

- (6) James C. Munch, "Bioassays" (1931).  
 (7) J. C. Munch and W. F. Reindollar, A statistical study of the chemical constants of *Oleum Chenopodii*, Paper read at Baltimore meeting, A. PH. A., 1930.  
 (8) L. W. Rowe, The colorimetric assay of *strophanthus*, *JOUR. A. PH. A.*, 16 (1927), 113-115; The colorimetric assay of *digitalis*, *Ibid.*, pages 510-516.  
 (9) K. Pearson, On the criterion that a given system of deviation from the probable in the case of a correlated system of variables is such that it can be reasonably supposed to have arisen from random sampling, *Phil. Mag.*, 5 (1900), 157-175.  
 (10) H. R. Tolley, The theory of correlation as applied to farm-survey data on fattening baby beef, *U. S. Dept. Agr. Bull.*, 504 (1917).

### PROPADIENE.\*

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

L. K. Riggs predicted that due to the presence of two double bonds in propadiene  $\text{CH}_2=\text{C}=\text{CH}_2$ , the gas should have very high anesthetic potency; and that since the molecular weight is low, it should not be highly toxic. His studies indicated that the gas is disappointingly toxic.<sup>1</sup>

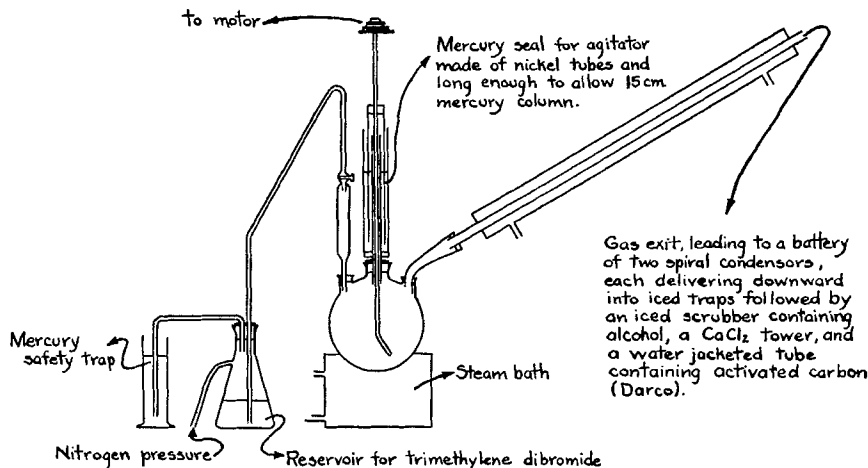


Fig. 1.

It seemed to the present authors that the method by which the material used in the above work was prepared did not adequately provide for the removal of vapors of 2,3-dibrompropene, and that the violent nervous symptoms noted by Dr. Riggs might be avoided by carefully removing these vapors from the propadiene.

In this laboratory we had already found that when propylene is prepared from propylene dibromide, incomplete removal of the propylene dibromide vapors causes the gas to be less satisfactory for anesthetic purposes. Likewise, in the case of cyclopropane we had much better results from that gas which we had rigidly purified from trimethylene dibromide.

\* Scientific Section, A. PH. A., Baltimore meeting, 1930.

<sup>1</sup> *Proc. Soc. Experimental Biology & Medicine*, 22 (1925), 269, and private communications.

Halogen substitution products of aliphatic hydrocarbons are very volatile even at temperatures far below their boiling points, and their vapors cannot be removed from a gas by condensation; especially when that gas is in rapid motion, *i. e.*, when it is being delivered from the apparatus in which it was made. This point is overlooked by many workers and was evidently overlooked by Henderson and Lucas in their recent work with cyclopropane.

In our work with cyclopropane we found that a battery of three spiral condensers above three cold ( $-15^{\circ}\text{C}.$ ) traps were insufficient to remove the trimethylene dibromide, but that a water jacketed column of activated carbon (Darco) was sufficient to remove every trace of bromide vapor.

We therefore decided to make propadiene in the same apparatus (diagram attached) used for the preparation of cyclopropane.

