CXXIX.—*Some Reactions of ω -Bromomethylfurfuraldehyde.*

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FENTON (Trans., 1898, **73**, 554) showed that ω -bromomethylfurfuraldehyde can condense with malonic esters in presence of alkali hydroxides or sodium ethoxide, giving a product which exhibits a blue fluorescence in solution, and that the reaction is so delicate that it may be used for the detection of traces of hexoses.

At Dr. Fenton's suggestion, the authors commenced an investigation of this reaction, and have continued the study of the properties of ω -bromomethylfurfuraldehyde.

The isolation of the fluorescent compound or compounds proved to be a matter of exceptional difficulty, as the course of the reaction appeared to be very erratic, and the same products were rarely obtained, even under what seemed to be identical conditions. For this reason, the preparation of new methylfurfuraldehyde derivatives became necessary, and unexpected products were obtained in two instances. These are described in the present communication.

I. Action of ω -Bromomethylfurfuraldehyde on Silver Cyanide in Presence of Alcohol.

An attempt to prepare the ω -nitrile or *iso*-nitrile by replacing the bromine by cyanogen by means of potassium or silver cyanide in alcoholic solution led to quite unexpected results; silver bromide was formed, but hydrogen cyanide distilled over quantitatively with the alcohol.

The product, after the removal of the alcohol and hydrogen cyanide, was a dark-coloured oil, which gave an oily precipitate with phenylhydrazine acetate, and which was readily oxidised with silver oxide, giving the crystalline *silver salt of ω -ethoxymethylpyromucic acid*:

On further examination, the oily product which gave the silver salt, was proved to be ω -ethoxymethylfurfuraldehyde. Its formation can only be explained by the interaction of the bromomethylfurfuraldehyde with the alcohol; the hydrogen bromide so liberated acts on the silver cyanide, and hydrogen cyanide is thus formed. Having regard to the extreme reactivity of the bromine in bromomethyl-

furfuraldehyde (compare Fenton and Gostling, *Trans.*, 1899, **75**, 427, 430, who showed that the bromine is quantitatively precipitated by alcoholic silver nitrate), such a reaction is intelligible.

That such is the correct explanation is most probable from the fact that, when an alcoholic solution of bromomethylfurfuraldehyde is allowed to evaporate in a vacuum desiccator, hydrogen bromide is liberated; further, when an alcoholic solution of bromomethylfurfuraldehyde is boiled, it rapidly becomes acid. *ω*-Ethoxymethylfurfuraldehyde may be most conveniently prepared by this method if means are taken to remove the hydrogen bromide as soon as it is formed, so that polymerisation and formation of humus cannot result. Thus, if an absolute alcoholic solution of bromomethylfurfuraldehyde is boiled with an excess of calcium carbonate, a good yield of ethoxymethylfurfuraldehyde is obtained. Even in the cold there is a considerable reaction and evolution of carbon dioxide. This method of formation is analogous to that described by Fenton and Gostling (*Trans.*, 1899, **75**, 431) for the preparation of *ω*-hydroxymethylfurfuraldehyde by heating bromomethylfurfuraldehyde in water in the presence of barium carbonate.

The reaction product from alcoholic bromomethylfurfuraldehyde and calcium carbonate on purification and fractionation gives a liquid boiling between 235° and 240°, which analysis and molecular-weight determination show to be *ω*-ethoxymethylfurfuraldehyde. The liquid has all the properties of an aldehyde, and gives crystalline *phenyl*- and *p*-bromophenyl-hydrazones.

On oxidation with silver oxide, *ω*-ethoxymethylfurfuraldehyde gives a crystalline silver salt, identical with that obtained by the oxidation of the product of interaction of bromomethylfurfuraldehyde and silver cyanide in alcoholic solution.

Both silver salts on acidification yield the same crystalline acid, which was proved to be *ω*-ethoxymethylpyromucic acid.

The bromine atom in bromomethylfurfuraldehyde is thus so reactive that it will react with ethyl alcohol directly, and the reaction appears to be a general one. For example, when bromomethylfurfuraldehyde is boiled in methyl-alcoholic solution with excess of calcium carbonate, *ω*-methoxymethylfurfuraldehyde is produced. The aldehyde itself was not actually isolated, but was oxidised directly with silver oxide to *ω*-methoxymethylpyromucic acid.

An attempt to convert the methoxy-aldehyde into the corresponding methoxy-acid by oxidation with alkaline permanganate gave an acid almost insoluble in water, and quite unlike the acid expected. This acid sublimes on heating, and on warming with ferric chloride gives a transparent jelly. It is, therefore, probably

dehydromucic acid (furan-2:5-dicarboxylic acid). Its preparation by a somewhat similar method, namely, by the oxidation of ω -chloromethylfurfuraldehyde, has already been described by Fenton and Robinson (*Trans.*, 1909, **95**, 1339).

