TETRAHYDROFURFURALDEHYDE AND RELATED COMPOUNDS

DISSERTATION

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I. INTRODUCTION

Several attempts have been made to prepare tetrahydrofurfuraldehyde. In most instances they have been quite unsuccessful. The main difficulty encountered was apparently the result of the great susceptibility of the tetrahydrofuran nucleus to ionic attack (25). During the course of the present investigation, four additional methods were tried in an attempt to effect a satisfactory synthesis.

\( \delta \)-Valerolactone, an isomer of tetrahydrofurfuraldehyde, has been identified as one of the products formed when tetrahydrofurfuryl alcohol is passed over metallic catalysts at high temperatures (1,2,3). The primary reaction, however, was elimination of the side chain with tetrahydrofuran as the main product. It was noticed that the catalysts of high copper content gave greater yields of the lactone. This fact suggested the intermediate formation of tetrahydrofurfuraldehyde. The lactone would then arise by the rearrangement of the aldehyde. This would be analogous to the rearrangement of cyclobutane-carboxaldehyde to cyclopentanone (26).

\( \delta \)-Valerolactone is also known to arise from cyclic dehydrogenation of 1,5-pentanediol under conditions similar to those which were present in the above reactions (4,5).
The mechanism of its formation has not been investigated but it must proceed through one or both of the dehydrogenation products of the diol. It has been shown (6) that \(\sigma\)-hydroxyvaleraldehyde exists in equilibrium with the cyclic acetal, the latter comprising ninety-five percent of the mixture.

These sequences of reactions were considered because (1) it is known that tetrahydrofurfuryl alcohol can be converted to 1,5-pentanediol by hydrogenolysis (7,8,9), and (2) 3,4-dihydro-2H-pyran is one of the products formed from tetrahydrofurfuryl alcohol upon dehydration and metal-catalyzed pyrolysis (33,6). Addition of water and subsequent dehydrogenation would yield the lactone.
The purpose of this investigation was to study the behaviour of tetrahydrofurfuraldehyde as the intermediate in side chain elimination and lactone formation and also the behaviour of the other proposed intermediates in the formation of $\alpha$-valerolactone.
II. HISTORICAL

Tetrahydrofurfuraldehyde -- In 1924, Scheibler, Sotscheck, and Friese (10) attempted to reduce the furan ring of furfural, but found that more than two mols of hydrogen were always taken up. The diethyl acetal and the diacetate of furfural were prepared, and reduction of the furan ring then effected. Better success was achieved using the diacetate derivative, and the pure derivative of tetrahydrofurfuraldehyde was obtained. Hydrolysis of the derivative yielded a small amount of crude aldehyde.

Minne and Adkins (11) also prepared the diethyl acetal of furfural, and were able to reduce the furan ring in good yield. However, a good deal of resinification occurred during the hydrolysis of the acetal, and some difficulty was experienced in separating the aldehyde from the water-alcohol mixture. The overall yield of tetrahydrofurfural was 4 percent based on furfural.

Hinz, Meyer, and Schücking (12) made several attempts to prepare tetrahydrofurfuraldehyde. They tried to reduce furfural diacetate by hydrogenation in ether with Raney nickel but obtained only furfuryl acetate and acetic acid. Reduction of the cyclic ethylene glycol acetal of furfural in ether solution with Raney nickel was accomplished in 96 percent yield. However, the hydrolysis of
of the tetrahydrofurural derivative resulted in a 9 percent yield of aldehyde. The bulk of the acetal was recovered unchanged.

These workers also oxidized tetrahydrofuranyl alcohol with chromium trioxide, but obtained poor (less than 10 percent) yields of the aldehyde, unchanged alcohol and tetrahydropyromucic acid. Attempted dehydrogenation of the alcohol with a copper catalyst yielded only a slight trace of tetrahydrofururaldehyde.

A very small yield of this aldehyde was obtained by Wilson (13) from the passage of tetrahydrofuranyl alcohol over nickel and nickel alloy catalysts, but only at low pressure. In attempting a synthesis, he pyrolyzed a mixture of barium tetrahydrofuroate and barium formate, but tetrahydrofuranyl alcohol was formed. Also attempted was a Stephens reduction of tetrahydrofururonitrile, but this reaction yielded 3-hydroxyvaleraldehyde. Two more approaches were investigated in which cases the 2,4-dinitrophenyldrazine was identified but no aldehyde was isolated. In the first instance furcin was formed, reduced to the pinacol, then oxidized in glacial acetic acid with lead tetraacetate. Secondly, tetrahydrofuranyl alcohol over copper chromite at 300-350° gave a fraction boiling 140-160° from which the derivative was obtained.

The most successful method reported to date is that
of Bremner and Coats (14). They claimed a 60 percent yield of tetrahydrofurfuraldehyde by the oxidation of tetrahydrofurfuryl alcohol. The reaction was carried out in the vapor phase by passing a mixture of alcohol, water and air over a silver-gauze catalyst.

Formation of $\alpha$-valerolactone -- Wilson (13) investigated the behaviour of tetrahydrofurfuryl alcohol over a variety of nickel and nickel alloy catalysts. Removal of the side chain was the main reaction observed, with tetrahydrofuran as the chief product. Among the gaseous products was carbon monoxide.

Other catalysts (2) 80 Co, 20 Cu; cupronickel (19.7 Ni, 80.3 Cu); ferry alloy (43.9 Ni, 54.3 Cu); 80 Ni, 20 Cu; 20 Co, 80 Cu gave similar results, but also small amounts of $\alpha$-valerolactone. Possible lactone formation by direct reaction of carbon monoxide and tetrahydrofuran in the vapor phase was investigated by Ballantyne (5), but no reaction was observed. Thomas (3) also found $\alpha$-valerolactone when tetrahydrofurfuryl alcohol was passed over iron-copper catalysts; the amount of lactone in the product increased with the copper content of the catalyst. Accompanying products were valeric acid and tetrahydrofurfuryl valerate. The presence of valeric acid was not unexpected since it was shown to arise from reductive fission of $\alpha$-valerolactone (2).
Several investigators have reported $\alpha$-valerolactone from 1,5-pentanediol. A 78 percent yield of crude lactone (15) was obtained by refluxing the diol over copper chromite at 210-245° for thirty minutes. Similarly, Bremner and Jones (4) obtained the lactone by refluxing the pentanediol at 180-230° over copper chromite. They also reported a vapor phase reaction yielding $\alpha$-valerolactone. This product was formed in 65 percent yield when the diol was passed over a copper-zinc oxide catalyst which had been reduced at 300° with hydrogen. Further vapor phase reactions were carried out by Ballentine (5). He investigated the behaviour 1,5-pentanediol over copper chromite, a 50Fe, 50Cu catalyst and a 50Ni, 50Cu catalyst, and obtained the lactone in all cases; the lactone was the main product when the chromite catalyst was used.

$\alpha$-Valerolactone was also formed by air oxidation of $\alpha$-hydroxyvaleraldehyde (16). The yield without a catalyst, at 100°, was 65 percent, and with a cobalt acetate catalyst was 76 percent at 80-90°.
III. EXPERIMENTAL

A. Tetrahydrofurfuraldehyde

1. McFadyen-Stevens Reaction (27)

\[ \text{CH}_2\text{CH}_2\text{O} + \text{H}_2\text{NNH}_2\text{H}_2\text{O} \rightarrow \text{CH}_2\text{CH}_2\text{O} + \text{MeOH} \]

\[ \text{CH}_2\text{CH}_2\text{O} \xrightarrow{\text{K}_2\text{CO}_3, \text{glycerol}} \text{CH}_2\text{CH}_2\text{O} \]

Methyl tetrahydrofuroate was prepared by reduction of methyl furoate under fifteen atmospheres pressure at 130°, using Raney nickel as the catalyst. In a typical reduction, four mols of the ester were reduced in eight hours. The average yield was seventy percent.

