

CXLVIII.—*Homologues of Furfuraldehyde.*

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IT has been shown in previous communications (Fenton and Gostling, *Trans.*, 1899, **75**, 423; 1901, **79**, 807) that the chloro- and bromo-derivatives of methylfurfuraldehyde are readily obtained by the action of the corresponding halogen acids on keto-hexoses or on cellulose. The yield from these carbohydrates is about 20 per cent. of the theoretical amount, whereas the aldo-hexoses give rise to mere traces only. The halogen atom in these compounds is extremely reactive, the interaction with silver nitrate, for example, being quantitative and practically instantaneous; when boiled with water in presence of barium carbonate, they are completely hydrolysed, yielding the hydroxy-derivative. Finely divided metallic silver readily removes the halogen from the bromo-derivative, the residual groups uniting to form difurylethanedialdehyde. Treatment with sulphurous acid converts the halogen compounds into a substance having the molecular formula $C_{11}H_8O_4$, to which the constitution of methylfuryl is provisionally assigned. This compound shows remarkable colour reactions with primary amines, with carbamides, and with strong bases, and various applications of these reactions have already been suggested (*Proc. Camb. Phil. Soc.*, 1906, **13**, 298). The action of malonic ester on the halogen derivatives in presence of alcoholic potash gives rise to a compound, still under investigation, which has strongly marked fluorescent properties; the formation of this compound affords a very delicate test for the mono- and poly-hexoses, and serves to distinguish them from the pentoses, etc. (*loc. cit.*, 1907, **14**, 24).

Investigation of the properties and relations of the various compounds here mentioned is now being continued, and in the present communication a brief account is given of some of the results which have recently been obtained.

Application of the Friedel and Crafts Reaction.

A mixture of chloromethylfurfuraldehyde (10 grams), anhydrous aluminium chloride (7 grams), and excess (25 c.c.) of benzene was heated in a reflux apparatus for about two hours. Reaction began at about 40° with copious evolution of hydrogen chloride, and the temperature was regulated so as to keep the liquid in a state of gentle ebullition. The resulting dark, nearly opaque mixture was then allowed to cool, poured on to powdered ice, and submitted to steam distillation. The first portions of the distillate contained some of the product of the reaction dissolved in excess of benzene; afterwards the main portion of the product passed over as an oil, which, on keeping, solidified to a crystalline mass. After recrystallisation several times from a mixture of ether and light petroleum, the product was obtained in large, colourless prisms, melting without decomposition at 30·5—31°. The total yield was about 6 grams:

0·1229 gave 0·3452 CO₂ and 0·0602 H₂O. C=76·65; H=5·44.

0·1917 „ 0·5403 CO₂ „ 0·0926 H₂O. C=76·86; H=5·37.

C₁₂H₁₀O₂ requires C=77·41; H=5·37 per cent.

The molecular weight was determined by the cryoscopic method, using acetic acid and benzene as solvents:

With benzene the results were as follows:

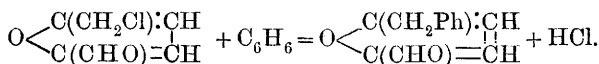
0·2946, in 16·34 benzene, gave $\Delta t = -0·495$. M.W.=182.

0·5043 „ 16·34 „ „ $\Delta t = -0·875$. M.W.=176.

0·1390 „ 15·18 acetic acid, gave $\Delta t = -0·205$. M.W.=174.

C₁₂H₁₀O₂ requires M.W.=186.

The mode of formation and molecular formula of this compound clearly indicate that it is benzylfurfuraldehyde, the change being represented thus:



Benzylfurfuraldehyde has a faint aromatic odour, somewhat resembling that of nitrobenzene; it is almost insoluble in cold water, but dissolves readily in alcohol, benzene, ether, petroleum, or acetic acid.

The aldehydic character is evidenced by the usual reactions; it yields a silver mirror on warming with ammoniacal silver nitrate, and reduces Fehling's solution only, however, on heating. Its solution in acetic acid yields with phenylhydrazine a milky precipitate, which

settles only to an oil ; if, however, the alcoholic solution is mixed with phenylhydrazine in slight excess and left in a vacuum desiccator, a crystalline mass is obtained, which, when washed with ether and recrystallised from a mixture of alcohol and toluene, melts at $199-204^{\circ}$.

The *phenylbenzylhydrazide* is more easily obtained ; acetic acid solutions of phenylbenzylhydrazine and benzylfurfuraldehyde when warmed together yield, after a time, a white or yellow precipitate, which, after washing with acetic acid and ether and recrystallising from benzene and light petroleum, melts at 133° :

0.2440 gave 16.6 c.c. N_2 at 15° and 760 mm. $N = 8.09$.

$C_{25}H_{22}ON_2$ requires $N = 7.66$ per cent.

The *oximes* of benzylfurfuraldehyde are obtained in a manner analogous to that employed by Goldschmidt and Zanolì (*Ber.*, 1892, 25, 2573) in the preparation of the oximes of furfuraldehyde.