By boiling bromomethylfurfuraldehyde with benzyl alcohol in the presence of calcium carbonate, a clear, yellow oil was produced, which boiled at 301—303°, and had the empirical formula $C_{23}H_{22}O_2$. (Benzyloxymethylfurfuraldehyde has the empirical formula $C_{18}H_{12}O_3$.) The constitution of this compound has not been satisfactorily determined, and the authors are engaged in investigating it.

II. *Action of Barium Carbonate on ω -Bromomethylfurfuraldehyde and Water.*

In repeating Fenton and Gostling's preparation (*loc. cit.*) of ω -hydroxymethylfurfuraldehyde by boiling ω -bromomethylfurfuraldehyde with water in the presence of barium carbonate, the present authors observed that under certain conditions a beautiful yellow, crystalline product, $C_{11}H_{10}O_4$, is produced, which melts at 111.5—112°.

It was first supposed that this compound might be identical with the anhydride, $C_{12}H_{10}O_5$, obtained by Kiermayer (*Chem. Zeit.*, 1895, **19**, 100) by eliminating one molecule of water from two molecules of hydroxymethylfurfuraldehyde. Kiermayer's anhydride melts at 112°, and is strongly aldehydic in character. It combines directly with two molecules of aniline and phenylhydrazine. No such combinations could be brought about with the authors' compound. Kiermayer's compound is insoluble in benzene or acetic acid, and readily reduces both ammoniacal silver nitrate and Fehling's solution. Further, the two compounds give somewhat different colour reactions with phenols, and a mixture of the two melts very indistinctly at 90—95°, showing that they were not identical.

A substance possessing the formula $C_{11}H_{10}O_4$ might conceivably be obtained from one molecule of bromomethylfurfuraldehyde and one molecule of lævulic acid, by loss of one molecule each of hydrogen bromide and water:

Since ω -bromomethylfurfuraldehyde on boiling with water gives ω -hydroxymethylfurfuraldehyde and hydrogen bromide, and ω -hydroxymethylfurfuraldehyde and mineral acids give lævulic and formic acids (Düll, *Chem. Zeit.*, 1895, **19**, 166, 217; Kiermayer, *ibid.*, 1003), the above reaction is a very possible one. If the yellow,

crystalline compound is a condensation product of ω -bromomethylfurfuraldehyde with lvulic acid, the addition of lvulic acid to the ω -bromomethylfurfuraldehyde and water before heating and adding barium carbonate should give a greatly increased yield of yellow crystals. Investigation shows that the addition of an equivalent quantity of lvulic acid increases the yield by about 50 per cent. Numerous experiments have also been carried out to bring about the formation of the crystals by the condensation of ω -hydroxymethylfurfuraldehyde and lvulic acid, but without success. Further investigation is therefore necessary before the constitution of this compound can be established.

EXPERIMENTAL.

ω -Bromomethylfurfuraldehyde was prepared from lvulose by the action of hydrogen bromide in chloroform solution (compare Fenton and Gostling, Trans., 1899, **75**, 425). The mixture was heated on a water-bath under a reflux condenser for one hour, cooled, and excess of anhydrous sodium carbonate added. It was found advisable to allow the product to remain overnight over sodium carbonate, as by this means a much purer preparation was obtained. The chloroform solution was filtered off, and the solvent removed by distillation at 50 under diminished pressure. The residual oil, on cooling, usually solidified to a mass of large needles, and further purification was not essential, but recrystallisation from dry ether, free from alcohol, was generally considered advisable.

Action of Silver Cyanide on ω -Bromomethylfurfuraldehyde in Alcoholic Solution.

A weighed quantity of ω -bromomethylfurfuraldehyde was dissolved in absolute ethyl alcohol with gentle warming, and the equivalent amount of well-washed and dried silver cyanide added. The mixture was heated on the water-bath for one to two hours, and allowed to cool; the precipitated silver bromide was collected, and well washed with absolute alcohol.

The filtrate was very dark coloured, and had a strong odour of hydrogen cyanide. The alcohol was distilled off on a water-bath, when the hydrogen cyanide passed over completely at the same time. The ethoxymethylfurfuraldehyde may be isolated by extraction with ether; or it may be distilled in a current of steam, and separated from the aqueous distillate by means of ether.

Interaction of ω -Bromomethylfurfuraldehyde and Ethyl Alcohol.

ω -Bromomethylfurfuraldehyde, purified by recrystallisation from dry ether, was dissolved in absolute alcohol; excess of finely powdered calcium carbonate was added, and the mixture heated on the water-bath under a reflux condenser. Since it was not possible to test the completion of the reaction by means of silver nitrate, use was made of Fenton's test, the boiling being continued until no fluorescence was obtained when a few drops of the reaction mixture were mixed with malonic ester and alcoholic potassium hydroxide.

