NOVEL REACTIONS OF GLYOXAL

By

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INTRODUCTION

The acid-catalyzed Prins type reaction of olefins with aldehydes and aldehyde-like compounds has been under active study by several members of the Department of Chemistry at Oklahoma A. and M. College for several years. Kohn (16) initiated the study. He was followed by Yuk (34) and prominently by Hawkins (11,12) and Sturzenegger (29).

The initial purpose of this investigation was to extend the Prins type reaction to glyoxal and to the simple aliphatic acetals of glyoxal. When it was learned that the commerical 30% solution of glyoxal does not react with isobutylene under acid conditions, and that preparation of tetramethyl and tetraethyl acetals of glyoxal from the commercial glyoxal solution is unsatisfactory because of low yields, the investigation resolved itself into the preparation of cyclic acetals of glyoxal from the commercial solution and all available aliphatic diols. After the reaction of glyoxal with several diols had been studied, the investigation was extended to include some alkanolamines and diamines which had not been tested in this reaction.

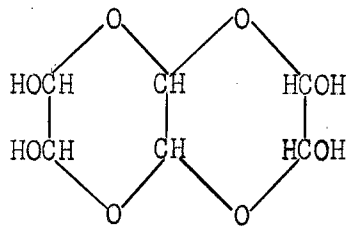
Since the fundamental purpose of this work was to find new reactions of the commercial glyoxal solution, little effort was expended in determining optimum conditions for the reactions.

HISTORICAL

Since Yuk (34) made a study of glyoxal acetals and related compounds in these laboratories and has written a thorough history of glyoxal in that connection, it seems that only a brief review and modernization of that history will be sufficient here.

Glyoxal in the monomeric state is the simplest known colored organic compound (31). The monomer was obtained by Hess and Uibrig (14) by heating polyglyoxal with anethole, phenetole, safrole, methyl nonyl ketone or benzaldehyde. Glyoxal monomer is a yellow, crystaline compound which melts to a green liquid at 15° and boils at 50° to give a green gas (31). The monomer was also prepared by distilling the polymer with phosphorus pentoxide (10), and by distilling the polymer at 150 mm. at 75° to 90° (30). The monomer is stable for only a few hours. Even at 0° it polymerizes to paraglyoxal. A small amount of water seems to catalyze the polymerization, but a large amount of water causes extensive hydration which represses polymerization.

Trimeric glyoxal has been prepared (10). Raudnitz (25) and Dyson (7) studied the structure of trimeric glyoxal. Although different structures were proposed, Raudnitz's structure for the trimeric glyoxal, 2,3,6,7-tetrahydroxy-p-dioxano-[b]-p-dioxane,



is generally accepted as correct.

Acetals of glyoxal have been prepared by various methods. Generally, glyoxal sulfate has been the source of glyoxal (2,8), though other methods are now known (18,27,34). Glyoxal sulfate was prepared by the action of fuming sulfuric acid on a symetrical tetrahaloethane. Impure tetraethyl acetal of glyoxal was obtained by heating sodium ethoxide with dichloroacetaldehyde (23) and by reacting trimeric glyoxal with absolute ethyl alcohol and hydrogen chloride at ordinary temperature (10).

A cyclic acetal of glyoxal, p-dioxano-[b]-p-dioxane, was formed by the reaction of ethylene glycol with glyoxal in the presence of hydrochloric acid as a catalyst (6). It was also obtained from the chlorination of ethylene glycol and by the reaction of ethylene glycol and 2,3-dichlorodioxane (3). The corresponding diethylenemercaptal, bis-trimethylenemercaptal, and tetraphenylmercaptal of glyoxal were prepared from 2,3-dichlorodioxane and the corresponding thiol (24). The mixed oxygen-sulfur compounds were not obtained.

The tetraacylals, also called tetraalkanoates, $(RCOO)_2CH\text{-}CH(OCOR)_2$, have been prepared from glyoxal and glyoxal derivatives (1,8,14).

Yuk (34) applied Henry's method (13) in the preparation of α-chloro ethers of glyoxal. The commercial 30% solution of glyoxal was evaporated to about half its original volume. The viscous material remaining was

dissolved in the desired alcohol, cooled to 0° to 10° and hydrogen chloride was passed into the solution. The water-soluble portion was extracted with ice water. The crude α-chloro ether which comprised the lower layer was distilled at reduced pressures. Molecular weight and chlorine content indicated that a slightly impure product was obtained. It has been suggested that the α-chloro ethers are too unstable to be kept at room temperature (27) or distilled even at reduced pressure (34). The α-chloro ether 1,2-dichloro-1,2-dimethoxyethane has been prepared by chlorinating 1,2-dimethoxyethylene (27). Here too, the α-chloro compound was not isolated. Instead, it was reacted with methanol or sodium methoxide to produce the tetramethyl acetal of glyoxal. Another example, 1,2-dibromo-1,2-diethoxyethane, was prepared by bromination 1,2-diethoxyethylene (19). The α-bromo ether decomposed readily to glyoxal, ethanol and hydrogen bromide. The sodium bisulfite addition product of glyoxal is known to react with acetic anhydride and hydrochloric acid to produce 1,2-dichloro-1,2-diacetoxyethane,

$$CH_3COOCH(Cl)-CH(Cl)OCOCH_3$$

EXPERIMENTAL

Prins Reaction of Glyoxal with Isobutylene

The boron trifluoride-catalyzed reaction between glyoxal, as found in the commercial 30% solution, and isobutylene was conducted in several steps. Thirty-five milliliters of water was distilled from 100 ml. of glyoxal solution. The remaining 65 ml. of glyoxal solution was placed in a three-necked flask fitted with a mechanical stirring apparatus. The solution was cooled to 0° to 10°. The temperature was kept within that range while boron trifluoride was bubbled into the solution for one hour. The mixture became dark reddish-brown. Isobutylene was then bubbled into the mixture for another hour. The ice bath was removed and stirring continued while the temperature was brought back slowly to room temperature. Finally, the reaction mixture was neutralized with a 10% sodium hydroxide solution.

