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Decomposition of $[\delta]^3$ -dihydropyran -dihydropyran over hot alumina

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BOSTON UNIVERSITY
GRADUATE SCHOOL

Thesis

DECOMPOSITION OF Δ^3 -DIHYDROPYRAN OVER HOT ALUMINA

by

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Submitted in partial fulfilment of the
requirements for the degree of
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1962

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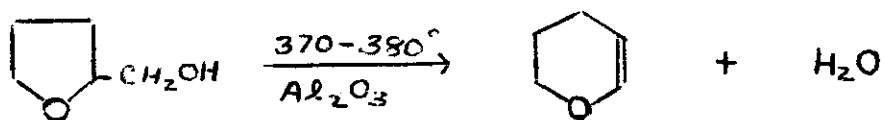
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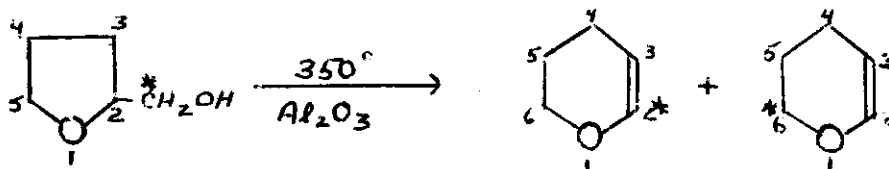
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I INTRODUCTION

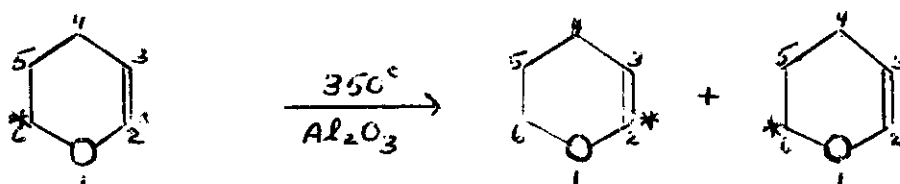
When Paul⁽¹⁰⁾ passed tetrahydrofurfuryl alcohol over alumina at 370-380°, he observed a ring expansion and dehydration to give Δ^2 -dihydropyran in 44% yield.



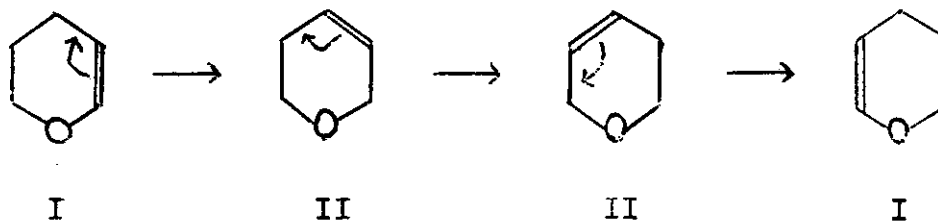
McLeod⁽⁷⁾ passed tetrahydrofurfuryl alcohol, labeled at the external methylene position with carbon-14, over hot alumina. The resulting Δ^2 -dihydropyran was labeled in approximately equal proportions on position 2 and 6.



Stouffer⁽⁸⁾ passed Δ^2 -dihydropyran, labeled with carbon-14 on position 6, over alumina under the same conditions as used by McLeod. The analysis of the reaction product showed a rearrangement had occurred. The Δ^2 -dihydropyran was now labeled in approximately equal proportions on position 2 and 6.



One way to account for the rearrangement is to postulate double bond migration around the carbon ring from one side to the other.



If this process is operating, Δ^3 -dihydropyran (II), when passed over alumina under the same conditions as used by Stouffer, should lead to Δ^2 -dihydropyran (I).

The subject of this thesis is the fate of Δ^3 -dihydropyran when passed over alumina under the same conditions as used by McLeod⁽⁷⁾ and Stouffer⁽¹⁸⁾ in the rearrangement of tetrahydrofurfuryl alcohol and Δ^2 -dihydropyran.

