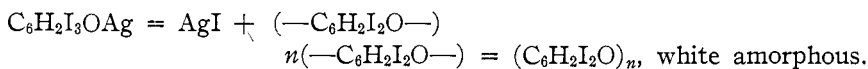


ences without atomic rearrangement, after polymerization of the benzenoid form.

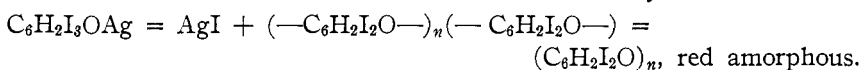
Summary.

The silver salt of triiodophenol has been prepared in a very pure state, but the colorless form described by Hantzsch has not been obtained, all the samples found being yellow.

This salt, when warmed, gives with ethyl iodide a reaction exactly like that shown by the silver salt of tribromophenol, yielding silver iodide and an unsaturated residue which polymerizes to a white oxide.



The salt, when treated with a very little iodine in water, gives instead of the white oxide, the red substance first described by Lautemann.



MINNEAPOLIS, MINN.

[CONTRIBUTION FROM THE LABORATORIES OF ORGANIC CHEMISTRY, UNIVERSITY OF ILLINOIS.]

STUDIES OF TRIMETHYLENE OXIDE.

I. PREPARATION AND CHARACTERIZATION.

BY C. G. DERICK AND D. W. BISSELL.¹

Received September 9, 1916.

I. Introduction. II. Preparation and Purification of Trimethylene Oxide. III. Properties of Trimethylene Oxide. IV. Proof of the Atomic Linking Structure. V. Experimental Part.

I. Introduction.

The use of ethylene oxide and its homologs in organic synthesis has been well established in the field of amino alcohols, and more recently their value in the Grignard reaction has been demonstrated by the work of Grignard,² Blaise,³ and Henry.⁴ In the study of the scale of influence of substitution, by the senior author and his students,⁵ it is necessary to synthesize substituted monobasic paraffin acids, in which the substituents are further removed from the carboxyl group than the delta position. It seemed probable that trimethylene oxide would be of great value in effecting these syntheses. With this in mind the only reported synthesis of this substance was studied.

¹ Presented at the Urbana meeting of the American Chemical Society, 1916. From a thesis, submitted in partial fulfilment of the requirements for the degree of Master of Science at the University of Illinois.

² *Compt. rend.*, **136**, 1260 (1903); **141**, 44 (1905); *Ann. chim.*, [8] **10**, 23 (1907).

³ *Compt. rend.*, **134**, 552 (1902).

⁴ *Chem. Zentr.*, II, 445 (1907).

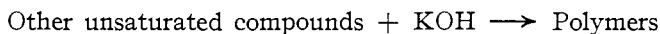
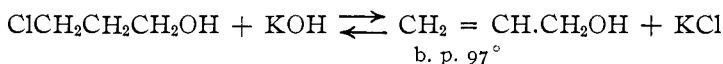
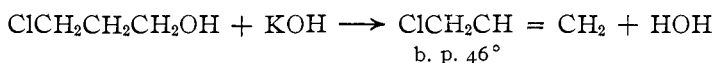
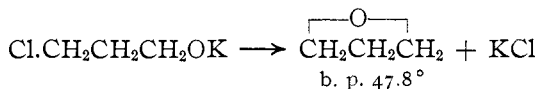
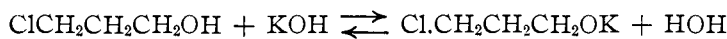
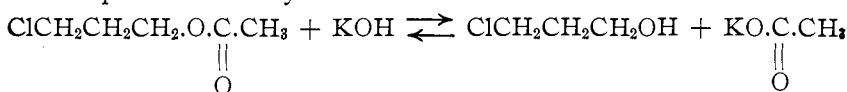
⁵ THIS JOURNAL, **33**, 1167 (1911); **38**, 400 (1916).

The synthesis of trimethylene oxide by the action of a very concentrated solution of potassium hydroxide upon trimethylene chlorohydrin reported by Reboul¹ was repeated. The yield was very poor and the product very impure, as Section II will show. At best a yield of only 5% of the pure product could be obtained, even after many repetitions. These experiments suggest that Reboul never obtained the pure substance and accordingly the following study was undertaken.

II. Preparation and Purification of Trimethylene Oxide.

Trimethylene oxide is best prepared by the action of potassium hydroxide containing 8% water upon gamma chloropropyl acetate at 100–110°. The desired products are condensed in a freezing mixture of hydrochloric acid and ice.