A portion of the mixture was distilled at atmospheric pressure. No reaction product of glyoxal and isobutylene was obtained. Instead, a quantity of highly polymerized glyoxal remained in the distilling flask. Salting out of the product with calcium chloride and sodium chloride failed to give any evidence that a reaction had taken place.

Since concentrating the glyoxal by distilling out water caused extensive polymerization, a suitable reaction of the polymer seemed unlikely. Another run was attempted without the initial distillation of water from the solution. The addition of boron trifluoride,

isobutylene and neutralization were conducted in the same manner as in the first run. Again, the desired reaction did not occur.

Preparation of Acyclic Acetals of Glyoxal

Tetramethyl acetal of glyoxal by alcoholysis of the tetrabutyl acetal.

$$(C_4H_9O)_2CHCH(OC_4H_9)_2 + 4CH_3OH \xrightarrow{H^+} (CH_3O)_2CHCH(OCH_3)_2 + 4C_4H_9OH$$

The tetrabutyl acetal of glyoxal was made from the commerical glyoxal solution in the manner described by Yuk (34). One hundred grams of the crude tetrabutyl acetal was dissolved in an excess of methanol to which 1 ml. of concentrated sulfuric acid had been added. The mixture was refluxed four hours and the catalyst neutralized with sodium bicarbonate. The reaction mixture was distilled at reduced pressure. A small yield of the tetramethyl acetal was obtained. A large portion of the reaction mixture distilled between the boiling points of the tetramethyl and tetrabutyl acetals. That boiling range indicated that the various possible mixed methyl butyl acetals had been produced. Since separation of these compounds at reduced pressure would have been difficult, this method of producing the tetramethyl acetal was abandoned.

Tetramethyl acetal of glyoxal from the α-chloro ether.

$$\begin{matrix} HC{=}O \\ HC{=}O \end{matrix} + 2CH_3OH + 2HCl \longrightarrow CH_3O\underset{Cl}{C}H-\underset{Cl}{C}HOCH_3 + 2H_2O$$

$$CH_3O\underset{Cl}{C}H-\underset{Cl}{C}HOCH_3 + 2CH_3OH \longrightarrow (CH_3O)_2CH-CH(OCH_3)_2 + 2HCl$$

Fifty milliliters of water was distilled from 100 ml. of glyoxal

solution. The remaining 50 ml. of amber, quite viscous, sticky glyoxal solution was dissolved in 75 ml. of anhydrous methanol. The alcoholic solution was placed in a three-necked flask fitted with a mechanical stirring apparatus. The mixture was cooled to 0° to 10° and kept within that temperature range for 20 minutes while anhydrous hydrogen chloride was passed into it. The mixture became dark brown. Stirring was continued for 30 minutes during which time the aspirator pulled air through the mixture to remove any excess, dissolved hydrogen chloride.

The mixture was distilled rapidly at 70 mm. without regard to fractionation. Forty milliliters of clear liquid was distilled and 15 g. of residue remained in the still pot. The residue was probably polymerized glyoxal. After standing overnight in the refrigerator, the distillate showed a light brown color. The odor of hydrogen chloride was easily discernible. The crude α-chloro ether was dried over calcium chloride. Without any further attempt at purification, it was dissolved in 50 ml. of anhydrous methanol. The mixture was heated to 60° and kept there until no more hydrogen chloride was given off. The reaction mixture was fractionated through a Todd column. No yield of the tetramethyl acetal was detected. The distillate had the odor of hydrogen chloride. It seemed that enough hydrogen chloride remained in the mixture to destroy any acetal which might have been formed.

Tetraethyl acetal of glyoxal from the α-chloro ether.

$$\begin{matrix} HC{=}O \\ | \\ HC{=}O \end{matrix} + 2C_2H_5OH + 2HCl \longrightarrow C_2H_5O\text{-}\underset{Cl}{\underset{|}{C}}H\text{-}\underset{Cl}{\underset{|}{C}}HOC_2H_5 + 2H_2O$$

$$C_2H_5O\underset{Cl}{\underset{|}{C}}H\text{-}\underset{Cl}{\underset{|}{C}}HOC_2H_5 + 2C_2H_5OH \longrightarrow (C_2H_5O)_2CHCH(OC_2H_5)_2 + 2HCl$$

Seventy-five milliliters of glyoxal solution was dissolved in 100 ml. of 95% ethanol. The alcoholic solution was cooled to 0° to 10° in a three-necked flask fitted with a mechanical stirring apparatus. Hydrogen chloride was passed into the solution for two hours at 0° to 10°. The ice bath was removed and the temperature rose slowly to that of the room.

Since the homologous compound prepared from propyl alcohol is insoluble in water, a separation of the ethyl homolog seemed possible. The ethyl compound, however, remained soluble even in ice water saturated with sodium chloride.