II DISCUSSION OF THE PROBLEM

A. Summary of the Problem and Discussion of Results.

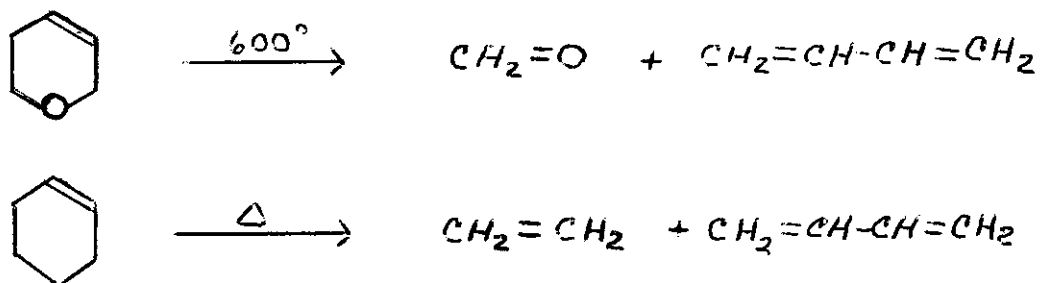
If Δ^3 -dihydropyran is an intermediate in rearrangement of Δ^2 -dihydropyran, passing Δ^3 -dihydropyran over hot alumina should produce Δ^2 -dihydropyran. Δ^3 -Dihydropyran was prepared and tested in this manner. The problem of detecting and distinguishing Δ^2 -dihydropyran in the presence of Δ^3 -dihydropyran was straight forward and made use of the difference in the behavior of the two compounds to dilute aqueous acid. Whereas Δ^2 -dihydropyran is readily hydrolyzed to delta-hydroxyvaleraldehyde which is easily identified as its 2,4-dinitrophenylhydrazone, Δ^3 -dihydropyran is inert under the same conditions⁽¹¹⁾.

In preliminary work, a series of experiments were carried out in which Δ^2 -dihydropyran, butadiene, and formaldehyde were isolated and identified with high precision under the same conditions used in the pyrolysis of Δ^3 -dihydropyran.

The experiments showed that Δ^2 -dihydropyran is not formed when Δ^3 -dihydropyran is passed over hot alumina. Instead butadiene and carbon dioxide were collected. Controlled experiments showed that aqueous formaldehyde on exposure to hot alumina produces carbon dioxide and an unidentified gas.

Accordingly Δ^3 -dihydropyran over hot alumina probably

pyrolysis to butadiene and formaldehyde. This kind of behavior of Δ^3 -dihydropyran at 600° in the absence of catalyst has been observed before⁽¹¹⁾ and has been compared to the reverse Diels-Alder reaction of cyclohexene at elevated temperature.

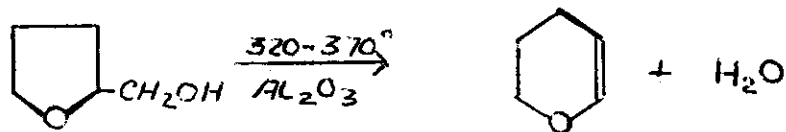


Other experiments established that no butadiene is formed when tetrahydrofurfuryl alcohol dehydrates to Δ^2 -dihydropyran and therefore renders highly unlikely the possibility that Δ^3 -dihydropyran is involved in the alumina transformation of tetrahydrofurfuryl alcohol to Δ^2 -dihydropyran.

The tabulated results for each pyrolysis experiment is given in Table 1 on page 52.

B. Review of the Experimental.

1. Preparation of Δ^2 -Dihydropyran.



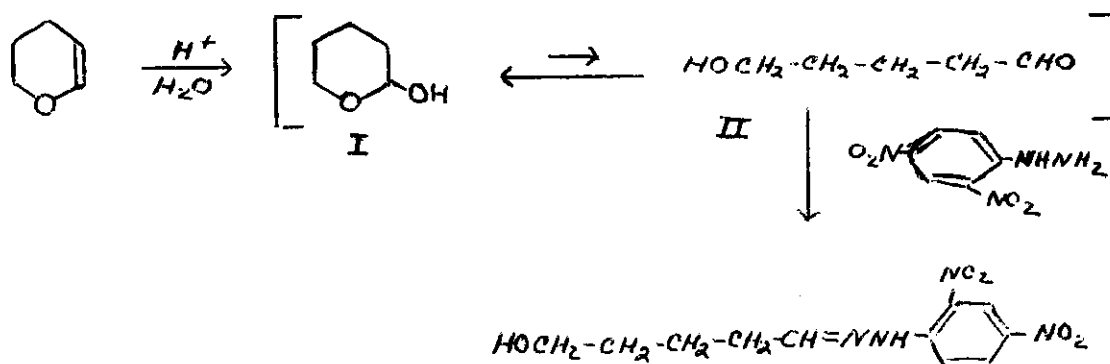
The catalytic dehydration and ring expansion of tetrahydrofurfuryl alcohol to Δ^2 -dihydropyran was first observed by Paul⁽¹⁰⁾. The yields of Δ^2 -dihydropyran vary with temperature, activity of the catalyst, and rate of addition of tetrahydrofurfuryl alcohol to the catalyst. Schnieff and Geller⁽¹⁴⁾ determined that the main factor in limiting yields and production rates was the exothermic reaction which occurred when the alumina catalyst came in contact with the hot (300°) alcoholic vapors. A temperature rise to 500°, carbonization, and inactivation of catalyst resulted. Pretreatment of the alumina with Δ^2 -dihydropyran under controlled conditions resulted in a stable catalyst, with which Δ^2 -dihydropyran could be obtained in yields up to 80%.

