Vollweiler.

Studies Of Trimethylene Oxide
STUDIES OF TRIMETHYLENE OXIDE

BY

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## INDEX

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>I. Introduction</strong></td>
<td>1.</td>
</tr>
<tr>
<td><strong>II. Historical</strong></td>
<td>3.</td>
</tr>
<tr>
<td>2. Trimethylene oxide</td>
<td>8.</td>
</tr>
<tr>
<td>3. Other oxides</td>
<td>9.</td>
</tr>
<tr>
<td><strong>III. Theoretical</strong></td>
<td>11.</td>
</tr>
<tr>
<td>A. Action of metallic oxides on trimethylene halides</td>
<td>12.</td>
</tr>
<tr>
<td>3. Action of silver oxide on trimethylene halides</td>
<td>15.</td>
</tr>
<tr>
<td>B. Action of heat on Cl-CH₂CH₂CH₂-OMgI</td>
<td>16.</td>
</tr>
<tr>
<td>C. Action of heat on Na-O-CH₂CH₂CH₂-Cl</td>
<td>20.</td>
</tr>
<tr>
<td><strong>IV. Experimental</strong></td>
<td>22.</td>
</tr>
<tr>
<td>A. Action of metallic oxides on trimethylene halides</td>
<td>22.</td>
</tr>
<tr>
<td>1. Action of lead oxide on trimethylene bromide</td>
<td>23.</td>
</tr>
<tr>
<td>a. Preparation of trimethylene glycol</td>
<td>23.</td>
</tr>
<tr>
<td>b. Preparation of trimethylene bromide</td>
<td>23.</td>
</tr>
<tr>
<td>d. Investigation of the polymers</td>
<td>27.</td>
</tr>
<tr>
<td>3. Action of silver oxide on trimethylene halides</td>
<td>33.</td>
</tr>
<tr>
<td>B. Action of heat on Na-O-CH₂CH₂CH₂Cl</td>
<td>36.</td>
</tr>
<tr>
<td>1. Preparation of trimethylene chlorhydrin</td>
<td>37.</td>
</tr>
<tr>
<td>2. Preparation of Na-O-CH₂CH₂CH₂Cl</td>
<td>38.</td>
</tr>
<tr>
<td>C. Action of heat on Cl-CH₂CH₂CH₂-OMgI</td>
<td>40.</td>
</tr>
<tr>
<td><strong>V. Conclusions</strong></td>
<td>48.</td>
</tr>
</tbody>
</table>
INTRODUCTION.

One of the problems being studied in this laboratory is the determination of the nature and magnitude of the influence of one atom upon another in organic compounds. Michael has formulated the following rule which he believes expresses the influence of one atom upon another: "If we number a certain atom in any fatty compound with a normal carbon chain by the figure 1, our present knowledge of the combined mutual influence between this atom and others in the molecule is expressed by the following scale of combined influence, the numbers indicating the degree of removal and the extent of the influence decreasing in the order given: 2-3-5-6-4-7-9-10-11-8."

Derick, on the other hand, believes that the scale of influence runs as follows: 2-3-4-5-6-7-8-9-10-. In conjunction with Brady and Hess, he has established this scale experimentally for the reaction ionization. These investigators studied the influence of the divalent oxygen atom and found that this divalent substituent did not obey the rule of thirds found by Derick for the monovalent negative substituents. Valence was, therefore, considered to be a factor in any scale of influence.

The present work was undertaken in an endeavor to determine the scale of influence for trivalent substituents and to determine further the manner in which valence enters into such a scale. The particular substituent with which this work is concerned is the trivalent nitrogen atom of the cyanide radical. This is to be moved out the chain of the aliphatic acids and the comparative effects upon the ionization constants of the acids noted. The general formula of the cyano-acids is $N\equiv C(\text{CH}_2)_x\text{COOH}$. 
It is evident that the first part of the problem is the synthesis of these acids, and some synthetic agent which supplies one or more methylene groups and which may readily be linked with other compounds to lengthen the chain, is necessary. It was thought that trimethylene oxide should be an excellent synthetic agent in these respects, for it can add three methylene groups all at once, and, having a four atomic ring structure, the ring should be broken with sufficient ease to make such a synthesis practicable.

The problem of a feasible synthesis of trimethylene oxide was attacked from the standpoint of the action of metallic oxides on trimethylene halides. Another method attempted was by the action of heat on the Grignard complex Cl-CH₂CH₂CH₂-O-Mg-I, and still another by the action of heat on the sodium alcoholate of trimethylene chlorhydrin. The results of this experimental work is given in the following thesis.
The polymethylene oxides have similar chemical properties, since they are members of the same homologous series. A study of the other members of the series will therefore make the method of attack of trimethylene oxide more clear and simple.

The first member of the series of polymethylene oxides is ethylene oxide, which was discovered by Wurtz\(^6\) about 1859, who appears to have been the first worker in the field. The first method by which he prepared ethylene oxide was by the use of the chlorhydrin of glycol. He prepared this substance by the action of hydrogen chloride on glycol in a closed vessel. This action eliminates water from the glycol as follows:

\[
\text{CH}_2\text{OH} + \text{HCl} \rightleftharpoons \text{CH}_2\text{Cl} + \text{H}_2\text{O}
\]

Upon treating the chlorhydrin with potassium hydroxide, Wurtz found that an instantaneous reaction took place with the precipitation of solid potassium chloride and the evolution of a gas or inflammable vapor which required a good cooling agent for condensation. He explains the reaction as taking place in the presence of potassium hydroxide as follows:

\[
\text{CH}_2\text{OH} \rightleftharpoons \text{CH}_2\text{Cl} \rightleftharpoons \text{CH}_2\text{O} + \text{HCl},
\]

and the reaction is driven to completion by the removal of the hydrochloric acid by the potassium hydroxide. Wurtz found that the quantitative analysis and vapor density checked the theory for ethylene oxide. Wurtz called attention to the fact that ethylene oxide is isomeric with acetaldehyde, and found that while some of its properties are the same as those of the aldehyde, others were quite different. (In the light of modern knowledge, it is evident that acetaldehyde may actually have been present in Wurtz's preparation. The
method of collision study developed in this laboratory shows that besides the collision given above, the following occur simultaneously:

\[
\begin{align*}
\text{Cl-CH}_2\text{CH}_2\text{-OH} + \text{KOH} & \rightleftharpoons \text{Cl-CH}=\text{CH}_2\text{+KOH} + \text{H}_2\text{O} \rightleftharpoons \text{KOH} + \text{H}_2\text{O}. \\
\text{Cl-CH}_2\text{CH}_2\text{-OH} + \text{KOH} & \rightarrow \text{CH}_3\text{OH} + \text{KCl} + \text{H}_2\text{O}.
\end{align*}
\]

That Wurtz's product may have been impure for this reason is borne out by the work of Bissell upon trimethylene oxide.) The pure oxide boils at 13.5° while acetaldehyde has a boiling point of 21°. Like acetaldehyde, he found that the oxide dissolves in water in all proportions, and with sodium bisulfite gives deliquescent crystals. But unlike the aldehyde, he found that ethylene oxide gives no crystals with ammoniacal ether, and is violently attacked by phosphorous halides, while acetaldehyde reacts only slowly with them:

\[
P\text{Cl}_5 + \text{C}_2\text{H}_4\text{O} \rightarrow P\text{OCl}_3 \text{C}_2\text{H}_4\text{Cl}_2
\]

The dichlor compound which he obtained boiled at 84° and had the same properties as the "oil of the four Dutch chemists", so that Wurtz entertained no doubt as to the course of the reaction.

