5. 1-Phenyl-4-chlorobutadiene absorbed one molecule of chlorine in the 3,4-positions to give 1-phenyl-3,4,4′-trichlorobutene. Its structure was proved by ozonization.
6. 1-Phenyl-3,4,4′-trichlorobutene was further chlorinated to give 1-phenyl-1,2,3,4,4′-pentachlorobutane.
7. Straus' work on the bromination of phenylbutadiene was confirmed in every particular.

CHICAGO, ILLINOIS

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE RICE INSTITUTE]

TETRAMETHYLENE GLYCOL AND TETRAMETHYLENE CHLOROHYDRIN

BY W. R. KIRNER AND G. HOLMES RICHTER

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Some work published by Bennett[1] suggested a new method for the synthesis of tetramethylene glycol. In the first two papers Bennett gives the preparation of δ-hydroxybutyl benzyl ether and in the last paper Bennett and Hock described an experiment in which the benzyl group in an entirely different series of benzyl ethers was removed by means of hydrogen bromide, forming benzyl bromide, the residual portion of the ether remaining as an alcohol. By applying this reaction to Bennett's δ-hydroxybutyl benzyl ether it was found that tetramethylene glycol could be obtained in good yield. The novelty of the reaction is the splitting of the benzyl ether with hydrogen bromide without converting either hydroxyl group of the glycol into a bromide. The glycol was characterized by preparing both the di-phenyl- and di-α-naphthylurethans.

Tetramethylene glycol has been a relatively rare substance and our purpose was to devise a method by which this valuable synthetic reagent might become more easily available. The older methods of synthesis are either very tedious or give poor yields. However, after this work had been completed an article appeared by Müller[2] describing the preparation of tetramethylene glycol by the Bouveault–Blanc reduction of diethyl succinate with a yield of 54%. This is a considerable improvement over the yield reported by Böeseken,[3] who obtained a 31% yield using the same method. Müller ascribes his higher yield to the use of thoroughly dry alcohol and a more efficient method of isolation of the final product. Müller's method thus appears to offer the cheapest and simplest method of preparing tetramethylene glycol which has been published to date.

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[1] Bennett, *J. Chem. Soc.*, **127**, 1279 (1925); Bennett and Hock, *ibid.*, 475, 481 (1927).

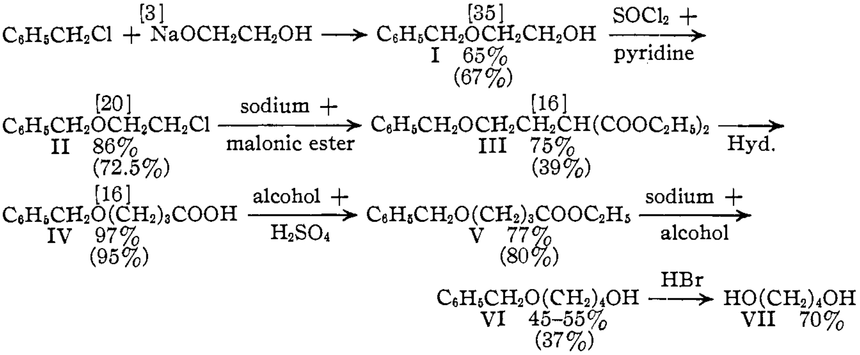
[2] Müller, *Monatsh.*, **49**, 27 (1928).

[3] Böeseken, *Rec. trav. chim.*, **34**, 101 (1915).

Tetramethylene glycol was converted into tetramethylene chlorohydrin by means of Darzens' reaction,[4] with a yield of approximately 50%. Bennett and Heathcoat[5] have very recently synthesized the chlorohydrin by the action of sulfur monochloride on the glycol but they state that their method gives the chlorohydrin "in poor yield and in an impure state." They obtained a fraction boiling at 86° at 15 mm. consisting of crude tetramethylene chlorohydrin which disappeared when redistilled under reduced pressure, producing much hydrogen chloride and presumably forming tetramethylene oxide. Our product boiled at 84–85° at 16 mm. and if distilled at a pressure much higher than this it also showed a tendency to lose hydrogen chloride. However, we succeeded in obtaining a pure product (by fractional vacuum distillation), as is indicated by the good agreement obtained between the calculated and observed values for the molecular refraction and in the chlorine content. The phenylurethan and α-naphthylurethan were prepared. The former is a new compound and melted at 54°. The α-naphthylurethan melted at 69–70°; Bennett and Heathcoat give the melting point as 66°.

