Effect of Other Absorbents than Fuller's Earth

One hundred-g. samples of α-pinene were refluxed for several hours with 40 g. of (*a*) iron gel, (*b*) silica gel, (*c*) activated charcoal. There was no evidence of any change whatever.

Summary

1. α-Pinene, in the presence of fuller's earth, first undergoes an intramolecular rearrangement, among the products formed being dipentene and terpinene. No camphene was found.

2. The second stage of the reaction is one of polymerization to dipinene and various polyterpenes.

3. At elevated temperatures, the dipinene so formed is slowly decomposed in the presence of fuller's earth, giving low-boiling paraffin hydrocarbons and some paracymene.

4. This reaction is a general one for terpenes and unsaturated oxygenated terpenes.

5. The effect of the diluents and conditions affecting the activity of the fuller's earth have been investigated.

6. The reaction is not promoted by iron gel, silica gel, or activated charcoal.

The writer wishes to express his appreciation to Messrs. André Deschamps, R. H. Bailey and E. C. Crocker, who contributed a large part of the experimental data described in this article.

CAMBRIDGE 39, MASSACHUSETTS

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

STUDIES ON CELLULOSE CHEMISTRY. III. PARABROMO-ACETALDEHYDE AND MONOBROMO-ACETALDEHYDE. THEIR PREPARATION, PROPERTIES AND UTILIZATION FOR THE SYNTHESIS OF BROMO- AND HYDROXY-CYCLIC ACETALS RELATED TO POLYSACCHARIDES

BY HAROLD HIBBERT AND HAROLD S. HILL[1,2]

Received August 29, 1922

The chemical inertness of cellulose has rendered a study of its molecular structure a matter of great difficulty. While the few reactions in which the cellulose molecule is involved have all helped to establish the fact of the close inter-relationship between this substance and glucose, they are of

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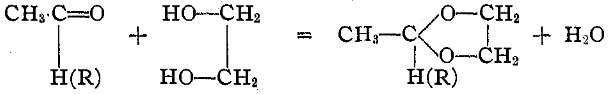
[1] This paper is constructed from Part 2 of a dissertation presented by Harold Sanford Hill (du Pont Research Fellow) in June, 1922, to the Faculty of the Graduate School, Yale University, in candidacy for the degree of Doctor of Philosophy. The thesis contains a review of the literature on bromo-acetaldehyde and related compounds.

[2] Communicated to the Cellulose Section of the American Chemical Society at the Birmingham (Ala.) meeting, April, 1922.

such a character as to offer only inconclusive evidence as to the exact nature of the "polymerized" molecule. Much has been learned concerning cellulose and starch through their decomposition reactions, but it seems probable that the actual elucidation of the structure of these polysaccharides may be brought to light largely by experimental work involving the synthesis, first of the simpler and later of the more complex derivatives.

That a quantitative relationship exists between cellulose and glucose has now been definitely established,[3] but there is as yet no conclusive evidence showing how the anhydro glucose residues are combined in the cellulose molecule.[4] In other words there are few or no data available at present to indicate how such a condensation is brought about. It is known that the free aldehyde and two hydroxyl groups of each glucose molecule disappear in the formation of the cellulose complex, the probability being that such condensation always occurs in the δ position as evidenced by the formation of 2,3,6-trimethyl glucose obtained by the hydrolysis of trimethoxy cellulose.[5] A knowledge of the properties of cyclic acetals (lactonyl derivatives) whether produced by an "intermolecular" condensation as in the case of an aldehyde and ketone with a polyalcohol,

(a)



$$\begin{matrix}CH_3\cdot C{=}O\\ |\\ H(R)\end{matrix} + \begin{matrix}HO{-}CH_2\\ |\\ HO{-}CH_2\end{matrix} = CH_3{-}\begin{matrix}C\\ |\\ H(R)\end{matrix}\begin{matrix}\diagup O{-}CH_2\\ \qquad |\\ \diagdown O{-}CH_2\end{matrix} + H_2O$$

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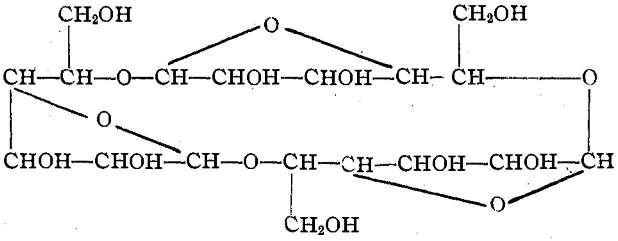
[3] (a) Willstätter and Zechmeister, *Ber.*, **46**, 2401 (1913). (b) Ost, *ibid.*, **46**, 2995 (1913). (c) Ost and Wilkening, *Chem.-Ztg.*, **34**, 461 (1910). (d) Monier-Williams, *J. Chem. Soc.*, 119, 803 (1921). (e) Irvine, *J. Soc. Chem. Ind.*, 41, 362R (1922).

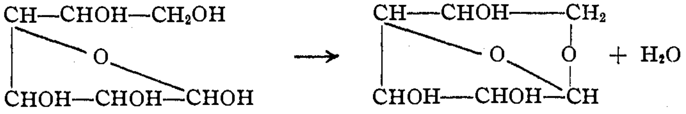
[4] During the correction of the manuscript of this article there appeared a short synopsis of the brilliant researches carried out by J. C. Irvine with the aid of his collaborators and pupils. The article (Ref. 3e) gives a summary of the author's conclusions on the constitution of cellulose, starch and inulin as presented to the Chemistry Section of the British Association for the Advancement of Science, in September, 1922. He advances convincing evidence that the formula for cellulose is



An examination of this shows it to be identical with that put forward by one of us some 3 years ago [*J. Ind. Eng. Chem.*, **13**, 256, 334 (1921)] although at that time it was naturally impossible to state definitely the exact number of anhydro dextrose units comprised in the cellulose molecule.

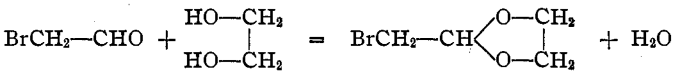
[5] Denham and Woodhouse, *J. Chem. Soc.*, **103**, 1735 (1913); **105**, 2537 (1914); 111, 244 (1917).

or by an "intramolecular" dihydroxy-aldehydic condensation as, for example, the conversion of glucose into *levo*glucosan,

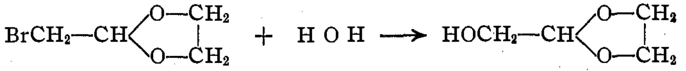


is thus of considerable interest.