After this first successful attempt to prepare ethylene oxide, Wurtz turned his attention to other methods of preparing the substance. He had come to the conclusion some time earlier that the oxide could not be prepared by the direct action of oxygen upon ethylene, but that indirect methods must be used. One of these was to use glycol diacetate, which he obtained by treating ethylene bromide or iodide with silver acetate. The oxide was obtained from the diacetate by the action of potassium or barium hydroxide. He
found that the product he obtained by this method was the same as that which he obtained from the chlorhydrin. A study of the chemical properties of ethylene oxide showed the oxide to be very reactive:

\[ \text{C}_2\text{H}_4\text{O} + \text{H}_2 \rightarrow \text{CH}_3\text{CH}_2\text{OH} \]

\[ \text{C}_2\text{H}_4\text{O} + \text{O}_2 \rightarrow \text{COOH} \]

\[ \text{C}_2\text{H}_4\text{O} + \text{Br}_2 \rightarrow \text{CH}_2\text{OBr} \]

\[ \text{C}_2\text{H}_4\text{O} + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{OH}, \text{red crystals} \]

\[ \text{C}_2\text{H}_4\text{O} + \text{H}_2\text{O} \rightarrow \text{CH}_2\text{OH}, \text{polymethylene alcohols} \]

\[ \text{C}_2\text{H}_4\text{O} + \text{NH}_3 \rightarrow \text{oxygen bases} \]

Wurtz found that ethylene oxide combines with ammonia to form several polymeric addition compounds. The series of molecular compounds which he thus obtained consists of the compounds \( \text{C}_2\text{H}_4\text{O} \cdot \text{NH}_3 \), \( (\text{C}_2\text{H}_4\text{O}) \cdot \text{NH}_3 \), \( (\text{C}_2\text{H}_4\text{O})_2 \cdot \text{NH}_3 \), and \( (\text{C}_2\text{H}_4\text{O})_3 \cdot \text{NH}_3 \).

Wurtz also found that ethylene oxide, when put into a flask with a concentrated solution of magnesium chloride, and sealed and allowed to stand, yields an abundant deposit of magnesium hydroxide together with ethylene chlorhydrin. In a like manner the oxide displaces aluminium, ferric oxide, and cupric oxide. The above reactions were believed by Wurtz to prove the structure of the oxide to be \( \text{CH} = \text{CH}_2\text{O} \), and in support of this he cited cases of the metallic oxides like barium oxide, manganese oxide, etc., which behave similarly in their combining capacities. From this series of experiments he concluded that he had broken down the barriers between organic and inorganic chemistry and that henceforth the same methods of study
could be applied to both branches of the subject.

In 1877, Green\textsuperscript{10}, working in Wurtz's laboratory, investigated the action of metallic oxides on ethylene bromide, chloride, and iodide. He found that at 150\textdegree C dry silver oxide acts very readily on ethylene iodide to give the oxide. If ethylene bromide is used in place of the iodide, the reaction goes if the temperature is kept at 250\textdegree C. Sodium oxide reacts readily with ethylene bromide to give the oxide, and ethylene chlor-iodide reacts equally well with the sodium oxide. By this method Green was able to prepare, in a sealed tube, 5 to 10 grams of pure oxide which he characterized with care.

In contrast to the action of the metallic oxides mentioned, however, Green found that the oxides of the diatomic elements, as barium and lead oxides, gave no ethylene oxide at all, even when the temperature was raised to 250\textdegree C and maintained there for a long time.

The last contribution which Wurtz\textsuperscript{11} appears to have made on the subject of polymethylene oxides was on the polymerization of the product. He accidentally found a polymer in a sealed tube in which ethylene oxide had been kept a year. In studying the conditions of this polymerization, he found that a very small piece of fused potassium hydroxide, or better still zinc chloride, caused the entire mass to become solid at the end of several months, while calcium chloride seemed to decompose the oxide without producing polymerization.

In 1874 Demole\textsuperscript{12} published a description of a method for preparing ethylene oxide which was similar to Wurtz's original
chlorhydrin method, but gave better yields of the oxide. He prepared the chloracetate of ethylene by the roundabout method of treating ethylene bromide with dry potassium acetate, which gave the brom-acetate; by treating this product with hydrochloric acid at 100° the bromine was replaced by chlorine, giving the chlor-acetate. The chlor-acetate was then treated with potassium hydroxide as Wurtz had done in using the chlorhydrin, and this yielded ethylene oxide. Demole found that, starting with 100 grams of ethylene bromide in each case, the chlorhydrin method gave 4 grams of ethylene oxide while the chlor-acetate method gave as much as 8 grams. He noticed that when he dried the oxide over potassium hydroxide, the materials heated up; he thought that this was due to a reaction with the ethylene oxide, and therefore dried his product by redistillation. He appears to have forgotten that the water which he was attempting to remove would react with potassium hydroxide with the evolution of heat.

Girard found that phosphonium iodide reacts with ethylene oxide as it does with an ordinary ether, and not as it does with the aldehyde isomeric with ethylene oxide:

\[
\text{CH}_2\text{CH}_2\text{I} + \text{PH}_4\text{I} \rightarrow \text{CH}_2\text{OH} + \text{PH}_3. \\
\text{CH}_2\text{OH} + \text{PH}_4\text{I} \rightarrow \text{CH}_2\text{I} + \text{PH}_3 + \text{H}_2\text{O}.
\]

**Trimethylene Oxide.**

Little work appears to have been done on trimethylene oxide. Reboul prepared it in what was probably an impure state by heating trimethylene chlorhydrin with solid potassium hydroxide.
He describes trimethylene oxide as being a colorless, very mobile liquid having a penetrating odor, soluble in water in all proportions and combining energetically with bromine. Bissell⁷ has shown, however, that pure trimethylene oxide does not react readily with bromine, and that the material which Reboul thought to be pure trimethylene oxide must have contained unsaturated compounds like allyl alcohol and chloride. Reboul gives the boiling point of the oxide as about 50° and finds that its quantitative analysis agrees very closely with the theoretical. He obtained an oil whose boiling point was above 326°, which he believed to be a mixture of polymers.

**TETRA-, PENTA-, AND DECA-METHYLENE OXIDES.**

Like trimethylene oxide, the higher polymethylene oxides have been little investigated. Dekkers¹⁵ obtained tetramethylene oxide as a by-product in the preparation of glycol from tetramethylenedinitramine and dilute sulfuric acid. The yield was very small. Its boiling point is 67° and it has an aromatic agreeable odor. Its quantitative analysis agrees fairly with the theoretical.

Hochstetter¹⁶ prepared pentamethylene oxide by heating pentamethylene bromide with twenty volumes of water in a sealed tube at 100°. The heating was continued for two weeks, when all but traces of the bromide had disappeared. From 38 grams of dibromide he obtained 10 grams of pure pentamethylene oxide. Its boiling point was found to be 61-82°.

What seems to have been decamethylene oxide was prepared by Alberti and Smieznyszenski¹⁷ by the action of solid sodium hydroxide upon decamethylene chlorhydrin, just as Wurtz prepared ethylene oxide from ethylene chlorhydrin. At the same time they obtained
a small quantity of an unsaturated alcohol. From 15 grams of the chlorhydrin they obtained 3.8 grams of the oxide. They found its boiling point to be 181°; the elementary analysis agreed with the theoretical; it did not add bromine, nor react with water when heated for ten hours at 200°; it was soluble in ether and alcohol but insoluble in water.
THEORETICAL.
ACTION OF METALLIC OXIDES ON TRIMETHYLENE HALIDES.
As has already been mentioned, Wurtz found that it was practically impossible to prepare ethylene oxide by the action of the oxides of divalent metals upon ethylene halides. As we go up the homologous series, however, we should expect, according to Baeyer's Strain Theory, that the compounds should be easier to prepare, for the strain in the 4, 5, and 6 atomic ring would be less than in the 3 atomic ring of ethylene oxide.