Tetrahydrofuroylhydrazide — Methyl tetrahydrofuroate, 65 g. (0.5 mol), and 1 mol of 100 percent hydrazine hydrate were placed in a 250-ml. Erlenmeyer flask. The flask was shaken at intervals for a few minutes until the evolution of heat subsided. The solution was transferred to a Claisen flask and the excess hydrazine, water and methanol removed under high vacuum. The remaining
material was then distilled under vacuum, yielding 63.0 g. of a colorless, viscous liquid, b.p. 126-128°/4-5 mm. The yield of product was 97 percent.

**Tetrahydrofuroyl-p-tolylsulfonhydrazole** -- Sixty-five grams (0.5 mol) of tetrahydrofuroylhydrazide were dissolved in 400 ml. of pyridine contained in a one-liter Erlenmeyer flask. The solution was cooled in ice water, and 104.5 g. (0.55 mol) of p-toluenesulfonyl chloride was added slowly. The mixture was stirred during the addition, which was accomplished in thirty minutes. The resulting solution was allowed to stand at room temperature for two hours, then poured onto ice and water. Immediate precipitation of a white, crystalline material resulted, but the mixture was stirred and allowed to stand for several hours to ensure complete precipitation. The precipitate was then collected on a Buchner funnel and washed with dilute hydrochloric acid and water. The sulfonhydrazole was recrystallized from aqueous alcohol, and dried in an oven at 80°. It melted from 136-138°. A sample was analyzed; calcd. for C\textsubscript{12}H\textsubscript{16}O\textsubscript{4}N\textsubscript{2}S: C, 50.70; H, 5.63. Found: C, 50.80; H, 5.60.

**Decomposition of tetrahydrofuroyl-p-tolylsulfonhydrazole** -- A solution of 94.7 g. (0.33 mol) of tetrahydrofuroyl-p-tolylsulfonhydrazole in 500 ml. of glycerol was added to a solution of 116 g. (0.83 mol) of potassium
carbonate in 500 ml. of glycerol in a two-liter Claisen flask. The apparatus was set for vacuum distillation and the pressure lowered to 30 mm. The solution was heated vigorously, and evolution of a gas started almost immediately. The evolution ceased after a couple minutes, by which time the bath temperature had reached 105°. Heating was continued as some material slowly distilled. Sixteen and six-tenths grams of distillate were collected, b.p. 42-49°/30 mm. No further distillate was observed below the boiling point of glycerol. The collected distillate boiled from 99-101° at atmospheric pressure and was found to be water with traces of other materials. A 2,4-dinitrophenylhydrazine derivative was formed when a sample was added to the reagent. After standing overnight, it was collected and washed with dilute acid and water, then dried and recrystallized twice from ethyl alcohol and ethyl acetate. It melted from 127.9-130.0°. A mixed melting point with an authentic sample of tetrahydrofurfuraldehyde dinitrophenylhydrazone melted from 128.0-129.9°.

The remaining material was polymeric. When the glycerol was removed by distillation, a dark tarry residue remained.

2. Rosenmund Reaction (28)
Tetrahydrofuroyl chloride -- One hundred milliliters of cold, dry ether, containing 5-7 drops of dry pyridine were placed in a 500-ml. suction flask. A calcium chloride tube was attached to the side arm. Twenty-six milliliters (about 0.33 mol) of thionyl chloride, followed by 34.8 g (0.3 mol) of tetrahydrofuroic acid were then warmed on the steam bath for fifteen minutes. At this point the drying tube was removed, a boiling chip added, and water-pump suction gradually applied to remove all the excess ether and thionyl chloride. During this period, the bath temperature was kept below 40°. Vacuum distillation of the remaining liquid produced 34.8 g of a colorless liquid, b.p. 66-67°/16.5-17.5 mm. The yield was 87 percent of theoretical.

Reduction of Tetrahydrofuroyl chloride -- The procedure followed for the reduction was essentially that described in organic syntheses (18). Twenty-three and four-tenths grams (0.174 mol) of tetrahydrofuroyl chloride and 75 ml of dry benzene were placed in a 250-ml. three-neck flask, and three grams of Pd-BaSO₄ catalyst (19) added. The air in the flask was displaced, the stirrer started, and heating began. The temperature was maintained at benzene reflux as the hydrogen was added. In four hours,
all the added base was neutralized.

The benzene was removed under vacuum, then the remaining material distilled. The only fraction collected was from 99-107°/3.5-4 mm. and contained 4 g. of distillate, identified as tetrahydrofuroic acid. Traces of tetrahydrofurfuraldehyde were observed from the formation of its 2,4-dinitrophenylhydrazone when the benzene distillate was added to the 2,4-dinitrophenylhydrazine reagent.

3. Oppenauer Oxidation —

\[
\begin{align*}
\text{CH}_2 = \text{CH}_2 &+ \frac{1}{3} \text{Al(OCH}_3)_3 \rightarrow \frac{1}{3} \text{Al(OH}_2\text{C-C}_3) \text{OCH}_3 + \text{CH}_3\text{C-CH-CH}_3 \\
\text{CH}_2 = \text{CH}_2 &+ \frac{1}{3} \text{Al(OH}_2\text{C-C}_3) \text{OCH}_3 \rightarrow \frac{1}{3} \text{Al(OH}_2\text{C-C}_3) \text{OCH}_3 + \text{C-COCH}_3
\end{align*}
\]

The procedure followed was the one described by Lauchnerauer and Schinz (29).

In a liter Claisen flask were placed 102 g. (1 mol) of tetrahydrofurfuryl alcohol and 66 g. (0.33 mol) of aluminum isopropoxide. The mixture was warmed rapidly to 65°, then gradually raised to 100-110° within forty-five to sixty minutes. The pressure was lowered but kept above 35°.
To complete the reaction the temperature was raised to 130-140°C. At this point it was sometimes necessary to add about 10 ml. of tetrahydrofurfuryl alcohol to aid the solution of the aluminum salts. When the last of the solid isopropylate disappeared, 50 g. of isopropanol had been collected. One hundred and seventy-seven grams of anisaldehyde were added all at once. The bath temperature was about 120°C at this point and was slowly raised. The pressure was kept so that any distillate came over at 70-90°C. Tetrahydrofurfuraldehyde was not forthcoming at the expected temperature and pressure, and could not be induced by either increasing the reaction temperature or reaction time. The presence of small amounts of aldehyde was detected (by the formation of the dinitrophenylhydrazone) in the aqueous distillate that was always present (20 ml. of water after heating the reaction mixture for forty-eight hours).

4. Sodium Trimethoxyborohydride Reduction of Tetrahydrofuroyl Chloride (30).

\[
\text{CH}_2-\text{CH}_2 \quad \text{CH}_2-\text{CH}_2
\]

\[
\text{CH}_2\text{O} \quad \text{C-C-Cl} + \text{NaHBO(OCH}_3)_3 \rightarrow \text{CH}_2\text{O} \quad \text{C-C-H} + \text{NaCl}
\]

Tetrahydrofuroyl Chloride -- The preparation of this compound has been described above.

Tetrahydrofurfuraldehyde -- Thirteen and four-tenths grams (0.1 mol) of tetrahydrofuroyl chloride was dissolved
in 35 ml. of tetrahydrofuran and placed in a three-neck flask equipped with a stirrer, a dropping funnel, and a low temperature thermometer. The solution was cooled to -40° in a dry ice-acetone bath, and maintained at that temperature while 13 g. (0.1 mol) of sodium trimethoxyborohydride in 55 ml. of tetrahydrofuran were added with stirring during twenty minutes. The cooling bath was then removed and the mixture allowed to come to room temperature (one hour). Formation of a white colloidal precipitate of sodium chloride occurred during this period. This precipitate was removed and washed by centrifugation.

At this point a 0.25-ml. aliquot from 25 ml. of solution was converted into the 2,4-dinitrophenylhydrazone (0.10 g.), indicating a 3.5 percent yield of aldehyde.