In order to purify the oxide it is necessary to know the different collisions of molecules that result in chemical reaction under the conditions of the experiment. They are as follows:



The physical properties of the substances resulting from the reactions show that this method of preparation gives trimethylene oxide contaminated with allyl alcohol, allyl chloride and water, but not with the higher boiling polymers.

To remove the unsaturated compounds, the distillate was carefully treated with liquid bromine until the reddish brown color was permanent. A subsequent distillation from the water bath removed the high boiling brominated compound. After drying the distillate over anhydrous sodium sulfate and redistilling the pure product was obtained. The yield of the pure product boiling from 48–50° (uncorr. at 750 mm.) was 22.5% of the theoretical amount calculated from gamma chloropropyl acetate.

¹ *Ann. chim.*, [5] 14, 496 (1878).

III. Properties of Trimethylene Oxide.

Since the properties of trimethylene oxide found by the authors differ decidedly from those reported by Reboul, a tabular comparison is given below:

| Physical property. | Authors. | Reboul. |
|---|----------------------------------|---------------------|
| Boiling point..... | 47.8° (corr. 760 mm.) | About 50° |
| Density..... | 0.8930 | |
| Molecular weight..... | 57.9 | |
| Index of refraction (N _D ²⁵ by Abbé)..... | 1.3897 ± 0.0008 | |
| Color..... | Colorless | Colorless |
| Odor..... | Pleasant—aromatic | Penetrating |
| Solubility in water..... | Completely miscible | Completely miscible |
| Chemical property. | | |
| Action of bromine..... | None, except after long standing | Vigorous |

Since Reboul did not obtain enough of his product to study it further, a few of the chemical properties of trimethylene oxide were compared to those of ethylene oxide. This latter oxide has been thoroughly studied by Wurtz,¹ Grignard,² and others. The following table will show the relation of the chemical properties of the two homologs:

| Chemical property. | Trimethylene oxide (Authors). | Ethylene oxide. |
|--|---|--------------------------------------|
| Action of bromine..... | Very slow | Forms red crystalline compound |
| Action of PCl ₅ | Vigorous—forms trimethylene chloride | Vigorous—forms ethylene chloride |
| Action of Grignard reagent | Reacts to synthesize higher alcohols | Reacts to synthesize higher alcohols |
| Action of FeCl ₃ solution.. | Gives brown ppt. | Gives red-brown ppt. |
| Action of acetyl chloride.. | Vigorous—forms gamma chloropropyl acetate | |

The physical properties given above demonstrate that a pure monomolecular form of trimethylene oxide was obtained by the authors, but not by Reboul. The chemical properties show that it is an oxide, and further that the impurities in Reboul's product were the unsaturated compounds discussed in Section II. These products were removed by the authors when the crude distillate was treated with bromine. With this definitely established, the excellent analysis of such a volatile product, reported by Reboul, must be attributed to a happy compensation of errors, since one of the main impurities is allyl alcohol, an *isomer* of trimethylene oxide, and the other is allyl chloride. Allyl chloride boils at 47° while the oxide boils at 47.8°, so it is obvious that Reboul could not have freed his product from the chloride by simple distillation, his method of purification. Moreover, the product obtained by the authors,

¹ *Ann. chim.*, [3] 55, 427 (1859).

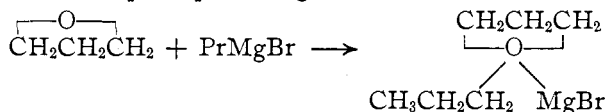
² *Compt. rend.*, 126, 1260 (1903).

after carefully repeating Reboul's experiment, always possessed three evidences of impurities, namely: reactivity toward liquid bromine, test for chlorine, and a sharp, unpleasant odor.

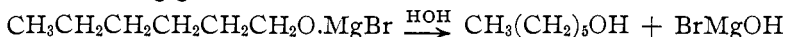
IV. Proof of the Atomic Linking Structure.

Trimethylene oxide was treated with phosphorus pentachloride, when a vigorous reaction took place forming trimethylene chloride. The latter was identified by its boiling point, insolubility in cold, concentrated sulfuric acid, and qualitative elementary analysis.

Like ethylene oxide, trimethylene oxide when treated with a magnesium alkyl halide reacts to cleave the ring, giving straight chain compounds. This reaction offers further proof of the structure of trimethylene oxide for, when the oxide is treated with magnesium propyl bromide in ether solution, a reaction takes place producing hexanol-1 as follows:



which on heating gives



The product hexanol-1 was identified by its boiling point, that of its acetate, and the characteristic odor of hexanol-1.

