

CXII.—*Furan-2:5-dialdehyde.*

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FENTON and Robinson (Trans., 1909, **95**, 1339) have shown that when ω -chloromethylfurfuraldehyde is oxidised by nitric acid, a very energetic reaction takes place, and dehydromucic acid (furan-2:5-dicarboxylic acid) is produced. Alberda van Ekenstein and Blanksma (*Ber.*, 1910, **43**, 2361) state that ω -hydroxymethylfurfuraldehyde on similar treatment gives dehydromucic acid.

While preparing a large quantity of this acid by Fenton and Robinson's method, the present authors observed that the yield varied within wide limits; and on investigating the cause of this

variation, it was noticed that the reaction product often contained a substance or substances extractable with organic solvents, such as benzene and chloroform, in which dehydromucic acid is practically insoluble. The chloroform extract, after drying, left a crystalline residue on evaporation.

This has been found to consist of furan-2:5-dialdehyde (I) mixed with a small quantity of a white, crystalline substance, which combines the properties of an aldehyde and an acid. It is most probably identical with furan-2-aldehyde-5-carboxylic acid (pyromucic aldehyde) (II) described by Hill and Sawyer (*Amer. Chem. J.*, 1898, **20**, 174), who obtained it by the hydrolysis with water of ω -dibromomethylpyromucyl bromide, prepared by the bromination of methylpyromucyl chloride. Hill and Sawyer give 201—202° as the melting point of their compound; the white, crystalline compound referred to above melts at 196—197°. A slight impurity would probably explain this difference, but, unfortunately, the yield was too small to enable the identity to be confirmed by analysis:



Furan-2:5-dialdehyde (I) has not been previously prepared, and, as the analogue of glyoxal, is a compound of interest and worthy of description.

Furan-2:5-dialdehyde shows all the usual properties of an aldehyde. It gives a diphenylhydrazone, a dianilide, and a dioxime. No attempt has yet been made to prepare the stereoisomerides of the oxime. An attempt to prepare the monoxime by the use of one equivalent of hydroxylamine hydrochloride gave the dioxime only. This behaviour is exactly analogous to that of glyoxal.

In addition to the above, the derivative with β -naphthylamine has also been prepared and analysed; as this reagent appears to be very suitable for the identification of aldehydes of the furan series. The β -naphthylamine derivatives are easily prepared, are crystalline, and the melting points of the various compounds differ more widely than those of other derivatives. The following have been prepared and their melting points determined for purpose of identification:

	M. p.
β -Naphthylamine derivative of furfuraldehyde	85° *
" " methylfurfuraldehyde	87—88°
" " ω -hydroxymethylfurfuraldehyde	131—132°
" " furan-2:5-dialdehyde	Above 230°

* Schiff, *Annalen*, 1887, **239**, 350.

The constitution of the dialdehyde follows from its mode of preparation, as well as from its easy conversion into dehydromucic acid by oxidation with silver oxide. Attempts to reduce it to 2:5-dihydroxymethylfuran, or to prepare it by the reduction of the methyl ester of dehydromucic acid, were not successful.

In common with other furanaldehydes, the dialdehyde gives striking colours on condensing with phenols, etc., by means of concentrated sulphuric acid. The most characteristic of these is the reaction with thymol. Addition of a few drops of concentrated sulphuric acid to a solution of the dialdehyde and thymol in alcohol produces a brilliant magenta colour. A large excess of acid changes this into a beautiful Prussian blue. On pouring into water, the colour changes into red, and a red dye is precipitated. The formation of the blue colour distinguishes the dialdehyde from other furanaldehydes, and, as it is extremely delicate, forms a convenient test for the new compound. A solution of 1 part of the dialdehyde in 50,000 parts of water gives the blue colour. The aldehyde acid gives a red colour with thymol, but the blue is not produced with excess of sulphuric acid.

As an analogue of glyoxal, the compound would be expected to polymerise readily, and investigations on this and other reactions are being made.