The oxides of monatomic metals like silver oxide should for the same reason give better yields of trimethylene oxide than can be obtained in the case of ethylene oxide.

Using lead oxide as an example of the series of the oxides used, the possible reactions which we might expect are as follows:

1. \[ \text{BrCH}_2\text{CH}_2\text{CH}_2\text{Br} + \text{PbO} \rightarrow \text{CH}_2\text{CH}_2\text{Br} + \text{PbBr}_2 \]

2. \[ \text{BrCH}_2\text{CH}_2\text{CH}_2\text{Br} \leftarrow \text{BrCH}_2\text{CH} = \text{CH}_2 + \text{HBr} \]

3. \[ \text{BrCH}_2\text{CH} = \text{CH}_2 \leftarrow \text{CH}_2 = \text{CH}_2 + \text{HBr} \]

4. \[ \text{PbO} + 2\text{HBr} \rightarrow \text{PbBr}_2 + \text{H}_2\text{O} \]

5. \[ \text{CH} = \text{CHCH}_2\text{Br} + \text{BrCH}_2\text{CH} = \text{CH}_2 + \text{PbO} \rightarrow \text{CH} = \text{CHCH}_2\text{Br} + \text{PbBr}_2 \]

6. \[ \text{BrCH}_2\text{CH}_2\text{CH}_2\text{Br} + \text{PbO} + \text{BrCH}_2\text{CH}_2\text{CH}_2\text{Br} \rightarrow \text{BrCH}_2\text{CH}_2\text{CH}_2\text{Br} + \text{PbBr}_2 + \text{H}_2\text{O} \]

7. Unsaturation from the products of (6), just as in (2) and (3).

8. Polymers from the oxide from (1).

**ACTION OF LEAD OXIDE ON TRIMETHYLENE BROMIDE.**

When lead oxide is allowed to act on trimethylene bromide at about 200°, a small amount of liquid is obtained which has a very sharp penetrating odor and boils at 50-100°. A high boiling liquid remains in the distilling flask, and part of this distills at about
180° under a pressure of 50 m.m.

The method used for the separation of the unsaturated compounds, from the trimethylenoxide, supposing the latter to be present, depended upon the reactivity of the unsaturated compounds with bromine in the cold. It is to be noted here that bromine in carbon tetrachloride reacts very slowly with unsaturated compounds like allyl alcohol, while pure bromine reacts violently with them. Trimethylenoxide will not react readily with bromine in the cold. It was found that when bromine was added to the fraction which boiled at 50-60°, the reaction was very violent and instant decolorization took place. The trimethylenoxide, if present, should be unaffected by the bromine, and should be salted out from the aqueous solution by potassium carbonate. This, however, did not occur, and the amount of trimethylenoxide present must have been very small.

The high boiling liquid which distilled at 180° under 50 m.m. pressure was thought to be perhaps the polymer of trimethylenoxide, and in order to test this out an attempt was made to prepare a derivative of it. By means of magnesium propyl bromide in the Grignard reaction, hexyl alcohol should be obtained if the product is really trimethylenoxide or one of its polymers. The reactions are as follows:

\[
\text{Mg} + \text{C}_3\text{H}_7\text{Br} \rightarrow \text{BrMgC}_3\text{H}_7. \\
\text{BrMgC}_3\text{H}_7 + \text{CH}_2\text{CH}_2\text{CH}_2 \rightarrow \text{C}_3\text{H}_7\text{CH}_2\text{CH}_2\text{CH}_2 - \text{OMgBr} \xrightarrow{\text{H}_2\text{O}} \text{CH}_3\text{(CH}_2\text{)}_5\text{OH} + \text{BrMgOH}. 
\]

About one c.c. of liquid, boiling constant at 155-157°, and giving the red ring test for alcohols with concentrated sulfuric acid and resorcinol, showed that the product obtained was actually hexyl
alcohol, and therefore the product started with must have been a polymer of trimethylene oxide.

ACTION OF MERCURIC OXIDE ON TRIMETHYLENE HALIDES.

Mercuric oxide would naturally be expected to react faster than lead oxide with trimethylene halides; and it was found that when trimethylene bromide was used it actually did largely increase the amounts of unsaturated products, although the amount of trimethylene oxide obtained was again inappreciable. The use of mercuric oxide introduces the further difficulty that the mercuric bromide produced is soluble in ether, making the extraction of the residue difficult. A large amount of charred organic material is also taken up by the ether and this is very difficult to remove.

When trimethylene chloride is refluxed with mercuric oxide the reaction is so slow that no products of any kind are obtained, and the trimethylene chloride is recovered unchanged. On the other hand when trimethylene iodide is heated with mercuric oxide, the trimethylene iodide is decomposed before any other reactions take place in appreciable amounts. This reaction also is therefore not a feasible one for the preparation of trimethylene oxide.

ACTION OF SILVER OXIDE ON TRIMETHYLENE HALIDES.

The trimethylene halides must be added to the silver oxide slowly in order to prevent the action from becoming violent. Trimethylene iodide, bromide, and chloride all give very small amounts of the same unsaturated products which were obtained when lead and mercuric oxide were used. The reaction is more difficult to control than in the case of lead and mercuric oxides and the yields are scarcely so good; hence this method was also abandoned.
THE ACTION OF HEAT ON CH \textsubscript{2}CH \textsubscript{2}CH \textsubscript{2}OMgI.
The Grignard reaction was the next method used in the attempt to prepare trimethylene oxide. When ethyl iodide is allowed to act on magnesium in ether solution, using a crystal of iodine as a catalyst, an almost quantitative yield of ethyl magnesium iodide is obtained. When this is treated with trimethylene chlorhydrin, the compound \( \text{Cl-CH}_2\text{CH}_2\text{CH}_2-\text{OMgI} \) is obtained from which the ether is evaporated and the residue heated. These reactions may yield products as follows:-

1. \( \text{I}_2 + \text{Mg} \rightarrow \text{MgI}_2 \).
2. \( \text{MgI}_2 + (\text{C}_2\text{H}_5)_2\text{O} \rightarrow \text{MgI}_2(\text{C}_2\text{H}_5)_2\text{O} \).
3. \( \text{C}_2\text{H}_5\text{I} + \text{Mg} + \text{MgI}_2(\text{C}_2\text{H}_5)_2\text{O} \rightarrow \text{C}_2\text{H}_5\text{MgI}(\text{C}_2\text{H}_5)_2\text{O} + \text{MgI}_2 \).
4. \( \text{C}_2\text{H}_5\text{MgI}(\text{C}_2\text{H}_5)_2\text{O} + \text{C}_2\text{H}_5\text{I} \rightarrow \text{C}_4\text{H}_{10} + \text{MgI}_2(\text{C}_2\text{H}_5)_2\text{O} \).
5. \( \text{C}_2\text{H}_5\text{MgI} \cdot (\text{C}_2\text{H}_5)_2\text{O} + \text{C}_2\text{H}_5\text{MgI}(\text{C}_2\text{H}_5)_2\text{O} \rightarrow \text{Mg}(\text{C}_2\text{H}_5)_2(\text{C}_2\text{H}_5)_2\text{O} + \text{MgI}_2(\text{C}_2\text{H}_5)_2\text{O} \).