A sweet smelling residue remained after the tetrahydrofuran was removed. A good deal of tarring occurred during the vacuum distillation, but 4.0 g. of distillate b.p. 69-73°/5 mm. was collected. The odor and the infrared spectrum suggested an ester, so the distillate was refluxed overnight with 10 ml. of 20 percent aqueous sodium hydroxide. The sweet odor disappeared, and tetrahydrofurfuryl alcohol and tetrahydrofurfurolic acid were identified as the components of the ester.
B. Preparation of tetrahydrofurfuraldehyde — The method of Bremner and his associates (14) was used to prepare the aldehyde required for the following experiments.

Distilled tetrahydrofurfuryl alcohol, boiling range 174-178°, was fed to the preheater as an 80 percent solution in water. To start the reaction a Bunsen flame was played on the combustion tube surrounding the catalyst until the gauze began to glow. The burner was then removed and the liquid and air rates adjusted so that the catalyst was maintained at a dull red heat.

The product was distilled under vacuum and a fraction boiling at 43°/15 mm. collected. Distillation at atmospheric pressure yielded tetrahydrofurfuraldehyde, boiling 144-145°.
C. Attempted Rearrangement of Tetrahydrofurfural

1. **In Ethanol, with Mercuric Chloride** -- Ten grams of tetrahydrofurfural and 20 ml. ethanol were mixed in a round-bottom flask and 0.1 g. of mercuric chloride added. The mixture was refluxed for six hours. The resulting mixture was then distilled under vacuum, the alcohol being removed under high vacuum. Unchanged tetrahydrofurfural distilled from 44-47°/15 mm, and the aldehyde acetal from 59-61°/4 mm. The latter was identified by its infrared spectra, which showed the absence of hydroxyl and carbonyl bands, and by the formation of the 2,4-dinitrophenylhydrazone of tetrahydrofurfuraldehyde. A sample, when added to the dinitrophenylhydrazine reagent, slowly formed a derivative. After allowing it to stand for several hours, the derivative was collected and recrystallized from a mixture of ethyl acetate and ethyl alcohol. The derivative was dried in an oven at 80°, and melted from 130.8-132.6°. A mixed melting point with authentic tetrahydrofurfuraldehyde dinitrophenylhydrazone showed no depression. Analysis of a sample yielded the following data: found C, 61.85; H, 10.46. Calculated for C₉H₁₆O₃: C, 62, 04; H, 10.41.

2. **In n-Pentanol, with Mercuric Chloride** -- Ten grams of tetrahydrofurfuraldehyde and 20 ml. of n-pentanol were mixed in a round-bottom flask and 0.1 g. of mercuric
chloride added. The mixture was refluxed for six hours. The pentanol was removed under vacuum, and then the remaining liquid likewise distilled. Two fractions were collected, the first distilling from 110-115°/3 mm. (3.3 g.), and the second from 123-128°/3 mm. (5.2 g.). Three grams of residue yet remained. Lactone formation was not observed, and the derivative of tetrahydrofuraldehyde was not formed when samples from either fraction was added to 2,4-dinitrophenylhydrazine solution. Further experiments to determine the nature of the products were not performed.

3. In Ether, with Phosphorus Pentachloride — Ten grams of tetrahydrofurfural and 20 ml. of dry ether were mixed in a round-bottom flask and 0.1 g. of phosphorus pentachloride added. The mixture was refluxed for six hours. The ether was removed under vacuum, then the remaining material vacuum distilled. Two grams of product, boiling 100-105°/2 mm. were collected. The remaining product was non-distilling residue. Tests for y-valerolactone gave negative results. The nature of the product collected was not determined.

4. Over acid-saturated pumice — A small furnace was used for this experiment. It was made by the Hoskins Manufacturing Company, Detroit, Michigan, Type FD 303, and was controlled by a Brown Electric Pyrometer. It was twenty-five inches in length and held a pyrex tube one
inch in diameter.

One hundred and twenty grams of pumice, with particles about 0.2 cm. in diameter, was stirred for several hours with a 60 percent sulfuric acid solution, then filtered and air dried for two hours. The catalyst was introduced into the catalyst tube, and the temperature slowly raised to 170-180°. About 20 ml. of water was collected during this period. Nitrogen (10 l./hour) was next passed over the catalyst, and then the addition of the aldehyde begun. The rate of flow was adjusted to 0.25 mol/hour.

The furnace product was collected in a receiver cooled in dry ice-acetone, and was found to be water. From 13 g. of aldehyde, 7 g. of water was collected.

D. Preparation of \( \delta \)-hydroxyvaleraldehyde

The procedure followed was essentially that of Woods (80) as modified by Dineen (22). To a one-liter flask fitted with an air-stirrer and condenser was added 36 g. (0.40 moles) of dihydropyran, 150 ml. of distilled water and portionwise 2 ml. of concentrated hydrochloric acid. The reaction was highly exothermic and had to be cooled by an ice-water bath. After twenty-five to thirty minutes, the suspension coalesced to one phase; the solution was agitated for another thirty minutes, and neutralized with
solid potassium carbonate to a light pink with phenolphthalein. A small amount of 2 N hydrochloric acid was added until the pink color just faded. The reaction mixture was then saturated with chemically pure sodium chloride and immediately hand extracted with five 100-ml. portions of diethyl ether, and dried over anhydrous sodium sulfate. The extract was filtered to remove the sodium sulfate and washed with ether which had been dried with calcium chloride. The filtrate was distilled to remove the ether and then distilled in vacuo from a 50-ml. flask.

E. Preparation of Glutaraldehyde

\[
\begin{align*}
\text{CH}_2 & \quad \text{CH}_2 \\
\text{CH} & \quad \text{OCH}_2\text{CH}_3 \\
\text{C} = \text{O} & \quad \text{CH} \quad \text{O} \\
\text{H} & \quad \text{CHOEt}
\end{align*}
\]

2-Ethoxy-3,4-dihydro-2H-pyran (31) -- 22.4 g. (0.4 mol) of acrolein and 28.8 g. (0.4 mol) of vinyl ethyl ether were heated in a 100-ml. steel pressure bomb for one hour at 190°. The resulting product was distilled and yielded 42.5 g. of 2-ethoxy-3,4-dihydro-2H-pyran, b.p. 142-144°.

Glutaraldehyde -- Fifty and two-tenths grams of 2-ethoxydihydropyran were added to 250 ml. of distilled water. The mixture was stirred as 15 ml. of concentrated hydrochloric acid was added in portions. After fifty to sixty
minutes, the suspension coalesced to one phase. Stirring was continued for another thirty minutes after which the solution was neutralized with solid potassium carbonate. The solution was then salted out with sodium chloride, and extracted with five 100-ml. portions of ether. The extract was dried over sodium sulfate, then filtered and distilled to remove the ether. The residue was distilled under vacuum and yielded 27.3 g. of glutaraldehyde, b.p. 64-66°/6 mm.

F. Pyrolysis Apparatus

1. Catalysts — The 90Cu, 10Fe and the 80Ni, 20Cu catalysts were 4-16 mesh granular sintered metals and were obtained from the Metals Disintegrating Corporation of Elizabeth, New Jersey.

   The copper chromite catalyst was a product of the Harshaw Chemical Company and was obtained in the form of small cylindrical shaped pellets of 4-20 mesh size.

2. Furnace — A detailed description of the furnace has been given by Ballantine (5). A temperature, constant to plus or minus 5° could be maintained over 40 in. of the furnace tube.

3. Catalyst Tube — The catalyst tube was made from a 60 in. length of 45-mm. pyrex glass tubing. This tube was constricted at one end and to this end was sealed a 24/40 ground glass inner joint. When in operation the
glass catalyst tube protruded about 6 in. from both ends of the furnace. The catalyst tube was fitted at the lower end with a spacer and catalyst support. This support was made of a nickel wire screen disc and rested on the spacer which was made from a 6-in. length of 25-mm. glass tubing. This spacer rested on the constriction of the catalyst tube and was flared at the upper end to support the nickel disc.