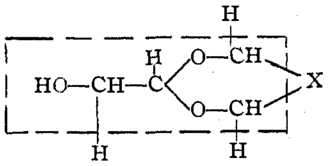
A product capable of serving as a logical starting-point in such an investigation would seem to be the cyclic acetal obtained from the condensation of the simplest sugar, glycollic aldehyde, with the simplest polyvalent alcohol, ethylene glycol. Unfortunately the former, on account of its unstable character, does not lend itself readily to such condensation reactions. There is, however, the possibility of overcoming the difficulty by substituting bromo-acetaldehyde for glycollic aldehyde, whereby a bromocyclic acetal should be formed.



and this, upon hydrolysis, should yield the corresponding hydroxy-derivative.

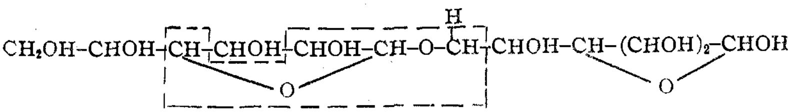


An examination of the structure of this acetal, whose type may be represented by the more general formula



and a comparison of it with anhydro-sugars and polysaccharides shows that the grouping enclosed within the dotted lines is the one present in a wide variety of important natural products.

1. *Maltose*
(Haworth and Leitch)[6a]



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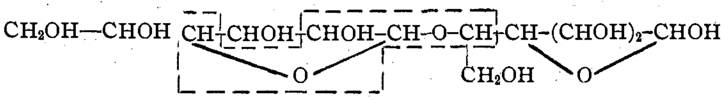
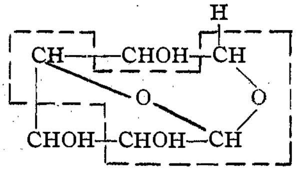
[6] (a) Haworth and Leitch, *J. Chem. Soc.*, **115**, 809 (1919). (b) Haworth and Hirst, *ibid.*, 119, 193 (1921). (c) Pictét, *Helvetica Chim. Acta*, **3**, 649 (1920). See also Irvine and Oldham, *J. Chem. Soc.*, **120**, 1752 (1921). (d) Karrer, *Helvetica Chim. Acta*, **5**, 187 (1922). (e) Hibbert, *J. Ind. Eng. Chem.*, 13, 256, 334 (1921).

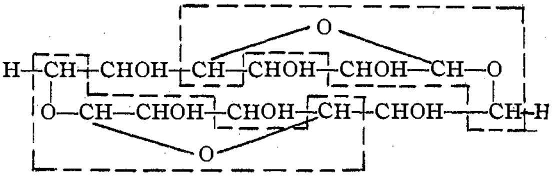
2. *Cellobiose*
(Haworth and Hirst)[6b]



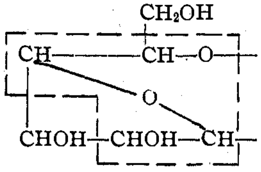
3. *Levoglucosan*
(Pictét)[6c]



4. *Diamylose*
(Karrer)[6d]



5. *Cellulose unit*
(Hibbert)[6e]



The key to the situation outlined is evidently the product, monobromo-acetaldehyde, which at the time this work was begun had never been isolated in a pure state.[7] Attention was therefore first concentrated on its synthesis and, after considerable effort (and some good fortune), it has been found possible to obtain, as indicated in the experimental part, a yield of 32% of a pure crystalline parabromo-acetaldehyde, $(CH_2BrCHO)_3$, by the bromination of paracetaldehyde under the stated conditions. Furthermore, this polymer on heating is converted directly into pure bromo-acetaldehyde.

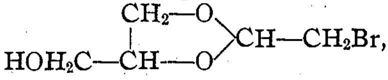
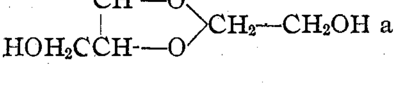
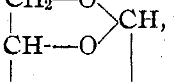
The bromination of paracetaldehyde is a reaction, the course of which is strongly influenced by the temperature as has been shown by various

[7] Just as the present investigation was about concluded, there appeared an article by Helferich and Speidel [(a) *Ber.*, **54**, 2364 (1922)] in which the isolation of pure para-bromo-acetaldehyde is described, the method used being a modification of that outlined by Natterer [(b) *Monatsh.*, **3**, 442 (1882)] for the synthesis of the corresponding chloro derivative. The method developed by the present authors differs considerably from that described by Helferich and Speidel in that it is a much more direct process.

investigators.[8] If the bromination is carried out between —5° and —12° the main products are mono- and parabromo-acetaldehyde. On the other hand, when the temperature is allowed to rise above +5°, "crotonization" occurs in the following manner: $CH_2Br\text{—}CHO + CH_2Br\text{—}CHO = CH_2Br\text{—}CH{=}CBr\text{—}CHO + H_2O$. This dibromocrotonaldehyde then adds on bromine to give the tetrabromobutyraldehyde: $CH_2Br\text{—}CH{=}CBr\text{—}CHO + Br_2 = CH_2Br\text{—}CHBr\text{—}CBr_2\text{—}CHO$, a yield of as high as 80% being obtainable.[9]

It is of interest that by a careful regulation of the conditions during bromination, followed by extraction of the product according to the method outlined later, the resulting crude mixture of para- and bromo-acetaldehyde is sufficiently pure for direct use in condensation reactions such as those with polyvalent alcohols.

Apparently no cyclic acetals have hitherto been prepared from bromo-acetaldehyde, although many such have been made from other aldehydes and ketones. In general it was found sufficient to heat together a mixture of either pure bromo-acetaldehyde, or the crude extracted mixture, with the polyvalent alcohol and a small amount of a catalyst, such as 40% sulfuric acid. In this way cyclic acetals of bromo-acetaldehyde with ethylene glycol, trimethylene glycol, α-bromo-hydrin, glycerol, and mannitol were prepared in a pure state in yields averaging 40–55%.

The acetals so obtained are all unstable in presence of dil. acids, especially on warming. Even continued boiling with water decomposes them into their original components. On the other hand, while the acetal grouping itself is relatively stable toward alkalies, it is possible, by continued boiling with dil. potassium hydroxide solution, to replace the bromine by an hydroxyl group, leaving the acetal group unchanged. Such an hydrolysis of the compound derived from glycerol, bromo-ethylidene glycerol,  $\begin{array}{l} \quad\;\; CH_2\text{—}O \\ \quad\;\;\; | \\ HOH_2C\text{—}CH\text{—}O \end{array}\!\!>CH\text{—}CH_2Br$, apparently yields two compounds, hydroxyethylidene glycerol and a dilactonyl derivative,  $\begin{array}{l} \quad\;\; CH\text{—}O \\ \quad\;\;\; | \\ HOH_2CCH\text{—}O \end{array}\!\!>CH_2\text{—}CH_2OH$ and  $\begin{array}{l} CH_2\text{—}O \\ | \\ CH\text{—}O \\ | \\ CH_2\text{—}O\text{—}CH_2 \end{array}\!\!>CH$, the identities of which, however, have not yet been definitely established.