Fractionation of the reaction mixture at 45 mm. through a Todd column gave a plateau at 52° to 54°. Twenty-five milliliters of the distillate from that cut was dissolved in 125 ml. of absolute ethanol and dried over anhydrous sodium sulfate for one day. The mixture remained acid. Calcium oxide was added to neutralize the acid and to take up any water present. The reaction products were fractionated at 45 mm. through a Todd column. The boiling point went no higher than 40°. Since the tetraethyl acetal boils from 90° to 92° at 17 mm., it seemed reasonable to conclude that no tetraethyl acetal had been produced by the above procedure. No attempt was made to identify or characterize the product(s) formed.

Another method of removing water from the glyoxal solution was attempted in the next run. Seventy-five milliliters of glyoxal solution, 200 ml. of 95% ethanol and 150 ml. of benzene were distilled. The distillate separated into two layers. The upper layer comprised about 84% of the total distillate and contained 85% benzene, 15% ethanol and only 0.5% water (20). The lower layer contained 32% water, 11.6% benzene and 58% ethanol. The upper layer was returned to the distilling flask. When no more water could be distilled, 100 ml. of absolute ethanol was added to the mixture to assure an excess. Anhydrous hydrogen chloride was passed into the mixture as in the previous run. The reaction mixture separated into two layers, but after saturation with hydrogen chloride the two layers became homogenous.

The reaction mixture was attached to a reflux condenser and heated to 60°. Air was pulled through the reaction mixture to remove the excess hydrogen chloride and the hydrogen chloride produced by the reaction of the α-chloro ether with ethanol. Air, however, did not remove all the hydrogen chloride. The reaction mixture was allowed to stand over calcium oxide to dry as well as to neutralize the acid present. It was fractionated at 45 mm. through a Todd column. A cut was taken between 115° and 118°. The boiling point and refractive index indicated that the tetraethyl acetal had been produced.

Since the removal of water from a 75-milliliter sample of glyoxal solution by the method described here required 56 hours of continuous distillation, production of the tetraethyl acetal in quantity by this procedure did not seem feasible. The ultimate yield of tetraethyl acetal of glyoxal based on the initial quantity of glyoxal was 20%.

Preparation of Glyoxal Tetraacetate

Since it is known that alcohols boiling above 100° convert acidified glyoxal solutions to the tetraacetals, and since acetic acid is cheap and boils above 100°, the conversion represented by the following equations was attempted:

$$\begin{matrix} HC{=}O \\ HC{=}O \end{matrix} + 4CH_3COOH \xrightarrow{H^+} (CH_3COO)_2CHCH(OCOCH_3)_2 + 2H_2O$$

Glyoxal tetraacetate is known (1,8,14), and would presumably function satisfactorily in the Prins reaction with olefins.

A flask containing 250 ml. of glyoxal solution, 450 ml. of glacial acetic acid and 1 ml. of concentrated sulfuric acid was attached to an Oldershaw column and the mixture distilled. Distillation was continued until 265 ml. of distillate had been collected below 104°. The reaction mixture became an amber color early in the distillation and grew progressively darker until it was almost black. It was discarded as being devoid of the expected compound.

Toluene was added in the second attempt so that the toluene-water azeotrope which boils at 84° to 85° (15) would prevent high temperatures during distillation. After the distillation had proceeded about two hours, a white solid appeared in granular form. The quantity of this material increased and the color darkened until the distillation was stopped. Even though the temperature went no higher than the boiling point of the toluene-acetic acid azeotrope, 103° to 104°, there was extensive charring. This reaction mixture was also discarded.

In the third attempt no catalyst was used. Water was distilled from 85 ml. of glyoxal solution, 100 ml. of acetic anhydride and 60 ml. of acetic acid. Here again extensive charring occured. No tetraacetate

of glyoxal was thought to have formed.

In the fourth attempt p-dioxano-[b]-p-dioxane was refluxed two hours with an acetylating mixture. The acetylating mixture contained three moles of acetic anhydride, two moles of acetic acid and one-half milliliter of orthophosphoric acid. Sodium acetate was added to destroy the catalyst. The acetic anhydride and acetic acid were removed by distillation. A white solid crystallized from the residue. It was identified by mixed melting point as the starting material p-dioxano-[b]-p-dioxane. No glyoxal tetraacetate was thought to have formed. For the preparation of p-dioxano-[b]-p-dioxane, see below.

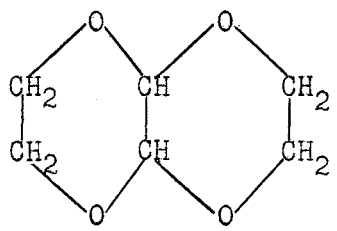
Preparation of Cyclic Acetals of Glyoxal

The procedure used in the preparation of the cyclic acetals is described in detail for the 1,2-ethanediol reaction and is referred to thereafter as the general procedure. Briefly, one-half mole of glyoxal, two moles of the diol and one-half milliliter of sulfuric acid were distilled until all the water was removed. The catalyst was neutralized with anhydrous sodium acetate. Purification methods are described separately.