Wilson⁽²²⁾ found that an overly active catalyst, e.g., hot, fresh alumina, converts the Δ^2 -dihydropyran product in part to green hydrocarbon material (C₅H₆)_n.

High yields (90-95%) of Δ^2 -dihydropyran from catalytic dehydration of tetrahydrofurfuryl alcohol have been obtained by working at reduced pressure (580-600 mm.)⁽⁸⁾.

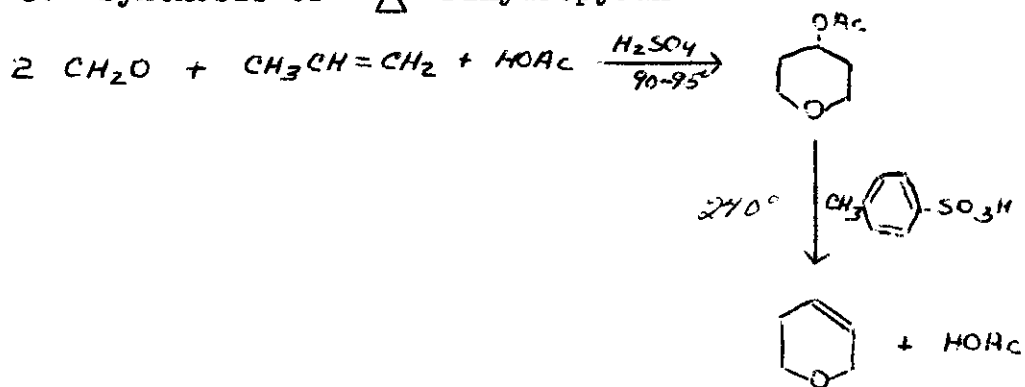
Fresh, unconditioned alumina was used in the present work. With this kind of catalyst, Δ^2 -dihydropyran was obtained in only 42% yield.

2. Hydrolysis of Δ^2 -Dihydropyran to delta-Hydroxyvaleraldehyde and Preparation of the 2,4-Dinitrophenylhydrazone.



Water readily adds to the double bond of Δ^2 -dihydropyran under mild acid conditions⁽¹¹⁾ to form an equilibrium mixture of 2-hydroxytetrahydropyran (I) and delta-hydroxyvaleraldehyde (II). The equilibrium mixture has been shown by absorption spectra⁽¹⁴⁾ to consist of 95% cyclic hemi-acetal (I), and 5% straight chain delta-hydroxyvaleraldehyde (II). The hydrolysis product can be isolated as the 2,4-dinitrophenylhydrazone of delta-hydroxyvaleraldehyde in high yields^(2,21).

3. Synthesis of Δ^3 -Dihydropyran.



Δ^3 -Dihydropyran has been synthesized by Olsen⁽⁹⁾, Hanschke⁽³⁾, and Stouffer⁽¹⁹⁾. The synthesis here was adapted from Stouffer and consists of two steps; (a) preparation of

4-acetoxytetrahydropyran, and (b) the elimination of the elements of acetic acid from 4-acetoxytetrahydropyran to form Δ^3 -dihydropyran.

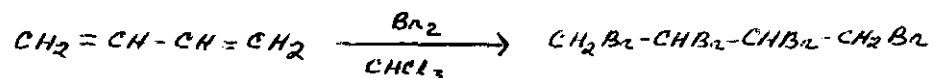
The first reaction, the addition of formaldehyde to propylene under strong acid conditions (Prins reaction⁽¹²⁾) in the presence of acetic acid gives as the major product 1,3-diacetoxybutane⁽⁹⁾. A yield of 17% 4-acetoxytetrahydropyran is also obtained.