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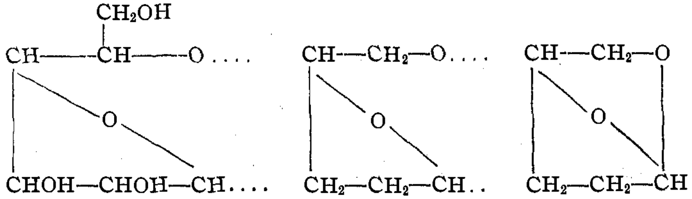
[8] Freundler and Ledru, (a) *Compt. rend.*, **140**, 794, 1693 (1905); (b) *Bull. soc. chim.*, [4] **1**, 66, 71 (1907).

For further work on bromination of acetaldehyde and paracetaldehyde see also: (c) Haarmann, *Ber.*, **3**, 758 (1870). (d) Pinner, *ibid.*, **7**, 1499 (1874); **5**, 149 (1872). (e) Wislicenus, *Ann.*, **192**, 112 (1878). (f) E. Fischer and Landsteiner, *Ber.*, **25**, 2551 (1892). (g) Braun, *ibid.*, **35**, 3388 (1902). (h) Burgarsky, *Z. physik. Chem.*, **48**, 63 (1904). (i) Mauguin, *Compt. rend.*, **147**, 747 (1908). (j) Franke, *Monatsh.*, **21**, 205, 210 (1900); (k) *Ann.*, **351**, 425 (1907).

[9] Ref. 8b, p. 68.

Attempted Synthesis of a Product Closely Related to Cellulose

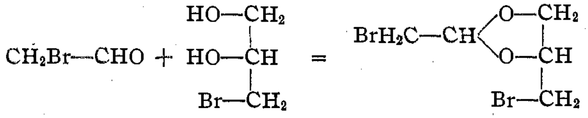
Much effort was spent in attempting to synthesize a product closely related to cellulose. If the formula for the latter proposed by Hibbert (I) is correct,



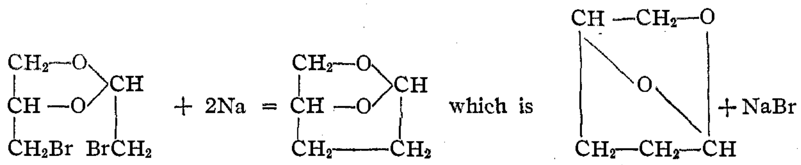
I II III

then a still simpler derivative, which might be expected to possess somewhat similar properties, would be that indicated by Formula II. It seemed possible that in this case the nucleus itself (III) might be capable of separate existence and it appeared of interest to attempt its synthesis by the following reactions.

1. Condensation of bromo-acetaldehyde with α-bromohydrin to give bromo-ethylidene bromohydrin.

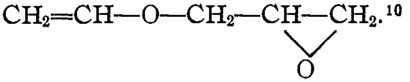


2. Removal of the 2 bromine atoms with formation of the desired ring compound.



The first stage was carried out with a yield of 55% of the cyclic acetal. This dibromo derivative, either alone or in the presence of solvents, (ether, xylene) reacts with apparent smoothness with metallic sodium, the bromine being quantitatively recoverable as the metallic salt, but in spite of numerous attempts to effect the desired ring-closure by the removal of the bromine in this manner, no definite reaction products could be isolated. Removal of the solvent by distillation, solution of the residue in water and acidification of the aqueous solution, caused the precipitation of a considerable quantity of a light-brown, amorphous solid free from bromine and inorganic matter. This solid was readily soluble in alkali, from which solution it was reprecipitated on addition of acids. It was also soluble in alcohol, acetone and ethyl acetate with formation of a reddish-brown solution, but on account of the difficulties attending its purification identification has not been found possible, as yet.

Fractionation of the solvent (ether, xylene) used in this experiment yielded a small amount of a mixture of unsaturated liquid hydrocarbons boiling below 100°. There was some evidence of the presence of a definite product boiling around 92°. This was a limpid, colorless liquid, free from bromine, unsaturated, and possessing a pungent odor. It was miscible with the common organic solvents, and its composition approximated that of vinyl glycide,



$$CH_2{=}CH{-}O{-}CH_2{-}\underset{\diagdown O \diagup}{CH{-}CH_2}$$.[10]

Molecular silver and copper do not react with bromo-ethylidene bromohydrin even on heating to 150°, while activated magnesium shows a behavior similar to that of metallic sodium.

Silver acetate and glacial acetic acid do not react even after heating for

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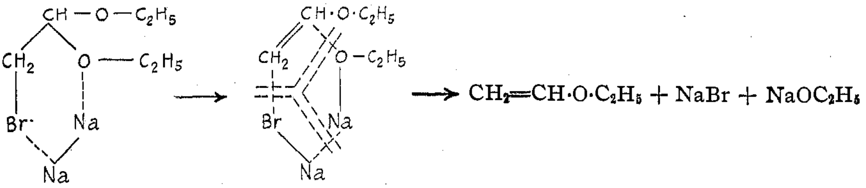
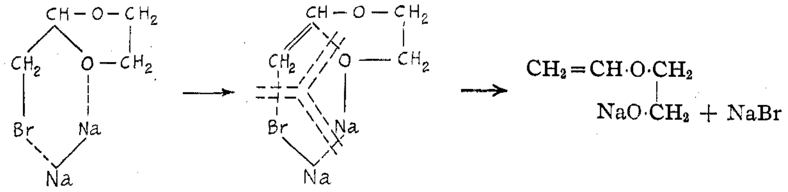
[10] Wislicenus (Ref. 8e, p. 106) showed that bromo-ethylal reacts at 130° with metallic sodium to form vinyl ethyl ether, according to the equation,

$$CH_2BrCH(OC_2H_5)_2 + Na = CH_2{:}CH{\cdot}O{\cdot}C_2H_5 + NaOC_2H_5$$

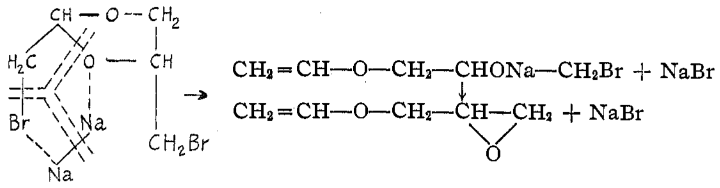
a change possibly explainable in the light of Erlenmeyer's theory of chemical reactions, [*Ann.*, **316**, 43 (1901)], as follows: the 2 atoms of sodium may be assumed to form a loose addition compound with the bromo-ethylal, giving a 6-membered ring which then breaks down.