In addition to some dehydromucic acid, other products of the oxidation of ω -chloromethylfurfuraldehyde are oxalic acid and a very considerable quantity of hydrocyanic acid. Other oxidising agents, such as potassium dichromate in acid solution, may be used instead of nitric acid. The authors have also obtained the dialdehyde by the restrained oxidation of ω -hydroxymethylfurfuraldehyde by nitric acid (D 1'3). During this investigation they have discovered a simplified method of preparation of ω -hydroxymethylfurfuraldehyde, which is described later.

Fenton and Gostling (*Trans.*, 1899, **75**, 430) first obtained ω -hydroxymethylfurfuraldehyde from ω -bromomethylfurfuraldehyde by precipitating in dilute alcoholic solution with slightly more than the calculated quantity of silver nitrate. Free nitric acid, which might conceivably have an oxidising action on the aldehyde, being produced by this method, Erdmann (*Ber.*, 1910, **43**, 2392) recommended the substitution of silver acetate for the nitrate. Fenton and Gostling further showed that ω -hydroxymethylfurfuraldehyde can be prepared by the hydrolysis of the corresponding bromo-compound with water in presence of barium carbonate. The present authors have since shown, however (*Trans.*, 1911, **99**, 1195), that this hydrolysis is not a simple one; a yellow, crystalline compound, $C_{11}H_{10}O_4$, is produced, the constitution of

which has not yet been determined, and, at the same time, there is a corresponding reduction in the yield of the hydroxy-aldehyde. The authors have found that a satisfactory method of preparing this aldehyde is by the hydrolysis of ω -chloromethylfurfuraldehyde by simply pouring the crude product into a large mass of almost boiling water, when hydrolysis results immediately; the hydroxy-aldehyde passes into solution, and may be extracted with ethyl acetate. If the volume of water is large, the concentration of hydrogen chloride liberated is not sufficiently great to react with the hydroxy-aldehyde. The method is not applicable to the bromo-analogue, as the liberated hydrogen bromide does react with the hydroxy-aldehyde.

EXPERIMENTAL.

Preparation of Furan-2:5-dialdehyde.

Fifty grams of crude ω -chloromethylfurfuraldehyde, prepared by a slight modification of the method described by Fenton and Robinson (Trans., 1909, **95**, 1339), namely, by the action of hydrogen chloride on levulose, are treated with 100 c.c. of concentrated nitric acid (D 1.3) in a large flask. The mixture is heated gently, with constant shaking, until the reaction commences, when the flask is immediately immersed in cold water. Even then the reaction is very violent, brown oxides of nitrogen and hydrogen cyanide being copiously evolved. When the reaction has subsided, the contents of the flask are diluted with water, filtered from a small quantity of brown, insoluble matter, and extracted with benzene or chloroform—preferably the latter. The extract is dried over ignited sodium sulphate, and the solvent distilled off from a water-bath; the dark, residual oil, on cooling, quickly solidifies to a brown mass of crystals, which consist of the dialdehyde mixed with a small quantity of the aldehyde-acid. The yield of the crude mixture varies between 25 and 30 per cent. of the theoretical. A partial separation of the dialdehyde and aldehyde-acid can be brought about by recrystallisation from carbon tetrachloride, in which the aldehyde-acid is only very sparingly soluble, and from which the dialdehyde crystallised in light yellow, thin plates. Complete separation, however, can only be accomplished by boiling the aqueous solution with barium carbonate, when the barium salt of the aldehyde-acid is produced and passes into solution. The aqueous solution is extracted with chloroform to remove the dialdehyde, after which the aldehyde-acid may be extracted from the residual liquid after acidification.

The dialdehyde can be conveniently purified by recrystallisation

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from carbon tetrachloride, but the solvent clings very tenaciously to the product.

It can be obtained in beautiful, feathery, iridescent plates from light petroleum containing about 2 per cent. of chloroform. From chloroform or ether it crystallises in characteristic aggregates, having the upper surface flat and the lower globular. Under the microscope these are found to consist of layers of extremely thin, waxy, transparent plates. The substance melts at $109.5-110^{\circ}$ (uncorr.).