1,2-Ethanediol and glyoxal. Water was distilled from a solution of 85 ml. of the commercial glyoxal, 124 g. of 1,2-ethanediol and 0.5 ml. of concentrated sulfuric acid. When all the water had been removed as indicated by a sudden increase in the boiling point, distillation was stopped. The catalytic effect of the acid was nullified with anhydrous sodium acetate. Distillation of the reaction mixture was resumed. The boiling point went to 190°. At that temperature 1,2-ethanediol and a clear liquid which crystallized to a white solid

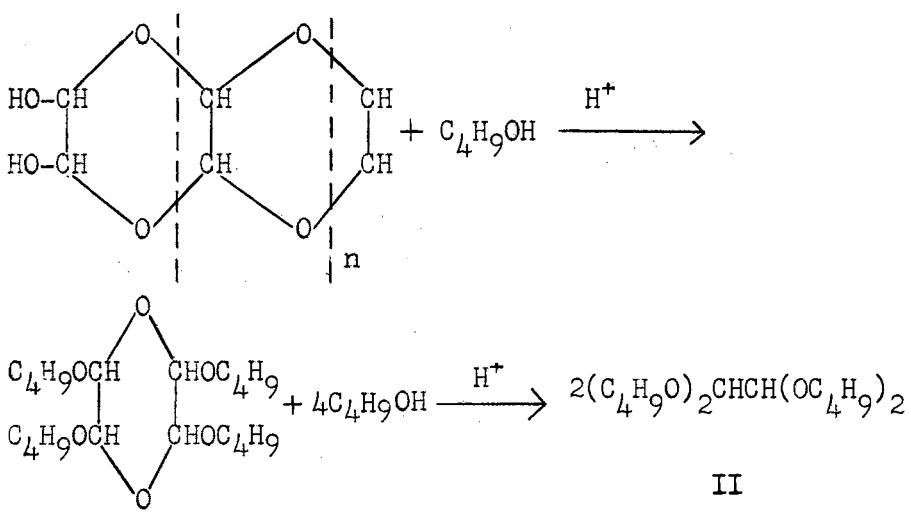
distilled. The boiling point ultimately reached 215°. Only a few grams of charred material remained in the still pot. The solid was filtered out of the 1,2-ethanediol and recrystallized three times from isopropyl ether containing 5% ethanol. It was recrystallized twice from benzene.

The melting point of the product became constant, though not sharp, at 106° to 110°. The melting point of the expected compound, p-dioxano-[b]-p-dioxane,

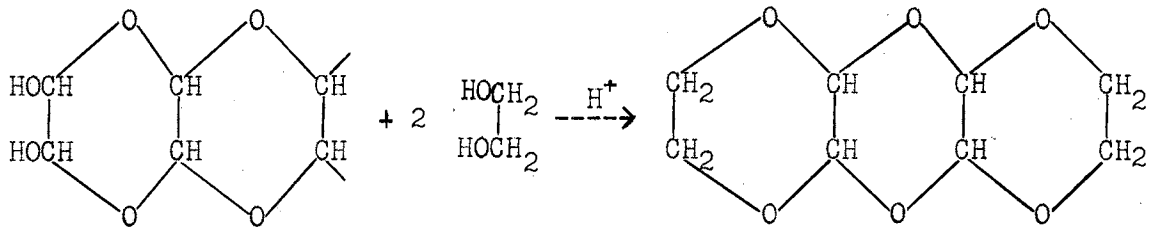


is reported in the literature as 134° to 135° (2,34).

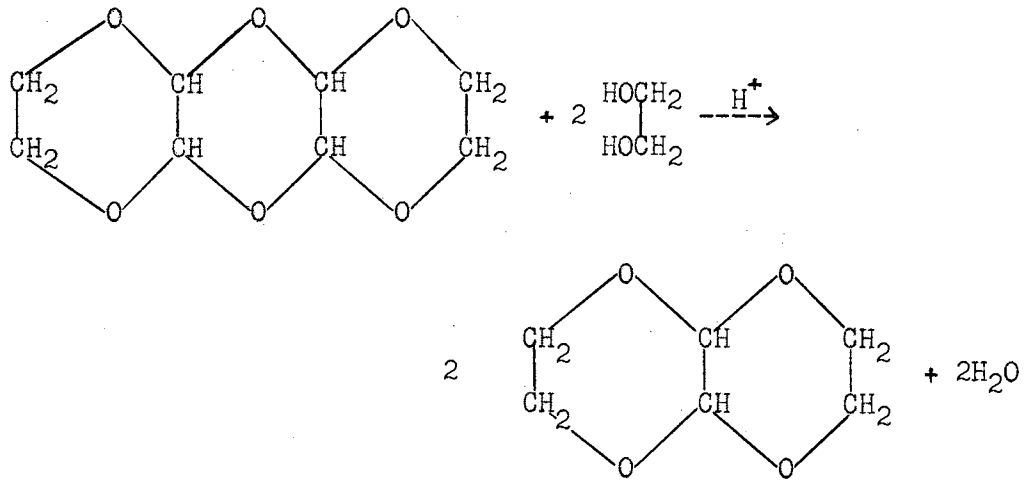
Since Yuk (34) found that 2,3,5,6-tetrabutoxy-1,4-dioxane (I) was produced by one of the side reactions, or more accurately, by an incomplete reaction in the preparation of tetrabutyl acetal of glyoxal,



it seemed likely that an analogous reaction could have taken place in the 1,2-ethanediol reaction with glyoxal