Bromo-ethylidene glycol in contact with sodium may possibly react in a similar manner giving the sodium salt of glycol-vinylin.



Bromo-ethylidene bromohydrin, however, might be expected to yield vinyl glycide.

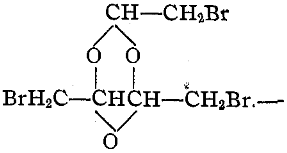


Various other reactions of this type are to be found in the literature and the subject is to be investigated further.

2 days at 120°. Alcoholic potash and sodium malonic ester appear to react smoothly but the products formed have not as yet been identified. Boiled with an excess of 0.1 *N* potassium carbonate solution for 10 hours, bromo-ethylidene bromohydrin is decomposed to the extent of 44%.

Experimental Part

Preparation of Parabromo-acetaldehyde,



This crystalline polymer was first isolated from the tarry mass left on distilling the reaction product from the condensation of crude bromoacetaldehyde with various polyalcohols.

The tarry mixture containing the crystalline product was dissolved in ether, the solution washed with a concentrated solution of sodium bisulfite to remove any free aldehyde, and then boiled for a short time with decolorizing charcoal. Evaporation of the ether left a white crystalline product which separated from hot alcohol as glistening needles, melting sharply at 104°. The crystals were odorless, possessed no aldehyde properties, and on analysis proved to be parabromo-acetaldehyde. In its chemical and physical properties it resembles the corresponding parachloro-acetaldehyde of Natterer,[7b] the paradibromo-acetaldehyde of Haarman, [8c] and the parabromo-*iso*butyraldehyde and parabromo-propionaldehyde of Franke,[8j] breaking down on heating into the pure monomolecular product, $CH_2Br.CHO$.

As parabromo-acetaldehyde was isolated from nearly all of the crude residues obtained in the preparation of different bromo-cyclic acetals from crude bromoacetaldehyde, it seemed probable, in spite of Franke's failure,[11] that it should be possible to obtain it by the direct bromination of paracetaldehyde. After numerous experiments this was accomplished despite the marked tendency towards undesirable side reactions, and the discomfort to the eyes caused by the extremely irritating and piercing vapors associated with the crude product.

Using the method outlined below, paracetaldehyde can be converted by the action of bromine in sunlight at a low temperature (—5° to —10°) into crystalline parabromo-acetaldehyde with a yield of 32%, which, however, could presumably be considerably increased by a more extended study of this complicated reaction.

As shown by Freundler and Ledru,[8] the temperature during bromination must be kept low in order to prevent "crotonization" of the monobromoacetaldehyde first formed, since this takes place nearly quantitatively if the temperature is allowed to rise much above 0°. As the unsaturated

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[11] Ref. 8j, p. 206. Ref. 8k. This author was able to isolate a very small quantity of a crude crystalline polymer, presumably the trimolecular derivative, although neither its melting point nor analytical data are in close agreement with those pertaining to parabromo-acetaldehyde.

dibromo-crotonaldehyde formed has a great affinity for bromine, its formation results in the removal of much of the halogen intended for bromination, as well as in the introduction of unstable by-products.

The formation of parabromo-acetaldehyde is apparently facilitated by direct sunlight, in that rapid bromination at a low temperature can thus be brought about with a consequent increase in the concentration of the monobromo-acetaldehyde, which in turn tends to favor the trimolecular reaction involved in the polymerization to the parabromo derivative. The following method was found to give the best yield.

One hundred and forty g. of pure dry paracetaldehyde were placed in a round-bottom flask equipped with a dropping funnel and a stirrer, and protected from moisture by a mercury seal and a calcium chloride tube. The flask was immersed in a freezing-mixture of ice and salt and so arranged that a maximum amount of direct sunlight could reach the contents; 400 g. of bromine was slowly dropped into the well-stirred aldehyde during a period of about 4 hours, and the temperature kept below —5°. After the last of the bromine had been added, the agitation was continued for a further half-hour, and the temperature still kept below —5°. A cold, aqueous sludge of sodium acetate crystals was then added, and the agitation continued; the sludge was prepared by dissolving 200 g. of crystalline sodium acetate in a small amount of hot water and agitating the solution during its subsequent cooling, in order to cause the product to separate as a thin paste of fine crystals. The slow addition of this cold paste to the red solution produced a rapid decoloration. Too vigorous agitation at this point was avoided and it was also found best to discontinue the stirring within a few minutes after the last of the acetate had been added.

The flask was allowed to remain overnight immersed in cold water which resulted in a separation of the liquid into 2 layers. The upper one was essentially an aqueous solution of sodium acetate, sodium bromide and hydrobromic acid, while the lower layer contained a semi-solid mixture of the excess of sodium salts, crystalline parabromo-acetaldehyde, and a certain amount of a heavy insoluble oil. The upper layer was removed and the mixture of solids washed with water, extracted with ether, the latter neutralized with dil. sodium hydroxide solution and then washed with a concentrated solution of sodium bisulfite. Removal of the ether under reduced pressure left a residue of white crystals mixed with a small amount of sirup, and on recrystallization from 90% alcohol, white, glistening needles of almost pure parabromo-acetaldehyde separated. The yield was 115 g., equivalent to about 32% of the calculated yield.[12]

Parabromo-acetaldehyde is an odorless product, which crystallizes in colorless needles; m. p., 104° (uncorr.). It is insoluble in water, slightly soluble in cold alcohol or ligroin, readily in the other common organic solvents and shows none of the reactions of the aldehyde group.

Analyses. Subs., 0.1845: AgBr, 0.2817. Calc. for C_2H_3OBr: Br, 65.04. Found: 64.99. Subs., 0.4064: benzene, 13.5 g., Δt, 0.425°. Calc. for $(CH_2BrCHO)_3$: mol. wt., 369. Found: 354.

The role of the sodium acetate in the preparation of parabromo-acetaldehyde is not thoroughly understood, but it is probably of a 3-fold nature: (1) it removes a large amount of hydrobromic acid; (2) it appears to stop

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[12] This represents the highest yield found thus far. Due to the interference of various factors, in general much lower yields were obtained, and the details of the process are being further investigated.

the undesirable "crotonization" reactions; (3) it furnishes a medium which at least is not unfavorable to the polymerization.

Other catalysts such as zinc chloride, zinc oxide, sulfur dioxide, sodium bisulfite, conc. sulfuric acid, water in various amounts, anhydrous sodium acetate, calcium chloride, and ether, were tried in place of the sodium acetate but with small success. The experiment with sodium bisulfite yielded a certain amount of the crystalline polymer but in this case there was an excess of sulfur dioxide formed by the action of the hydrobromic acid which rendered the extraction more than ordinarily difficult.

