INFORMATION TO USERS

This manuscript has been reproduced from the microfilm master. UMI films the text directly from the original or copy submitted. Thus, some thesis and dissertation copies are in typewriter face, while others may be from any type of computer printer.

The quality of this reproduction is dependent upon the quality of the copy submitted. Broken or indistinct print, colored or poor quality illustrations and photographs, print bleedthrough, substandard margins, and improper alignment can adversely affect reproduction.

In the unlikely event that the author did not send UMI a complete manuscript and there are missing pages, these will be noted. Also, if unauthorized copyright material had to be removed, a note will indicate the deletion.

Oversize materials (e.g., maps, drawings, charts) are reproduced by sectioning the original, beginning at the upper left-hand corner and continuing from left to right in equal sections with small overlaps.

ProQuest Information and Learning
300 North Zeeb Road, Ann Arbor, MI 48106-1346 USA
800-521-0600

UMI®
NOTE TO USERS

This reproduction is the best copy available.

UMI
A STUDY
OF
THE BROMINATION
OF
SATURATED ORGANIC COMPOUNDS

by

James C. Schiller, M. A.

Submitted in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

The Rice Institute
1941
# Table of Contents

## PART I: THE BROMINATION OF SATURATED HYDROCARBONS

### A. A Preliminary Discussion

1. Historical ...................................... 1
2. An Introduction to the Experimental ........ 3

### B. Experimental

1. Reagents ....................................... 7
2. The Bromination Procedure .................. 9
3. Distillation of the Products ............... 12
4. Identification of the Products ............ 15
   2-Bromopentane ................................ 16
   2-Bromo-2-methylbutane ...................... 16
   2-Bromohexane ................................ 17
   2-Bromo-2-methylpentane .................... 17
   Bromocyclohexane ............................ 18
   Debromination ............................... 19
   Ozonolysis .................................. 20
   2,3-Dibromopentane ......................... 20
   2,3-Dibromo-2-methylbutane ............... 22
   x,x,x-Tribromo-2-methylbutane ............ 23
   2,3-Dibromohexane ......................... 23
   2,3-Dibromo-2-methylpentane .............. 24
   1,2-Dibromocyclohexane .................... 24
   1,2-Dibromobutane ......................... 25
   Stereoisomerism of the Products .......... 26
PART II: THE BROMINATION OF ALIPHATIC ALCOHOLS

A. Introduction........................................30
B. A Description of the Reaction.........................32

1. Bromination Using Copper Powder................32
2. Iodination Using Copper Powder.................33
3. Stoichiometry.......................................34
4. Bromination Using Cupric Bromide............35

C. Theoretical........................................38

SUMMARY................................................42

ACKNOWLEDGMENTS.....................................43

BIBLIOGRAPHY..........................................44
PART I

THE BROMINATION OF SATURATED HYDROCARBONS
A Preliminary Discussion
Historical

When one looks in any modern textbook of organic chemistry under "Reactions of Paraffin Hydrocarbons", he is certain to find that halogenation by substitution with chlorine or bromine is one of the very few reactions exhibited by this series of homologs. And yet if one continues his search by going back to the original literature, he will discover, surprisingly enough, that almost nothing is known concerning the configuration of the products obtained or the conditions influencing the speed or type of substitution. The reports in the literature are scanty and conflicting in their nature, and are almost worthless as far as making any predictions.

Egloff\textsuperscript{11} has compiled a very good review of halogenation experiments through 1931. From this summary it is evident that although chlorination has been studied extensively, the results are by no means useful; and the field of bromination has been touched hardly at all. At the conclusion of this review Egloff makes a number of suggestions as to the course future researches in paraffin bromination should take. And yet, strangely enough, since that time only one case of a study of this kind has been reported. In this report Floerke\textsuperscript{14} simply makes the statement that the photochemical bromination of hexane is possible, a fact which has been known\textsuperscript{48} since 1863.

It might be expedient to mention a few of the more
important of the older studies to be found in the literature. Only the bromination of liquid hydrocarbons will be considered, particularly of hexanes and pentanes.

Schorlemmer was perhaps the first to attempt to prove the structure of a bromination product. He reacted gaseous hexane and bromine in the presence of sunlight and found, by the conversion of the product to the alcohol and the oxidation of it to acetic and butyric acids, that the main portion had been 2-bromohexane. "Not a trace of a primary bromide" could be found. Previously, Pelouze and Cahours had reported the formation of only a dibromohexane. The same workers said that bromine had no action on pentane.

