

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

FURAN REACTIONS. II. FURAN FROM FURFURALBY CHARLES D. HURD, A. R. GOLDSBY AND E. N. OSBORNE¹

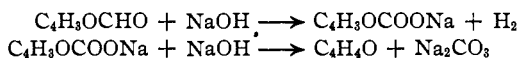
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The present method² for making furan from furfural involves two steps: namely, a Cannizzaro oxidation of furfural to furoic acid, followed by thermal decarboxylation of the acid. In searching for a method which would give furan directly from furfural, two reactions were studied. One of these, which was very successful, consisted in allowing furfural to react with hot alkali. Furan was also formed in the pyrolysis of furfural, but the yields were less satisfactory than in the first reaction.

Furan from Furfural by Hot Alkali.—Fused alkali is an oxidizing agent capable of converting aldehydes into acids (as salts). Thus, acetaldehyde³ gives rise to sodium acetate. With salts it is also a decarboxylating agent and it is pertinent that Limpricht⁴ first prepared furan by heating barium furoate with soda lime. In the present investigation, excellent yields of furan were realized by dry-distilling an intimate mixture of sodium furoate and sodium hydroxide.

To ascertain if these two effects might be combined in the case of furfural in accordance with the equations



the behavior of fused sodium hydroxide and hot soda lime on furfural was investigated. Using this plan, excellent yields of furan were realized.

The flow method seemed to be the better of the two plans tried. In it, furfural vapors were passed through a hot iron pipe which was packed with soda lime. With a rapid flow, furan was isolated in yields as high as 86% of the theoretical. With the other method, furfural was dropped onto a molten mixture of sodium and potassium hydroxides. Yields of about 60% of furan were obtained. Encrustation of the surface of the molten alkali, due to carbonate formation, introduced difficulties which were not encountered in the flow method. Considerable quantities of carbon monoxide and traces of methylacetylene (or acetylene) accompanied the hydrogen in the gas. That these were secondary products of decomposition was established since they were also formed when furan (not furfural) was dropped on the fused alkali.

Pyrolysis of Furfural.—At high temperatures benzaldehyde breaks

¹ Holder of a Quaker Oats Fellowship, 1929–1930, administered through the Miner Laboratories, Chicago.

² Wilson, "Organic Syntheses," John Wiley and Sons, New York, 1927, Vol. VII, p. 40.

³ Fry and Schulze, *THIS JOURNAL*, **48**, 958 (1926).

⁴ Limpricht, *Ann.*, **165**, 281 (1873).

down chiefly into carbon monoxide and benzene.⁵ With a similar type of pyrolysis, furfural should yield carbon monoxide and furan. Preliminary work⁶ demonstrated that no gases were formed as furfural was heated for three hours in a sealed tube at 200 or 275°. Most of the furfural was recoverable, leaving only a small amount of tarry residue on distillation. Using a flow method, 565° was found to be the initial decomposition temperature for a contact time of twenty seconds. With a reduced nickel catalyst, the decomposition temperature was lowered to 345°, which is somewhat higher than the temperature reported by Padoa and Ponti.⁷ However, their catalyst may have been different and their contact time may have been longer.

With the flow method, furfural was found to give fair yields of furan. With a contact time of 0.2 second, only one-twentieth of the furfural decomposed at 660° and one-half at 900°. By increasing the contact time to four or five seconds, two-fifths of it decomposed at 725° whereas four-fifths was altered at 800° and three seconds. At 555° and sixty seconds furfural was found to decompose somewhat but over four-fifths of it was recoverable. The best conditions for furan production by pyrolysis were found to be 725° and a contact time of about five seconds. This gave a 16.5% yield.