Experimental

The following equations illustrate the method which was used for the preparation of the tetramethylene glycol. The yield in each step is indicated under the substance prepared and Bennett's yield is given in parentheses. The figures in brackets above the various compounds indicate the number of times the quantities given by Bennett were multiplied and shows the rather large scale on which these reactions were run. The over-all yield is 11%.



$$\overset{[3]}{C_6H_5CH_2Cl + NaOCH_2CH_2OH} \longrightarrow \underset{\substack{\text{I}\ \ 65\%\\(67\%)}}{\overset{[35]}{C_6H_5CH_2OCH_2CH_2OH}} \xrightarrow[\text{pyridine}]{SOCl_2\ +}$$

$$\underset{\substack{\text{II}\ \ 86\%\\(72.5\%)}}{\overset{[20]}{C_6H_5CH_2OCH_2CH_2Cl}} \xrightarrow[\text{malonic ester}]{\text{sodium}\ +} \underset{\substack{\text{III}\ \ 75\%\\(39\%)}}{\overset{[16]}{C_6H_5CH_2OCH_2CH_2CH(COOC_2H_5)_2}} \xrightarrow[\text{Hyd.}]{}$$

$$\underset{\substack{\text{IV}\ \ 97\%\\(95\%)}}{\overset{[16]}{C_6H_5CH_2O(CH_2)_3COOH}} \xrightarrow[H_2SO_4]{\text{alcohol}\ +} \underset{\substack{\text{V}\ \ 77\%\\(80\%)}}{C_6H_5CH_2O(CH_2)_3COOC_2H_5} \xrightarrow[\text{alcohol}]{\text{sodium}\ +}$$

$$\underset{\substack{\text{VI}\ \ 45\text{–}55\%\\(37\%)}}{C_6H_5CH_2O(CH_2)_4OH} \xrightarrow{HBr} \underset{\text{VII}\ \ 70\%}{HO(CH_2)_4OH}$$

In the preparation of β-chloro-ethyl benzyl ether (II) by Darzens' reaction we used pyridine whereas Bennett used dimethylaniline. In our work the temperature was not allowed to rise above 55° during the addition of the thionyl chloride and the mixture was not heated to drive

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[4] Darzens, *Compt. rend.*, **152**, 1314 (1911).

[5] Bennett and Heathcoat, *J. Chem. Soc.*, 272 (1929).

off sulfur dioxide but was merely allowed to stand overnight. This illustrates another case where good yields of a chloride can be obtained by this method without heating the reaction mixture.[6]

The improved yield of diethyl-β-benzyloxyethylmalonic ester (III) is ascribed to the use of thoroughly dried alcohol which was used in the malonic ester condensation. A good grade of absolute alcohol was further dehydrated by the irreversible hydrolysis of ethyl acetate as recommended by Smith,[7] and distilled directly into the apparatus used for the reaction. The mixture was merely stirred and refluxed over a period of five days and not heated under pressure as recommended by Bennett and Hock.

In the reduction of the ethyl-γ-benzyloxybutyrate (V) thoroughly dry alcohol was also used. About 100 g. of ester was reduced in each run. It was found that small amounts (4–6 g.) of the glycol, which was probably formed by the splitting of the benzyl ether by the metallic sodium,[8] could be recovered from the aqueous solutions by saturating them with anhydrous potassium carbonate and then extracting with alcohol.

Bennett and Hock's procedure for the splitting of benzyl ethers was modified as follows and found to give better yields: 66 g. of the benzyl ether were treated with 175 cc. of concentrated hydrobromic acid and allowed to stand for three days (without adding any hydrogen bromide). Potassium carbonate was added until the mixture was just neutral and any unreacted material was extracted with benzene, the benzene extract being washed with water to remove any glycol. The aqueous solution, plus that obtained from washing the benzene layer, was saturated with potassium carbonate and extracted with alcohol. On distilling off the alcohol, carbonate precipitated out; this was again extracted with alcohol and the alcohol distilled off. A residue is thus obtained which is distilled in vacuum and which yields the glycol; 20.7 g. of glycol was obtained and 6.2 g. of unchanged benzyl ether was recovered. This corresponds to a yield of 69% based on the ether which reacted; boiling point of tetramethylene glycol, 107–108° at 4 mm.; melting point, 19–19.5°; $d_4^{20} = 1.0171$; n_D^{20}, 1.4467; M_D (calcd.), 23.722; M_D (found), 23.651. The di-phenylurethan was prepared according to the directions of Hamonet.[9] Crystallization from chloroform gave a product melting at 179.5°. Hamonet gives the melting point as 180–181°. The di-α-naphthylurethan was also prepared by warming the glycol with α-naphthyl isocyanate. Crystallized from xylene it melted at 198.5–199°. Bennett and Heathcoat give the melting point as 198°.