A solution of 3.14 grams of sodium hydroxide in 20 c.c. of water was mixed with 1.1 grams of hydroxylamine hydrochloride in 5 c.c. of water, and to the well-cooled mixture, 2 grams of benzylfurfuraldehyde, dissolved in a little ether, were gradually added. The resulting mixture was continuously shaken, and a stream of carbon dioxide was passed into it, during which process the liquid becomes yellow. After extraction with ether and evaporation of the ethereal solution, the product separates in pale yellow needles or prisms, which melt at $96-97^{\circ}$; these when repeatedly crystallised from light petroleum become colourless and then melt at 99° . This product is practically insoluble in water, but dissolves easily in organic solvents :

0.2695 gave 15.7 c.c. N_2 at 12° and 757 mm. $N = 6.95$.

$C_{12}H_{11}O_2N$ requires $N = 6.99$ per cent.

By this method of treatment Goldschmidt and Zanolì (*loc. cit.*) obtained the *anti*-aldoxime of furfuraldehyde ; Fromherz and Meigen, proceeding in the same way with methylfurfuraldehyde, obtained a product which was at first considered to be a mixture, but which on further investigation was shown in all probability to be the *anti*-aldoxime. In order to prepare methylfurfuraldehyde *syn*-oxime, the authors named treated the *anti*-compound in ethereal solution with hydrogen chloride, and decomposed the resulting salt with sodium hydroxide. The benzylfurfuraldehyde compound obtained in the manner described above was therefore subjected to a similar treatment ; on passing the gas into the colourless solution, crystals separated, and the liquid became pale yellow. The ethereal solution on evaporation deposited a mass of crystals ; these were washed with a little ether and with water, mixed with excess of aqueous sodium hydroxide, and warmed for five minutes on a water-bath. The rather

yellow liquid so obtained, on cooling, deposited lustrous, silver-white prisms, which melted at 121—122° and, after recrystallisation from light petroleum, at 124° :

0.2245 gave 13.7 c.c. N_2 at 22° and 755 mm. $N = 7.04$.

$C_{12}H_{11}O_2N$ requires $N = 6.99$ per cent.

From analogy to the methylfurfuraldehyde compounds, there appears to be little doubt therefore that the two compounds here described are the *anti*- and *syn*-oximes respectively of benzylfurfuraldehyde. Both compounds when dissolved in dry ether, mixed with slight excess of phenylcarbimide, and kept for twenty-four hours, yield crystalline products; the properties of the derivatives appear also to be different, but they have not yet been thoroughly studied.

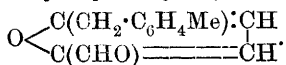
The properties of benzylfurfuraldehyde are in many other respects analogous to those of methylfurfuraldehyde; thus, when concentrated sulphuric acid is carefully added to a dilute solution of benzylfurfuraldehyde in alcohol, a bright blue colour is developed (Maquenne's reaction for methylfurfuraldehyde gives a green colour). Phloroglucinol in presence of concentrated hydrochloric acid gives an orange-red colour; resorcinol produces a somewhat similar effect, and with pyrogallol the colour is crimson; when warmed with carbamide and hydrochloric acid a violet colour results. Aniline acetate gives a yellow colour changing to red.

The oxidation of benzylfurfuraldehyde to benzylpyromucic acid has been attempted in various ways; the method of oxidation by silver oxide in presence of sodium carbonate, which was employed by Hill in the preparation of methylpyromucic acid from methylfurfuraldehyde, yields a colourless, crystalline acid, which has a penetrating frankincense-like odour. The same product is obtained by oxidation of the aldehyde with alkaline potassium permanganate at 20°, according to the method used by Volhard in the preparation of pyromucic acid (*Annalen*, 1891, 261, 379); also, by heating the aldehyde with alcoholic potassium hydroxide, evaporation, extraction with ether, and acidification of the aqueous solution which remains. In all cases, however, the yield is extremely poor and the purification difficult. The partly purified acid melted at 167—169°. The authors intend to make a further study of this acid, when a further supply of material is available, with the object of obtaining benzylfurane.

It is evident that this synthetical method of preparing substituted furfuraldehydes may, if desired, be greatly extended, and the authors propose to make further experiments in this direction.

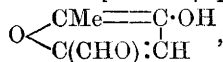
When toluene and chloromethylfurfuraldehyde interact in presence of aluminium chloride, a product is obtained, on steam distillation, which solidifies to a white solid melting at 74.5°. It is nearly insoluble

in water, but dissolves easily in most organic solvents, and its solutions show aldehydic properties. From its mode of formation and properties, this product is presumably *tolylmethylfurfuraldehyde*,



Constitution of Hydroxymethylfurfuraldehyde.

It was shown by Dull in 1895 (*Chem. Zeit.*, **19**, 216) that inulin when heated with a solution of oxalic acid under pressure yields hydroxymethylfurfuraldehyde as a colourless syrup. This substance was afterwards more thoroughly examined by Kiermayer (*loc. cit.*, p. 1003), who obtained it also from sucrose. No positive evidence was forthcoming to indicate the position of the hydroxy-group, but the author considered it probable that it occupied the β -position; this constitution,



has since been universally accepted.