The second reaction consists of the pyrolysis of 4-acetoxytetrahydropyran at 240° in the presence of p-toluenesulfonic acid. The major product is Δ^3 -dihydropyran. On pyrolysis of 4-acetoxytetrahydropyran at 250° in the presence of potassium dihydrogenphosphate, Hanschke⁽³⁾ obtained butadiene in addition to Δ^3 -dihydropyran.

To ensure that no Δ^2 -dihydropyran is present in the Δ^3 -dihydropyran, the Δ^3 -dihydropyran was treated under mild conditions with 0.1 N hydrochloric acid. Paul and Tchelitcheff⁽¹¹⁾ hydrolyzed Δ^2 -dihydropyran to delta-hydroxyvaleraldehyde with 0.1 N sulfuric acid at room temperature. Under these conditions Δ^3 -dihydropyran is inert, and could be recovered unchanged.

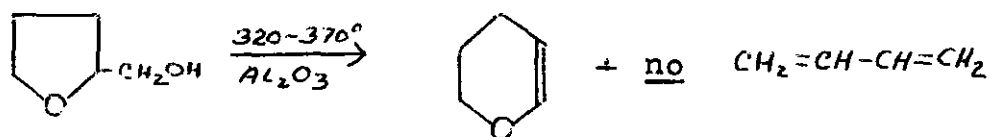
The infrared spectrum of Δ^3 -dihydropyran showed no absorption at 6.09 μ . McLeod⁽⁷⁾ reports absorption at 6.09 μ due to the vinyl ether bond in Δ^2 -dihydropyran.

4. Preparation of dl-1,2,3,4-Tetrabromobutane.



In anticipation of butadiene from Δ^3 -dihydropyran, a suitable means of identification was sought. Bromination of butadiene in cold chloroform containing excess bromine gives two isomeric tetrabromobutanes in approximate ratios of 2 to 1 and melting at 117° and 38° respectively^(4,6). Schubert and Lanka⁽¹⁵⁾ Report a yield of 88% meso and dl-1,2,3,4-tetrabromobutane when butadiene is absorbed in carbon tetrachloride containing excess bromine. The high melting isomer, which can be isolated by crystallization from cold ligroin or alcohol⁽⁶⁾, has been identified by Raman spectra (Slobodin and Zabojev⁽¹⁷⁾) as dl-1,2,3,4-tetrabromobutane. The low melting isomer is meso-1,2,3,4-tetrabromobutane.

In the present work, bromination of butadiene gave dl-1,2,3,4-tetrabromobutane in 59% yield, a result in reasonable agreement with previously reported yields under similar experimental conditions^(4,6,15).

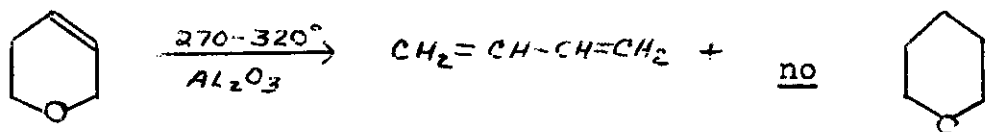
5. Tetrahydrofurfuryl Alcohol over Activated Alumina at $320-370^\circ$.

Tetrahydrofurfuryl alcohol was passed over hot, fresh alumina using nitrogen as a carrier gas, and the reaction

products collected. The Δ^2 -dihydropyran was hydrolyzed to delta-hydroxyvaleraldehyde⁽¹¹⁾ and isolated as the 2,4-dinitrophenylhydrazone in 14% yield. The low yield of Δ^2 -dihydropyran is due to the small amount (5.0 g.) of tetrahydrofurfuryl alcohol passed over the overactive catalyst. See page 5 for a discussion of yields.

The reaction products were also bubbled through a cold chloroform-bromine solution. No butadiene, as the 1,2,3,4-tetrabromo., was detected.

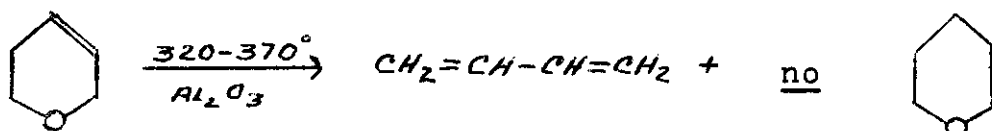
6. Δ^3 -Dihydropyran over Activated Alumina at 270-320°.