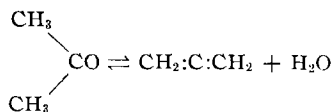
Two and a half liters of 80% alcohol were introduced into the reaction flask, and 2100 Gm. zinc dust were added to the alcohol, while stirring (to prevent caking). After the alcohol had been brought to boiling, 1381 Gm. of 2,3-dibromopropene were added, slowly and uniformly, through a dropping tube by use of nitrogen pressure, as shown. About 27 gallons of gas were collected by displacement of water, or approximately a 70% yield. This gas was diluted somewhat with air, but the hydrocarbon content was pure propadiene except for some small quantities of methyl acetylene, an isomer probably formed indirectly from propadiene. A sample taken just before the reaction stopped contained 7-8% methyl acetylene, but in the samples used for physiological tests the isomer was present in a considerably smaller quantity. The gases used for anesthetic studies contained 90-95% propadiene.

The brief physiological studies<sup>1</sup> made on this sample of propadiene indicated that it is capable of producing surgical anesthesia in white rats in concentrations between 12% and 25% with practically no irregularity in the respiratory rate, and without alarming depression of that rate. There seems to be some promise that more extensive studies with larger samples of the pure gas may prove it to be a good anesthetic.

No concentrations higher than 25% have been used, so that the concentration at which propadiene becomes definitely toxic has not been established.

The preparation of the 2,3-dibromopropene used for the generation of the propadiene involved (*a*) the preparation and purification of large quantities of tribromopropane by careful bromination of propylene dibromide, (*b*) the laborious preparation of 2,3-dibromopropene therefrom in small batches, by the removal of HBr with KOH, and (*c*) the repeated distillation of the 2,3-dibromopropene. Therefore, it was decided that further physiological studies must await the development of a better method of preparing the gas.

An attempt was made to do this by the dehydration of acetone.



<sup>1</sup> By Messrs. H. Holaday and B. L. Thomas of the Biological Laboratories, E. R. Squibb & Sons, New Brunswick, N. J. Not yet published.

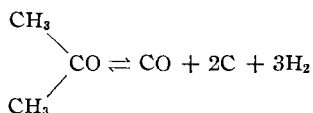
Acetone vapor was passed over pumice impregnated with pyrophosphoric acid, in an iron converter of the usual type, at temperature of 350–375° C. The acetone was recondensed quantitatively at the exit end of the converter and no gaseous product collected. However, when the temperature in the converter was raised gradually to 425–450° C. the evolution of a gaseous product began. At 475° C. no more acetone was condensed and the conversion to the gas was complete.

Analysis of this gas, which was somewhat diluted with air, was as follows:

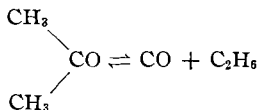
Oxygen	2.6 %
Nitrogen	10.0 %
Carbon dioxide	1.5 %
Carbon monoxide	22.9 %
Hydrogen	59.8 %
Olefin (calculated as ethylene)	1.75%
Saturated hydrocarbon (calculated as ethane)	1.53%

At the conclusion of the experiment, the dehydrating catalyst was interspersed with great quantities of retort carbon.

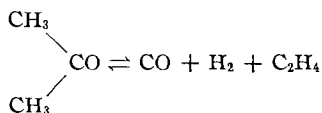
This analysis indicates that the acetone suffers thermal decomposition; probably according to the following equation:



A small portion may have decomposed in the following manner.



And a smaller portion may have decomposed in still another manner.



The work had to be dropped at this point but will be continued again at an early date.

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#### CINCHONA PRODUCTION AND SENNA IMPORTS.

Cinchona bark production in Netherland East Indies increased in 1930 to 11,121,000 kilos, a gain of 481,000 kilos over the 1929 production. Java produced 9,542,000 kilos, while Sumatra produced 1,580,000 kilos. (Trade Commissioner Richard P. Hendren, Batavia.)

Exports of senna from the Sudan for the first 11 months of 1930 aggregated 706 tons as against 552 tons for the corresponding period 1929. Of the 1930 total, 453 tons were shipped to the United States, 193 tons to Great Britain and 60 tons to Egypt. (Assistant Trade Commissioner Gabriel D. Ferrante, Cairo.)