III



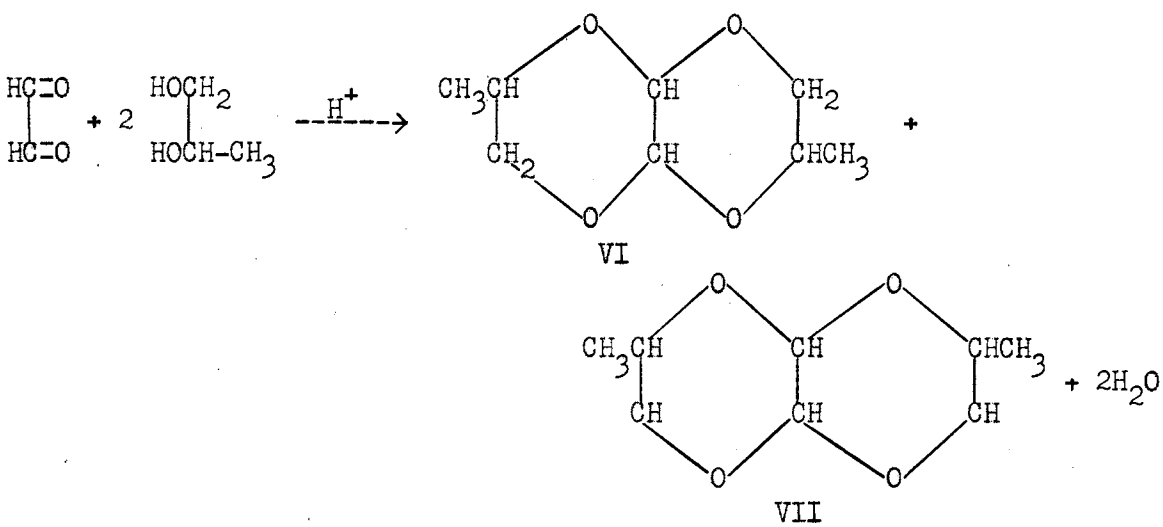
IV

Another run was made to produce an adequate quantity of the product(s) for fractionation through a Todd column. The results of the second run exactly duplicated those of the first.

The solid was fractionated at atmospheric pressure in anticipation of a more thorough separation. The distillate was divided into five fractions although the boiling point varied only 3.5° --from 212° to 215.5°. The melting points of the first and fifth cuts were found to be identical and found not to have changed from the 106° to 110° range. Molecular weight determinations by the freezing point depression of benzene were made on the first and fifth cuts. They were found to be 145 to 143 respectively. The theoretical molecular weight of IV is 146.14. The molecular weights as determined agreed so well with the

theoretical value that it was assumed IV had been produced as the major product.

<u>1,2-Propanediol and glyoxal</u>. After the general procedure was applied to this reaction mixture, forty milliliters of crude product was rapidly distilled. This crude product was fractionated at atmospheric pressure through a Todd column. Twenty-one milliliters of distillate was collected at 218° to 218.5°. A reflux-ratio of eight-to-one was used. The take-off rate was eight milliliters an hour. The boiling point increased steadily to 230° after the 218° fraction was taken. Distillation was stopped. Two milliliters of liquid residue remained in the still pot. A small quantity of white solid crystallized from the residue when it cooled. No attempt was made to identify or characterize this solid. Two structural isomers, 2,6-dimethyl-*p*-dioxano-[b]-*p*-dioxane (VI) and 2,7-dimethyl-*p*-dioxano-[b]-*p*-dioxane (VII),

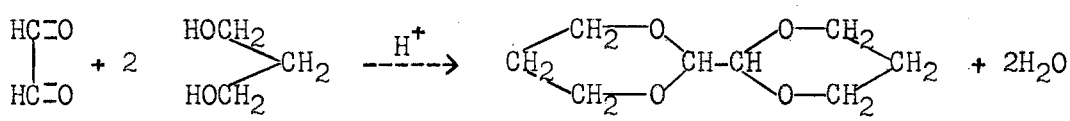


However, no effort was expended in their separation. Characterization of the fraction collected at 218° to 218.5° was conducted as though it were one pure compound. It probably contained the two isomers.

Properties of the 1,2-propanediol-glyoxal reaction product(s)

	Found	Theoretical
Molecular weight	175	174.19
Carbon content, %	55.3, 54.9	55.16
Hydrogen content, %	7.9, 8.3	8.10
Refractive index, $n_D^{20^\circ}$	1.4417	
Molecular refraction	41.7	41.32
Density, g./ml. at 20°	1.107	
Boiling point at 744 mm.	218-218.5°	

1,3-Propanediol and glyoxal. The general procedure was applied and the reaction product was distilled at 120 mm. and 180° to 225°. A white solid crystallized out of the water-clear distillate. The solid was filtered out of the excess diol and recrystallized four times from isopropyl ether containing 5% ethanol. The predicted reaction



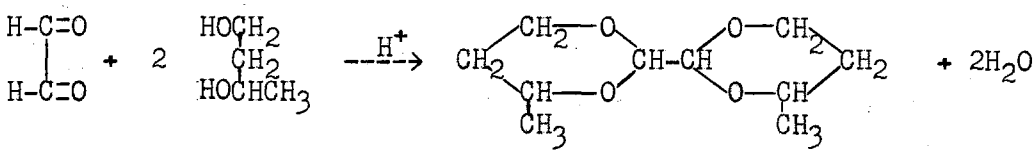
VIII

is believed to have produced 2,2'-bi-1,3-dioxane (VIII).