V. Experimental Part.

Preparation of Trimethylene Chlorohydrin by the Chlorohydrin Method.

Preparation of the Chlorohydrin by the Action of Hydrogen Chloride upon Trimethylene Glycol.—Dry hydrogen chloride was prepared by dropping concentrated sulfuric acid upon 37% hydrochloric acid, and drying the evolved gas by passing it through concentrated sulfuric acid. The gas was passed into trimethylene *chlorohydrin* which was kept at a temperature of 100°. At the end of three hours, the product was distilled, the fraction boiling between 150° and 175° containing the chlorohydrin. This was redistilled, and from 130 g. of glycol, 25 g. of trimethylene chlorohydrin boiling at 160–164° were obtained. A large amount of the glycol was recovered unchanged. This method was used by Reboul.

Action of Sulfur Chloride on Trimethylene Glycol.—Carius¹ prepared the chlorohydrin of ethylene glycol by the action of sulfur chloride on glycol. The procedure in preparing trimethylene chlorohydrin by this method was as follows:

In a liter flask was placed 250 g. of trimethylene glycol and 450 g. of sulfur chloride. After the mixture had been thoroughly shaken it became warm and there was a lively evolution of sulfur dioxide, while sulfur was precipitated. Without heating, but with occasional shaking, the

¹ *Ann.*, 124, 257 (1862).

lively reaction continued for an hour. When the spontaneous action had ceased, the mixture was heated on the water bath for six hours, using a reflux condenser, and was finally heated for half an hour over the free flame. By this time sulfur dioxide had ceased to be evolved. The cessation of the evolution of sulfur dioxide is adopted as a criterion of the completion of the reaction. The contents of the flask were then cooled and ether added. After removing the ether solution the crystallized sulfur was washed with ether, and the ether extracts combined, and shaken with a saturated solution of sodium carbonate to remove sulfur dioxide. The two liquid layers were then separated and the ether layer dried over anhydrous sodium sulfate. After distilling off the ether, the crude trimethylene chlorohydrin was distilled. The portion boiling $140-180^{\circ}$ was redistilled and a yield of 160 g. of trimethylene chlorohydrin boiling at $160-164^{\circ}$ was obtained, this being about 60% of theory. The chlorohydrin is a colorless oil, slightly soluble in water, and has an agreeable odor.

Preparation of Trimethylene Oxide by the Action of Potassium Hydroxide upon Trimethylene Chlorohydrin.

The method of Reboul¹ was followed rather closely. A 500 cc. flask was fitted with a dropping funnel, and a thermometer so arranged that the bulb of the thermometer was in the reacting mixture. The side neck was connected with the two U-tubes in series, both immersed in a freezing mixture of hydrochloric acid and ice. In the flask were placed 100 g. of potassium hydroxide and 10 g. of water. The temperature of the mixture was brought to 130° where it was maintained throughout the experiment. 50 g. of trimethylene chlorohydrin were added drop by drop through the dropping funnel over a period of 45 minutes. As each drop of the chlorohydrin struck the hot potassium hydroxide, a lively action resulted, and a vapor was evolved which condensed mainly in the first receiver.

Purification of Trimethylene Oxide.—After all the chlorohydrin had been added the generating flask was allowed to cool and water was added to dissolve the potassium hydroxide and potassium chloride. The residue was then extracted with ether and the ether extract worked up for high boiling products. The treatment of this residue will be discussed later.

The product which condensed in the receivers was a colorless mobile liquid, soluble in water and having a sharp odor. It was observed that the substance at this stage is very reactive toward liquid bromine. Bromine was added drop by drop to the ice-cold distillate until a permanent bromine color remained. At first the bromine acted instantly and violently, the solution being immediately decolorized. When the permanent

¹ *Ann.*, [5] 14, 496 (1878).

color had been obtained, water was added until the water layer was four times greater in volume than the oily layer. The two layers were then thoroughly mixed by shaking, and the heavy bromide allowed to separate out. This was drawn off and the aqueous layer saturated with potassium carbonate. The solution separated into two layers, the lighter containing the trimethylene oxide. The potassium carbonate solution was drawn off and the crude oxide dried over anhydrous sodium sulfate, and distilled from the water bath. The distillate was redistilled and gave 2 g. of pure trimethylene oxide boiling at 48-49° (uncorr.). It was noticed that the sharp, unpleasant odor of the crude distillate had entirely vanished, and that the odor was now sweet and aromatic.