Δ^3 -Dihydropyran was passed over hot, fresh alumina using nitrogen as a carrier gas, and the reaction products passed through a series of collecting flasks (see Figure 4, page 35). Butadiene was isolated as the dl-1,2,3,4-tetrabromo derivative in 24% yield. From the yield of 59% of dl-1,2,3,4-tetrabromobutane from pure butadiene, the yield of butadiene from Δ^3 -dihydropyran is estimated at 40%. The low yield may be due a temperature range not high enough to cause complete pyrolysis of Δ^3 -dihydropyran; dimerization of butadiene may also have occurred. Kistiakowsky and Lacher⁽⁵⁾ report partial dimerization of butadiene at 155-330°.

The contents of the collecting flasks were tested with dimedone and 2,4-dinitrophenylhydrazine reagents. No formaldehyde or Δ^2 -dihydropyran was detected either as the dimedone or as the 2,4-dinitrophenylhydrazone derivatives.

7. Δ^3 -Dihydropyran over Activated Alumina at 320-370°.

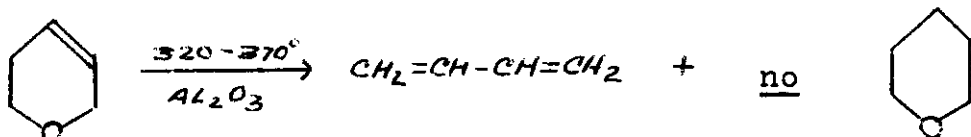


Δ^3 -Dihydropyran was passed over the very same alumina used in the preceding pyrolysis experiment using nitrogen as a carrier gas. The reaction products were passed through a series of collecting flasks (see Figure 4, page 35).

The butadiene was isolated as the dl-1,2,3,4-tetrabromo derivative in 39% yield. From the yield of 59% of dl-1,2,3,4-tetrabromobutane from pure butadiene, the yield of butadiene from Δ^3 -dihydropyran is estimated at 65%.

No formaldehyde or Δ^2 -dihydropyran was detected either as the dimedone or as the 2,4-dinitrophenylhydrazone derivatives.

8. Δ^3 -Dihydropyran over Activated Alumina at 320-370° in the Absence of Nitrogen.

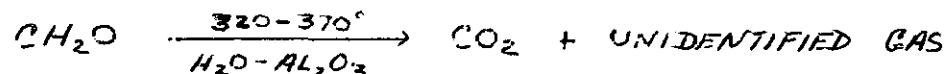


Δ^3 -Dihydropyran was passed over the very same hot alumina used in the preceding pyrolysis experiment but in the absence of

nitrogen as a carrier gas. As in the previous experiment, the reaction products were collected in a series of collecting traps (see Figure 4, page 35). The butadiene was isolated as the dl-1,2,3,4-tetrabromo derivative in 22% yield. The low yield of butadiene may be ascribed to the longer contact time in the reaction tube. Since no carrier gas was used to flush the tube during the pyrolysis, the gases formed had to leave the reaction tube under their own pressure.

The contents of the collecting flasks were tested with dimedone and 2,4-dinitrophenylhydrazine reagents. No formaldehyde or Δ^2 -dihydropyran was detected either as the dimedone or as the 2,4-dinitrophenylhydrazone derivatives.

9. Aqueous Formaldehyde over Activated Alumina at 320-370°.

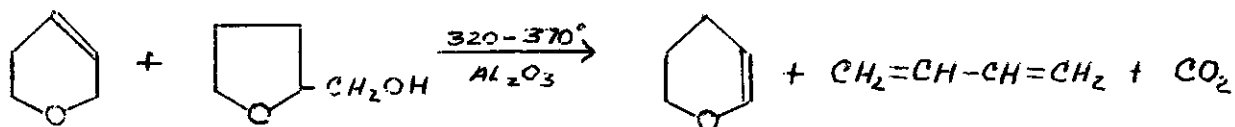


Aqueous formaldehyde solution was passed over hot, fresh alumina in the presence, and in the absence of nitrogen as a carrier gas. The collecting system was similar to that of the previous experiment so that an attempted identification of formaldehyde would be under similar conditions as experienced in the preceding experiment. In anticipation that carbon dioxide is formed when formaldehyde is in contact with hot alumina, an additional flask containing a clear, saturated calcium hydroxide solution was added to the collecting system.

