7. L. B. Richardson, "General Chemistry" (1927), 730.

8. J. Kendall, "Smith's College Chemistry" (1923), 665.

9. Bourgoin, quoted by J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," IV (1923), 911.

10. F. P. Treadwell and W. T. Hall, "Analytical Chemistry," 5th Edition, I (1920), 210.

11. A. R. L. Dohme, JOUR. A. PH. A., 9 (1920), 312.

12. Joseph Rosin, *Ibid.*, 6 (1917), 951.

13. W. H. Schulze, *Ibid.*, 15 (1926), 464.

14. W. H. Schulze, *Ibid.*, 15 (1926), 965.

15. E. Goodman, PROC. A. PH. A., 37 (1889), 100.

16. Wm. Procter, Jr., *Amer. J. Pharm.*, 19 (1847), 93.

17. "British Pharmaceutical Codex," (1923), 157.

18. L. A. Brown, *Ky. Ag. Exp. Sta. Bull.*, No. 150, p. 154; through JOUR. A. PH. A., 14 (1925), 509.

19. H. V. Arny, "Principles of Pharmacy," 3rd Edition (1926), 516.

20. E. Warburg and W. Rump, *Z. Physik*, 47 (1928), 305–322; through *Chem. Abstr.*, 22 (1928), 1912.

21. Guyot, *Bull. soc. pharm. Bordeaux*, 63 (1925), 214–216; through *Chem. Abstr.*, 20 (1926), 965.

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### ABSTRACT OF DISCUSSION.

E. Fullerton Cook inquired if it is desirable to widen the range of possible deterioration, because of deterioration of the product.

W. J. Husa replied that this would hardly seem feasible since the solution commonly shows 30 to 50 per cent deterioration. So many methods of increasing the stability have been found that it is difficult to select the best one. Further work is in progress in which ten solutions stabilized in different ways have been stored under drug store conditions and are being analyzed every three months. He concluded by saying that unless the formula is changed the solution should be freshly prepared.

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# THE PREPARATION OF CYCLOPROPANE.*

## BY W. A. LOTT AND W. G. CHRISTIANSEN.

Trimethylene (cyclopropane) is the simplest cyclic hydrocarbon; its preparation in the pure state and in large quantities has been studied by a number of investigators whose various results are not entirely in agreement. We found none of the recorded methods entirely satisfactory.

All of the practical methods are based on the reduction of[1] trimethylene dibromide with metallic zinc in an alcoholic solution.

$$BrH_2C \overset{CH_2}{\diagup} \diagdown CH_2Br + Zn \rightleftharpoons H_2C \overset{CH_2}{\diagup} \diagdown CH_2$$
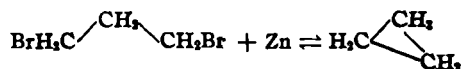
Freund, (*J. prakt. Chem.* (2), 26 (1886), 368) reduced trimethylene dibromide with sodium, in alcoholic solution. His product was not entirely pure, but he mentioned only propylene, its more stable isomer, as an impurity.

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* Scientific Section, Rapid City meeting, 1929.

[1] Made according to method outlined in Organic Syntheses, Vol. I, R. Adams.

A little later, Gustavson (*J. prakt. Chem.* (2), 36, 300) described the preparation of this hydrocarbon from trimethylene dibromide using zinc dust as the reducing agent and 75% ethyl alcohol as the solvent. He obtained a rapid evolution of the gas at 50–60° C. and pointed out that the analogous reduction of propylene dibromide to form propylene is even more rapid. The use of absolute alcohol decreases the rate of delivery of the gas. The trimethylene obtained by this method contained only small quantities of propylene and hydrogen.

Wolkoff and Menschutken (*Centralblatt* (1900), II, 43) repeated the work of Gustavson but claimed to have obtained about 25% of the isomer, propylene, and some propane and hydrogen as impurities. They also disclaimed the practicability of Freund's method. These authors later again discussed Gustavson's work (*Berichte*, 31 (1898), 3067); they prepared pure trimethylene by passing the gas (evolved by the reduction of the bromide) through bromine water which removes propylene as the dibromide but does not affect trimethylene.