After cooling, the excess of calcium carbonate was filtered off, and the alcohol removed by distillation. The residue was diluted with water to dissolve the calcium bromide, and the solution completely extracted with ether. After removing the ether, an oil was obtained which was distilled under diminished pressure; most of the oil distilled below $145^{\circ}/34$ mm., and the distillate was then fractionated under the atmospheric pressure. The following fractions were collected: up to 90° ; $90-100^{\circ}$; $100-220^{\circ}$; $220-225^{\circ}$; $225-230^{\circ}$; $230-235^{\circ}$; $235-240^{\circ}$.

The residue in the flask was very dark and viscous, and not completely soluble in ether; it was probably a polymerised product, as the aldehyde polymerises very easily. Owing to this fact, it was decided not to attempt a finer fractionation.

In order to ascertain which fraction contained the desired substance, the molecular weights of the fractions $220-225^{\circ}$ and $235-240^{\circ}$ were determined by the cryoscopic method, using benzene as solvent.

Fraction.	Weight of solvent, grams.	Weight of substance, gram.	Depression of freezing point.	M. W.
$220-225^{\circ}$	I. 21.52	0.2779	0.490°	131.8
$220-225$	II. 21.52	0.5936	0.997	130.3
$235-240$	I. 21.24	0.5947	0.907	154.3
$235-240$	II. 22.52	0.5708	0.827	153.2

$C_8H_{10}O_3$ requires M. W. = 154. The fraction $235-240^{\circ}$ was therefore analysed.

I. 0.1718 gave 0.3923 CO_2 and 0.1038 H_2O . C = 62.28; H = 6.71.

II. 0.1660 „ 0.3824 CO_2 „ 0.0987 H_2O . C = 62.70; H = 6.66.

$C_8H_{10}O_3$ requires C = 62.34; H = 6.50 per cent.

 *ω -Ethoxymethylfurfuraldehyde.**

ω -Ethoxymethylfurfuraldehyde, as obtained by either of the two foregoing methods, is a yellow oil, D_{16}^{25} 1.1096, readily soluble in the

* Since this work on ω -ethoxymethylfurfuraldehyde was carried out, Erdmann (*Ber.*, 1910, 43, 2391) in his paper on ω -hydroxymethylfurfuraldehyde mentions the

usual organic solvents; it is soluble in hot petroleum, but insoluble in cold, and is moderately soluble in water. If rapidly distilled, it boils without decomposition under the ordinary pressure at 235—240°, but prolonged heating induces polymerisation. Under 35 mm. pressure it boils at 145°.

The substance shows the usual properties of an aldehyde. It is readily oxidised by silver oxide or Fehling's solution, and restores the colour to Schiff's reagent. With aniline acetate paper it gives a bright yellow colour. With β -naphthylamine in glacial acetic acid (1:4) a yellow colour is produced, similar to that given by hydroxymethylfurfuraldehyde and the same reagent. With an alcoholic solution of thymol and a few drops of concentrated sulphuric acid, a fine magenta colour is developed. An alcoholic solution of phloroglucinol gives, in the presence of concentrated sulphuric acid, a fine reddish-purple colour with the ethoxy-aldehyde, and a greenish-yellow with furfuraldehyde.

The *phenylhydrazone* was obtained as a pink, oily precipitate, which solidified after decanting the supernatant liquid, washing the residual oil by decantation, drying it by warming over a flame with stirring, and then scratching with a glass rod. Once it has been obtained in the solid condition, it can be recrystallised from various solvents. The most convenient of these is light petroleum, from which it crystallises in long, slender, yellow needles, melting at 55·5—56·2°:

0·1928 gave 0·4847 CO₂ and 0·1172 H₂O. C=68·56; H=6·75.

0·5069 „ 50·0 c.c. N₂ (moist) at 8·9° and 754·9 mm. N=11·77.

C₁₄H₁₆O₂N₂ requires C=68·85; H=6·50; N=11·48 per cent.

The *p*-bromophenylhydrazone crystallises in shining silken needles, which soften at 103°, and melt at 104—105°.

ω -Ethoxymethylpyromucic Acid.

ω -Ethoxymethylfurfuraldehyde, prepared by either of the two methods described, is mixed with water, and heated with a large excess of freshly precipitated silver oxide for three hours, and filtered. The residue is washed with boiling water until no more silver salt is extracted. The yellow filtrate crystallises readily on cooling in small, nodular, grey crystals.

The *silver* salt is moderately soluble in hot water, but not very readily in cold. When recrystallised several times from water, it is

formation of ω -ethoxymethylfurfuraldehyde by precipitating an alcoholic solution of bromomethylfurfuraldehyde with alcoholic silver nitrate, but he gives no details or properties.

obtained in colourless, shining nodules. It can also be purified by precipitation from its aqueous solution by absolute alcohol:

0.2274 gave 0.2896 CO_2 , 0.0702 H_2O , and 0.0856 Ag. $\text{C}=34.73$; $\text{H}=3.43$; $\text{Ag}=39.00$.