Herzfelder postulated certain generalizations with regard to bromination. He believed that the introduction of successive bromine atoms into a molecule takes place in such a way that adjacent carbon atoms are substituted, and further that no more than one bromine atom can be attached by ordinary means to each carbon atom. While the experimental data to be presented in this thesis would seem to uphold this idea, at the time Herzfelder made these statements there was almost no evidence from which such sweeping assertions could be made.

A little later Michael and Garner modified Schorlemmer's method by dropping the bromine through a condenser to hexane which was refluxing in the attached flask. They identified 2-bromohexane and 3-bromohexane in the main fraction of product.

Pon undertook the only study reported of the
bromination of pentane. The petroleum fraction used boiled from 0° to 10° and four products were identified, two mono- substituted isomers and two disubstituted, although the evidence offered in support of their structures was scanty.

In 1923 Wertshkowsky attempted to extend the old substitution rules of Markownikov and Victor Meyer to cover all the available data to that time, particularly with regard to his own work on the use of catalysts in paraffin bromination. This coordination was very much to be desired, but the rules are so generalized and the evidence so scattered that they may not be considered proved. It may be significant that Wertshkowsky found that the use of catalysts in bromination seemed to lead to the formation of more of the unsymmetrical polysubstituted isomers than was the case when pure bromine was used without a catalyst. However in this instance also the structures of the various isomers are not sufficiently well-known to accept these findings without reservations.

An Introduction to the Experimental

It would appear from this brief survey of the earlier work on paraffin bromination that several factors were responsible for the confusion and lack of substantial experimental data.

First, in no reported case was a reasonably pure hydrocarbon employed in the experiments. In most instances a petroleum fraction boiling over several degrees was used.
This fact considerably complicated the separation of the bromination products, as the author can testify. In preliminary experiments in this laboratory a "pentane fraction" boiling 38° to 41° was used. Rectification graphs of the products were very unsatisfactory, more so than the small amounts of other hydrocarbons present in the original sample would seem to justify.

A second source of difficulty encountered by the older investigators lay in connection with the fractionation of the products themselves. Distillation apparatus was rather unrefined, and the problem of the identification of the various fractions obtained was further complicated by the fact that they were nearly always impure mixtures.

Thirdly, characterizing derivatives and methods of analysis of the products had not been developed to any large degree. Physical constants alone were relied on in most cases, and these were untrustworthy because of the fractionation problems.

Lastly, the conditions under which the various experiments were carried out were by no means standardized. Catalyzed and non-catalyzed brominations were performed, both types at various temperatures, and both under varying conditions of activation by light. These variations certainly did not make for coordination of results, and they complicated attempts like those of Herzfelder and Mereshkovsky at generalizations of any kind.

These enumerated difficulties of the earlier workers were borne in mind when the experiments reported in this thesis
were undertaken.

Before the work was carried out, which is reported on in detail in the next section, a series of preliminary experiments was performed. These were designed to show the effects of various physical and chemical agents on the speed of the bromination and the configuration of the products.

It was found that the addition of almost any solid to the hydrocarbon to be brominated very greatly increased the time necessary for the bromination to take place. This was true with iodine, anhydrous AlCl₃, powdered sulphur, and powdered glass. The use of benzoyl peroxide and myristoyl peroxide as catalysts were failures in that these materials also slowed down the rate of substitution. All of these instances are probably examples of the breaking of the chain reaction of bromination. Inert liquid foreign materials, such as nitrobenzene and ethyl acetate, also slowed down the reaction, probably for the same reason.

Only two factors were noticed which would materially speed up the bromination. First, the presence of small amounts of water very greatly reduced the time required for bromination, but when the products were distilled it was found that they consisted very largely of polysubstituted derivatives. This is in line with the findings of several earlier investigators.² Secondly, as to be expected, it was found that intense activation of the reactants by light, greatly increased the speed of the reaction.

Using this preliminary work as a guide, the experiments
to be described in the next section were devised. It appeared that the most desirable conditions would be those of a constant temperature, highly-activated bromination, using hydrocarbons of unquestionable purity. Insofar as possible, the products would be carefully fractionated and identified, the identification to be both of a chemical and a physical nature. In this way it was hoped that a definite contribution could be made to the knowledge of paraffin bromination.
Experimental
Reagents

The hydrocarbons used in these bromination procedures include n-pentane, isopentane, n-hexane, isohexane and cyclohexane. In addition to the above, n-butyl bromide was also employed. All of these materials were of the highest purity obtainable by reasonable methods.

