presence of sodium chloride may be due to the increase in concentration of chloride ions thereby exerting a mass effect in the concluding step of the addition. The behavior of methylenecyclopentane under the same conditions may be due to an attack by the chlorine molecule on the dichloride with the resultant formation of a Cl$_3^-$ ion. Treatment of 1-chloro-1-chloromethylcyclohexane under the same conditions as the addition, resulted in the formation of some chloro-olefin and a large amount of polymeric material. The chlorination of methylenecyclohexane in the presence of sodium nitrite yielded mostly the chloro-nitrites as would be expected from a stepwise process. The ratio of the two isomers agrees with that predicted by the I-strain theory. The instability of some of the products formed in the case of methylenecyclopentane makes the assignment of orientation of the nitrite group quite uncertain but a stepwise process is clearly indicated.
IV. SUMMARY

"So much to do; so little done."

Rhodes

The effects of ring size on the orientation of addition reactions of a series of methylenecycloalkanes (methylenecyclobutane, methylenecyclopentane, methylenecyclohexane and methylenecycloheptane) were investigated.

Ionic and free radical additions of hydrogen bromide were found to proceed normally; i.e., ionic additions led to tertiary bromides and radical additions to primary bromides. Unfavorable energy contributions due to the formation of an intermediate or transition state with a trigonal ring carbon are not sufficient to cause abnormal orientations. Rearranged products were obtained in the ionic addition of hydrogen bromide to methylenecyclobutane but the isomeric bromomethylcyclobutane was not detected. The rearranged products were attributed to a rearrangement of the strained cyclobutyl carbonium ion to a more sterically favorable structure.

In the addition of hypochlorous acid, both isomeric chlorohydrins were formed. The predominating product is the one predicted by the I-strain theory developed by Brown, Brewster and Shechter; i.e., 1-chloro-1-hydroxymethylenecycloalkane for the 4- and 6-membered ring systems and 1-chloromethylcycloalkanol for the 5- and 7-membered ring systems.

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The addition of hypobromous acid yielded the 1-bromo-1-hydroxymethylcycloalkane (90-99%) and some cycloalkane-carboxaldehyde (1-10%) in all cases. Repulsion between non-bonded atoms in the transition state due in part to the steric requirements of the cycloalkane ring, the great tendency of bromine to participate in neighboring group displacement reactions and the preference of $S_{N}2$ attack at the least-substituted carbon atom may be responsible for the addition going non-Markownikoff regardless of ring size.

The addition of hydrobromic acid to methylenecycloalkane oxides (not carried out with methylenecyclobutane oxide) gave 1-bromo-1-hydroxymethylcycloalkanes and cycloalkanecarboxaldehydes regardless of ring size. The varying amount of aldehyde formed was attributed to I-strain effects in the intermediate or transition state.

The addition of chlorine to methylenecyclobutane yielded the dichloride in addition to some rearranged products attributed to transannular participation in the cyclobutane ring$^{105}$. The addition to the other methylenecycloalkanes gave mainly chloromethylcycloalkene probably by way of a transient ring intermediate$^{130}$. The products formed in the presence of extraneous anions were attributed either to mass effect or I-strain.
V. BIBLIOGRAPHY


(60) Isaac, Ann., 347, 328 (1906).


(68) Wallach, Ann., 345, 139 (1906).


(76) Dumjancic, Far., 40, 4959 (1907).

(77) Tatevosyan and Melikyan, Bull, Armenian Branch Acad. Sci., U.S.S.R., No.5/6, 23 (1944); C. A., 40, 3406 (1945).


(87) Markownikoff, Ann., 327, 59 (1903).
(90) Demjanow and Dojarenko, Ber., 55B, 2730 (1922).
(91) Tiffeneau, Weill and Tchoubar, Compt. rend., 205, 144 (1937).


(124) Bordwell and Hewett, Abstract of Papers, 126th A.C.S. Meeting at New York, N.Y., 1954, p. 6-0.


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