Preparation of Pure Monobromo-acetaldehyde, (CH_2Br-CHO).—Parabromo-acetaldehyde on heating, behaves in a manner similar to that of the other halogenated paraldehydes; for example, parachloro-acetaldehyde,[7b] parabromo-*iso*butyraldehyde, and parabromo-propionaldehyde,[13] yielding the monomolecular derivative which, however, shows a great tendency to undergo repolymerization.

Method.—A 50cc. distilling bulb was filled with crystals of pure parabromo-acetaldehyde, and carefully heated over a small flame. The crystals melted to a colorless liquid and on continued heating a product began to distil at a temperature of 107°, as indicated by the thermometer in the neck of the flask. By using an oil-bath it was found that the temperature of the bath necessary to produce this distillation was about 165°. However, a small flame was found more convenient. The temperature as indicated by the thermometer rose slowly from 107° to 112°, the liquid distilling within this range, but in order to assure this, it was necessary to interrupt the heating, allow the mixture to cool, and then to reheat. The product thus obtained was a limpid, colorless liquid, the vapor of which had an extremely irritating effect on the eyes and mucous membrane. It dissolved readily in water and in alcohol with evolution of heat, but unlike chloro-acetaldehyde, showed no tendency to form a crystalline hydrate, even on long standing with a small volume of water. The aqueous solution exerted a strong reducing action on cold ammoniacal silver nitrate and in agreement with the observation of Fischer and Landsteiner,[8f] completely lost its sharp odor in contact with a dilute solution of barium hydroxide, glycollic aldehyde being formed.

The distillate from parabromo-acetaldehyde had, in fact, all the properties to be expected of a monomolecular derivative.

Analysis. Subs., 0.1374: AgBr, 0.2107. Calc. for C_2H_3OBr: Br, 65.04. Found: 65.26.

Bromo-acetaldehyde Semicarbazone, $CH_2Br.CH{:}N.NH.CO.NH_2$.—This semicarbazone was prepared by dissolving the freshly-distilled aldehyde in twice its volume of absolute alcohol, and mixing with an excess of an alcoholic solution of sodium acetate and semicarbazide hydrochloride. Upon allowing the mixture to stand a short time, long, flat, white needle-shaped crystals separated, which, after filtration and washing with cold alcohol and hot benzene, and drying at 80°, melted with decomposition at about 128°. They were readily soluble in hot alcohol but only slightly in hot benzene. Analysis proved that the product was the semicarbazone of bromo-acetaldehyde.

Analysis. Subs., 0.1996: AgBr, 0.2092. Calc. for $C_3H_6OBrN_3$: Br, 44.20. Found: 44.6.

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[13] Ref. 8j, p. 211.

Polymerization of Bromo-acetaldehyde.—When the distillate from the crystalline polymer (m. p. 104°) was allowed to stand for about 12 hours it became noticeably viscous and was then only partially soluble in water. After a week it completely repolymerized to the same crystalline trimolecular derivative.[14]

The polymerization of the free aldehyde was brought about at low temperature somewhat more quickly by means of concentrated acids, although with these reagents there was a tendency for side reactions to occur. Conc. sulfuric acid polymerized the mono derivative at —10° to —15° in the course of an hour, although with some loss. With conc. hydrochloric and hydrobromic acids the polymerization took place more slowly, extending over a number of hours.

That the actual formation of the free aldehyde in the distillation of the crystalline polymer was due merely to a depolymerization was shown by the fact that at any time during the distillation, if the flask were allowed to cool, the entire contents would crystallize again to almost colorless needles of the trimolecular derivative.

Judging from analogy with the other halogenated aldehydes which have been studied previously, it would seem that by carefully freeing the vapors of the parabromo-acetaldehyde distillation product from moisture by means of copper sulfate (as described by Natterer[15] for the preparation of chloro-acetaldehyde) and protecting the product from the air, a fairly stable bromo-acetaldehyde might be obtained which would doubtless have a sharp, constant boiling point. The wide range observed, 107–112°, was presumably due to the continuous re-production of a small amount of the trimolecular polymer, for on redistillation the liquid monomolecular derivative was found to boil within the same limits. The product from the distillation of parabromo-acetaldehyde if used directly, and at temperatures of 100° or over, may be considered, without appreciable error, to consist entirely of monomolecular bromo-acetaldehyde. At temperatures below 100°, a continual repolymerization takes place to the more stable, crystalline, para derivative.

It should be noted that for the preparation of monobromo-acetaldehyde, the crystalline polymer used must be pure. Thus it is necessary that the latter in the course of its preparation should have been washed with a concentrated solution of sodium bisulfite to remove any traces of dibromocrotonaldehyde and other unstable aldehydes formed as by-products in the bromination of paracetaldehyde and which are likely to be retained as impurities. Any small amounts of these compounds present during the

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[14] This result is not in agreement with the observation of Helferich and Speidel (Ref. 7a) who claim that some other polymer is formed although no m. p. determinations are given.

[15] Ref. 7b, p. 464.

distillation undergo decomposition and the hydrobromic acid liberated causes the free bromo-acetaldehyde to "crotonize" to some extent. The subsequent decomposition of the unstable dibromo-crotonaldehyde gives rise to dark colored products, so that unless the crystals at the start are quite pure, the distillate of bromo-acetaldehyde will be dark colored, besides containing a variety of impurities.

It was found that a preliminary heating of the pure, crystalline parabromo-acetaldehyde at 170° under a reflux condenser offered no advantage in the above preparation of bromo-acetaldehyde.

It is of some interest that when parabromo-acetaldehyde was heated under reduced pressure (15 mm.), only a slight depolymerization into the monomolecular aldehyde took place, the polymer distilling for the most part unchanged and resolidifying immediately in the condenser.

Cyclic Acetals from Bromo-acetaldehyde and Polyhydroxy Derivatives

Condensations between bromo-acetaldehyde and polyalcohols have not hitherto been carried out. Freundler and Ledru[8] showed that ethyl and methyl bromo-acetals can be obtained with a yield of 50% by adding an excess of the corresponding alcohol directly to the cooled mixture of crude bromo-acetaldehyde and hydrobromic acid obtained from the bromination of paracetaldehyde. It seemed possible that a similar crude product might also be used for the synthesis of cyclic acetals (condensation with polyalcohols) and this, as indicated below, was found to be the case.

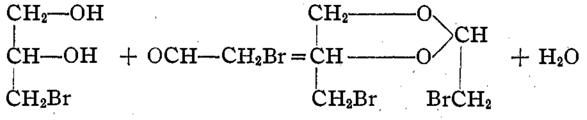
Condensation of Bromo-acetaldehyde with α-Bromohydrin

Formation of Bromo-ethylidene Bromohydrin

Preparation of α-Monobromohydrin.—Pure α-bromohydrin was prepared by Carré's method[16] of heating an aqueous solution of glycerol and hydrobromic acid; yield, 50–54%; b. p., 127° at 12 mm. Carré gives 134° at 16 mm.