Experimental Part

Furfural and Hot Alkali

Fused Alkali.—An iron flask about 30 cm. tall was improvised from a small gas-storage cylinder by removing the connections and drilling away the threads so as to leave a smooth hole in the top. A rubber stopper, bearing a reflux condenser tilted at an angle of 45°, was fitted into this hole. In the top of the condenser was a 2-holed rubber stopper which carried a dropping funnel the stem of which was drawn out to a capillary tip and a tube leading to another condenser which was directed downward for condensation. The first condenser was filled with hot water (about 75°) so as to let the furan escape but to return the furfural. The second condenser, which was cooled with tap water, was connected to a helical lead pipe which was surrounded by a freezing mixture of ice and salt. The condensed furan dropped into a cooled flask. The uncondensed furan was scrubbed out of the escaping gas by conducting it through four bottles (in series) of furfural (50 cc. each), all immersed in a freezing mixture at -20°.

Two moles of furfural were placed in the dropping funnel. In the iron flask were placed two moles of technical sodium hydroxide and two of potassium hydroxide. The furfural was added at the rate of about 0.4 g. per minute after the temperature of the salt-bath surrounding the iron flask reached 300°. Eight hours was taken for the addition. Gas evolution continued for about thirty minutes after all the furfural was introduced.

Of the 192 g. of furfural which was taken, 164 g. was decomposed since 28 g. was recovered. The liquid which distilled below 40° on the first fractionation was considered to be furan. It weighed 67.5 g., which was a 59% yield based on the decomposed furfural.

⁵ Hurd and Bennett, *THIS JOURNAL*, 51, 1197 (1929).

⁶ With John W. Garrett.

⁷ Padoa and Ponti, *Atti accad. Lincei*, [2] 15, 610 (1906).

Several different modifications were tried without material benefit. The yields ranged from 54 to 64%. When the flask was heated by a direct flame considerable carbonization ensued although the yield of furan did not suffer. Curiously, only about 25–30% yields of furan were obtainable if the furfural which had been used for scrubbing was used directly on the hot alkali. One hundred cc. of this "scrubbing" furfural was found to contain 8 g. of water, 79 g. of furfural and 8 g. of a tarry residue. After redistillation this furfural again gave furan satisfactorily.

Other Products of the Reaction.—In a similar experiment wherein 29.0 g. of furfural was treated with 23.2 g. of fused sodium hydroxide, 19.7 g. of furfural was recovered. The 9.3 g. (0.097 mole) of furfural which underwent decomposition gave rise to 4.2 g. of furan (a 56% yield), 905 cc. of gas, and a carbonate residue. The gas was 71% hydrogen (0.029 mole), 22.2% carbon monoxide (0.009 mole), 4.2% methylacetylene or acetylene (0.0017 mole), and 2% carbon dioxide. The carbonate residue on acidification gave 1618 cc. of carbon dioxide. The carbonates in the original alkali gave but 20 cc. of carbon dioxide, hence 1598 cc. was generated in the reaction.

Similarly, when 9.44 g. of furan was dropped onto 10.2 g. of the fused alkali, 6.94 g. of furan was recovered and 137 cc. of gas was collected. *Anal.* CO, 67.14% or 0.0041 mole; H₂, 24.83, 0.0015; acetylenes, 7.94, 0.0005.

The gas formed when a mixture of 13.5 g. of sodium furoate and 4.0 g. of sodium hydroxide was dry distilled at 350–360° was similar. In all, 178 cc. was collected. It analyzed as follows (per cent. and mole): CO, 65.17, 0.0052; H₂, 26.42, 0.0021; acetylenes, 8.37, 0.0007. The yield of furan in this experiment was 6.2 g. or 92.6%.

Flow Method with Soda Lime.—Furfural (760 g.) was distilled during three hours into an iron pipe, 120 × 5 cm., which was about half filled with soda lime. Rubber stoppers were used for the connections. The pipe was heated for about half of its length and an inside temperature of 350–360° was maintained, as shown by a thermometer inside the pipe.

Furfural and furan were condensed from the effluent gas as previously described and the uncondensed gas was stored in a gasometer. On working up the products, 696 g. of furfural was recovered and 39 g. of furan formed, a yield which is 86% of the theoretical.