Add the above to \( \text{Cl-CH}_2\text{CH}_2\text{CH}_2\text{OH} \).
6. \( \text{C}_2\text{H}_5\text{MgI-\text{Et}_2\text{O} + \text{HO(CH}_2)_3\text{Cl} \rightarrow \text{C}_2\text{H}_6 + \text{IMgO(\text{CH}_2)_3\text{Cl} \).
7. \( \text{I-Mg-O(\text{CH}_2)_3\text{Cl} \rightarrow \text{CH}_2\text{CH}_2\text{CH}_2 + \text{IMgCl} \).
8. \( \text{Cl(\text{CH}_2)_3\text{Cl} + I-Mg-C_2H_5 \rightarrow Cl-(\text{CH}_2)_4\text{CH}_3 \) (or \( I-(\text{CH}_2)_4\text{CH}_3 \)).

Evaporate off the ether cautiously, then heat.
9. \( \text{Cl-(CH}_2)_3\text{OMgI} \rightarrow \text{CH}_2\text{CH}_2\text{CH}_2 + I-Mg-\text{Cl} \).
16. \( \text{Cl-(CH}_2)_3\text{O-Mg-I} \rightarrow \text{Cl-CH}_2\text{CH=CH}_2 + I-Mg-\text{OH} \).
11. \( \text{Cl-(CH}_2)_3\text{O-Mg-I + H}_2\text{O} \rightarrow \text{Cl-(CH}_2)_5\text{OH} + I-Mg-\text{OH} \).

Contrary to expectations, the reactions did not yield trimethylene oxide at all, but gave a large amount of trimethylene
iodide and a mixture of some iodine compounds boiling from 50-100°. They decomposed on distillation, giving free iodine, but they have not yet been fully investigated.

If the residue in the flask is distilled with steam instead of heating directly, trimethylene iodide is again obtained with some low boiling iodine compounds.

These peculiar reactions may be explained in several ways. If the residue is heated directly, in the absence of water, the following reactions are probably the source of the trimethylene iodide;

1. \(\text{Cl-CH}_2\text{CH}_2\text{CH}_2-0-\text{Mg}-I + \text{I-Mg-O-CH}_2\text{CH}_2\text{CH}_2-\text{Cl} \rightarrow \text{I-CH}_2\text{CH}_2\text{CH}_2-0\text{MgI} + \text{Cl-CH}_2\text{CH}_2\text{CH}_2-0-\text{Mg}-\text{Cl}\).

2. \(\text{I-CH}_2\text{CH}_2\text{CH}_2-0-\text{Mg}-I \leftrightarrow \text{CH}_2=\text{CH}\text{CH}_2\text{O-Mg}-I + \text{HI}\).

3. \(\text{I-CH}_2\text{CH}_2\text{CH}_2-0-\text{Mg}-I \leftrightarrow \text{I-CH}_2\text{CH}=\text{CH}_2 + \text{I-Mg-OH}\).

4. \(\text{I-CH}_2\text{CH}=\text{CH}_2 + \text{HI} \rightarrow \text{I-CH}_2\text{CH}_2\text{CH}_2\text{I}\).

If the above is the explanation, however, it is difficult to see why some trimethylene chloride should not be obtained in the same way.

If the residue is distilled with steam, several explanations for the production of trimethylene iodide are possible:

1. \(\text{Cl(CH}_2)_3\text{O-Mg-I} + \text{I-Mg-0(CH}_2)_3\text{Cl} \leftrightarrow \text{I(CH}_2)_3\text{O MgI} + \text{ClMgO(CH}_2)_3\text{Cl}\).

2. \(\text{I(CH}_2)_3\text{OMgI} + \text{H}_2\text{O} \rightarrow \text{I(CH}_2)_3\text{OH} + \text{IMgOH}\).

3. \(\text{I-Mg-OH} + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2 + \text{HI}\).

4. \(\text{I(CH}_2)_3\text{OH} + \text{HI} \rightarrow \text{I(CH}_2)_3\text{I} + \text{H}_2\text{O}\).

or,

1. \(\text{I-Mg-0(CH}_2)_3\text{Cl} + \text{H}_2\text{O} \leftrightarrow \text{I-Mg-OH} + \text{HO(CH}_2)_3\text{Cl}\).

2. \(\text{I-Mg-OH} + \text{H}_2\text{O} \leftrightarrow \text{HI} + \text{Mg(OH)}_2\).

3. \(\text{Cl(CH}_2)_3\text{OH} + \text{HI} \leftrightarrow \text{Cl(CH}_2)_3\text{I} + \text{H}_2\text{O}\).

4. \(\text{I(CH}_2)_3\text{Cl} + \text{HI} \leftrightarrow \text{I(CH}_2)_3\text{I} + \text{HCl}\).
The latter explanation seems to agree better with the experimental results, for according to it we get no trimethylene chloride, as was actually found to be the case; while according to the first explanation we should expect to get at least some trimethylene chloride.
ACTION OF HEAT ON Na-O-CH₂CH₂CH₂Cl.
When trimethylene chlorhydrin is treated with sodium, it reacts to give sodium alcoholdate according to the reaction:

\[
\text{Cl-CH}_2\text{CH}_2\text{CH}_2\text{OH} + \text{Na} \rightarrow \text{Cl-CH}_2\text{CH}_2\text{CH}_2\text{O-Na} + \text{H}
\]

and this sodium alcoholdate might break up on heating as follows:

\[
\text{Cl-CH}_2\text{CH}_2\text{CH}_2\text{O-Na} \rightarrow \text{NaCl} + \text{CH}_2\text{CH}_2\text{CH}_2
\]

Instead of giving trimethylene oxide, however, it gives products which are nearly all unsaturated. These unsaturated products have not been characterized.
EXPERIMENTAL.
PREPARATION OF TRIMETHYLENE OXIDE BY THE ACTION OF LEAD OXIDE ON TRIMETHYLENE HALIDES.
THE PREPARATION OF TRIMETHYLENE OXIDE BY THE ACTION OF LEAD OXIDE ON TRIMETHYLENE BROMIDE.

I. PREPARATION OF TRIMETHYLENE GLYCOL.

The first method which was tried for making trimethylene oxide was the action of lead oxide on trimethylene bromide. When the commercial by-product of the soap industry known as "Blizzard Oil" was fractioned four or five times, nearly 50% of the crude product was obtained as a clear, syrupy liquid with a constant boiling point of about $210^\circ_{750}$ (uncorrected). This substance is trimethylene glycol.

II. PREPARATION OF TRIMETHYLENE BROMIDE.

To prepare the dibromide from the glycol, 157 grams of the glycol was added to 1000 grams (3 moles) of constant boiling hydrobromic acid in a 2-liter flask. This mixture was then refluxed four or five hours; during the operation some trimethylene bromide separated out as a heavy layer and this was separated. The upper layer was then put back into the flask, weighed, and gaseous hydrobromic acid, generated by the action of bromine and phosphorous and water, was passed in until the weight of the contents of the flask indicated that two moles of hydrogen bromide had been absorbed. The mixture was then refluxed about four or five hours more, the dibromide layer separated, and the remainder of the liquid distilled, which caused more dibromide to separate.

The trimethylene bromide was purified as follows: first washed three times with 100 c.c. water, then once with 30 c.c. concentrated sulfuric acid, keeping the contents cool with ice; after being again treated with 20 c.c. concentrated sulfuric acid, it was
washed twice with water, then with 1-1 potassium hydroxide until alkaline, and finally with water. This treatment removes glycol and the monobrom derivative, and leaves a clear, slightly yellow liquid which nearly all comes over constant at $163^\circ_746$ (uncorrected). The yields of trimethylene bromide by this procedure sometimes run as high as 80%, but the average yield obtained was not above 65%.