The top end of the catalyst tube was fitted with a two hole rubber stopper; one hole was for the entrance of a dropping funnel through which feed was introduced and the other for the insertion of a thermocouple well.

The thermocouple well, made from 7-mm. pyrex glass tubing sealed at one end, extended through the rubber stopper and rested on the catalyst support disc.

The thermocouple was made from a chromel-alumel pair fused at one end. The couple was encased in a chain of 1.5 in. pieces of two-hole porcelain sleeving and was extended over a pulley above the furnace. The pulley permitted the thermocouple to be raised or lowered easily so that a record of the temperature at any point in the catalyst tube was readily obtained. The thermocouple was connected to a Wheelco Capacitrol which served as a temperature indicator.
4. Constant Rate Addition Funnel — The liquid feed and carrier gases were added by means of a specially constructed dropping funnel. The main portions were made from a 200-ml. round-bottom pyrex flask and a piece of capillary tubing. The rate was controlled by raising or lowering the position of a wire in the capillary section and with moderate care constant rates could be obtained over many hours.

5. Control of a Carrier Gas — The rate of gas flow was controlled by a needle valve and was measured by a flowmeter provided with a set of capillary tubes. The flowmeter was filled with dibutyl phthalate and was calibrated for each gas used.

6. Activation of the Catalyst — The various catalysts were activated by air oxidation followed by reduction with hydrogen. The oxidations were carried out by first raising the catalyst temperature to approximately 500°. Air was then pushed through the catalyst bed at a controlled rate, about 1-3 l./hour for the first few hours. Then the flow was increased to 5-10 l./hour. The oxidation was strongly exothermic and with too rapid a stream of air the temperature rose sufficiently high to melt the glass catalyst tube. The catalysts with a high percentage of iron were most easily oxidized and required careful adjustment of the air flow, while the nickel catalyst was much less
easily oxidized. The progress of the oxidation could be closely followed because a hot band appeared at the point when oxidation was occurring. This hot band, about 1/2 in. in depth, was as much as 60° higher than the average temperature in the catalyst bed. The hot spot appeared first at the top and moved slowly downward requiring generally 48-72 hours for complete oxidation of a 40 in. bed.

The oxidation was followed by reduction at 350°. This operation was much less sensitive and the hot band was much less pronounced. Hydrogen, added at the rate of 20 l./hour, was used for the reduction. The water formed in the reduction was caught in a flask attached to the bottom of the catalyst tube. Reduction was continued until no further water formation was noted and the amount of water formed was taken as a rough estimate of the activity of the catalyst being used.

G. Behaviour of Proposed Intermediates in Lactone Formation

1. Tetrahydrofurfuraldehyde over 90Cu, 10Fe Catalyst —
The aldehyde was added to an activated catalyst (yield of water-88 ml.) at a constant rate after the desired temperature had been reached and the carrier gas flow maintained at 10 l./hr. After the addition was completed, the gas flow was maintained for at least two hours in order to clear the catalyst tube of reacted products.
The receiver was a 100-ml, round-bottom 2-neck flask, with 19/38 and 10/30 ground glass outside joints. It was joined to the catalyst tube by a 24/40 to 19/38 adapter. Leading from the second neck was a 8 in. piece of 6 mm. pyrex tubing in the shape of an inverted U, terminated at one end by a 10/30 ground glass inside joint. A short piece of rubber tubing connected this to the dry ice trap. The trap was made in the following manner. Fourteen-inch lengths of 50-mm. pyrex tubing were sealed at one end, and 11.5 inches from the bottom was placed a side arm. Inserted in these tubes were Number 10 rubber stoppers which were pierced by 19/40 ground outer joints joined to 6.5-inch lengths of 35-mm. pyrex tubing. The large opening was to prevent the trap from becoming stopped by frozen material.

Reaction products were collected in the receiver, and in the dry ice trap. The materials were combined, then distilled from a small distilling flask. A rough separation was made by collecting fractions at the following temperatures: 50-75°, 95-104°, 120-160°, 170-185°, 200-235°.

Fraction 1— The first fraction was small in all cases. The yields from several runs were combined and placed over solid sodium hydroxide pellets. After several hours, a sample was added to an excess of a 2 N
hydrochloric acid solution of 2,4-dinitrophenylhydrazine. The dinitrophenylhydrazone of \( \gamma \)-hydroxybutyraldehyde was formed, indicating the presence of dihydrofuran. This means of identification is described elsewhere in this work. Tetrahydrofuran was identified by infrared spectroscopic analysis, as will also be described.

**Fraction 2** — This fraction contained water and small amounts of tetrahydrofurfuraldehyde from the water-aldehyde azeotrope (114). The aldehyde was detected and identified by the formation of the 2,4-dinitrophenylhydrazone derivative.

**Fraction 3** — This fraction consisted mainly of tetrahydrofurfuraldehyde. Refractionation of the combined products from several runs yielded material boiling from 110-115°. This was unchanged tetrahydrofurfuraldehyde as identified by the formation of its 2,4-dinitrophenylhydrazone.

**Fraction 4** — This fraction, after drying over calcium sulfate, was tested for tetrahydrofurfuryl alcohol by formation of its 3,5-dinitrobenzoate according to a procedure described in Shriner and Fuson (24), m.p. 82.5-84.5°, m.m.p. 82.6-84.5° with an authentic sample, m.p. 83.5-85.0°. The alcohol was found to make up the bulk of the fraction. In some instances, a trace of acidic material was detected. The amount was estimated by titration with
standard alkali after being identified as n-valeric acid by the formation of its p-bromphenacyl derivative, m.p. 70.2-71.5°, m.m.p. 70.5-71.5° with an authentic sample, m.p. 71.0-72.0°.

**Fraction 5** — $\beta$-Valerolactone was the only product observed in this fraction. Its presence was confirmed by formation of the ammonia derivative, m.p. 103.8-105.0°, m.m.p. 104.0-105.0° with an authentic sample, m.p. 104.0-105.0°. A search was made for 1,5-pentanediol, but no evidence was found for its presence. The results of these experiments are presented in Table II.

2. **Dihdropyran and water over 90Cu, 10Fe Catalyst** — For these runs, a third hole was made in the stopper in the catalyst tube and a small addition funnel inserted. Dihdropyran was added from the constant rate addition funnel and the distilled water added simultaneously from the other funnel. The rate of flow was adjusted by setting the stopcock to the desired position. Activation of the catalyst yielded 288 ml. of water. Nitrogen was used as the carrier gas to minimize reduction of dihydropyran to tetrahydropyran.

The product was collected and found to be in two layers. They were separated, and the top layer dried over calcium sulfate. The bottom layer distilled at 99-100°, leaving 2-3 g. of residue. The top layer distilled at 84-89°, and also left a couple grams of residue. The
residues were combined, and dried with calcium sulfate. After drying, the product was distilled under vacuum and a distillate collected from 50-70°C/4 mm. \( \delta \)-Hydroxyvaleraldehyde distills at 56-57°C/4 mm. and gives a dinitrophenylhydrazine derivative melting at 11.8-113.8°C. A sample of this product gave a dinitrophenylhydrazone melting at 110.6-112.6, and the mixed melting point was 110.8-113.0°C. Valeric acid constituted the other part of the product. It was identified and estimated as described above. The results of these experiments are presented in Table III.

3. \( \delta \)-Hydroxyvaleraldehyde over 90Cu, 10Fe Catalyst

Experiments were performed with this catalyst in different states of activity. The experimental procedure, however, was otherwise the same throughout. After the desired temperature had been reached and the gas flow set at 10 l./hour, the \( \delta \)-hydroxyvaleraldehyde was added to the catalyst tube at the rate of 0.5 mol/hour. Following completion of the addition, the gas flow was maintained for two hours to clear the catalyst of reaction products.