The n-pentane and isopentane samples were those isolated by Marsh\textsuperscript{23} in this laboratory by distillation procedures. The n-hexane and isohexane samples were furnished by the Shell Oil Company, Houston Refinery. Both isomers had been treated by distillation only. They were further purified in this laboratory by fractionation, at a reflux ratio at least equal to 20:1, through a Bruun 100-plate glass bubble-cap column.

The temperature in the column was measured with a calibrated copper-constantan thermocouple and by means of a Leeds and Northrup type K potentiometer. For more details the original work is cited.\textsuperscript{23}

In addition to the fractionation the n-hexane was given a preliminary nitration\textsuperscript{5} to remove traces of benzene, followed by a treatment with chlorosulfonic acid to remove branched isomers. The n-hexane was then washed, dried, and distilled as described.

The cyclohexane and n-butyl bromide were Eastman Kodak Company's highest purity and were distilled at a reflux ratio of 20:1 through a 1 m. packed column, which will be described in detail in the section on the distillation of the
products.

The bromine was obtained in 1 lb. ampules from Mallickrodt, and was used without further treatment.

A table of physical data on these reagents follows. The hydrocarbon constants check very closely with those most generally accepted today.\textsuperscript{10}
# Physical Properties of the Hydrocarbons Brominated

<table>
<thead>
<tr>
<th>Compound</th>
<th>B.p. @ 760 mm. corrected</th>
<th>$n_D^{20^\circ}$ (Pulfrich)</th>
<th>$d_4^{20^\circ}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Pentane</td>
<td>36.06 - 36.09</td>
<td>1.35768</td>
<td>0.6262</td>
</tr>
<tr>
<td>2-Methylbutane</td>
<td>27.92</td>
<td>1.35392</td>
<td>0.6197</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>68.88 - 68.92</td>
<td>1.37501</td>
<td>0.6594</td>
</tr>
<tr>
<td>2-Methylpentane</td>
<td>60.34</td>
<td>1.37160</td>
<td>0.6530</td>
</tr>
<tr>
<td>Cyclohexane (M.p. = 6.61\textdegree)</td>
<td>80.85</td>
<td>1.42650</td>
<td>0.7806</td>
</tr>
<tr>
<td>n-Butyl bromide</td>
<td>71.0 - 71.2 @ 500 mm.</td>
<td>1.43960</td>
<td>1.2758</td>
</tr>
</tbody>
</table>
The Bromination Procedure

The procedure was standardized as much as possible. The proportion of the reagents employed was 1.35 mols of hydrocarbon to 0.97 mols (50 c.c.) of bromine. The bromine was added intermittently in small portions from a funnel placed in the top of an ice-water-cooled reflux condenser to the flask attached below which contained the hydrocarbon. The stem of the funnel extended through the entire condenser to about one inch from the surface of the hydrocarbon in the flask.

The addition of the bromine was controlled so that the color of the mixture in the flask remained a bright cherry red. The liberated HBr was conducted through a Y-joint in the top of the condenser to an absorption flask containing a strong KOH solution. In this way the amount of HBr released could be determined fairly accurately.

In the case of the low-boiling pentanes, a trap cooled by ice and HCl was placed before this absorption flask, so as to condense the hydrocarbon and bromine vapors carried over by the HBr. These were returned to the reaction flask from time to time.

The mixture of hydrocarbon and bromine in the flask was activated during bromination by the following means:

A frustrum of a cone was made from sheet metal. An inlet and an outlet for circulating water were constructed. The activator in the form of a C. I. Mazda #2 Photoflood lamp was inserted into the smaller opening in the cone through a
water-tight rubber stopper. These lamps proved to have a life of 12 to 15 hours when cooled with circulating ice water, and they were easily replaceable.

The cone was coated with aluminum paint to increase the reflection, and the reaction flask was placed inside the larger opening so that it was also immersed in the ice-water, about one inch from the top of the Photoflood lamp. It was observed that the temperature in the flask during all of these brominations took values between 25° and 31°.

A sketch of the apparatus is included.