III. ACTION OF LEAD OXIDE ON TRIMETHYLENE BROMIDE.

The reaction between lead oxide and trimethylene bromide was carried out in a 500 c.c. round bottom flask to which was attached a 2-foot reflux condenser; the top of this was connected by glass tubing to two U-tubes containing bromine covered with water which served to retain the unsaturated gases. All the U-tubes were set into a freezing mixture of ice and water. The flask was heated by means of a Wood's metal bath.

For the reaction, 55 grams of lead oxide and 48 grams of trimethylene bromide were put together into the flask and the temperature of the Wood's metal bath maintained at 175-180°. At the end of eight hours heating about one-half c.c. of a colorless, mobile liquid with an exceedingly penetrating odor had collected in the first U-tube receiver. Continued heating at the same temperature for four hours more yielded no further distillate. The temperature of the Wood's metal bath was then raised to 185-190°, and at the end of eight hours about 1 c.c. more of the distillate had come over. Continued heating, even at 200°, gave no further distillate.

A number of such runs were made with about the same amount of product being obtained each time. It was found that the best
and most economical method was to heat to 190-200° for about eight hours. A higher temperature caused trimethylene bromide to distill over; a lower temperature made the reaction very slow.

When about 3 c.c. of distillate had been obtained in this way, it was distilled, using a short condenser and a side neck test tube immersed in a bath of ice and crude hydrochloric acid (1.2) as receiver. The heating was done on a water bath. About 2 c.c. of the product came over rather slowly at 50-65°, while the remainder could not be distilled with a water bath. The distillate still had the same penetrating odor as the original liquid. The odor was very similar to that of allyl bromide. When tested for halogens with a clean copper wire, it gave an intense green coloration which lasted for some time. An aqueous solution of potassium permanganate was instantly decolorized by the liquid, and when bromine was dropped into it, a violent reaction took place with noise and spattering. All the above reactions show the presence of unsaturated compounds in considerable amount, probably partly allyl bromide, which boils at 70°.

The remainder of the distillate which had come over at 50-65° was then treated with bromine until no further reaction was noticeable. Ten volumes of water were then added and when shaken, a small fractional part of the substance dissolved. The bromide was separated from the water layer, and solid potassium carbonate was added to the latter. About one-half c.c. of a thick, syrupy, yellow substance was salted out which was too small in volume for characterization. The bromide layer was dried, but it too was too small in volume for characterization.
The next method used was to drop the trimethylene bromide on to the hot lead oxide, instead of mixing the entire quantities at once, but this gave no appreciably better yields.

The residue left in the flask from each run had been extracted with ether and filtered, and these extracts were now combined and the ether evaporated off. Distillation under 745 m.m. gave only a few drops up to $165^\circ$, but from $165-180^\circ$ about 10 c.c. of distillate came over which was trimethylene bromide. The remainder of the liquid was then distilled under diminished pressure, and the temperature gradually rose to $180^\circ$. This fraction had the odor of trimethylene bromide, and probably the main part of it was this substance. About a third of the total amount of the substance had come over in this temperature range. The temperature now remained practically constant at $180-185^\circ$ until 4 grams of distillate had come over. This distillate was light yellow in color and of a syrupy consistency. The temperature then slowly rose, but only a few grams more came over, leaving a tarry liquid in the flask which could not be distilled under a vacuum of 1 m.m. when the temperature of the bath was $350^\circ$.

In order to obtain a vacuum less than that mentioned above, a side tube containing cocoanut charcoal which had been previously heated was attached to the distilling bulb. Even with this addition, however, very little of the residue distilled over.

The residues from six more runs were then extracted, and after the ether had been evaporated off, about 70 grams of liquid remained. This yielded the following distillates under the pressures given:
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>To 70°</td>
<td>-----</td>
<td>Atmospheric</td>
<td>2 grams.</td>
</tr>
<tr>
<td>70-155°</td>
<td>170°</td>
<td>&quot;</td>
<td>0&quot; &quot;</td>
</tr>
<tr>
<td>155-163°</td>
<td>200°</td>
<td>&quot;</td>
<td>35 &quot;</td>
</tr>
<tr>
<td>I.50-80°</td>
<td>160°</td>
<td>4 m.m.</td>
<td>5.5 grams.</td>
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<tr>
<td>II.105-110°</td>
<td>170°</td>
<td>2 m.m.</td>
<td>16.2 &quot;</td>
</tr>
<tr>
<td>III.110-130°</td>
<td>180-220°</td>
<td>3 m.m.</td>
<td>1.5 &quot;</td>
</tr>
<tr>
<td>IV.150-165°</td>
<td>270-300°</td>
<td>1 m/m.</td>
<td>1 &quot;</td>
</tr>
<tr>
<td>Residue (black solid)</td>
<td></td>
<td>3 &quot;</td>
<td></td>
</tr>
</tbody>
</table>

Fraction I had the odor of trimethylene bromide, and fraction IV partly solidified in the receiver. The only fraction which distilled practically constant was II, which probably corresponds to the fraction coming over at 183° under a pressure of 45-50 m.m. in the previous distillation.

IV. INVESTIGATION OF THE POLYMERS.

In order to find whether the fraction boiling constant at 183° was a polymer of the monomolecular trimethylene oxide, the Grignard synthesis was chosen to prove its atomic linking structure. If trimethylene oxide or its polymer is treated with propyl magnesium bromide according the Grignard reaction, and the product then hydrolyzed, hexyl alcohol should be obtained.

PREPARATION OF PROPYL MAGNESIUM BROMIDE.

To 1.6 grams of magnesium, freshly scraped, 32 c.c. of anhydrous ether was added. 8.5 grams of propyl bromide, and a small crystal of iodine which served to speed up the reaction, were added to the magnesium and the contents of the flask refluxed until no
more magnesium would go into solution. This required about an hour
and at the end of that time a few small pieces of magnesium still
remained undissolved.

ACTION OF PROPYL MAGNESIUM BROMIDE ON THE POLYMER
OF TRIMETHYLENE OXIDE.

To the propyl magnesium bromide in the flask, 4.4 grams
of the substance boiling at 183° under 50 m. m. was slowly added
through the top of the condenser. A reaction was apparent when the
liquid was dropped in, for the material in the flask boiled slightly.
When all the substance had been dropped in, it was refluxed for a
half hour, and then allowed to stand over night.

The ether was then distilled from the Grignard complex,
and when it had nearly all been driven over, about 500 c.c. water
added and the product steam distilled. This broke up the complex,
giving hexyl alcohol which came over dissolved in the water and was
salted out with potassium carbonate. A layer whose volume was
slightly over 1 c.c. came to the surface, and this was separated and
and dried with anhydrous sodium sulfate. When it was distilled ,
nearly the entire amount came over constant at 155-157°(uncorrected)
under 748 m.m. The boiling point of pure hexyl alcohol is 157-158°
under 760 m.m. The alcohol had a rather sweet odor, resembling that
of freshly cut wood. A hot copper spiral was dipped into a small
portion of the liquid, a drop of aqueous resorcinol added, and then
concentrated sulfuric acid added by carefully pouring it down the
side of the test tube so as to form two layers. A very definite
purple line appeared between the two layers, indicating the presence
of an alcohol.
Since the product obtained was thus evidently hexyl alcohol, the product started with must have been some polymer of trimethylene oxide. Since the process of making trimethylene oxide by the lead oxide method is so slow, however, and gives such small yields, it could scarcely be used as a feasible synthesis and was not further investigated.