The material in the flask and in the dry-ice trap were combined, then separated roughly by distillation under vacuum from a Claisen flask. Three fractions were collected, the first collected at room temperature as the pressure was lowered, the second from 50-70°C/4 mm. and the third from 75-90°C/4 mm. A few grams of residue were always
observed.

Fraction 1 — This fraction consisted of two layers, an aqueous bottom layer and an organic upper layer. The two were separated by means of a small separatory funnel.

The top layer was dried over calcium sulfate and potassium hydroxide for several hours. After drying, the material was distilled from a small distilling flask and boiled from 84-87°. It was tested for dihydropyran by adding a sample to an excess of a solution of 2,4-dinitrophenylhydrazine in 2 N hydrochloric acid. The acid causes fission of the dihydropyran ring to \( \sigma \)-hydroxyvaleraldehyde, which then forms a derivative by reaction with the reagent. The mixture was allowed to stand for twenty-four hours, then the precipitate collected. The derivative was recrystallized from ethanol, and melted from 110.6-112.6°. An authentic sample of the 2,4-dinitrophenylhydrazine formed from dihydropyran melted from 11.8-113.8°, and the mixed melting point was 110.8-113.0°.

Fraction 2 — The main products observed in this fraction were unreacted aldehyde and valeric acid. The amount of \( \sigma \)-hydroxyvaleraldehyde was accurately determined by a quantitative estimation of its 2,4-dinitrophenylhydrazine derivative. A known weight of this fraction was added to a large excess of the 2,4-dinitrophenylhydrazine reagent. The mixture was stirred well during the addition,
and the stirring continued for a few minutes after. Then it was allowed to stand for twenty-four hours. The derivative was transferred quantitatively to a tared sintered glass funnel, washed with dilute acid and water, and dried in an oven at 80° to constant weight. A correction factor for the solubility of the derivative in the acid solution was applied. This factor was 0.044 g./100 ml. of 2 N hydrochloric acid (5).

Identification of the valeric acid was made by formation of the p-bromphenacyl ester. The procedure followed was the one described by Shriner and Puson (20). This derivative melted from 70.5-72.0°. An authentic valeric acid derivative was prepared in the same way and melted from 71.0-72.0°. The melting point of a mixture was from 70.5-72.0°, showing no depression.

Estimation of the valeric acid was accomplished by titration with 0.1 N sodium hydroxide. Phenolphthalein indicator was used, alkali being added until a fading pink endpoint was reached.

**Fraction 3**—This fraction consisted mainly of \( \alpha \)-valerolactone, with valeric acid and condensation products of \( \alpha \)-hydroxyvaleraldehyde also present. The valeric acid was identified and estimated as described above, as were the products from \( \alpha \)-hydroxyvaleraldehyde which gave the 2,4-dinitrophenylhydrazone of that aldehyde. \( \alpha \)-Valero-
lactone was identified by the formation of an ammonia derivative. About 1 g. of the fraction was dissolved in 10 ml. dry benzene, and the solution cooled in ice and water. Excess (5 ml) liquid ammonia was added and the solution allowed to stand at room temperature. The excess ammonia boiled off leaving a white solid. This precipitate was collected and washed with ether. The dried derivative melted from 104-105°C. A derivative from an authentic sample of \( \delta \)-valerolactone was prepared in like manner, and it melted from 104-105°C. The mixed melting point showed no depression. It was noticed that valeric acid formed a solid derivative with ammonia also, but it was unstable in air at room temperature, losing ammonia and leaving a liquid residue. Therefore, in those cases in which the acid derivative formed together with the lactone derivative, the filtered precipitates were allowed to stand until the odor of ammonia could not be detected. The liquid residue was removed during the washings with ether. The amount of lactone was determined by titration. A measured excess of 0.1 N alkali was added to a known amount of sample. The solution was allowed to stand for several hours, then back titrated with standard acid to a phenolphthalein end point.

This fraction formed a waxy white solid on standing for several days, characteristic of \( \delta \)-valerolactone (21).
In some instances a fraction boiling above the third was observed. It was shown by the index of refraction and infrared analysis to be the condensation product of \( \alpha \)-hydroxyvaleraldehyde described by Dineen\( ^{22} \). See Table IV for these results.

4. \( \alpha \)-Hydroxyvaleraldehyde over Copper Chromite Catalyst—\( \alpha \)-Hydroxyvaleraldehyde was reacted in contact with this catalyst in same manner as it was added to the copper-iron catalyst. The rate of addition was 0.5 mol/hour, and the catalyst bed was cleared of reaction products by sweeping it for two hours with the carrier gas.

It was found that the main products formed in these runs were equivalent to those formed from the preceding series of runs. Analysis and identifications were therefore carried out in a like manner. After combining the products from the receiver and the dry ice trap, they were distilled under vacuum. The first fraction was removed without the application of heat as the pressure was lowered, the second collected from 50-70°/4 mm. and the third from 75-90°/4 mm.

Fraction one again occurred in two layers and was found to consist of water and dihydropyran. Fraction two was dried for several hours, then analysed. It consisted of valeric acid and unchanged aldehyde. These products were identified as described before. The third fraction
was mainly $\delta$-valerolactone. See Table V for these results.

5. $\delta$-Hydroxyvaleraldehyde over 80Ni, 20Cu Catalyst
The mode of addition of the aldehyde to this catalyst was the same as described for the 90Cu, 10Fe catalyst. Activation of this catalyst had yielded 106 g. of water.

The material in the flask and in the dry ice trap were combined. Two layers were always present, and they were separated by use of a separatory funnel. The bottom layer distilled mainly from 99-100°C, with a trace of dihydropyran identified in a forerun.

The top layer was then distilled under vacuum from a Claisen flask. Two fractions were collected, the first removed at room temperature as the pressure was lowered. The second was collected from 50-70 degrees at 4 mm. pressure. A few grams of residue were always present. Fraction consisted of pyrans with traces of water, so it was dried with anhydrous calcium sulfate for several hours, then analyzed as described before. The second fraction was mainly composed of valeric acid and $\delta$-hydroxyvaleraldehyde. These products were analyzed as described before. See Table VI for these results.

6. Glutaraldehyde over Copper Chromite Catalyst
Copper chromite was chosen as the catalyst for this series of experiments since it afforded the best yields of $\delta$-valerolactone from 1,5-pentanediol (5). Nitrogen was used as
the carrier gas to minimize the possible reduction of the aldehyde groups. The aldehyde was added to the catalyst chamber in a similar manner as the materials previously described. The catalyst when activated yielded 85 ml. of water.

Fifteen grams of glutaraldehyde were added to the catalyst chamber in the temperature range 250-300°. The results from each run were almost identical, from 1.5 to 3.5 g. of product being collected. The product was water with traces of resinous material.

H. Side Chain Elimination of Tetrahydrofurfuraldehyde

1. 80Ni-20Cu Catalyst -- In this series of experiments, the gas flow was maintained at 20 l./hour. The aldehyde was added at the rate of 0.5 mol/hour. Activation of the catalyst had yielded 129 ml. of water.

The products observed were dihydrofuran, tetrahydrofuran, water, and tetrahydrofurfuryl alcohol. A separation was made by distilling until most of the water was off. The remaining material was then distilled and the bulk came over from 166-188°.

Fraction 1 -- Solid potassium hydroxide pellets were added to this fraction in order to resinify any carbonyl compounds and to prevent the addition of acids or alcohols to 2,3-dihydrofuran. The water layer was removed after a
few hours and more potassium hydroxide pellets added. After standing overnight, the mixture was filtered and the filtrate distilled. The distillate was collected from 50-70°, then analyzed for 2,3-dihydrofuran. A known weight of sample was added with stirring to an excess of a 2 N hydrochloric acid solution of 2,4-dinitrophenylhydrazine. Fission of the dihydrofuran ring to α-hydroxybutyraldehyde occurred and that reacted with the reagent. The 2,4-dinitrophenylhydrazone was collected, dried and weighed. The amount of dihydrofuran present in this fraction was calculated by the following formula:

\[
\text{Amount of 2,3-dihydrofuran} = 26.12 \times \frac{\text{corrected weight of hydrazone}}{\text{weight of sample taken}}
\]

The corrected weight of the hydrazone was obtained by applying a solubility correction of 0.043 g./100 ml. (23). After recrystallizing the derivative from ethyl alcohol, its mixed melting point with an authentic derivative of α-hydroxybutyraldehyde was taken, and there was no depression.