In a similar experiment wherein 600 g. of furfural was admitted during twelve hours (thus, a slower rate of flow), 318 g. was recovered and 94.5 g. of furan was formed. Here the percentage yield is only 47.5.

A 63% yield (18.5 g.) of furan was realized at 450° (a thermocouple used for the inside temperature) by distilling 192 g. (151 g. recovered) of furfural during three hours through a Pyrex tube which contained a charge of soda lime.

Pyrolysis of Furfural

Apparatus.—The apparatus used was similar to the one described for the pyrolysis of furan, furfural being introduced by displacement with mercury (see preceding paper). The 2-cm. quartz tube was used in most of the experiments but a tube of 0.55 cm. bore was used for the experiments with contact times of less than one second. Furfural and some furan was condensed from the effluent gas by cooling it to –15°. The remaining furan was removed either by cooling in a coil at –80° or by scrubbing with furfural at –15°. The effluent gas was metered and stored over salt solution in a gasometer. The essential data for six characteristic runs are given in Table I.

Gas.—The gas from each run was analyzed, a typical case showing 80% carbon monoxide, 3% carbon dioxide, 6.5% unsaturated hydrocarbons, 10% hydrogen plus saturated hydrocarbons. Generally, about one-fifth of the unsaturated hydrocarbons was ethylene; two-fifths was a mixture of methylacetylene and acetylene, chiefly the former; the remaining two-fifths was absorbed in 82.4% sulfuric acid and was a mixture

TABLE I
 DATA FOR THE PYROLYSIS OF FURFURAL

Furfural taken, g.....	88.5	115	115	259	805	115
Furfural decomposed, g....	83.5	46	26.5	142.5	658	63.5
Extent of decompn., %...	94	40	23	55	82	55
Temperature, °C.....	680	725	755	780	800	900
Duration of expt., min....	112	93	100	184	425	60
Contact time, seconds....	19.4	4.9	0.40	4.0	2.9	0.21
Gas formed (0°), liters....	36.2	24.3	11.5	112	308
Benzene isolated, g.....	2.6	0.9	0.4	...	19	0.2
Toluene isolated, g.....	2.5	5.5
Carbon formed, g.....	17
Furan yield, g.....	2.0	5.4	2.0	8.2	22	0.2
Furan yield, %.....	3.4	16.5	10.0	8.1	4.7	0.4

of propylene, allene, butadiene and cyclopropene. The methylacetylene was established through the mercury derivative, $(\text{CH}_3\text{C}\equiv\text{C})_2\text{Hg}$.

In several runs, the unsaturated content of the gas was converted into bromide derivatives. The dibromide fraction was found by refractive index measurements to be a mixture of about equal weights of ethylene and propylene bromides. For each cc. of dibromides there was produced about 1.5 cc. of tetrabromides. From the latter, butadiene tetrabromide, m. p. 116–116.5°, separated easily. Its identity was confirmed by a mixed melting point determination with an authentic specimen prepared from phosphorus pentabromide and erythritol. In the experiment wherein 805 g. of furfural was taken, 11 g. of pure butadiene tetrabromide was secured and, of course, more was held in the mother liquor. The latter contained tetrabromides of methylacetylene, acetylene, allene and cyclopropene. This material evolved hydrogen bromide⁸ at room temperature.

The mixture of tetrabromides from which the butadiene tetrabromide had been filtered off was added dropwise on zinc dust and boiling alcohol. Analysis of the unsaturated hydrocarbons which were thus regenerated showed the presence of 20% acetylenes and 80% other gases which were soluble in 82% sulfuric acid. The latter points to allene, cyclopropene or butadiene inasmuch as propylene should have been largely eliminated.

Liquid Products.—Furan, benzene and toluene were separated from the liquid products by distillation. Yields of 13–16.5% of furan were realized at 725° and about five seconds contact time. Higher temperatures, even with a diminished contact time, lessened the yield.