THE PREPARATION OF TRIMETHYLENE OXIDE BY THE ACTION OF MERCURIC OXIDE ON TRIMETHYLENE BROMIDE.

The action of mercuric oxide upon trimethylene bromide was first carried out by just the same method as was used in the case of lead oxide. 30 grams of trimethylene bromide and 35 grams of mercuric oxide were put into the generating flask of the apparatus described under lead oxide. The mixture was heated to 175° for three hours but during this time no distillate had collected in the receiver. The mixture now suddenly began to froth and turn black, and quickly blew up the apparatus. It was thus apparent that this method would have to be modified before it could be used. Hence, instead of mixing the trimethylene bromide all at once with the mercuric oxide, it was dropped in from a dropping funnel through the top of the condenser. The rate of dropping was such that 100 grams were dropped in within two hours. The Wood's metal bath was kept at 200° for about six hours; during this time about 5 c.c. of distillate had been produced from the 100 grams of trimethylene bromide and 120 grams of mercuric oxide which were used. Continued heating during six hours produced no further amount of distillate.

The residue in the flask was extracted with ether and the extract filtered off from the solid residue. The filtrate came over
black, however, due to a black suspension which repeated filtration could not entirely remove. The ether also dissolves some of the mercuric bromide which is formed in the course of the reaction, and this is difficult to remove. Carbon tetrachloride, on the other hand, was found to dissolve very little of the mercuric bromide. Its use might be open to objection however since it may not extract the residue as completely as ether. These extracts were not characterized.

The combined distillates from a number of runs by the mercuric oxide method, which had a total weight of 17 grams, were distilled. The fractions taken were as follows:

I. 50-60° 5.5 grams.
II. 60-80° 3.2 "
III. 80-100° 1.6 "
IV. 100-160° 3.8 "

Each of the above fractions gave a strong Beilstein test for halogens. All of them had the very sharp, penetrating odor of unsaturation which the products of the lead oxide method had. The boiling point of the first fraction indicated that it might be allyl bromide, while the boiling points of the second and third would lead us to expect a mixture of allyl bromide and allyl alcohol.

To fraction I, keeping it cold, bromine was added and it acted very energetically. 2 c.c. of bromine were required to produce a permanent color. When this brominated product was heated on the water bath, nothing distilled over; but when the distilling flask was heated with a free flame, 1.3 grams of distillate came over from 50-100°; it still had a trace of the sharp penetrating
odor. Its volume was too small for further characterization. To the liquid which still remained in the distilling bulb, ten times its volume of water was added and shaken; about 1 c.c. of it dissolved in the water but none of it could be salted out again with potassium carbonate. The weight of the bromide layer was 3 grams; when it was dried and distilled the temperature rose steadily from 120° to 150°, and was thus undoubtedly a mixture of bromine addition products of several unsaturated compounds. On the assumption that Fraction II was mainly allyl alcohol, an attempt was made to prepare its 1-3-5-dinitro-benzoic acid derivative as recommended in Vol. I of Mullikin's "Identification of pure Organic Compounds". The melting point of the solid derivative was found to be 80°, whereas that of allyl alcohol was found to be 41-44°.

Portions of Fractions II and III were then treated with acetyl chloride, and both became slightly warm, indicating a chemical reaction. The products were then washed with water to remove excess acetyl chloride, extracted with ether, dried, and the ether finally evaporated off. Only a few drops of yellow liquid remained in each case, and each had an ester odor resembling that of ethyl acetate. The volumes of the esters were too small for boiling point determinations.

It is thus apparent that if the reaction of mercuric oxide on trimethylene bromide yields any trimethylene oxide at all, it is too small in amount and mixed with too many unsaturated impurities for profitable isolation and characterization.
THE ACTION OF MERCURIC OXIDE ON TRIMETHYLENE IODIDE.

In investigating the action of trimethylene iodide on mercuric oxide the apparatus described under the previous method was used. 7.2 grams of trimethylene iodide, whose preparation will be described later, was dropped on 5 grams of mercuric oxide heated to 200°. The mixture slowly turned black and iodine vapors were given off, but no distillate collected in the receiver. The method does not appear to be feasible, due to the ease of decomposition of the trimethylene iodide when heated.

THE ACTION OF MERCURIC OXIDE ON TRIMETHYLENE CHLORIDE.

The trimethylene chloride used in this experiment was obtained as a side product in the preparation of trimethylene chlorhydrin, which will be discussed later. The apparatus used was the same as that used for the mercuric oxide and trimethylene bromide. 95 grams of mercuric oxide were put into the flask and 50 grams trimethylene chloride dropped in, the temperature being maintained at 160-170°. The trimethylene chloride in the flask boiled vigorously, since its boiling point is about 125°, but at the end of three hours heating there had been no apparent reaction with the mercuric oxide and not a drop of distillate had come over. Judging from these results, any method of treating mercuric oxide with trimethylene chloride which permits the latter substance to boil and reflux cannot be feasible; the velocity of the reaction of the chloride with mercuric oxide is too slow.
THE ACTION OF SILVER OXIDE ON TRIMETHYLENE BROMIDE.

I. PREPARATION OF SILVER OXIDE.

The silver oxide used in this reaction was prepared as follows: the calculated amount of silver nitrate crystals were dissolved in about twice their weight of water, and then a slight excess of 1-1 potassium hydroxide solution added. This precipitated a brown substance, which was filtered with suction. The precipitate of silver oxide (or silver hydroxide) was then spread on a watch glass and dried by heating on a watch glass for two hours.

II. TREATMENT OF SILVER OXIDE WITH TRIMETHYLENE BROMIDE.

25 grams of the freshly prepared, dry silver oxide was mixed with 22 grams of trimethylene bromide and heated. The reaction mixture burst into flame and this method of mixing trimethylene bromide with silver oxide cannot be used for the preparation of trimethylene oxide.

THE ACTION OF SILVER OXIDE ON TRIMETHYLENE CHLORIDE.

Instead of mixing all the metallic oxide with the dihalogen compound at once, as was done above, the trimethylene chloride was dropped on to the silver oxide. 41 grams of silver oxide and 20 grams of trimethylene chloride were used. The first few drops were allowed to fall on the silver oxide without applying any heat. When the drops struck the silver oxide, it changed from its original brown color to a grayish white. No further change took place, even when more drops were allowed to fall on the silver oxide. Heat was then gradually applied to the flask with a Wood's metal bath until the temperature reached 80-100°. When about 2 c.c. of trimethylene
Chloride had been dropped in, the material in the flask suddenly became warm, white fumes were evolved, and some gases bubbled through the bromine water in the last U-tube receiver. The reaction quickly died down when the flask was removed from the Wood's metal bath, and the heating was then continued. The temperature was then maintained at 150° and the remainder of the trimethylene chloride dropped in, but refluxing for six hours produced no further change. About three drops of liquid collected in the first receiver, and this had the odor of the unsaturated compounds already mentioned. The residue in the flask was extracted with ether, which was evaporated off; the remaining liquid, which had the odor of trimethylene chloride, was distilled. The following fractions were thus obtained:

I. 60-125° 3 grams.
II. 125-143° 4 "
III. 143-175° 2 "
IV. 175-200° 1 "

While fraction I was coming over the temperature rose so steadily that the isolation of a pure product from the small amount of material at hand was out of the question. It had the odor of trimethylene chloride, as did the second and third fractions. These two intermediate fractions were mainly trimethylene chloride. The fourth fraction was too small in volume to work with.

The action of silver oxide on trimethylene iodide.