For the analysis, the substance, after several recrystallisations from carbon tetrachloride, was crystallised once from ether, and dried under diminished pressure over sulphuric acid:

0.1823 gave 0.3886 CO_2 and 0.0558 H_2O . $\text{C}=58.13$; $\text{H}=3.40$.

0.1333 in 20.1 benzene gave $\Delta t = -0.263^{\circ}$. $\text{M.W.}=126.1$.

0.1110 „ 21.74 „ „ „ $\Delta t = -0.206^{\circ}$. $\text{M.W.}=123.9$.

$\text{C}_6\text{H}_4\text{O}_3$ requires $\text{C}=58.06$; $\text{H}=3.23$ per cent. $\text{M.W.}=124$.

It is somewhat soluble in water, readily so in alcohol, ether, ethyl acetate, or benzene, and extremely so in chloroform; it does not dissolve in light petroleum. It is easily volatile in steam, and also in the vapours of chloroform and benzene. It sublimes below 100° in a most characteristic manner; the sublimate resembles cotton-wool, and when viewed under the microscope this is found to consist of aggregations of glistening plates.

The compound cannot be conveniently purified by this method, as the unsublimed portion rapidly liquefies and darkens, probably due to polymerisation.

The compound quickly colours Schiff's reagent, and readily reduces ammoniacal silver nitrate or Fehling's solution on warming. It dissolves easily in cold aqueous sodium hydroxide or barium hydroxide, forming an acid, as it cannot be extracted from these solutions by organic solvents.

It is also soluble in ammonium hydrate (D 0.880), giving a brown solution, from which a flocculent precipitate soon separates.

No hydrogen sulphite compound could be obtained.

Besides the colour with phenols, already described, the dialdehyde gives a beautiful blue when condensed with dimethylaniline by heating with zinc chloride.

With anthraquinone and concentrated sulphuric acid an olive-green colour is obtained.

The Phenylhydrazone.—Four grams of the dialdehyde were dissolved in ethyl acetate, and 9 grams (rather more than 2 mols.) of phenylhydrazine, also in ethyl acetate, were added. After the addition of anhydrous potassium carbonate, the mixture was boiled and filtered, and part of the solvent removed by distillation. Petroleum of high boiling point was added to the residue, when

the *phenylhydrazone* separated as a yellow, crystalline precipitate. It was purified by recrystallisation from benzene containing a little methyl alcohol, when it melted at 206—207° (uncorr.):

0.1817 gave 0.4733 CO₂ + 0.0908 H₂O. C=71.04; H=5.55.

0.2549 „ 41.0 c.c. N₂ (moist) at 15° and 748 mm. N=18.5.

C₁₈H₁₆ON₄ requires C=71.05; H=5.26; N=18.4 per cent.

The Dianilide.—Two grams (1 mol.) of the dialdehyde were triturated with 3 grams (2 mols.) of aniline. The aldehyde soon dissolved, and the warm mixture quickly solidified. Excess of ether was added, and the insoluble anilide collected. Four grams of crude anilide were obtained, and this was purified by crystallisation from absolute alcohol, from which it separated in light yellow, glistening plates melting at 160—161° (uncorr.). The alcoholic solution on boiling readily gave a red dye:

0.3645 gave 32.2 c.c. N₂ (moist) at 18° and 758 mm. N=10.2.

C₁₈H₁₄ON₂ requires N=10.2 per cent.

The Di-β-naphthylamine Derivative.—Three grams of the dialdehyde in alcohol were added to 9 grams of β-naphthylamine, also in alcohol. There was an immediate, yellow, crystalline precipitate, which, as the mixture became heated, changed to red. It was collected and washed, first with alcohol and afterwards with ether, when it was obtained in glistening, golden-yellow plates. It was purified for analysis by extraction with alcohol, and drying the residue in a vacuum desiccator. It is a yellow, crystalline solid, almost insoluble in the ordinary organic solvents with the exception of glacial acetic acid:

0.3722 gave 24.5 c.c. N₂ (moist) at 16° and 752 mm. N=7.6

C₂₆H₂₀ON₂ requires N=7.4 per cent.