The benzene fraction was characterized by converting it into *m*-dinitrobenzene, m. p. 89°. In the 105–115° fraction, toluene was identified as 2,4-dinitrotoluene, m. p. 69–70°.

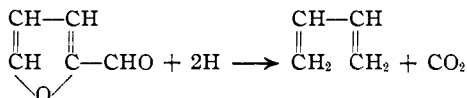
After distillation of the unused furfural, considerable residue boiling above 185° remained. This was largely phenolic. From the 88.5 g. (of furfural) run at 680° and 19.4 sec., 15 g. of this residue was encountered. Eleven grams of this was extracted with 10% sodium hydroxide solution whereupon 6 g. of phenolic material was obtained. Another 3 g. of similar material was extracted from the residue by refluxing for half an hour with 50 cc. of 20% sodium hydroxide solution. This material was not soluble in sodium bicarbonate solution. Hence, it could not have been furoic acid and, therefore, furfuryl furoate could not have been present in the original mixture. It will be recalled that under certain conditions of pyrolysis benzaldehyde changes into benzyl benzoate.

⁸ Freundler, *Compt. rend.*, **124**, 1157 (1897), reported that cyclopropene tetrabromide behaved in this way.

The tarry material which was not soluble in alkali would have contained any difuryl. α, α' -Difuryl is reported⁹ to distil at 240° and 7 mm. Our residue gave no distillate in this range.

Distillation of the phenolic portion gave a fraction, b. p. 183–190°. This was identified as phenol, for it yielded pure tribromophenol readily with bromine. An unidentified phenolic fraction was collected between 205–245° but the 245–250° fraction solidified on cooling. The latter melted at 46°, which suggests 2,6-dimethylphenol, m. p. 49°. The α -naphthyl isocyanate derivative¹⁰ of this phenol is not listed, but the higher melting 2,5-dimethylphenol gives a derivative melting at 172–173°. Our 46° material gave a derivative which melted at 174–175°. Molecular weight evidence on the 46° material was satisfactory for a xylenol. Trinitrotoluene was used as a cryoscopic solvent¹¹ and to test the method cresol gave a value of 104.5 as compared with the theoretical value of 108. The 46° crystals gave a value of 115, whereas the mol. wt. of xylenol is 122.

Dilution Experiment with Hydrogen.—No carbon dioxide was formed in the pyrolysis of furan (see preceding paper) but with furfural it comprised 2 to 3% of the gas. Since its formation was approximately equivalent to that of butadiene, it suggested the following equation



Accordingly, it was of interest to study the effect of hydrogen on furfural at high temperatures. The results showed a minor increase in the total unsaturated gases but in general no marked change resulted. For example, using a temperature of 750°, 245 g. of furfural was passed through the furnace in 218 minutes together with a current of dry hydrogen, introduced at a rate of 50–300 cc. per minute. There were formed 6 g. of furan, 4 g. of benzene and 3.5 g. of butadiene tetrabromide. The other liquid and gaseous products were also similar to those obtained without the admixed hydrogen.

Summary

Toward heat alone, furfural changes above 550° into furan and its decomposition products, carbon monoxide, methylacetylene, etc. Also, butadiene, benzene, toluene, phenol and a xylenol were identified. Excellent yields of furan were realized by passing furfural vapors through soda lime at 350° or through fused sodium hydroxide. Hydrogen was liberated and the hydroxide was changed to carbonate. The hot alkali converted a small portion of the furan into gaseous products.

EVANSTON, ILLINOIS

⁹ Kondo and Suzuki, *J. Pharm. Soc. Japan*, No. 544, 501 (1927).

¹⁰ French and Wirtel, *THIS JOURNAL*, 48, 1736 (1926).

¹¹ Pastak, *Bull. soc. chim.*, 39, 82 (1926).