The trimethylene iodide used in this experiment was obtained by the action of heat upon the Grignard complex IMgO-CH₂CH₂CH₂-Cl, and the method of obtaining it will be described in detail later.
13 grams of trimethylene iodide and 100 grams of silver oxide were used. The apparatus was the same as that used for mercuric oxide, the iodide being dropped on to the silver oxide. No reaction took place in the cold, and the flask was then heated to 150-170°. White fumes came off at this temperature for a few minutes, and then the reaction died down again. The heating was continued four hours and at the end of that time only about three drops of distillate had collected in the receiver. This distillate had the sharp odor of unsaturation noted in the previous experiments. The flask was then again heated to 170-180°, which caused iodine vapors to be formed in the flask, but yielded no distillate.

The difficulties of using trimethylene halides with silver oxide are thus apparent. If the halide is mixed with the silver oxide and heated, the reaction becomes violent; if the chloride is dropped on to the silver oxide, it is too non-reactive to keep reacting after it has once stopped; and if the iodide is used, it decomposes if heated above 170°.
THE ACTION OF HEAT UPON THE SODIUM ALCOHOLATE OF

TRIMETHYLENE CHLORHYDRIN.
PREPARATION OF TRIMETHYLENE CHLORHYDRIN.

To 230 grams of trimethylene glycol in a two-liter flask 480 grams of sulfur chloride, $S_2Cl_2$, was carefully added. If the sulfur chloride is not added carefully, or if it becomes well mixed with the glycol at once, the reaction is liable to become violent. Sulfur is precipitated as soon as the sulfur chloride comes in contact with the glycol.

The flask was connected to a reflux condenser to the top of which a tube was attached which led to a hood or out of doors. Sulfur trioxide was evolved at first in large quantities, especially on shaking a little. It was found necessary to have a pan of cold water at hand in order to cool the flask if the reaction became violent. After the reaction had been allowed to proceed for about one or two hours, with occasional shaking, the reaction became slower, and the flask was heated with an electric heater capable of keeping the temperature at 100°. This heater was merely a large 100 watt carbon incandescent bulb which was attached to the bottom of a well insulated vessel.

The material in the flask was kept gently boiling until no more sulfur dioxide fumes were evolved. This required from six to ten hours continuous heating. By this time a layer of melted sulfur was on the bottom of the flask and the layer above it was of a clear dark amber color. The flask was allowed to cool, whereupon the sulfur solidified; the liquid layer was poured off and dissolved in one to two times its volume of ether. To neutralize the sulfur dioxide which remained in the liquid, a saturated solution of potassium carbonate was carefully added, care being taken to prevent too
violent frothing during the neutralization. When the liquid reacted alkaline towards litmus paper, it was separated from the water layer, washed once with a little water, and dried with anhydrous sodium sulfate.

After the ether had been distilled off on a water bath, the remainder was distilled. A small amount came over from 120-160°, and this upon fractionation gave a product boiling nearly constant at about 130°, which was trimethylene chloride. The remainder of the liquid nearly all came over at 160-165°, while a small amount of unchanged glycol remained in the flask. The boiling point of pure trimethylene chlorhydrin is given by Beilstein as 163°. The yields vary from 60 to 80%.

PREPARATION OF THE SODIUM ALCOHOLATE OF TRIMETHYLENE CHLORHYDRIN.

To prepare the sodium alcoholate of the chlorhydrin, 5 grams of sodium cut in small pieces was dropped into 25 grams of the chlorhydrin in a small flask. This was attached to a reflux condenser whose top was connected to two U-tubes set in a freezing mixture. The sodium acted quite slowly at first, but after five minutes shaking the reaction suddenly became violent, white fumes being evolved. The reaction mixture reached a temperature of 140°. Nothing was carried over into the U-tube receivers during the reaction, and when it had ceased, the flask was heated with a flame in order to break up the product to give trimethylene oxide. The water flowing through the condenser was turned off during this heating. A sweet odor somewhat resembling that of ether was noted at the exit tube and a gas was evolved which burned with a bluish flame.
This did not condense at all, and was probably impure hydrogen which was formed by the reaction of the sodium chlorhydrin which had not yet been entirely been used up.

The heating was continued until the water in the condenser had become hot and about 5 c.c. of distillate had come over. The lumps of sodium had become coated with a white layer and reacted with difficulty, hence 2 grams of finely cut sodium were added, and on heating the reaction again went violently. The heating was continued for another hour, water being kept trickling through the condenser. 4.2 grams of distillate had collected in the first receiver, and was distilled. The boiling point rose steadily from 50 to 150°. The distillate had the strong sharp odor of unsaturation, and was brominated. It reacted rapidly with bromine, and 1 to 2 c.c. of bromine was required to produce a permanent color. Ten volumes of water were then added and about two thirds of the material dissolved. The water layer was then separated, salted out with potassium carbonate, whereupon 2 to 3 c.c. of a slightly yellow, viscous liquid separated. This was dried and distilled. About 1 c.c. came over from 75 to 110°, but the volume was too small for further purification. The method thus seems to yield mainly unsaturated products and is not a feasible one for the preparation of trimethylene oxide.
ACTION OF HEAT UPON THE GRIGNARD COMPLEX Cl-CH₂CH₂CH₂-OMgI.
To prepare the complex Cl-CH₂CH₂CH₂OMgI, trimethylene chlorhydrin, magnesium, and ethyl iodide were used. The preparation of the chlorhydrin has already been described; the ethyl iodide was prepared by the action of phosphorous and iodine on ethyl alcohol.

PREPARATION OF ETHYL MAGNESIUM IODIDE.

To 7 grams of freshly scraped magnesium was added 49 grams of ethyl iodide and 100 c.c. anhydrous ether. The reaction started without the addition of iodine but a crystal of iodine was added to make the reaction faster. The reaction became so violent that it became necessary to cool with ice water. After the reaction had slowed up somewhat, it was found necessary to reflux and to add 5 to 7 grams more ethyl iodide to get the magnesium into solution. Even then a little magnesium remained undissolved.

PREPARATION OF Cl-CH₂CH₂CH₂OMgI.

28 grams of trimethylene chlorhydrin were now dissolved in 100 c.c. anhydrous ether in a flask surrounded by ice. A reflux condenser bearing a dropping funnel and an exit tube protected by calcium chloride was attached to the flask, and the ether solution of ethyl magnesium iodide added in a small stream, keeping the flask well shaken and cooling only when the flask became warm. The ethyl magnesium iodide must be kept away from the open air as much as possible, as it is exceedingly hygroscopic and a white precipitate of magnesium hydroxide comes down very quickly. The reaction took place quickly with a hissing sound, and the reaction products turned yellow. The addition of the entire amount required about twenty minutes.
DECOMPOSITION OF Cl-CH₂CH₂CH₂-MgI BY HEAT.

The ether was then distilled off; when most of it had been driven over, the contents of the flask began to froth, but shaking prevented this. When the ether in the flask had about ceased coming over, the residue was powdered with a glass rod. The flask was then heated with a Wood's metal bath and the following fractions were collected:

I. To 240° 10 c.c. (ether).
II. 240-260° 5 grams.
III. 260-290° 0.5 "
IV. 290-306° 0.2 "

At a higher temperature the contents of the flask began to fuse and vapors of iodine were given off.

Upon distilling Fraction II, the liquid began coming over at 47° and the temperature rose slowly to 53° where most of the product distilled. At 60° receivers were changed and from 60° to 80° 6 grams of product came over. Upon brominating Fraction I, there was little reaction, but when the product was extracted with water and salted out with potassium carbonate, only a very small amount separated out; and on attempting to distil any low boiling product from the water layer, none came over. 4 c.c. of product had been lost by the above treatment.