Gustavson (*J. prakt. Chem.*, 59 (1899), 302) rediscussed his earlier work and offered certain improvements. He explained Wolkoff and Menschutken's failure to obtain trimethylene free from propylene as lying in the incomplete removal of propylene dibromide from the trimethylene dibromide and disclosed some later results in which he was able to obtain trimethylene free from propylene by discarding the gas evolved at the beginning of the reaction; pointing out that propylene dibromide is reduced so much more readily than is trimethylene dibromide that it will react completely before the trimethylene dibromide is materially attacked.

Fornoe (*Berichte*, 21, 1283) repeated the before-mentioned Gustavson's experiment and confirmed his result. Haehn (*Arch. Pharm.*, 245, 518) used amyl alcohol instead of ethyl alcohol with somewhat poorer results. Willstäter and Bruce (*Berichte*, 40 (1907), 4456) also repeated Gustavson's work and confirm that pure trimethylene *can* be prepared by his method provided the precautions outlined in his later work are adhered to.

Trautz and Winkler (*J. prakt. Chem.*, 104 (1922), 37) in a review of the subject throw doubt upon the purity of the trimethylene prepared by the earlier methods and describe a method for the preparation of the gas in large quantities. They use amyl alcohol for the solvent and zinc wool for the reducing agent. They advise a rather higher temperature 130° C., which is probably necessitated by the less finely dispersed form of zinc. They obtained a very pure product by a very burdensome fractional distillation which requires a very complicated apparatus.

A number of trials, in this laboratory, with the method of evolution used by Trautz and Winkler gave small yields of gas which were about 95% absorbed by fuming sulphuric acid; in each run additional portions of gas were obtained which were contaminated by saturated hydrocarbons and hydrogen. In one experiment in which smooth delivery of gas was obtained at 110° C., two carboys of about 40 liters each, obtained from 1600 Gm. of trimethylene bromide, were 69% and 29% absorbable by fuming sulphuric acid. The remainder of the gas was largely saturated hydrocarbon and hydrogen.

In one attempt with Gustavson's method smooth evolution of gas began at 48° C., but the temperature had to be progressively increased to the boiling point of the alcohol. The product was 95.5% absorbed by fuming $H_2SO_4$; but only a

very small quantity was collected before evolution stopped, due to the settling and caking of the zinc dust. The substitution of zinc shavings reduced the quality of the product.

It was evident, therefore, that the reaction used by Trautz and Winkler gave a product which was unsatisfactory unless the separation of large quantities of lower boiling hydrocarbons by the very inconvenient fractional distillation at low temperature was performed; the boiling point of trimethylene being —34° C. Also, the method of Gustavson was not useful without considerable modification for the preparation of fairly large quantities of material.

The following apparatus was used with what was otherwise essentially Gustavson's method, and very satisfactory results were obtained.

The trimethylene bromide was fed into the reaction flask at uniform speed by nitrogen pressure from the reservoir. This allows the boiling temperature of the solvent to be used uniformly throughout the reaction, without violent evolution at
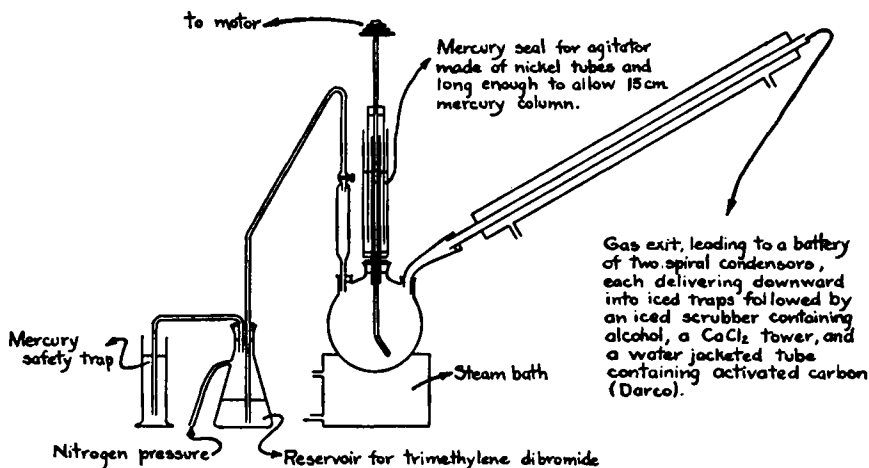