Several modifications of this method of preparing trimethylene oxide have been tried. An experiment was run in which the temperature of the flask was kept at 160-180°, and the result was a preponderance of unsaturated products and very little trimethylene oxide. The next modification was to use a more dilute solution of potassium hydroxide. Instead of 10 cc. of water to 100 g. of potassium hydroxide, 20 cc. were used. The yield of distillate was very much lessened in this case. Another experiment was run using alcohol as a solvent. Again it was found that mainly unsaturated products were formed. Moreover a considerable quantity of ethyl alcohol distilled over with the low boiling products and the complete separation of the oxide was extremely difficult.

While the chlorohydrin method gave some trimethylene oxide, the quantity was so small that the process could hardly be called a feasible one. In all, seven runs were made, and the average yield was only 5-6% of theory.

Preparation of Trimethylene Oxide by the Action of Gamma Chloropropyl Acetate upon Potassium Hydroxide.

Preparation of Gamma Chloropropyl Acetate.—A flask having a capacity of 1500 cc. was connected with an upright condenser fitted at the top with a dropping funnel and an outlet tube leading into an absorption apparatus filled with water. In the generating flask was placed 300 g. of trimethylene chlorohydrin. Through the dropping funnel was added slowly 250 g. of acetyl chloride. The hydrogen chloride liberated was absorbed in the absorption train. After all the acetyl chloride had been added the contents of the flask were boiled gently until there was no further evolution of hydrogen chloride. The crude ester was then redistilled, yielding 375 g. of gamma chloropropyl acetate boiling at 160-166°.

Preparation of Trimethylene Oxide.—The same apparatus in which the oxide was made by the chlorohydrin method was used in this experiment. 150 g. of solid potassium hydroxide were placed in the 500 cc. generating flask. To this was added 12 cc. of water and the temperature

brought to 100°, the bulb of the thermometer being immersed in the potassium hydroxide mixture. Through the dropping funnel was then added slowly, 75 g. of gamma chloropropyl acetate. A lively reaction took place at once, and no further heating was necessary throughout the experiment. The heat evolved by the reaction kept the temperature of the mixture at 100–110°. Continued shaking was necessary throughout the experiment to maintain a thorough mixture of the reacting substances. In an hour all the ester had been added, and the mixture was then heated for ten minutes at 120°. At this time a marked *odor of the unsaturated compounds*, referred to above, was noticed, and the heating was discontinued. The experiment was duplicated and the products of the two reactions combined. The total weight of the crude distillate from 150 g. of ester was 29 g. It was noticeable that this distillate did not possess nearly so strongly the sharp odor of allyl compounds as did the crude product obtained by the chlorohydrin method, although this odor could still be detected. The whole was placed in a small flask kept cold by immersion in a freezing mixture. Bromine was then added slowly, a much smaller quantity being required to produce the permanent color than in any of the previous experiments. When no more bromine was acted on in the cold, the product was distilled from the water bath and the distillate condensed in a receiver immersed in a freezing mixture. The distillate was colored slightly yellow from the excess bromine. Anhydrous sodium sulfate was added and the products was allowed to stand for 24 hours in a glass-stoppered bottle. At the end of that time the color had disappeared. The crude trimethylene oxide was distilled, giving 14 g. of pure trimethylene oxide boiling at 48–50° (uncorr.). This is 22.5% of the amount predicted by theory.

Study of the Chemical Properties of Trimethylene Oxide.

Synthesis of Hexanol-1.—Magnesium propyl bromide was prepared by the action of 4.3 g. of magnesium ribbon upon 24 g. of propyl bromide in absolute ether. To this was added 10 g. of trimethylene oxide in 25 cc. of absolute ether. This was added slowly, to prevent too rapid reaction. When all had been added, the mixture was refluxed for an hour, using an upright condenser. The water was then drawn from the condenser and the ether evaporated. As the last traces of ether were evaporated the mass became porous and metallic looking. Suddenly a violent reaction took place, evolving a good deal of heat and leaving the residue somewhat charred and in the form of a hard cake. Water was then added to the cooled mixture, causing a slight heating. When the product was distilled with steam, about 2 cc. of an oil were obtained which had an odor much like that of hexanol-1. The volume was not great enough, however, to permit of purification by redistillation.