The Dioxime.—Four grams of the dialdehyde were dissolved in warm 50 per cent. alcohol, 4.4 grams of hydroxylamine hydrochloride (2 mols.) added and dissolved, and finally 6.2 grams of anhydrous potassium acetate were dissolved in the mixture. The substance crystallised out immediately on cooling in very fine needles radiating from a common nucleus and melting at 212.5—213° (uncorr.). For analysis it was recrystallised from dilute methyl alcohol and dried at 95°:

0.2183 gave 33.9 c.c. N₂ (moist) at 18° and 769 mm. N=18.2.

C₆H₆O₃N₂ requires N=18.2 per cent.

Attempt to Prepare the Monoxime.—Two grams of the dialdehyde were dissolved in 50 per cent. alcohol and heated with 1.1 grams of hydroxylamine hydrochloride (1 mol.) and 1.6 grams of anhydrous potassium acetate in the manner described in the preparation of

the dioxime. The solution darkened somewhat, and on cooling gave a good crop of yellowish-brown crystals.

These crystallised from water in characteristic, microscopic, flat, dentate needles radiating from a common point, and melting at 212—213°. Analysis showed that this compound was the dioxime.

Oxidation of the Dialdehyde to Dehydromucic Acid, C₆H₄O₆.

For this purpose the dialdehyde was heated with excess of freshly precipitated well washed silver oxide and water for three hours on a boiling-water bath. After removing the silver oxide, the soluble silver was precipitated with a slight excess of hydrochloric acid, and the filtrate therefrom concentrated to a small bulk. After several hours the acid crystallised out.

As considerable difficulty was experienced in purifying the acid directly, it was converted into its barium salt, which was recrystallised twice from water, and then the acid regenerated from it by exact precipitation with sulphuric acid. It was thus obtained in shining, white plates. (Found, C=46·10; H=2·74. Calc., C=46·15; H=2·56 per cent.)

The acid does not melt below 220°; it sublimes easily, and gives the characteristic red jelly on warming with ferric chloride solution.

β-Naphthylamine Derivative of Methylfurfuraldehyde.

The methylfurfuraldehyde was prepared by the reduction of ω-bromomethylfurfuraldehyde by means of stannous chloride (Fenton and Gostling, *Trans.*, 1901, **79**, 811). The crude aldehyde so obtained was triturated with slightly more than two parts of well powdered β-naphthylamine. The mixture became warm, and quickly solidified. The mass was extracted with ether, in which the required derivative is very soluble, filtered, and the crystalline residue therefrom recrystallised from 50 per cent. alcohol. Soft, almost white, microscopic needles separated, which melted at 87—88° (uncorr.). The compound is very readily soluble in all the usual organic solvents. After being dried over sulphuric acid:

0·5925 gave 30·5 c.c. N₂ (moist) at 16·5° and 760 mm. N=6·0.

C₁₆H₁₃ON requires N=6·0 per cent.

β-Naphthylamine Derivative of ω-Hydroxymethylfurfuraldehyde.

One part of ω-hydroxymethylfurfuraldehyde dissolved in ethyl acetate was mixed with slightly more than one part of β-naphthylamine, also in ethyl acetate. The mixture was boiled with anhydrous potassium carbonate, and filtered. After the removal

of most of the solvent by distillation, the residue solidified on cooling. The crystals were collected, washed with ethyl acetate, dissolved in benzene, and precipitated by the addition of light petroleum. On recrystallisation from heavy petroleum, yellow, glistening, flat needles were obtained, which melted at 131—132° (uncorr.). After being dried in a vacuum :

0.6112 gave 30.0 c.c. N_2 (moist) at 21° and 768 mm. $N=5.7$.

$C_{16}H_{18}O_2N$ requires $N=5.6$ per cent.

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