$\text{C}_8\text{H}_9\text{O}_4\text{Ag}$ requires $\text{C}=34.65$; $\text{H}=3.25$; $\text{Ag}=38.98$ per cent.

ω -Ethoxymethylpyromucic acid was prepared from the silver salt by dissolving the latter in hot water, and precipitating the silver with sodium carbonate solution. The silver carbonate was removed, and the filtrate, after concentrating, was acidified with sulphuric acid (1:3) and extracted with chloroform, in which the small quantity of dehydromucic acid, also formed, is insoluble. The chloroform extract was dried, and evaporated, when a yellow syrup remained, which after some days solidified to a mass of needles. These, after being collected and washed with ether, became practically white.

The acid can be purified by dissolving in dry ether and adding dry petroleum to the solution. As the ether slowly evaporates, the acid separates in small, shining needles. The most convenient method of purification is crystallisation from carbon disulphide, or by precipitation from chloroform solution with petroleum; the product is obtained in this way in very long, shining needles, melting at $57.5-58.5^\circ$:

0.2270 gave 0.4705 CO_2 and 0.1212 H_2O . $\text{C}=56.53$; $\text{H}=5.96$.

$\text{C}_8\text{H}_{10}\text{O}_4$ requires $\text{C}=56.47$; $\text{H}=5.88$ per cent.

The acid is also soluble in benzene, alcohol, or water. Solutions of its ammonium salt give no precipitate with calcium chloride, lead acetate, basic lead acetate, or copper sulphate.

ω -Methoxymethylpyromucic Acid.

ω -Methoxymethylfurfuraldehyde was prepared by boiling bromomethylfurfuraldehyde in methyl-alcoholic solution with calcium carbonate, and proceeding as in the preparation of the ethoxy-compound. The aldehyde was not isolated, but, after the removal of the calcium bromide, was oxidised with silver oxide. The acid was prepared from the silver salt in the usual manner, and was extracted by chloroform. It was best purified by precipitating from chloroform with petroleum:

0.1955 gave 0.3850 CO_2 and 0.0913 H_2O . $\text{C}=53.71$; $\text{H}=5.18$.

0.2960 „ 0.4413 AgI. $\text{OMe}=19.67$.

$\text{C}_6\text{H}_5\text{O}_3\cdot\text{OMe}$ requires $\text{C}=53.84$; $\text{H}=5.13$; $\text{OMe}=19.87$ per cent.

The properties of ω -methoxymethylpyromucic acid are similar to those of the ethoxy-compound. It crystallises in long, silken needles, which melt at $67.5-68.5^\circ$.

Preparation of the Compound $C_{11}H_{10}O_4$.

In order to obtain this compound, ω -bromomethylfurfuraldehyde is melted under water, the mixture heated to 60° , and barium carbonate added little by little, care being taken to maintain the solution always slightly acid. The aqueous solution quickly becomes coloured a canary-yellow, and the melted aldehyde gradually passes into solution. When this occurs, a large excess of barium carbonate is added, the mixture heated nearly to boiling, and filtered hot. The yellow filtrate deposits an oil on cooling, which, on remaining overnight, becomes a mass of crystals. The yield varies greatly, and is rarely large. It appears to depend largely on the temperature to which the reaction mixture is heated. The compound, which usually crystallises in canary-yellow needles, but sometimes in plates, may be crystallised from hot water, but more readily from hot alcohol or benzene. It is best purified by dissolving in glacial acetic acid, and precipitating with dry petroleum, when it is obtained in microscopic needles. These are then recrystallised from carbon tetrachloride. The compound melts at $111.5-112^\circ$. Its solutions in all solvents are yellow, possessing a slight green tinge. It is neutral to litmus, but sodium carbonate solution extracts it from an ethereal solution. The crystals do not readily reduce either ammoniacal silver nitrate or Fehling's solution, considerable boiling being necessary. With phenylhydrazine acetate, a very slight precipitate is obtained after some time. The compound does not restore the colour to Schiff's reagent. From these reactions it does not appear to be aldehydic in nature; neither does it contain bromine:

0.1902 gave 0.4471 CO_2 and 0.0828 H_2O . $C=64.11$; $H=4.83$.

0.1909 „ 0.4477 CO_2 „ 0.0832 H_2O . $C=63.96$; $H=4.84$.

0.921 in 29.2 acetic acid gave $\Delta t=0.12$. M.W.=204.

$C_{11}H_{10}O_4$ requires $C=64.08$; $H=4.85$ per cent. M.W.=206.

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