In order to determine a means of preventing this violent decomposi-

tion, a modification of this method was tried. Half the above quantities were used and the magnesium propyl bromide was prepared in the same manner as before. To the ether solution was added 5 g. of trimethylene oxide in 10 cc. of ether, and the mixture refluxed as before. Instead of distilling off the ether at this point, 100 cc. of dry benzene were added to the mixture, and the ether evaporated from this leaving the benzene as the solvent for the reacting substances. While the ether was being evaporated a thermometer was suspended in the upright condenser. When the temperature of the distilling vapors had reached 70° , the mixture was refluxed under the water cooler for four hours. The complex which had been precipitated as a gray solid, on the addition of the trimethylene oxide, became pasty under this treatment. No change of color, however, was noticeable. The mixture was now cooled and water added, without visible evidence of heat effect. As the gray mass went into solution a white precipitate formed at the bottom of the flask, and the liquid portion separated into two layers. The precipitate was dissolved in 30% sulfuric acid and the mixture distilled with steam. The distillate collected in two layers, and after separation, the oil was dried over anhydrous sodium sulfate and redistilled. After the benzene had passed over, 5 cc. of a liquid distilling constant at 155° were obtained. This was identified as hexanol-1.

Action of Phosphorus Pentachloride.—When trimethylene oxide was treated with phosphorus pentachloride, a violent reaction took place and an oil insoluble in water and in cold concentrated sulfuric acid was formed. The liquid was identical in its properties with trimethylene chloride.

Action of Acetyl Chloride.—Acetyl chloride reacts violently with trimethylene oxide to form gamma chloropropyl acetate.

Physical Properties of Trimethylene Oxide.

Determination of the Boiling Point.—The boiling point of trimethylene oxide was determined by the equilibrium method. The following table shows the readings of the thermometer, together with those readings corrected for emergent stem, for calibration and for variation of the atmospheric pressure from 760 mm.:

| | | | | |
|-------------------|-------|-------|-------|-------|
| Readings..... | 47.35 | 47.45 | 47.40 | 47.50 |
| B. p. 760 mm..... | 47.77 | 47.87 | 47.82 | 47.92 |

Determination of the Specific Gravity.—The specific gravity of trimethylene oxide was determined in an ordinary specific gravity bottle. The determinations were made at 25° . Densities are compared to water at 4° .

| Wt. bulb with oxide, g. | Wt. bulb empty, g. | Volume of bulb, cc. | Wt. of oxide, g. | Sp. gr. of oxide. |
|-------------------------|--------------------|---------------------|------------------|-------------------|
| 10.6760 | 6.0086 | 5.2272 | 4.6674 | 0.8930 |
| 10.6770 | 6.0086 | 5.2272 | 4.6684 | 0.8931 |

Determination of the Index of Refraction.—The index of refraction of trimethylene oxide was determined by the Abbé refractometer using ordinary (white) light. The following readings were taken:

n_{24}° . . . 1.3900, 1.3895, 1.3899, 1.3899, 1.3897, 1.3892, 1.3901, 1.3895, 1.3898, 1.3899.

Determination of the Molecular Weight.—The molecular weight of trimethylene oxide was determined by the method of Victor Meyer. Three determinations were made with the following results: 61.5; 56.8; 55.5. The calculated molecular weight is 58.

Residues from the Preparation of Trimethylene Oxide (Chlorohydrin Method).—After the trimethylene oxide had been driven from the generating flask, the residues were cooled and the water solutions extracted with ether. The ether solution was dried over anhydrous sodium sulfate, and the ether distilled over. The residue was subjected to fractional distillation. A considerable quantity of the liquid distilled over below 100° . This portion was treated with bromine and found to add that substance quantitatively. From 100 to 150° little distilled over, but from 150 to 190° there was an increased quantity of distillate. It was this portion that Reboul considered to be the unchanged chlorohydrin. But it was found that this fraction also reacted vigorously and completely with bromine to form heavy oils, while the chlorohydrin under similar conditions will not react at all. From 200° under ordinary pressure to 270° under 30 mm. several fractions were obtained, all of which formed heavy bromides with bromine. The latter fractions were viscous oils which seemed to have minute crystals in the liquid. However, they did not crystallize further on standing for three months.

URBANA, ILL.

[CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF CORNELL UNIVERSITY.]

THE NITRATION PRODUCTS OF PHENOLTETRACHLOROPHTHALEIN AND SOME OF THEIR DERIVATIVES.

BY W. R. ORNDORFF AND J. J. KENNEDY.

Received September 8, 1916.

The investigation of the nitration products of phenoltetrachlorophthalein and their derivatives was undertaken to study the effect of introducing negative groups into the phthalein molecule.

The phenol used in this investigation was a pure crystallized product. This was distilled, the first fraction being rejected, and only that distilling between 180° and 181° was used. This product was perfectly colorless and melted sharply at 42° . Commercial tetrachlorophthalic acid was purified by the method described by Delbridge.¹ The purity of the acid

¹ *Am. Chem. J.*, 41, 414 (1909).