Later it was found by Fenton and Gostling (*Trans.*, 1899, **75**, 430) that bromomethylfurfuraldehyde when treated with the calculated quantity of silver nitrate in aqueous-alcoholic solution, or when boiled with water in presence of barium carbonate, yields a syrup, the properties of which are closely analogous to those of Dull's hydroxymethylfurfuraldehyde. When oxidised with silver oxide, however, the bromo-derivative and the hydroxy-derivative both yield a hydroxymethylpyromucic acid melting at $162\text{--}163^\circ$, which is identical with that obtained by Hill and Jennings (*Amer. Chem. J.*, 1893, **15**, 162) from the bromo-acid, and was shown to be the ω -hydroxy-compound. From this result, and also from the extremely reactive character of the bromine atom in bromomethylfurfuraldehyde, there appears to be little doubt that the hydroxymethylfurfuraldehyde obtained by Fenton and Gostling is also the ω -hydroxy-compound, and it was concluded therefore that it must differ from Dull's product. This conclusion was supported by the fact that Kiermayer obtained, by oxidation of the latter product, a hydroxymethylpyromucic acid melting at 148° . Further, the phenylhydrazone obtained from this hydroxyaldehyde was crystalline, melting at 138° , whereas the corresponding product obtained from Fenton and Gostling's compound appeared to be a liquid. Further investigation now shows, however, that the phenylhydrazone from the latter compound is also crystalline, and that the melting point is the same.

There still remains the fact that the hydroxymethylpyromucic acids derived from the two products appear to be different, and some further evidence is therefore desirable in order to clear up the discrepancy,

especially since the two modes of formation of the hydroxy-aldehyde are so closely allied.

The present authors have now obtained a result which affords a fairly conclusive proof of the correctness of the formula previously assigned to chloro- and bromo-methylfurfuraldehyde, and consequently to the hydroxy-compound which these compounds yield on hydrolysis. When the chloro-derivative is warmed with excess of nitric acid (D about 1·3), a violent action ensues, and the resulting liquid, on evaporation, yields a white, crystalline mass. This product, which is free from chlorine, is very sparingly soluble in cold water, but dissolves easily in boiling water; it crystallises from the latter in needles or prisms, which partly sublime when heated, and show no signs of melting at the boiling point of concentrated sulphuric acid:

0·1005 gave 0·1697 CO₂ and 0·0258 H₂O. C = 46·05; H = 2·85.

C₆H₄O₅ requires C = 46·15; H = 2·57 per cent.

The properties of this product agree entirely with those of furan-2:5-dicarboxylic acid (dehydromucic acid); ferric chloride, for example, gives the well-known characteristic reaction; an aqueous solution of the acid is mixed with a few drops of the reagent and warmed, when a transparent jelly separates.

This result then clearly indicates that the halogen must have occupied the ω -position, and is altogether irreconcilable with the formula suggested for Dull's compound.

The authors consider that, on the whole, the balance of evidence strongly favours the view that the two hydroxymethylfurfuraldehydes mentioned are identical, and that the position commonly assigned to the hydroxyl group in Dull's compound is incorrect.

Preparation of Chloromethylfurfuraldehyde.

Many attempts have been made to improve on the methods previously given for the preparation of the halogen derivatives of methylfurfuraldehyde. Although the yield obtained by these methods is good, the process of extraction is very troublesome when lævulose or sucrose is used, owing to the presence of tarry "humus" substances, and also to the large excess of acid which is necessarily present. The preparation from cellulose avoids these difficulties to some extent, but in this case the operation has to be performed under pressure, and is attended with some danger. Although no substantial improvement has been effected in the preparation of the products on a fairly large scale, the following simple process is found to be very rapid and convenient when only small quantities are required, since it permits the use of aqueous acids.

Lævulose is mixed with about twice its weight of solid calcium

chloride, and the mixture is made into a thin paste by stirring it with concentrated aqueous hydrochloric acid. It is then warmed for a few minutes on a water-bath with constant stirring, until the whole mass is dark brown or nearly black, and is suddenly cooled before actual charring takes place. The excess of acid is then removed by careful addition of solid sodium carbonate, and the mixture is extracted with chloroform. On distilling off the chloroform, the chloromethylfurfuraldehyde remains as a syrup, which, when well cooled and rubbed with a rod, often sets to a crystalline mass. In most cases, however, it is best to purify the product by recrystallisation from hot petroleum, and to promote crystallisation by contact with a trace of the compound which has been previously prepared.

The bromo-compound can be prepared in a similar way, using calcium bromide, or even potassium bromide, and concentrated aqueous hydrogen bromide.

An attempt to obtain the fluoro-compound in this way, using potassium hydrogen fluoride and hydrofluoric acid, has not so far been successful. If calcium chloride and hydrofluoric acid are used, the chloro-compound only results.

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