Anal. Calcd. for $C_{26}H_{24}O_4N_2$: N, 6.55. Found: N, 6.49.

Tetramethylene Chlorohydrin.—Twenty grams of the glycol was dissolved in pyridine (17.6 g.) in a 200-cc. three-necked flask fitted with a stirrer, dropping funnel and reflux condenser. The flask was placed in a water-bath maintained at 55° and 26.4 g. of thionyl chloride was added drop-wise during one hour. The temperature of the bath was then raised to 80° for one hour to drive off the sulfur dioxide. The reaction mixture was then worked up in the usual way; yield, 11.4 g. (47%). Tetramethylene chlorohydrin boils at 84–85° at 16 mm. If distilled at a pressure much higher than this it tends to lose hydrogen chloride, presumably forming tetrahydrofuran; d_4^{20}, 1.0883; n_D^{20}, 1.4518; M_D (calcd.), 27.064; M_D (found), 26.893.

Anal. Subs., 0.3175: AgCl, 0.4176. Calcd. for C_4H_9OCl: Cl, 32.67. Found: Cl, 32.54.

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[6] See Kirner, THIS JOURNAL, **50,** 1959 (1928).

[7] Smith, *J. Chem. Soc.*, 1288 (1927).

[8] Schorigin, *Ber.*, **56,** 176 (1923); **57,** 1627 (1924).

[9] Hamonet, *Bull. soc. chim.*, [3] **33,** 525 (1905).

The phenylurethan, crystallized from petroleum ether, melted at 54°. This is a new compound.

Anal. Subs., 0.0608: AgCl, 0.0381. Calcd. for $C_{11}H_{14}O_2NCl$: Cl, 15.58. Found: Cl, 15.50.

The α-naphthylurethan prepared similarly and crystallized from petroleum ether melted at 69–70°. Bennett and Heathcoat give the melting point as 66°.

Anal. Subs., 0.3401: AgCl, 0.1768. Calcd. for $C_{15}H_{16}NO_2Cl$: Cl, 12.78. Found: Cl, 12.85.

Summary

1. A new method of synthesis of tetramethylene glycol has been devised. Müller's method (published after this work had been completed), involving the reduction of diethyl succinate, appears to be cheaper, simpler and more rapid.
2. Tetramethylene chlorohydrin was isolated in a pure state for the first time; its physical properties were determined and its phenylurethan and α-naphthylurethan were made, the former being a new derivative.

HOUSTON, TEXAS

[CONTRIBUTION FROM THE DEPARTMENT OF AGRICULTURAL CHEMISTRY, UNIVERSITY OF WISCONSIN, AND THE OFFICE OF CEREAL CROPS AND DISEASES, BUREAU OF PLANT INDUSTRY, UNITED STATES DEPARTMENT OF AGRICULTURE]

THE CHEMICAL COMPOSITION OF CORN (ZEA MAYS) SEEDLINGS. I. THE ISOLATION OF XYLAN AND CELLULOSE FROM THE CELL WALLS[1,2]

BY KARL PAUL LINK

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Introduction

In the course of a general investigation on the nature of corn (Zea Mays) seedling blight, it was deemed expedient to investigate the chemical com-

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[1] Published with the permission of the Director of the Wisconsin Agricultural Experiment Station.

[2] This publication comprises part of a thesis submitted to the Graduate Faculty of the University of Wisconsin in June, 1925, in partial fulfilment of the requirements for the degree of Doctor of Philosophy. The research was concluded during 1925–1927 while the author was a Fellow of the International Education Board posted at the University of St. Andrews, Scotland, and the University of Graz, Austria. The author wishes to acknowledge his indebtedness to Sir James Irvine, D.Sc., F.R.S., Principal and Vice Chancellor of the University of St. Andrews, for the privilege of extending the research while a student in his laboratory and for advice and help received. The author is likewise indebted to Professor Fritz Pregl, Director of the Medico-chemical Institute of the University of Graz, under whose personal direction the micro-analytical analyses were conducted. To the Board of Directors of the International Education Board, New York City, the author wishes to extend his thanks for the Fellowship grant received which enabled him to complete the work in the laboratories mentioned.