Properties of the 1,3-propanediol-glyoxal reaction product

	Found	Theoretical
Molecular weight	172	174.19
Carbon content, %	55.2, 55.6	55.16
Hydrogen content, %	8.4, 8.3	8.10
Melting point	155-156°	

1,3-Butanediol and glyoxal. The general procedure was followed and the reaction mixture was distilled rapidly at reduced pressure. The crude product was fractionated at 11 mm. through a Todd column. The boiling point increased steadily to 140° and leveled off. After five milliliters of distillate was collected at 140° a white solid appeared in the take-off head and made further distillation impossible. The distillate collected at 140° also solidified. It was recrystallized once from isopropyl ether in preparation for characterization. The compound, 2,2'-bi-(4-methyl-1,3-dioxane) (IX), is believed to have been produced by the following reaction:



IX

Properties of the 1,3-butanediol-glyoxal reaction product

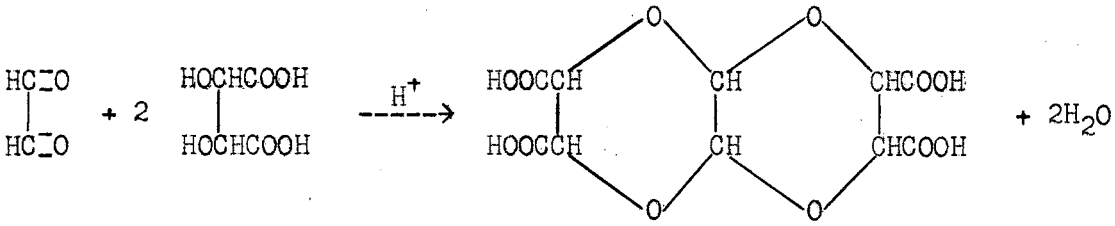
	Found	Theoretical
Molecular weight	198	202.24
Carbon content, %	59.2, 59.5	59.38
Hydrogen content, %	9.3, 9.3	8.97
Melting point	94-95°	
Boiling point at 11 mm.	140°	

2,3-Butanediol and glyoxal. While the general procedure was being applied, the reaction mixture became quite dark and viscous. Distillation of the reaction product was attempted, but pyrolysis occurred even at 5 mm.

Another run using a milder catalyst was made. The sulfuric acid generally used was replaced by orthophosphoric acid. The results of the first run were duplicated.

1,2,3,-Propanetriol (glycerol) and glyoxal. The expected reaction did not take place when the general procedure was applied to these reactants. Instead 75 to 80 grams of brown resin was produced. From the difference between the amount of the triol added initially and that recovered it appeared that nearly the theoretical amount had reacted. Characterization of the resin was not undertaken. No other attempt was made to produce the desired reaction.

2,3-Dihydroxybutane-1,4-dicarboxylic acid (tartaric acid) and glyoxal. The racemic form of the acid was used in the general procedure. The expected reaction was as follows:



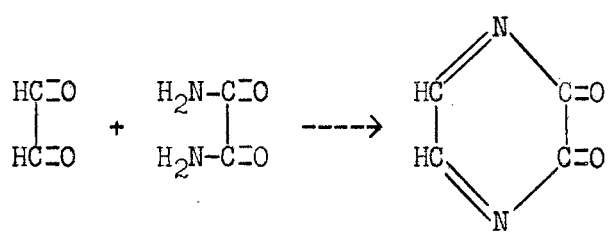
but as water was removed by distillation the mixture became quite dark and viscous and gave the oror of caramel. A black, brittle solid was produced. Its chemical character was not determined.

Miscellaneous Reactions Attempted

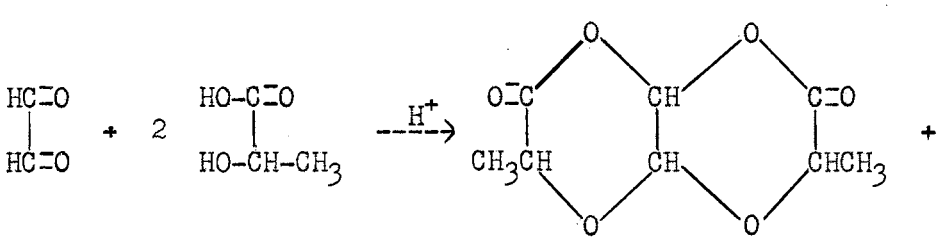
2-Hydroxyethylamine and glyoxal. The reaction mixture comprised 80 ml. of glyoxal solution and 122 ml. of 2-hydroxyethylamine (ethanolamine). It was expected to give the following reaction:

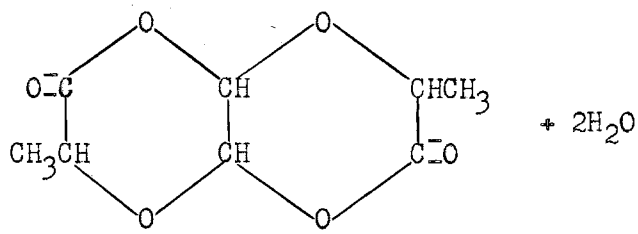
The glyoxal solution was cooled to 0° to 10° and stirred thoroughly while the amine was added slowly. The reaction mixture became quite hot even though it was kept in an ice bath. After all the amine had been added, the mixture was stirred for 30 minutes. It was fractionated at 20 mm. through a Todd column. A fraction which comprised nearly 80% of the mixture was taken at 85° to 86°. This fraction was identified as 2-hydroxyethylamine by its refractive index (17) and by its picrate derivative (28). It appeared that little or no reaction between the amine and glyoxal had taken place even though an unusually large amount of heat was produced when the two compounds were mixed.