The residue left in the flask in which the reaction had been carried on was covered with water, and distilled with steam. 31 grams of a heavy layer came over with the water. Nothing could be salted out with potassium carbonate from the water layer. The
heavy layer was dried and fractioned as follows:

I. 120-205°  4.5 grams.
II. 205-220°  6 "
III. 220-230° 7.8 "

Each fraction was washed with sodium carbonate solution to remove iodine, and dried. None of the fractions were appreciably soluble in concentrated sulfuric acid, showing that they could not be trimethylene iodhydrin or any hydroxy compound. All three fractions gave strong flame tests for halogens with a copper wire. Upon re-fractionation, the following fractions were obtained:

I. 135-205°  2 grams.
II. 205-220°  3 "
III. 220-230° 7.2 "

Each fraction turned dark on distillation, and III evolved purple vapors of iodine. The last fraction was redistilled under 160-170 m.m. pressure and it distilled constant at 165 to 167°. The boiling points of trimethylene iodide as given by Beilstein are 227° under 760 m.m. with decomposition, and 170° under 170 m.m. The boiling points and the other tests made can leave no doubt that the substance is trimethylene iodide.

Another run was made using just double the quantities used in the experiment just described. The experiment was carried on just as before, except that instead of distilling the residue in the flask with steam, it was extracted with ether. This gave 29.5 grams of a heavy red liquid, which upon fractionation yielded:
I. 80-100 0.8 grams.  
II. 100-215 0.6 "   
III. 215-220 11.4 "   
IV. 220-230 14.2 "   

The last three fractions distilled with decomposition, giving iodine vapors during the distillation. When the last two fractions were purified with sodium carbonate and dried, they were distilled as before and again found to be trimethylene iodide.

To the residue from which the above ether extract had been obtained, water was added. This water extract gave an alkaline reaction due to magnesium hydroxide. When potassium carbonate was added a white gelatinous precipitate came down which did not settle even after standing for a few days.

A third run was made in the same manner as the two already described, using 14 grams of magnesium ribbon and 100 grams ethyl iodide dissolved in 200 c.c. anhydrous ether. 15 grams more ethyl iodide was added to dissolve the magnesium which had not gone into solution, but even so a little remained undissolved. This compound was then added to 58 grams trimethylene chlorhydrin dissolved in 100 c.c. ether, the addition requiring about twenty minutes. The ether was then distilled off as well as possible on a water bath, the pasty mass in the flask pushed down and compacted, and the flask heated with an electric heater.

CONSTRUCTION OF ELECTRIC HEATER.

A tin can six inches in diameter and ten inches high was wrapped once with wet asbestos paper. When the paper was dry, two heavy copper wires were wrapped around the two ends; these served
as terminals. One end of a ten foot length of #30 nichrome wire was attached to one of these terminals, and the wire was then spirally wrapped around the can and the other end attached to the second terminal. Another layer of asbestos paper was then put on in the same manner as the first, another ten foot length of nichrome wire wrapped around spirally and attached to the same two terminals as the first coil. A third layer of asbestos paper was wrapped around this and finally the entire thing put into a cylinder of asbestos steam pipe covering which thus gave an insulation material more than an inch in thickness. The outer covering was allowed to extend an inch below the bottom of the can, which was covered with several thicknesses of asbestos board. A final covering of sheet aluminum was then put around the heater. The coils may thus be used either singly or together; if both are used, they are connected in parallel. The ordinary 110 volt A.C. lighting current is used.

HEATING OF THE COMPLEX Cl-CH₂CH₂CH₂-OMgI.

Only one coil was used in the heating of the flask; the temperature of the air just below the flask was constant at 271°. The solid material in the flask soon began to fuse and a colorless distillate came over at first, but the later distillate was colored yellow. Receivers were changed when 14.8 grams of distillate had been obtained. Purple iodine vapors were formed in the flask, especially after it had been heated for half an hour. The distillate came over quite rapidly at the end of an hour's heating; the color gradually changed from brown to almost black. Fumes with an irritating odor like that of hydrochloric acid came over and could not
be condensed at \(-5^\circ\). At the end of four hours heating, nothing more came over. The second fraction, which was a black, heavy liquid, weighed 53 grams. Nothing could be extracted with ether from the dry residue in the flask. The first distillate, weighing 14.6 grams, was fractioned as follows:

I. \(35-45^\circ\) 3 grams.
II. \(45-60^\circ\) 4 "
III. \(60-96^\circ\) 2.3 "
IV. \(96-105^\circ\) 3 "

Decomposition took place during the distillation of the last fraction as was indicated by the vapors of iodine evolved and the brown color of the distillate.

The boiling point and odor of fraction I showed it to be ether. The second fraction was brominated but there was no apparent reaction. Solid potassium carbonate and 1 c.c. water were added to remove the excess bromine, whereupon the liquid separated into two layers; this was then distilled, without separation, on a steam bath and yielded 1 to 2 c.c. of slightly yellow liquid which on redistillation came over at \(35-40^\circ\); hence fraction II was mainly ether. About 1 c.c. bromine was taken up by fraction III. None of this product was soluble in water. The excess bromine was then removed with sodium carbonate solution; the residue was dried and distilled. The temperature rose steadily from \(135^\circ\) to \(200^\circ\) and the distillate partly solidified on standing. Fraction III was thus evidently a mixture of unsaturated compounds which on bromination gave a mixture of bromine derivatives which are difficult to identify.
The 53 grams of distillate gave the following fractions on redistillation:

I. 50-100° 16 grams.  
II. 100-125° 10.6 "  
III. 125-150° 3 "  
IV. 150-200° 2.5 "  
V. 200-210° 9.2 "  

The last fractions decomposed during the distillation and gave solid iodine. Iodine vapors were formed copiously while the last three fractions were coming over. Upon refractionation of the above products, the following fractions were obtained:

I. 75-85° 0.5 grams.  
II. 85-90° 3.5 "  
III. 90-95° 5.0 "  
IV. 120-130° 1.3 "  
V. 175-190° 1.3 "  
VI. 190-212° 2.8 "  

Fractions II and III contained iodine, but no chlorine. They were united and distilled. The product began coming over at 70°, and the temperature steadily rose to 90°. About half of the material came over during this interval and the remainder decomposed at 90°, as shown by the copious vapors of iodine given off. When heated further it merely decomposed and iodine sublimed into the condenser. There thus seems to be a little ethyl iodide in the fractions, together with a higher boiling material which decomposes at about 100°.
CONCLUSIONS.

1. The action of lead oxide on trimethylene bromide yields only inappreciable amounts of monomolecular trimethylene oxide, but gives some polymeric form of the oxide. The main products of the reaction are unsaturated compounds.

2. The action of mercuric oxide on trimethylene bromide gives larger quantities of unsaturated compounds than when lead oxide is used, but in this case the polymeric form is more difficult to purify.

3. The reaction of mercuric oxide on trimethylene chloride is too slow to be feasible, and when trimethylene iodide is used it decomposes, giving free iodine.

4. Silver oxide reacts too violently with trimethylene halides when mixed with them all at once, and too slowly when the halides are dropped on the silver oxide, to be feasible.

5. When the sodium alcoholate of trimethylene chlorhydrin is heated it gives only unsaturated products in appreciable amounts.

6. When the Grignard complex Cl-CH₂CH₂-OMgI is heated, it yields no appreciable amounts of trimethylene oxide, but gives good yields of trimethylene iodide.

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10. Comptes rendus 85, 624 (1877).
15. Receuil 9, 102 (1890).
17. Monatshefte der Chemie 27, 414 (1906).