Fig. 1.

any time. At this temperature the reduction of the bromide to trimethylene is so rapid that side reactions are precluded. Rapid agitation prevents caking of the zinc dust and allows the exposure of fresh zinc surface to the bromide at all times and thereby deters side reaction and prevents the premature cessation of the desired reaction.

A series of spiral condensers and iced traps serve to retain the larger portions of the trimethylene dibromide, which in spite of its high boiling point is very volatile even at ordinary temperature. The last traces of these vapors are removed by a water-cooled column of granular activated carbon (Darco). The gas is dried by a $CaCl_2$ tower previous to exposure to this absorbent. Now the product may be collected as a gas or liquified in a copper coil surrounded by solid $CO_2$.

The agitator must be protected by a mercury seal in which the mercury column is about 15 cm. high, in order to prevent the leakage of gas when the reaction is well under way.

Three thousand cc. ethyl alcohol (95%) and 300 cc. water are placed into the

3-neck 5-liter Pyrex flask. The agitator is started, and 2000 Gm. zinc dust added. This precaution prevents any caking. The temperature is now raised to the boiling point of the diluted alcohol by a steam-bath, and 1600 Gm. of trimethylene dibromide (boiling at 162–164° C. uncorrected) which has been treated previously with 160 Gm. of zinc dust at room temperature is fed into the flask at a rate which will just maintain a smooth flow of gas. The gas so obtained was 99.5–100% absorbed by fuming sulphuric acid, and a 100-cc. sample left an acidified solution of 20 cc. $N/5$ $KBrO_3$ unaffected; indicating freedom from propylene.

We condensed the trimethylene from a typical experiment by a coil cooled by solid $CO_2$ and collected about 250 Gm. of liquid. This represents a yield of approximately 80%. No attempt was made to collect the largest possible yield.

Even though trimethylene is capable of producing anæsthesia when administered by inhalation, our results indicate that the margin of safety is too small for practical use.

### SUMMARY.

A convenient method of preparing trimethylene with a high degree of purity and in substantial quantities has been developed, without recourse to burdensome methods of purification.

Preliminary tests indicate that this gas is not suitable for use as a general anæsthetic because of its low margin of safety.

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# A THOUGHT ON THE PLACE OF VOLATILE OILS IN PLANT ECONOMY.*

BY FREDERICK E. MARSH AND WILMA K. MAUS.

One of the most constant observations of the student of living things is the purposeful intent of the various devices of nature. While some seem quite obscure and some uncertain, the obviousness of others seems to guarantee a certain definite usefulness for all. Thus it is commonly accepted. The purpose of many devices is traditionally accepted, of many we find divergent and changing views, of some we will probably always be in doubt.

The question of the purpose of the class of products commonly termed volatile oils occurred to us several years ago. A class of secretions so widely distributed in the plant kingdom, consistently found in many species and produced with such definite intent, as the special structures which bear them would indicate, must certainly be developed for a very definite purpose to the plant. Certain general values have been ascribed to volatile oils and traditionally accepted, such as the attraction of insects to aid in pollination, the repulsion of animal life which might be detrimental to the species (6), etc. These go unchallenged. Nor is it the intent of this paper to challenge them, but we intend to show that volatile oils as a class serve an added and very important purpose.

In the literature of the past we find very few references made to the biological function of volatile oils. In Asa Gray's "Introduction to Structural and Syste-

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* Scientific Section, A. PH. A., Rapid City meeting, 1929.