Analysis. Subs., 0.4063: AgBr, 0.4836. Calc. for $C_3H_7O_2Br$: Br, 51.61. Found: 51.63.

Condensation of α-Bromohydrin with (Crude) Bromo-acetaldehyde.—



$$\begin{array}{l} CH_2\text{—}OH \\ | \\ CH\text{—}OH \\ | \\ CH_2Br \end{array} + OCH\text{—}CH_2Br = \begin{array}{l} CH_2\text{———}O \\ | \\ CH\text{———}O \\ | \\ CH_2Br \end{array} \!\!\!> \begin{array}{l} CH \\ | \\ BrCH_2 \end{array} + H_2O$$

The best yield was obtained in the following manner: 150 g. of pure, dry paracetaldehyde was brominated with 480 g. of bromine as described in the preparation of parabromo-acetaldehyde, except that in this experiment the stirring in the cold was continued after all the bromine had been added, until decolorization was nearly complete. At this point 280 g. of bromohydrin (60% of the amount calculated on the weight of paracetaldehyde taken) was run into the flask rather rapidly, and the agitation continued, the temperature rising somewhat in spite of the surrounding freezing mixture. The cooling bath was then removed, the mixture stirred at ordinary temperature for an hour, and allowed to stand overnight. The straw-colored lower layer was extracted with

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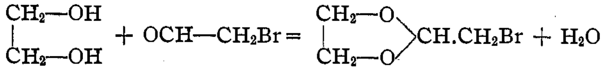
[16] Carré, *Bull. soc. chim.*, [4] 7, 835 (1910).

ether, the ether solution washed with water, and then neutralized by shaking with 5% caustic soda solution. It was then washed with a concentrated solution of sodium bisulfite, and finally dried over sodium sulfate. The ether was removed under diminished pressure, and the reddish residue fractionated under reduced pressure. A small amount of low-boiling material came over between 40° and 125° (15–25 mm.). The main fraction distilled constantly at 125° (15 mm.), the temperature rising near the end to 135° (15 mm.). There was a large amount of dark residue left in the flask. The fraction between 125° and 130° (15 mm.), was redistilled and a pure product obtained which boiled sharply at 118–120° (10 mm.). The yield of bromo-ethylidene bromohydrin was 250 g., which represented 56% of the value calculated on the weight of bromohydrin taken. The product thus obtained was a heavy oil, insoluble in water but readily soluble in organic solvents. It was colorless when first distilled, but on standing changed to a light, straw color.

Analyses. Subs., 0.1826: AgBr, 0.2630. Calc. for $C_5H_8O_2Br_2$: Br, 61.54. Found: 61.30. Subs., 0.4219: benzene, 18.43 g., Δt (cryoscopic method), 0.459°. Calc. for $C_5H_8O_2Br_2$: mol. wt., 260. Found: 249.

Preparation of Bromo-ethylidene Glycol.—This was prepared by the same method, using an equivalent amount of ethylene glycol.



$$\begin{matrix}CH_2-OH\\ |\\ CH_2-OH\end{matrix} + OCH-CH_2Br = \begin{matrix}CH_2-O\\ |\\ CH_2-O\end{matrix}\!\!>CH.CH_2Br + H_2O$$

The yields obtained varied from 25–28%, calculated on the weight of glycol taken. In this case the final refractionation was best accomplished under ordinary pressure. The product was a heavy, colorless oil, b. p. 63–65° at 12 mm., or 175° at atmospheric pressure, and possessed an odor somewhat resembling ethylene bromide, although somewhat irritating. It dissolved readily in organic solvents but was insoluble in water.

Analysis. Subs., 0.1975: AgBr, 0.2234. Calc. for $C_4H_7O_2Br$: Br, 47.91. Found: 48.16.

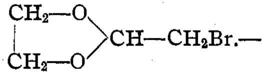
An attempt to prepare the corresponding condensation products of bromo-acetaldehyde with glycerol and mannitol failed to give appreciable yields, due probably to the large amount of hydrobromic acid present in the crude bromination product. This acid, while an excellent condensing agent, would undoubtedly tend to favor the formation of other undesirable reactions of the glycols and glycerol, such as bromohydrin formation, etc., a danger obviously much less pronounced in the case of bromohydrin itself.

Preparation of Cyclic Acetals from "Crude Extracted" Bromo-acetaldehyde

A simpler and more convenient method—giving better yields and purer products—for obtaining the condensation products of bromo-acetaldehyde with ethylene glycol, trimethylene glycol, and glycerol was found to consist in the use of a "crude extracted sirup" containing a high percentage of bromo-acetaldehyde, and prepared as follows.

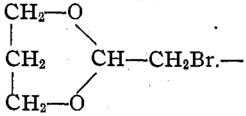
One hundred g. of pure paracetaldehyde was brominated in the same manner as in the preparation of parabromo-acetaldehyde, except that the experiment was performed in diffused light, and also after the addition of the entire quantity of bromine, the agitation of the cooled mixture was continued until the color of bromine had practically disappeared. At this point an aqueous sludge containing about 150 g. of finely divided, crystalline sodium acetate was slowly added, and the temperature kept at about —5° to 0°. After the mixture had been stirred for a short time it was allowed to stand overnight at about 0°. Sufficient ice-water was added to dissolve the excess of sodium salts, and the mixture extracted four times with ether. The ether solution was cautiously neutralized with cold 5% sodium hydroxide solution, a rise in temperature being carefully avoided by cooling, washed free from alkali with a small amount of water, and dried over anhydrous sodium sulfate. Removal of the ether under reduced pressure left 175 g. of a light yellow sirup, which smelled strongly of bromo-acetaldehyde. The yield of crude bromo-acetaldehyde calculated on the weight of paracetaldehyde taken amounted to 71%. This material is the "crude extracted sirup" referred to in the following experiments.

