S 4. *Tetrahydrofurfuraldehyde. Part I. A New Method of Preparation.*

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Tetrahydrofurfuraldehyde can be readily prepared in 60% yield by the oxidation of tetrahydrofurfuryl alcohol with air in the vapour phase over a silver-gauze catalyst.

TETRAHYDROFURFURALDEHYDE cannot be prepared by partial hydrogenation of furfuraldehyde since the aldehyde group is first attacked, forming furfuryl alcohol (cf. Bremner and Keeys, *J.*, 1947, 1068; Owen, *Ann. Reports*, 1945, **42**, 157). If the aldehyde group is protected, as by working with a diacetal (Minne and Adkins, *J. Amer. Chem. Soc.*, 1933, **55**, 299) or diacetate derivative (Scheibler, Sotscheck, and Friese, *Ber.*, 1924, **57**, 1443), tetrahydrofurfuraldehyde is obtained but in poor yield (cf. Hinz, Meyer, and Schucking, *Ber.*, 1943, **76**, 676; Wilson, *J.*, 1945, 52). Somewhat surprisingly, the dehydrogenation of tetrahydrofurfuryl alcohol also gives only small yields of the aldehyde (Hinz, Meyer, and Schucking, *loc. cit.*; Wilson, *loc. cit.*). Furthermore, the chemical oxidation of tetrahydrofurfuryl alcohol with acidified sodium dichromate (Hinz, Meyer, and Schucking, *loc. cit.*) or of decahydrofuroin (Wilson, *loc. cit.*) also appears unattractive. Owen (*loc. cit.*) has pointed out that no satisfactory method for the preparation of tetrahydrofurfuraldehyde has yet been disclosed.

We have confirmed the statements that the hydrogenation of the diacetal and diacetate of furfuraldehyde, the dehydrogenation of tetrahydrofurfuryl alcohol, as also the pyrolysis of tetrahydrofurfuryl vinyl ether (cf. Sheng-Nien Wang and Winkler, *Canadian J. Res.*, 1943, **21**, *B*, 97), and the hydrogen interchange between tetrahydrofurfuryl alcohol and aceto- or benzo-phenone (cf. Hickinbottom, " The Reactions of Organic Compounds ", 1941, 131) are all unattractive as preparative methods. The difficulty attending the chemical oxidation of tetrahydrofurfuryl alcohol to the aldehyde is apparently due to the greater susceptibility of the tetrahydrofuryl nucleus than the hydroxymethyl group to ionic attack (cf. F.I.A.T. Final Report 293, Faragher, Chaffle, Schindler, and Howes; 3/10/45).

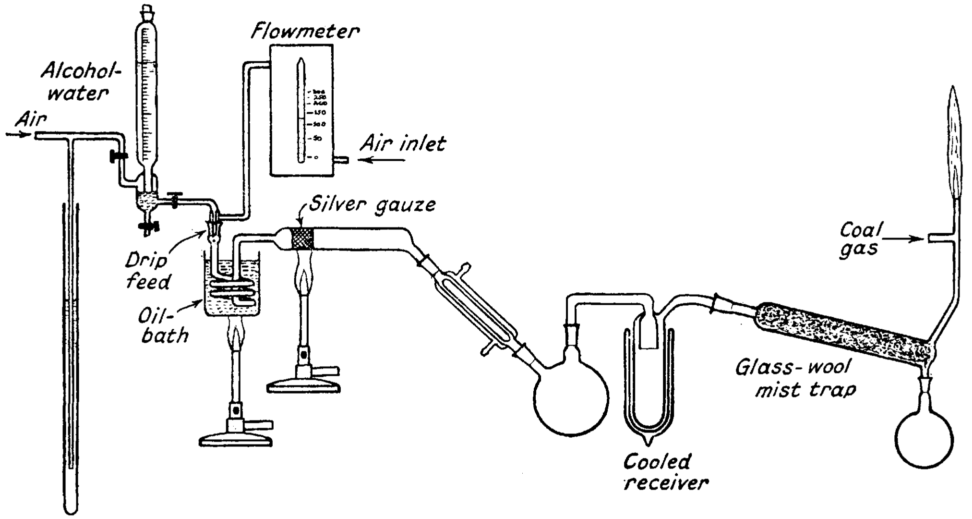
We now describe a convenient method for the preparation of tetrahydrofurfuraldehyde in good yield, using a simple apparatus which can be worked at atmospheric pressure. The process comprises the oxidation of tetrahydrofurfuryl alcohol (B.P. 593,617)—itself readily prepared from furfuraldehyde—by passage with air over a silver-gauze catalyst (see Fig.). Further advantages of this process are that the alcohol is almost completely converted in one passage over the catalyst, and, in consequence, the aldehyde formed can readily be isolated, especially as the by-products of the reaction are carbon oxides and water. The process may, moreover, be worked autothermally, for the heat evolved can, in part, be dissipated by dilution of the alcohol vapour with steam.

EXPERIMENTAL.

Tetrahydrofurfuryl Alcohol.—The distilled material prepared by hydrogenation of furfuraldehyde had $d_{4^\circ}^{20^\circ}$ 1·050, $n_D^{20^\circ}$ 1·450, b. p. 177—178°.

Catalyst.—Silver gauze of 40-mesh size, containing 0·05% of copper, was cut into a strip 1″ × 36″ and rolled to fit closely into the combustion tube of 1″ diameter.