Tetrahydrofuran was identified by infrared spectroscopic analysis, after hydrolysis of the dihydrofuran.

**Fraction 2** -- The high boiling fraction consisted almost entirely of tetrahydrofurfuryl alcohol. It was identified by the formation of the 3,5-dinitrobenzoate
according to the procedure in Shriner and Fuson (24). The derivative melted from 82.3°-84.6° and did not depress the melting point of an authentic derivative. The amount present was estimated by an acetylation procedure described by Goodings (2). See Table VII for these results.
**TABLE I**

**Reaction of Tetrahydrofurfuraldehyde in Ethanol with Mercuric Chloride**

<table>
<thead>
<tr>
<th>Tetrahydrofurfuraldehyde (g.)</th>
<th>Alcohol (ml.)</th>
<th>H₂O (ml.)</th>
<th>Time (hrs.)</th>
<th>Product* (g.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>20</td>
<td>--</td>
<td>6</td>
<td>6.8</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>10</td>
<td>6</td>
<td>0.5</td>
</tr>
<tr>
<td>10</td>
<td>20</td>
<td>--</td>
<td>12</td>
<td>6.3</td>
</tr>
<tr>
<td>10</td>
<td>10</td>
<td>10</td>
<td>12</td>
<td>trace</td>
</tr>
<tr>
<td>10</td>
<td>20</td>
<td>--</td>
<td>24</td>
<td>6.1</td>
</tr>
</tbody>
</table>

**abs. alc.**

| 10 | 20 | -- | 18.5 | 8.1 |

* diethylacetal of tetrahydrofurfuraldehyde
TABLE II

Reaction of Tetrahydrofurfuraldehyde
over 90Cu, 10Fe Catalyst

Input: 30 g. of tetrahydrofurfuraldehyde.
Rate of addition: 0.5 mol/hour.
Activation of the catalyst yielded 88 ml. of water

<table>
<thead>
<tr>
<th>Carrier Gas: N&lt;sub&gt;2&lt;/sub&gt;</th>
<th>Furans (g.)</th>
<th>tetrahydrofurfuraldehyde (g.)</th>
<th>tetrahydrofurfuryl alcohol (g.)</th>
<th>n-valeric acid (g.)</th>
<th>d-valerolactone (g.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>0.9</td>
<td>2.9</td>
<td>10.2</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>350</td>
<td>1.3</td>
<td>2.3</td>
<td>9.7</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>305</td>
<td>0.6</td>
<td>2.1</td>
<td>8.4</td>
<td>trace</td>
<td>0.5</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Carrier Gas: H&lt;sub&gt;2&lt;/sub&gt;</th>
<th>Furans (g.)</th>
<th>tetrahydrofurfuraldehyde (g.)</th>
<th>tetrahydrofurfuryl alcohol (g.)</th>
<th>n-valeric acid (g.)</th>
<th>d-valerolactone (g.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temp. (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>0.4</td>
<td>7.6</td>
<td>19.5</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>305</td>
<td>0.9</td>
<td>3.2</td>
<td>12.4</td>
<td>0.6</td>
<td>0.8</td>
</tr>
<tr>
<td>350</td>
<td>1.9</td>
<td>0.5</td>
<td>6.1</td>
<td>0.4</td>
<td>1.7</td>
</tr>
</tbody>
</table>
TABLE III

Reaction of Dihydropyran and Water over 90Cu, 10Fe Catalyst

Rate of addition: 0.5 mol dihydropyran/hour
Activation of the catalyst yielded 288 ml. of water
Carrier gas: N₂

<table>
<thead>
<tr>
<th>Dihydropyran (g.)</th>
<th>H₂O (g.)</th>
<th>Temp. (°C)</th>
<th>Pyrans (g.)</th>
<th>H₂O (g.)</th>
<th>Δ-hydroxyvaleraldehyde (g.)</th>
<th>Valeric Acid (g.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>4.5</td>
<td>250</td>
<td>14.8</td>
<td>6.6</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>21</td>
<td>21</td>
<td>250</td>
<td>9.8</td>
<td>19.6</td>
<td>4.7</td>
<td>0.9</td>
</tr>
<tr>
<td>21</td>
<td>21</td>
<td>300</td>
<td>12.7</td>
<td>19.0</td>
<td>1.5</td>
<td>0.8</td>
</tr>
</tbody>
</table>
TABLE IV

Reaction of \( \delta \)-Hydroxyvaleraldehyde

over 90Cu, 10Fe Catalyst

Input: 34 g. of \( \delta \)-hydroxyvaleraldehyde.
Rate of addition: 0.5 mol/hour.

<table>
<thead>
<tr>
<th>Temp. ((^\circ\text{C}))</th>
<th>Carrier gas</th>
<th>H(_2)O (g.)</th>
<th>Pyrans (g.)</th>
<th>( \delta )-hydroxyvaleraldehyde (g.)</th>
<th>valeric acid (g.)</th>
<th>( \delta )-valerolactone (g.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A) 265</td>
<td>N(_2)</td>
<td>1.2</td>
<td>3.2</td>
<td>1.0</td>
<td>--</td>
<td>2.4</td>
</tr>
<tr>
<td>A) 305</td>
<td>H(_2)</td>
<td>4.3</td>
<td>2.0</td>
<td>2.6</td>
<td>1.2</td>
<td>2.7</td>
</tr>
<tr>
<td>B) 250</td>
<td>N(_2)</td>
<td>1.4</td>
<td>3.4</td>
<td>5.4</td>
<td>1.2</td>
<td>5.5</td>
</tr>
<tr>
<td>B) 280</td>
<td>N(_2)</td>
<td>1.6</td>
<td>3.0</td>
<td>10.8</td>
<td>2.1</td>
<td>1.0</td>
</tr>
<tr>
<td>B) 300</td>
<td>N(_2)</td>
<td>2.9</td>
<td>8.1</td>
<td>6.3</td>
<td>4.2</td>
<td>--</td>
</tr>
<tr>
<td>C) 250</td>
<td>N(_2)</td>
<td>1.8</td>
<td>2.0</td>
<td>5.2</td>
<td>7.1</td>
<td>trace</td>
</tr>
<tr>
<td>C) 300</td>
<td>N(_2)</td>
<td>1.2</td>
<td>3.8</td>
<td>5.0</td>
<td>9.0</td>
<td>--</td>
</tr>
<tr>
<td>C) 300</td>
<td>H(_2)</td>
<td>3.2</td>
<td>4.4</td>
<td>4.0</td>
<td>5.1</td>
<td>--</td>
</tr>
</tbody>
</table>

A) Activation of catalyst yielded 88 ml. of water
B) Activation of catalyst yielded 147 ml. of water
C) Activation of catalyst yielded 354 ml. of water
TABLE V

Reaction of $\alpha$-Hydroxyvaleraldehyde

over Copper Chromite Catalyst

Input: 30 g. of $\alpha$-hydroxyvaleraldehyde.

Rate of addition: 0.5 mol/hour.