It is possible that this "crude product," besides serving admirably for condensation reactions between bromo-acetaldehyde and polyalcohols, as indicated below, may also find a wide application in many synthetic operations involving the use of bromo-acetaldehyde.[17]

Preparation of Bromo-ethylidene Glycol, .—Seventy g. of "crude extracted sirup" prepared as above, and 32 g. of pure ethylene glycol were placed in a round-bottom flask equipped with a good stirrer, 10 drops of 40% sulfuric acid added, and the mixture was heated on the steam-bath with thorough agitation for 10 hours. Two layers were present from the start but the relative amount of the upper one increased progressively, due to the water formed in the reaction. There was no apparent decomposition or charring, the mixture at the end possessing a clear, light, straw color. It was extracted with ether, the latter solution neutralized with dil. sodium hydroxide solution, washed with a small amount of sodium bisulfite solution, washed again with water, and dried over anhydrous sodium sulfate. After the ether had been removed under reduced pressure, the temperature rose rapidly to 63° (12 mm.), about 75% of the entire amount distilling over constantly at 63–66° (12 mm). The distillation was stopped at this point, the residue in the flask being a light colored oil, from which on standing overnight a white crystalline product separated. This on purification proved to be parabromo-acetaldehyde (m. p., 104°), the yield of the polymer being 5 g. The bromo-ethylidene glycol on redistillation under ordinary pressure gave 35 g., (equivalent to a yield of about 42%), of a pure product boiling at 174–176°, and identical with that obtained by condensing glycol directly with the crude bromination product from paracetaldehyde.

Analysis. Subs., 0.1802: AgBr, 0.2041. Calc. for $C_4H_7O_2Br$: Br, 47.91. Found: 48.22.

When heated with an excess of 0.5 *N* aqueous potassium hydroxide at 100° and agitated vigorously for 24 hours bromo-ethylidene glycol undergoes a practically quantitative decomposition, the bromine being removed as potassium bromide. Extraction of the liquid with ether yields a viscous oil, presumably hydroxy-ethylidene glycol.

Preparation of Bromo-ethylidene-trimethylene Glycol,  Seventy g. of "crude extracted sirup," 40 g. of pure trimethylene glycol, and 10 drops of 40% sulfuric acid were heated together as described in the preceding experiment, and the reaction product extracted in a similar manner. There was obtained 48 g. of the crude cyclic acetal (b. p., 80–86° at 12 mm.), which upon distillation under ordinary

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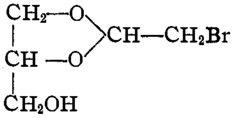
[17] It is intended to use this reagent for the further synthesis of various cyclic acetals and other derivatives related to the polysaccharides, and to study the properties of such derivatives and their corresponding hydroxy compounds.

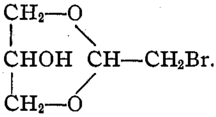
pressure gave 35 g. (40% yield) of the pure product, (b. p. 191–194°). It resembled closely in all its properties the lower homolog obtained in the preceding experiment.

Analysis. Subs., 0.1702: AgBr, 0.1786. Calc. for $C_5H_9O_2Br$: Br, 44.2. Found: 44.6.

Preparation of Bromo-ethylidene Glycerol,



or



—This was prepared from 125 g. of the "crude extracted sirup," 94 g. of pure glycerol, and 20 drops of 40% sulfuric acid, by the same procedure as described in the last two experiments. Fractionation of the crude product under reduced pressure (18 mm.) yielded, in addition to a small amount of a lower-boiling fraction, 105 g. of a liquid boiling at 140–150°, from which on refractionation, there was obtained 92 g. of pure bromo-ethylidene glycerol (b. p., 137–140 at 15 mm.) equivalent to a yield of 46%, calculated on the weight of the glycerol taken.

Analysis. Subs., 0.1740: AgBr, 0.1660. Calc. for $C_5H_9O_3Br$: Br, 40.6. Found: 40.6.

Bromo-ethylidene glycerol[18] is a colorless, viscous sirup, somewhat soluble in water,

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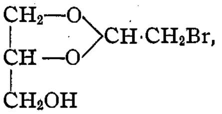
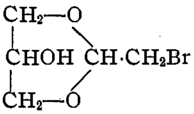
[18] Regarding the question as to whether this represents a 5- or 6-membered cyclic acetal, it seems probable, judging from analogy with other condensation products, such as *iso*propylidene glycerol [Irvine, McDonald and Soutar, *J. Chem. Soc.*, **107**, 337 (1915)], methylene glycerol [Peacock, *ibid.*, **107**, 815 (1915)], benzylidene glycerol, etc., that the product in this case contains a 5- and not a 6-membered ring; that is

(A)

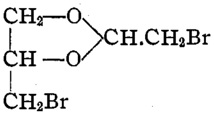


rather than: (B)

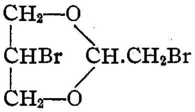


A definite decision could probably be reached by replacing the remaining hydroxyl group with Br, thus giving either

(C)

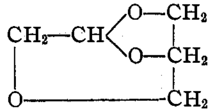


or (D)

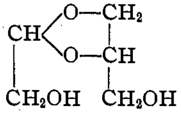


the constitution of (C) having already been established by direct synthesis as previously outlined. A number of researches are in progress in this Laboratory for the purpose of determining the relative stability and ease of formation of different cyclic acetal configurations. As will be shown in a forthcoming publication when a mixture of a 1,2-glycol (1 mole) and a 1,3-glycol (1 mole) is condensed with an aldehyde (1 mole) an "intermolecular partition" takes place, a much larger amount of the 6- than of the 5-membered ring being formed in each case. The condensation of glycerol (1 mole) with an aldehyde (1 mole) represents an "intramolecular partition" and it seems logical to assume that in these reactions 2 isomers (namely, a 5- and a 6-membered cyclic acetal) will be formed in each case, the relative amounts being dependent on the molecular configuration of the aldehyde employed. An investigation of such reactions is being carried out. H. H.

and readily soluble in alcohol or ether. When the substance was heated with 3.5% aqueous potassium hydroxide and vigorously agitated for 18 hours all of the bromine was removed as potassium bromide. Saturation of this alkaline liquid with potassium carbonate, extraction with ether, and fractionation of the anhydrous liquid left after evaporation of the ether yielded 2 products in approximately equal quantity: (a) a substance distilling at 70° (15 mm.) and rapidly solidifying to colorless crystals; and (b) a clear viscous sirup, b. p. 145° (15 mm.). The first product melted at about 30°, was readily soluble in all of the common solvents, and possessed a remarkably high vapor pressure at room temperature. It seems highly probable, from the mode of formation and properties that this was the bicyclic lactonyl derivative (IV), while the second was presumably hydroxyethylidine glycerol (V).[19]

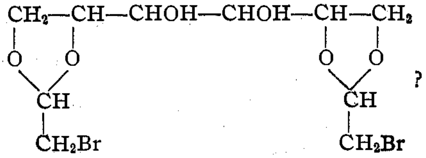


IV



V

Preparation of Di-(bromo-ethylidene) Mannitol,



—Attempts to prepare this condensation product by the use of the "crude bromo-acetaldehyde" were not successful, but good results were obtained by employing the pure product obtained by the distillation of parabromo-acetaldehyde, and adapting the procedure used by Meunier[20] for the preparation of tribenzylidene and tri-ethylidene mannitol.