Apparatus.—A calibrated reservoir contains the alcohol–water mixture which drips into a glass helix preheater immersed in an oil-bath at 250° (see Fig.). Inlet air is passed through a differential flow-meter to the preheater. Exit vapours from the preheater pass into a horizontal Pyrex-glass combustion tube (6″ × 1″). It contains the close-fitting roll of silver gauze. The products of oxidation pass through a double-surface condenser which is water-cooled, and the condensed product is collected in a glass receiver immersed in solid carbon dioxide–methanol. Mist is removed from the exit gas by a trap (10″ × 1½″) packed with glass-wool which drains into a glass receiver. The exit gas may be vented outside or, because of its acrid nature, mixed with coal-gas and burned.



Analysis of Products.—Gaseous products were analysed in an Orsat apparatus. The liquid products in the two receivers were mixed and then fractioned at reduced pressure in a column equivalent to about 20 plates. Tetrahydrofurfuraldehyde in the fractions was determined by titration of the acid liberated on reaction with hydroxylamine hydrochloride : the aldehyde was readily oximated at room temperature (Found : CHO, 28·8. Calc. for $C_4H_7O{\cdot}CHO$: CHO, 29·0%).

Procedure.—Tetrahydrofurfuryl alcohol was fed to the preheater as an 80% solution in water. The rate was adjusted to 150—200 ml./hr., air being admitted at 150—250 l./hr. The reaction was initiated by playing a Bunsen flame on the combustion tube surrounding the silver gauze until the catalyst began to glow. Both for the initiation and for the subsequent operation it is convenient to work in a darkened room since the gauze quickly melts by over-heating. Even with thermocouples embedded in the catalyst, local over-heating is possible in equipment of this size. When the gauze glows, the burner is removed, and the liquid and air rates adjusted so that the catalyst is maintained at a dull red heat. A small asbestos case can now be placed round the combustion tube, as it serves, by minimising heat loss from the periphery of the roll, to maintain a more even catalyst temperature. The amount and position of the asbestos can be adjusted to give autothermal operation.

Characterisation of Products.—All four fractions reacted with a 2N-hydrochloric acid solution of 2 : 4-dinitrophenylhydrazine in the cold to give the same (mixed m. p.) dinitrophenylhydrazone; m. p. 134° from ethanol (Hinz *et al.*, *loc. cit.*, record m. p. 135—136°; Wilson, *loc. cit.*, records m. p. 131°) (Found : C, 47·6; H, 4·3; N, 20·0. Calc. for $C_{11}H_{12}O_5N_4$: C, 47·2; H, 4·3; N, 20·0%). Fraction 3 (see table), b. p. 43°/15 mm., consists essentially of tetrahydrofurfuraldehyde (Found : C, 59·9; H, 8·0. Calc. for $C_5H_8O_2$: C, 60·0; H, 8·0%).

Results.—The results obtained in two typical experiments with an 80% solution of tetrahydrofurfuryl alcohol in water are given in the table. The terms pass conversion and yield are used to denote, respectively, the percentage of the tetrahydrofurfuryl alcohol oxidised and the theoretical yield, based on the amount of alcohol converted.

Atmospheric oxidation of tetrahydrofurfuryl alcohol.

Tetrahydrofurfuryl alcohol fed (g.)	420	420
Water fed (g.)	100	100
Air rate (l./hr.)	200	120—150
Duration of experiment (hrs.)	2·5	3·3
Analysis of exit gas (vol. %) :		
O_2	0	0
CO	6·0	3·0
CO_2	4·3	3·2
N_2	86·6	91
H_2	0·6	0·8
C_nH_{2n}	2·5	1·6
Liquid products recovered (g.)	485	506
Distillation of liquid products :		
Fractions 1 and 2, b. p. 31—54°/30 mm. (g.)	176	130
,, ,, $C_4H_7O\cdot CHO$ content (%)	13·3	14·8
Fraction 3, b. p. 57°/30 mm. (g.)	131	165
,, $C_4H_7O\cdot CHO$ content (%)	96	97
Fraction 4, b. p. 82—85°/30 mm. (g.)	98	82
,, $C_4H_7O\cdot CHO$ content (%)	20	25
Total $C_4H_7O\cdot CHO$ (g.)	170	200
Pass conversion (%)	80	85
Yield (%)	52	60

The liquid product was distilled to give four main fractions. The first is a water–tetrahydrofurfuraldehyde azeotrope (b. p. 30°/25 mm.) which contains 15% of aldehyde. The second fraction is viscous (b. p. 40°/15 mm.) and contains $\sim$84% of tetrahydrofurfuraldehyde; it is a hydrate of the aldehyde. Next, a mobile fraction (b. p. 43°/15 mm.) containing 98·6% of tetrahydrofurfuraldehyde distils over. Finally, another mobile fraction (b. p. 43—46°/15 mm.) and containing 20% of tetrahydrofurfuraldehyde is obtained. The first two fractions contain aldehyde and water, the third consists essentially of tetrahydrofurfuraldehyde, and unchanged tetrahydrofurfuryl alcohol comes over with the aldehyde in the final fractions. The distillation of the viscous hydrate at atmospheric pressure gives first the aldehyde–water azeotrope (b. p. $\sim$100°/760 mm.)—of similar composition to that obtained at reduced pressure—and then the anhydrous aldehyde distils over at 145°. As is to be expected, the addition of water to tetrahydrofurfuraldehyde gives the viscous hydrate with a considerable evolution of heat.

The properties of tetrahydrofurfuraldehyde are discussed in Part II (following paper).

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