Activation of the catalyst yielded 88 ml. of water.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Carrier gas</th>
<th>$\text{H}_2\text{O}$ (g.)</th>
<th>Pyrans (g.)</th>
<th>$\alpha$-hydroxyvaleraldehyde (g.)</th>
<th>n-valeric acid (g.)</th>
<th>$\alpha$-valerolactone (g.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>$\text{H}_2$</td>
<td>1.0</td>
<td>1.5</td>
<td>2.1</td>
<td>--</td>
<td>5.0</td>
</tr>
<tr>
<td>260</td>
<td>$\text{H}_2$</td>
<td>1.2</td>
<td>4.0</td>
<td>1.2</td>
<td>--</td>
<td>11.2</td>
</tr>
<tr>
<td>270</td>
<td>$\text{N}_2$</td>
<td>1.9</td>
<td>3.1</td>
<td>1.6</td>
<td>0.9</td>
<td>6.0</td>
</tr>
<tr>
<td>285</td>
<td>$\text{H}_2$</td>
<td>4.7</td>
<td>3.7</td>
<td>7.2</td>
<td>1.2</td>
<td>4.2</td>
</tr>
<tr>
<td>290</td>
<td>$\text{N}_2$</td>
<td>5.2</td>
<td>5.7</td>
<td>2.4</td>
<td>2.3</td>
<td>1.0</td>
</tr>
<tr>
<td>315</td>
<td>$\text{N}_2$</td>
<td>5.3</td>
<td>9.9</td>
<td>1.6</td>
<td>0.3</td>
<td>1.5</td>
</tr>
</tbody>
</table>
TABLE VI

Reaction of $\alpha$-Hydroxyvaleraldehyde

over 80Ni, 20 Cu Catalyst

Input: 34 g. of $\alpha$-hydroxyvaleraldehyde.
Rate of addition: 0.5 mol/hour.
Activation of the catalyst yielded 106 ml. of water.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Carrier gas</th>
<th>$\text{H}_2\text{O}$ (g.)</th>
<th>Pyrans (g.)</th>
<th>n-valeric acid (g.)</th>
<th>$\alpha$-hydroxyvaleraldehyde (g.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>250</td>
<td>$\text{N}_2$</td>
<td>2.4</td>
<td>5.9</td>
<td>4.8</td>
<td>5.6</td>
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<td>300</td>
<td>$\text{H}_2$</td>
<td>4.1</td>
<td>16.1</td>
<td>0.4</td>
<td>1.6</td>
</tr>
<tr>
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<td>$\text{N}_2$</td>
<td>3.4</td>
<td>8.9</td>
<td>2.2</td>
<td>3.5</td>
</tr>
<tr>
<td>300</td>
<td>$\text{H}_2$</td>
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<td>11.0</td>
<td>0.3</td>
<td>1.1</td>
</tr>
<tr>
<td>350</td>
<td>$\text{H}_2$</td>
<td>4.2</td>
<td>5.8</td>
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<tr>
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<td>2.5</td>
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</tr>
<tr>
<td>350</td>
<td>$\text{H}_2$</td>
<td>5.1</td>
<td>6.4</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>
TABLE VII

Reaction of Tetrahydrofurfuraldehyde
over 80Ni, 20Cu Catalyst

Input: 30 g. of tetrahydrofurfuraldehyde.
Rate of addition: 0.5 mol/hour
Activation of the catalyst yielded 130g. of water.

Variation of Carrier Gas

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Carrier Gas</th>
<th>(DHF - THF) (g.)</th>
<th>DHF of (DHF - THF) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>270</td>
<td>N₂</td>
<td>22.8</td>
<td>49.1</td>
</tr>
<tr>
<td>270</td>
<td>N₂</td>
<td>19.7</td>
<td>64.8</td>
</tr>
<tr>
<td>270</td>
<td>H₂</td>
<td>23.4</td>
<td>46.7</td>
</tr>
</tbody>
</table>

Effect of Temperature Changes

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Carrier Gas</th>
<th>(DHF - THF) (g.)</th>
<th>DHF of (DHF - THF) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>240</td>
<td>N₂</td>
<td>25.2</td>
<td>76.2</td>
</tr>
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<td>N₂</td>
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<td>69.9</td>
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<tr>
<td>280</td>
<td>N₂</td>
<td>20.7</td>
<td>67.8</td>
</tr>
<tr>
<td>300</td>
<td>N₂</td>
<td>15.3</td>
<td>34.5</td>
</tr>
<tr>
<td>320</td>
<td>N₂</td>
<td>7.0</td>
<td>13.8</td>
</tr>
</tbody>
</table>

#DHF - THF-dihydrofuran plus tetrahydrofuran
Spectra

Figure 2. Tetrahydrofurfuraldehyde
sample cell - sandwich cell
reference cell - sodium chloride window

Figure 3. Diethylacetal of tetrahydrofurfuraldehyde
sample cell - sandwich cell
reference cell - sodium chloride window

Figure 4. α-Hydroxyvaleraldehyde
sample cell - sandwich cell
reference cell - sodium chloride window

Figure 5. Condensation product of α-hydroxy-valeraldehyde (22)
sample cell - sandwich cell
reference cell - sodium chloride window

Figure 6. Dihydrofuran
sample cell - 0.025 mm. cell
reference cell - sodium chloride window

Figure 7. Tetrahydrofuran
sample cell - 0.025 mm. cell
reference cell - sodium chloride window
WAVE NUMBERS IN CM\(^{-1}\)

WAVE LENGTH IN MICRONS

WAVE NUMBERS IN CM\(^{-1}\)

WAVE LENGTH IN MICRONS

WAVE NUMBERS IN CM\(^{-1}\)

WAVE LENGTH IN MICRONS
V. DISCUSSION

On the basis of the experiments performed, it is probable that the formation of $\alpha$-valerolactone from tetrahydrofurfuryl alcohol proceeds through $\alpha$-hydroxyvaleraldehyde, which has as its predecessor, 1,5-pentanediol. The reasons for this conclusion are presented in the following discussion of the experimental results.

Experiments attempting to show a rearrangement of tetrahydrofurfural yielded negative results. The aldehyde was stable at 250°, and in the presence of hydrogen was easily reduced to tetrahydrofurfuryl alcohol. At higher temperatures, over the metal catalyst, small amounts of $\alpha$-valerolactone were formed, but in these cases tetrahydrofurfuryl alcohol was the main product formed. Since reduction of the aldehyde was so easily accomplished, it can be safely assumed that that occurred first and the lactone was subsequently formed by further reaction of the alcohol.

The experiments performed in the liquid phase also yielded no evidence of rearrangement. At low temperatures in alcohol solution with a mild catalyst, the carbonyl function was mainly affected, the acetal being formed. At higher temperatures or with phosphorus pentachloride in ether, ring opening and subsequent polymerisation occurred. The results were not wholly unexpected since there have
been no reports in the literature suggesting this reaction of the aldehyde. The idea is not entirely without foundation, however, as such a rearrangement has been demonstrated in the case of cyclobutanecarboxaldehyde. Venus-Danilova (26) obtained 30-55 percent yield of cyclopentanone by (1) refluxing the aldehyde in aqueous alcohol in the presence of mercuric chloride or (2) heating it to 130-135° for 30 minutes in the presence of pumice saturated with 60 percent sulfuric acid. A similar reaction of tetrahydrofurfuraldehyde in the vapor phase over acid-saturated pumice resulted only in decomposition.

It has been shown that water does add to dihydropyran in the vapor phase in the presence of a metallic catalyst, but not to a great extent (Table III). Indeed, when equimolar amounts of the two substances were added, no addition was observed. However, a slight excess of water can be expected since small amounts of water are formed during the passage of dihydropyran alone over a copper-iron catalyst. (3). To be considered as an intermediate in lactone formation, one would expect a greater tendency for water and dihydropyran to combine, otherwise dihydropyran would be found in large amounts. As noted by Thomas (3), only trace amounts were detected.

The possibility of a Cannizaro type of reaction of glutaraldehyde could not be excluded, though it had not
been detected in any previous experiments. Reppe, in his work with butanediols, suggested the formation of succindialdehyde as intermediate in the recovered product, butyrrolactone. Here, again, no evidence was found for its presence. That open-chain dialdehyds can form lactones was shown by Smith (32), who obtained an 84 percent yield of $\beta$-valerolactone by treatment of glutaraldehyde with aluminum isopropropoxide in carbon tetrachloride. This was, of course, a liquid phase reaction.