Five g. of mannitol was dissolved in about 5 cc. of conc. hydrochloric acid, and to this solution (cooled by immersion in water) 9.3 g. of pure bromo-acetaldehyde (freshly prepared by the distillation of pure parabromo-acetaldehyde) was added. The mixture was shaken vigorously and after about 5 minutes began to thicken, and soon solidified. It was allowed to stand for an hour, and then stirred vigorously with an excess of cold water. The crude, colorless solid was washed free from acid with dil. sodium hydroxide solution, then shaken with water and finally air-dried at about 70°. It was found to be very insoluble in cold, but somewhat more soluble in hot benzene. This solvent was used for its purification, any crystalline parabromo-acetaldehyde present remaining in the mother liquor. The pure di-(bromo-ethylidene) mannitol separated from the filtered benzene solution in slender, white needles (m. p., 137–141°), the dried product having the appearance of a network of silk fibres. The crystals were readily soluble in hot water and alcohol much less soluble in cold; they were also moderately soluble in ether. A second recrystallization from benzene produced no change in the melting point (137–141°), or in the appearance of the crystals.

Analysis. Subs., 0.1677: AgBr, 0.1612. Calc. for $C_{10}H_{16}O_6Br_2$: Br, 41.0. Found: 40.9.

A repetition of the above experiment, using an excess of either bromo-acetaldehyde

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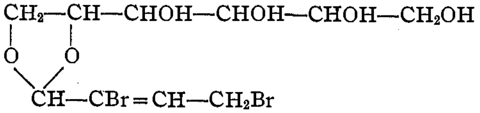
[19] The products obtained in these and analogous reactions are being investigated with a view to determining both the physical and chemical properties of such ring structures.

[20] Meunier, *Compt. rend.*, **107**, 910 (1888); **108**, 408 (1889).

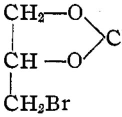
or mannitol, yielded a product identical with the above. There was no evidence of the formation of either a tri- or a monobromo-ethylidene derivative.

The product obtained gave no evidence of being unsaturated, which precludes the possibility of its being an isomer of a somewhat different type, such as



formed by a preliminary "crotonization" of bromo-acetaldehyde, $CH_2Br-CHO + CH_2Br-CHO \longrightarrow CH_2Br-CH=CBr-CHO + H_2O$, and condensation of the latter product with mannitol.

Condensation of Acetaldehyde with α-Bromohydrin. Use of Iodine as Catalyst,



—Forty g. of α-bromohydrin was mixed with 30 g. of acetaldehyde, a trace of iodine was added as a catalyst,[21] and the mixture heated gently on the steam-bath for 5 to 6 hours, during which a separation into 2 layers gradually took place. The heavier oil was separated from the aqueous layer, washed with water, dried over calcium chloride, filtered and fractionated under ordinary pressure. The greater part distilled within the range 165–170°, and on refractionation yielded 30 g. of a colorless oil, boiling constantly at 168–169°, and corresponding to a yield of 70%.

It was insoluble in water, soluble in ether and alcohol and possessed a somewhat pleasant odor. On standing it acquired a faint yellow color.

Analysis. Subs., 0.2703: AgBr, 0.2773. Calc. for $C_5H_9O_2Br$: Br, 44.2. Found: 43.7.

Summary

1. Methods are described for the preparation from paracetaldehyde of pure parabromo-acetaldehyde and monobromo-acetaldehyde. An account is given of their properties including the conversion of the one into the other.

2. A simplified process is given for the manufacture of a "crude bromo-acetaldehyde" which can be employed in place of the pure product for various condensation reactions.

3. The preparation of new cyclic acetals by the condensation of ethylene glycol, trimethylene glycol, glycerol, glycerol bromohydrin, and mannitol with bromo-acetaldehyde is described, and the behavior of such acetals towards chemical reagents indicated.

4. These acetals on treatment with alkalies yield the corresponding hydroxy derivatives, the configuration of the latter being closely related to that of various anhydro-sugars and polysaccharides.

In conclusion the authors desire to express their hearty thanks to E. I. du Pont de Nemours and Company, through whose goodwill this work was rendered possible, as well as to acknowledge gratefully the kind as-

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[21] See Hibbert, This Journal, **37**, 1762 (1915).

sistance rendered to them in the form of a grant from the Warren Fund of the American Academy of Arts and Sciences for the purchase of supplies.

New Haven, Connecticut

[Contribution from the Chemical Laboratory of Washington University]

THE DECOMPOSITION OF THE AMINOBENZOIC ACIDS BY BOILING WATER

By L. McMaster and R. L. Shriner

Received October 2, 1922

The decomposition of anthranilic acid, when heated above its melting point, into carbon dioxide and aniline is well known. Fritzsche[1] identified the gas evolved as carbon dioxide and Liebig[2] showed that the oily distillate obtained was aniline. Powlewski[3] studied this decomposition and found it to be complete when the acid was heated for 1 hour at 205–210°.

The *m*-aminobenzoic acid yields carbon dioxide, aniline and ammonia on treatment with caustic potash[4] and the *p*-aminobenzoic acid gives aniline and carbon dioxide when treated with conc. hydrochloric acid.[5] However, no mention is made of the effect of heating aqueous solutions of these acids.

The object of this investigation was to study not only the decomposition of the aminobenzoic acids by boiling water but also to determine the rate of decomposition and the volatility of the acids with steam.

Experimental Part

Products of Decomposition.—The presence or absence of aniline and carbon dioxide as products of the decomposition was ascertained by boiling 5g. samples of the pure acids[6] with water under a short reflux condenser for 3 hours, the gases evolved being led into a tube of lime-water protected by a tube of soda lime. The solutions were then neutralized with sodium hydroxide, extracted with ether, and the ether extracts tested for aniline. It was found that the *ortho* and *para* acids gave aniline and carbon dioxide while the *meta* acid did not.

Rate of Decomposition.—Weighed samples of the acids were placed in Erlenmeyer flasks and distilled water was added. The flasks were heated just to boiling over the Bunsen flame, and then transferred to an electric hot plate, where gentle boiling was maintained for the desired length of time. During this period the carbon dioxide and aniline escaped from the

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[1] Fritzsche, *Ann.*, **39**, 86 (1841).

[2] Liebig, *ibid.*, **39**, 94 (1841).

[3] Powlewski, *Ber.*, **37**, 592 (1904).

[4] Beilstein, "Handbuch der Organischen Chemie," Voss **1896**, II, 1256.

[5] Weith, *Ber.*, 1, 105 (1879).

[6] We wish to thank the Monsanto Chemical Works of St. Louis for the anthranilic acid which was prepared and purified by them for us.