Oxamide and glyoxal. The reaction mixture was made up of 80 ml. glyoxal solution and 50 g. of oxamide. It was refluxed for six hours. The mixture darkened considerably. The oxamide remained insoluble, and altogether evidence of any favorable reaction was lacking. By analogy, the reaction as follows was expected:



2-Hydroxypropionic acid (lactic acid) and glyoxal. The general procedure was applied in the expectation of the following reaction:

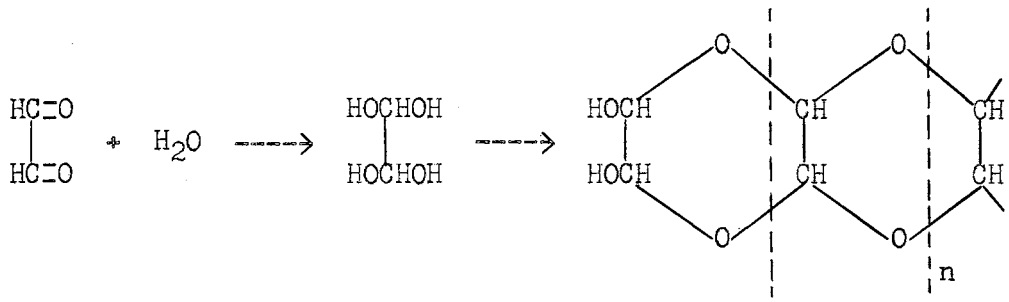




As water was distilled from the reaction mixture, however, the color of the mixture became progressively darker until it was almost black. The tarry mass remaining in the distilling flask solidified upon cooling. It was discarded as devoid of the wanted product(s).

DISCUSSION

Glyoxal in very dilute solutions exists as the hydrated monomer, but as the concentration increases the hydrate also increases in molecular weight.



At a 30% concentration glyoxal is believed to exist largely as a trimer or tetramer (4). The Prins type reaction of glyoxal with isobutylene is thought to have failed because of the stability of the hydrated trimer or tetramer. Depolymerization of these polymers is evidently much more difficult than the depolymerization of formaldehyde chains in formalin.

Yuk (34) learned that 1-butanol would not degrade the glyoxal polymer at 35°. Temperatures above 100° seem to be necessary for depolymerization of glyoxal. Slow and incomplete degradation resulted with 1-butanol (B.P. 117°) but excellent results were noted with 1,2-ethanediol (B.P. 197.4°) Difficulty of removal of water from the reaction mixtures and insufficiently high temperatures for degradation of the glyoxal polymers are contributing factors in the near failure of ethanol to produce the tetraethyl acetal.

Alcoholysis of tetrabutyl acetal of glyoxal by methanol is, no doubt, an equilibrium reaction of several steps. The experimental results discussed previously support that conclusion. Since the 1-butanol could not be conveniently removed from the reaction mixture as it was produced, the reaction could not be forced to completion. The reaction equilibrium is unfavorable for the formation of the tetramethyl acetal of glyoxal.

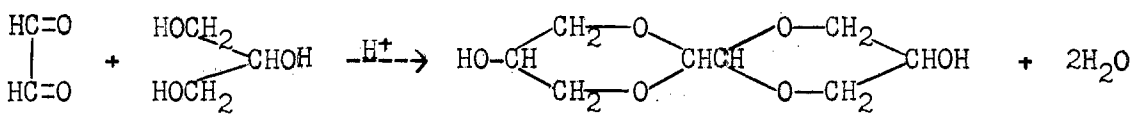
The consistent failure of formation of the tetraacetate is not adequately understood. The formation was tried at both high and low temperatures, with and without a catalyst. The reaction of acetic anhydride and acetic acid with p-dioxano-[b]-p-dioxane could produce several equilibria. The possible intermediate compounds in route to the formation of the tetraacetate are equilibrium possibilities. Since the tetraacetate is quite sensitive to acids and bases, the reaction would be forced far to the left. The failure of this specific method for producing the tetraacetate is therefore attributed to unfavorable equilibrium conditions.

Though no quantitative determination of yield was made on any of the cyclic acetal preparations, evidence of excellent yields of IV and VIII from 1,2-ethanediol and 1,3-propanediol respectively was noted. The yields of VI and IX in the cases of 1,2-propanediol and 1,3-butanediol respectively were comparatively low. There was a complete lack of expected products from the 2,3-butanediol and the 2,3-dihydroxybutane-1,4-dicarboxylic acid reactions. In review it may be observed that primary hydroxyl groups have reacted exceptionally well, whereas secondary hydroxyl groups have reacted with

difficulty in two cases and not at all in two other cases. It was also noted that in the two cases of positive reaction of secondary hydroxyl groups that a primary hydroxyl group was also present. This is in keeping with the relative ease of converting the several types of alcohols into simple acetals.

From the analogous reactions of mercapto compounds with glyoxal (24,26), it appears that the oxygen in the acetal is supplied by the alcohol. Since alcohols lose the hydrogen from the hydroxyl group with difficulty decreasing in the order tertiary > secondary > primary (5,9), the low yields of VI and IX can be explained. The failure of 2,3-butanediol and 2,3-dihydroxybutane-1,4-dicarboxylic acid to give the expected analogous reactions can be attributed to the same effect.

Because primary hydroxyl groups reacted so well, it was predicted that 1,2,3-propanetriol would react



and the secondary hydroxyl group would remain inactive. The failure of the reaction to give the desired product is ascribed to cross-linking and polymerization.

The reaction of 2-hydroxypropionic acid with glyoxal probably failed because of the polymerized nature of both reactants. Quite possibly glycolic acid, $HOCH_2COOH$, would have succeeded in the reaction. The compound then to be expected is known (8).