From our experiments in the vapor phase, we find that the glutaraldehyde is almost entirely decomposed or polymerized on the catalyst bed. Nitrogen was used as the carrier gas, to minimize any reduction of the aldehyde groups.

The results from the passage of $\beta$-hydroxyvaleraldehyde over the metal catalysts indicate that it is most likely the intermediate in the transformation of the pentanediol to the lactone. (Tables IV, V, VI). For all three catalysts used, there was found the competing reactions of dehydoration versus dehydrogenation:

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{CH}_2\text{O}\text{H} & \quad \text{CH}_2\text{CH}_2\text{CH}_2 \\
\text{CH}_2\text{OH} & \quad \text{CH}_2\text{CH}_2\text{OH} \\
\text{CH}_2\text{OH} & \quad \text{CH}_2\text{OH}
\end{align*}
\]
In the case of the 80Ni, 20Cu catalyst no lactone as such was detected, but valeric acid constituted a major product. It is noticed that as the temperature was raised, the yield of water increased, indicating a temperature dependence for dehydration. The yield of dihydropyran was initially increased, but dropped at 350°, as its thermal decomposition was initiated. Both nitrogen and hydrogen were used as carrier gases, but had no noticeable effect. It is interesting to note the decrease in yield of valeric acid as the temperature was raised. Ballantine (5), investigating the reaction of 1,5-pentanediol over a 50Ni, 50Cu catalyst, found valeric acid as the major product. He called attention to the fact that the yield of acid decreased with increased temperature, attributing it to thermal decomposition.

The products formed from \( \gamma \)-hydroxyvaleraldehyde with the copper chromite catalyst were those of dehydration and dehydrogenation (Table V). In this case, substantial yields of \( \gamma \)-valerolactone were found, constituting the major product at the lower temperatures. As the temperature was increased, dihydropyran was formed at the expense of the other products. Also, as the temperature was
increased, valeric acid began to appear, but was only present in small amounts. In the work with 1,5-pentanediol, \( \Delta \)-valerolactone was the major product. Valeric acid and pyran material were also isolated. Two observable trends were reported; the yield of valeric acid and pyran materials increased with increasing temperature.

The behaviour of \( \Delta \)-hydroxyvaleraldehyde was studied over the 90Cu, 10Fe catalyst (Table IV) since Thomas (3) found \( \Delta \)-valerolactone, n-valeric acid, and tetrahydrofurfurylvalerate as the main products when tetrahydrofurfuryl alcohol was passed over this catalyst. The catalyst was used in varying states of activity, and though the proportions changed somewhat, the products formed did not vary. Using the catalyst of lowest activity, we found \( \Delta \)-valerolactone and pyrans as the major products, with valeric acid appearing at the higher temperature. In these experiments, the reaction products were distilled at atmospheric pressure, causing the major portion of the unchanged aldehyde to be converted into high boiling and decomposition products. As the activity of the catalyst was increased, its dehydrogenating ability increased and \( \Delta \)-valerolactone was formed in larger amounts. At the same time, valeric acid was also formed to a larger extent. As the temperature was increased, it increased at the expense of the lactone. With the catalyst in its highest state of
activity, only a trace of $\alpha$-valerolactone could be found. Valeric acid, however, was a major product, demonstrating the effect of catalyst activity on the varying amounts of valeric acid and valerolactone formed. In all three cases considered, water and dihydropyran were consistently formed, the same trends being noticed as mentioned above.

Comparing the results obtained from these experiments with those from the work with 1,5-pentanediol (5), we note many similarities. The main products obtained in each case were dihydropyran, $\alpha$-valerolactone and n-valeric acid. Certain trends observed in this work were reported for pentanediol, all lending support for the postulate that $\alpha$-hydroxyvaleraldehyde is intermediate in the formation of the lactone.

The question still remains concerning the conversion of tetrahydrofurfuryl alcohol to 1,5-pentanediol. It is known that tetrahydrofurfuryl alcohol can be converted to pentanediol in good yield, but the diol has not been isolated under the conditions employed by Wilson and Thomas (3), though a special search was made for it. However, a product believed derived from it, 4-pentenol-1, has been isolated.

It should be remembered in discussing any proposed intermediate that its concentration during the reaction would be small, and with an active catalyst is likely to
be completely converted to the end products observed. A case in point is that of tetrahydrofurfuraldehyde in the elimination of the side chain of tetrahydrofurfuryl alcohol. It was postulated and sought for by Wilson (13). In his experiments with nickel catalysts, no trace of tetrahydrofurfuraldehyde could be found among the products. However, when operating under reduced pressure with a nickel catalyst and with the nickel alloy catalysts at ordinary pressure, very small amounts of the aldehyde were detected by formation of the 2,4-dinitrophenylhydrazone.

In this work experiments indicate that the aldehyde is intermediate in side chain elimination. The conditions employed in this reaction approximated as closely as possible those of Ragan (23), who studied the elimination reaction in great detail. The main interest was to obtain the greatest percentage of dihydrofuran in the dihydro-tetrahydrofuran mixture. Tetrahydrofurfuraldehyde was shown to behave in the same manner as tetrahydrofurfuryl alcohol (Table VII). It was postulated by Wilson that dihydrofuran was the predecessor of some, if not all, of the tetrahydrofuran. In such a case, a change from nitrogen to hydrogen as the carrier gas should decrease the amount of dihydrofuran. Such an effect was demonstrated in the aldehyde reaction. The effect of temperature was that predicted, the yield of hydrogenated furans decreasing with
increasing temperature. It has been shown that both di- and tetrahydrofuran would undergo increased decomposition as the temperature was raised (2).
VI. SUMMARY

An attempt was made to prepare tetrahydrofurfuraldehyde by four different approaches. They included the McFadyen-Stevens reaction, the Rosenmund reaction, a hydrogen exchange reaction, and the reduction of the acid chloride of tetrahydrofuroic acid by sodium trimethoxyborohydride. None of the four proved satisfactory as a method of synthesis.

Tetrahydrofurfuraldehyde was investigated as the probable intermediate in the vapor phase side chain elimination reaction of tetrahydrofurfuryl alcohol, and was found to behave as anticipated. When passed over a 80Ni, 20Cu catalyst it yielded dihydrofuran and tetrahydrofuran in percentages and amounts comparable to those obtained using tetrahydrofurfuryl alcohol.

The behaviour of various proposed intermediates in the vapor phase reaction involving the formation of D-valerolactone from tetrahydrofurfuryl alcohol was also investigated. Several attempts were made to rearrange tetrahydrofurfuraldehyde to D-valerolactone, but they met with no success. The dehydrogenation products of 1,5-pentanediol, D-hydroxyvaleraldehyde and glutaraldehyde were passed over metal catalysts in the same manner as tetrahydrofurfuryl alcohol and 1,5-pentanediol had been reacted.
Glutaraldehyde was entirely decomposed or polymerized, but \( \alpha \)-hydroxyvaleraldehyde yielded \( \alpha \)-valerolactone, \( n \)-valeric acid, and dihydropyran. These products had been obtained from \( 1,5 \)-pentanediol and tetrahydrofurfuryl alcohol, and indicated that the hydroxyaldehyde was intermediate in lactone formation. The conclusion drawn, therefore, was that tetrahydrofurfuryl alcohol underwent reductive fission to \( 1,5 \)-pentanediol, which was then successively dehydrogenated to \( \alpha \)-hydroxyvaleraldehyde and \( \alpha \)-valerolactone.
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VIII. AUTOBIOGRAPHY

I, Albert C. Antoine, was born in New York City, N.Y., January 14, 1925. I received my secondary school education in the public schools of New York City. My undergraduate training was obtained at The College of the City of New York, from which I received the degree Bachelor of Science in 1946. During the period 1944-46, I served in the Army of the United States. I enrolled in the graduate school of the Ohio State University in 1948. From 1950-1953, I served as a Research Assistant in the Department of Chemistry at the Ohio State University. I expect to receive the degree Doctor of Philosophy in August, 1953.