When all the bromine had been added and the color discharged, the products were removed and weighed before treatment. The HBr absorption flask was also weighed. A table of results follow:

<table>
<thead>
<tr>
<th>Material Brominated</th>
<th>Time in Hours for Complete Reaction</th>
<th>% Recovery Products</th>
<th>HBr</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Pentane</td>
<td>8</td>
<td>34.5</td>
<td>88.0</td>
</tr>
<tr>
<td>Isopentane</td>
<td>5*</td>
<td>91.6</td>
<td>84.2</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>8</td>
<td>32.0</td>
<td>92.0</td>
</tr>
<tr>
<td>Isohexane</td>
<td>3/4</td>
<td>95.0</td>
<td>90.5</td>
</tr>
<tr>
<td>Isohexane (With 12 c.c. Nitro-benzene)</td>
<td>6</td>
<td>93.5</td>
<td>91.0</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>16</td>
<td>99.5</td>
<td>94.5</td>
</tr>
<tr>
<td>n-Butyl bromide</td>
<td>10</td>
<td>99.3</td>
<td>93.5</td>
</tr>
</tbody>
</table>

*Not significant. The bromine had to be added very slowly because of the high volatility of the isopentane and the tendency of the HBr to sweep out a large amount of it.
These bromides were washed thrice with cold 10% Na₂CO₃ solution, thrice with cold water, and then they were dried over anhydrous CaCl₂ before being fractionated.

This treatment had been ascertained to hydrolyze none of the products⁵¹.
Distillation of the Product

The fractionating apparatus consisted of a glass column 1 m. x 18 mm., fitted with standard interchangeable ground glass connections at both ends, and packed for 90% of its length with 3 mm. spiral single-turn glass helixes. The column was insulated with 85% magnesia standard pipe covering one inch thick, which in turn was covered with a layer of smooth tin foil. Since the column was only rarely to be operated at temperatures above 80°C it was thought unnecessary to heat the column externally to balance the heat losses.

The still head was a total-condensation variable take-off type manufactured by Ace Glass, Incorporated. The head was so designed that fractions could be removed, when operating at reduced pressures, without breaking the pump connection to the column and thus disturbing the equilibrium. In testing the column efficiency under total reflux with various mixtures of benzene and carbon tetrachloride, the graphical method of McCabe and Thiele was followed, using the data of Rosanoff and Easley\textsuperscript{39}. The values obtained for the number of theoretical plates in the column, operating under total reflux, varied from 27 to 31.

In fractionating the products the excess hydrocarbon was in each case removed at atmospheric pressure, the temperature being measured with a 100°C thermometer calibrated in
0.1°. To prevent decomposition and rearrangement of the bromides, the distillation was continued at reduced pressures, the pressure being controlled to within 0.5 mm. with an electrically controlled manostat of the U-type manometer, using a tungsten contact in the open arm side. The Cenco Pyvac pump was operated intermittently by the manostat through a magnetic relay. A five gallon bottle was introduced into the system to increase the sensitivity. The bromides were distilled from a flask containing a capillary side-arm to prevent bumping, and the temperature in the column was measured by means of a 150° C calibrated ace thermometer with a ground glass joint.

The distillation graphs are included. As is evident no more than three flat portions corresponding to pure components were obtained in any case. Assuming these flats to represent the amounts of mono-, di-, and trisubstituted compounds, as will be proved in the next section, the percentage of the total amount of Br substituted which was present as each type of product was calculated.

Isobenzene containing 12 c.c. of nitrobenzene was also brominated. The products obtained were the same in configuration as those for pure isobenzene, as indicated by the distillation graph (not shown), but the ratio of their occurrence was considerably changed.

A table of calculated values follows:
<table>
<thead>
<tr>
<th>Material Brominated</th>
<th>Monobromides</th>
<th>Dibromides</th>
<th>Tribromides</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>n</em>-Pentane</td>
<td>50.2</td>
<td>35.5</td>
<td>14.3</td>
</tr>
<tr>
<td>Isopentane</td>
<td>47.6</td>
<td>46.8</td>
<td>6.6</td>
</tr>
<tr>
<td><em>n</em>-Hexane</td>
<td>53.2</td>
<td>29.4</td>
<td>17.4</td>
</tr>
<tr>
<td>Isohexane</td>
<td>55.1</td>
<td>38.4</td>
<td>6.5</td>
</tr>
<tr>
<td>Isohexane (with nitrobenzene)</td>
<td>6.7</td>
<td>82.7</td>
<td>10.6</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>7.0</td>
<td>79.3</td>
<td>13.7</td>
</tr>
<tr>
<td><em>n</em>-Butyl bromide</td>
<td>-</td>
<td>65.5</td>
<td>36.5</td>
</tr>
</tbody>
</table>