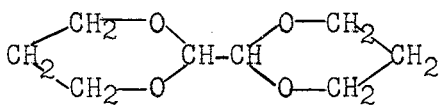
The obvious failure of the melting point of IV to agree with literature values may be attributed to the presence of a little di(p-dioxano)-[b,e]-p-dioxane (III), which could have been produced by the reaction.

SUMMARY

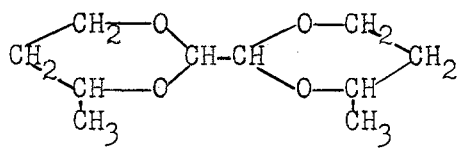
The glyoxal trimer or tetramer found in the 30% commerical solution was found to be inactive toward isobutylene in the Prins type boron trifluoride-catalyzed reaction.

A known compound, p-dioxano-[b]-p-dioxane, was produced by a simplified method.

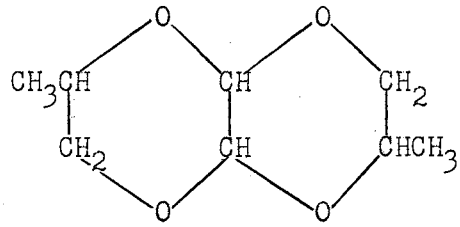
Three new compounds, 2,2'-bi-1,3-dioxane (I), 2,2'-bi-(4-methyl-1,3-dioxane) (III), and 2,6-dimethyl-p-dioxano-[b]-p-dioxane (III),



I



II



III

were prepared from glyoxal and characterized. The 2,7-dimethyl isomer of III was probably also present with it, but was not isolated.

Glyoxal tetraacetate was not obtained from aqueous glyoxal and acetic acid by simple dehydrative distillation nor from p-dioxano-[b]-p-dioxane by acid-catalyzed acetolysis in acetic acid and acetic anhydride.

BIBLIOGRAPHY

(1) Baer and Fischer, J. Am. Chem. Soc., 69, 1463-5 (1947).

(2) Baker and Field, J. Chem. Soc. 1932, 86.

(3) Boeseken, Tellegen and Henriquez, Proc. Roy. Soc. Amsterdam 34, 631 (1931); Rec. trav. chim. 50, 909-14 (1931); Brit. Chem. Abstracts 1931, A, 1162.

(4) Carbide and Carbon Chem. Co., Tech. Bull. F-7607, New York.

(5) Day, "Electronic Mechanisms of Organic Reactions", Boston, American Book Co., 1950, p. 72.

(6) Donciu, Monatsh. 16, 8 (1895).

(7) Dyson, Chemistry and Industry 1944, 342.

(8) Fischer and Taube, Ber. 59, 853 (1926).

(9) Fuson, "Advanced Organic Chemistry", New York, Wiley and Sons, Inc., 1950, p. 99.

(10) Harris and Femme, Ber. 40, 165-72 (1907).

(11) Hawkins, Master's Thesis, Okla. A. and M. College (1949).

(12) Hawkins, Doctor's Thesis, Okla. A. and M. College (1952).

(13) Henry, Bull. soc. chim. 2 44, 458 (1885).

(14) Hess and Uibrig, Ber. 50, 365-8 (1917).

(15) Horsley, Ind. and Eng. Chem. Anal. Ed. 19, 508-600 (1947).

(16) Kohn, Master's Thesis, Okla. A. and M. College (1948).

(17) Lange, "Handbook of Chemistry", 7th ed., Sandusky, Ohio, Handbook Publishers, Inc. (1949)

(18) MacDowell and McNamee, (to Carbide and Carbon Chemicals Corp.) U.S. 2,360,959 (1944); C.A. 39, 2080 (1945); and Brit. 559,362 (1944); C.A. 40, 355 (1946).

(19) McElvain and Stammer, J. Am. Chem. Soc. 73, 915-7 (1951).

(20) Morton, "Laboratory Technique in Organic Chemistry", New York, McGraw-Hill Book Co., 1938, p. 10.

(21) Ott, M. (to Chemische Fabriken vorm. Weiler-ter-Meer), Ger. 362,743 (1919); C.A. 18, 991 (1924).

(22) Perkins, (to E. I. dePont de Nemours and Co.), U.S. 1,999,995 (1935); C.A. 29, 4026 (1935).

(23) Pinner, Ber. 5, 147 (1872).

(24) Prostenik and Balenovic, J. Org. Chem. 17, 379-80 (1952).

(25) Raudnitz, Chemistry and Industry 1944, 324,366.

(26) Ryzheva, Biokhimiya, 11, 391-400 (1946); C.A. 41, 2696 (1947).

(27) Schreyer, J. Am. Chem. Soc. 73, 2962 (1951).

(28) Shriner and Fuson, "The Systematic Identification of Organic Compounds, 3rd ed., New York, Wiley, 1948.

(29) Sturzenegger, Doctor's Thesis, Okla. A. and M. College (1953).

(30) Walker, (to E. I. duPont de Nemours and Co.) U. S. 2,379,555 (1945); C.A. 40, 90 (1946).

(31) Whitmore, "Organic Chemistry", 2nd ed., New York, D. Van Nostrand Co., 1951, p. 354.

(32) Wohl and Mylo, Ber. 45, 330 (1912).

(33) Wolthius and Lawler, (to General Aniline and Film Corp.), U. S. 2,415,397 (1947); C.A. 41, 3118 (1947).

(34) Yuk, Master's Thesis, Okla. A. and M. College (1949).

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