The carbon dioxide formed in the reaction was passed through a series of four traps and absorbed in the fifth trap (see Figure 4, page 35) which contained a clear, calcium hydroxide solution. The contents of the first four traps did not react with 2,4-dinitrophenylhydrazine reagent. It is concluded that no formaldehyde survived the reaction.

When nitrogen was not used as a carrier gas, a gas was observed which was not soluble in any of the solutions in the traps and which escaped from the fifth trap. This gas was not identified.

10 Δ^3 -Dihydropyran over Activated Alumina at 320-370°
in the Presence of Tetrahydrofurfuryl Alcohol.



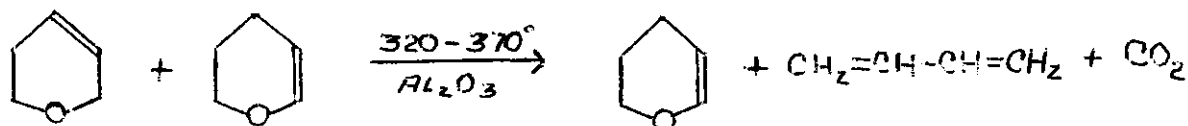
To ensure that Δ^3 -dihydropyran pyrolysis in the presence of tetrahydrofurfuryl alcohol, and that the butadiene formed in the decomposition can be identified, a homogeneous solution of Δ^3 -dihydropyran and tetrahydrofurfuryl alcohol was passed over hot, fresh alumina. The reaction products were passed through a series of five collecting flasks (see Figure 4, page 35). The carbon dioxide was absorbed in the fifth trap which contained a saturated calcium hydroxide solution.

The Δ^2 -dihydropyran was hydrolyzed to delta-hydroxyvaleraldehyde and isolated as the 2,4-dinitrophenylhydrazone

in 1.3% yield. The small yield of Δ^2 -dihydropyran may be ascribed to the overactive catalyst for the production of Δ^2 -dihydropyran from tetrahydrofurfuryl alcohol with unconditioned alumina (see the discussion of dehydration of tetrahydrofurfuryl alcohol on page 5).

The butadiene was absorbed in a cold chloroform-bromine solution and isolated in 34% yield as the dl-1,2,3,4-tetrabromo derivative. From the yield of 59% of dl-1,2,3,4-tetrabromobutane from pure butadiene, the yield of butadiene from Δ^3 -dihydropyran is estimated at 57%.

11. Δ^3 -Dihydropyran over Activated Alumina at 320-370° in the Presence of Δ^2 -Dihydropyran.



To ensure that Δ^3 -dihydropyran pyrolysis in the presence of Δ^2 -dihydropyran, and that the butadiene formed in the decomposition can be identified, a homogeneous solution of Δ^3 -dihydropyran and Δ^2 -dihydropyran was passed over hot, fresh alumina. The reaction products were passed through a series of five collecting flasks (see Figure 4, page 35). The carbon dioxide was absorbed in the fifth flask which contained saturated calcium hydroxide solution.

The Δ^2 -dihydropyran was hydrolyzed to delta-hydroxyvaleraldehyde and isolated as the 2,4-dinitrophenylhydrazone in a small yield (3%). The small yield of recovered Δ^2 -dihydro

pyran may be ascribed to the activity of the alumina catalyst. Wilson⁽²²⁾ States Δ^2 -dihydropyran can be dehydrated to green hydrocarbon material (C_5H_6)_n when passed over hot (300°), fresh alumina. (See the discussion of the rearrangement of tetrahydrofurfuryl alcohol to Δ^2 -dihydropyran on page 5.)

The butadiene was absorbed in a cold chloroform-bromine solution and isolated in 30% yield as the dl-1,2,3,4-tetrabromo derivative. From the yield of 59% of dl-1,2,3,4-tetrabromobutane from pure butadiene, the yield of butadiene from Δ^3 -dihydropyran is estimated at 49%.

III EXPERIMENTAL

A. Preparation of Δ^2 -Dihydropyran.

The procedure followed was that of Sawyer and Andrus⁽¹³⁾ with modifications.

Tetrahydrofurfuryl alcohol (Eastman Practical), which was slightly yellow, was distilled from a 300 ml. round-bottom flask connected to a six inch Vigreux column and a water condenser. A clear, colorless liquid (90 g.) b.p. 80-81° (20 mm.), n_D^{25} 1.4497 was collected. Burdick and Adkins⁽¹⁾ report b.p. 80-82° (20 mm.) and n_D^{25} 1.4505.

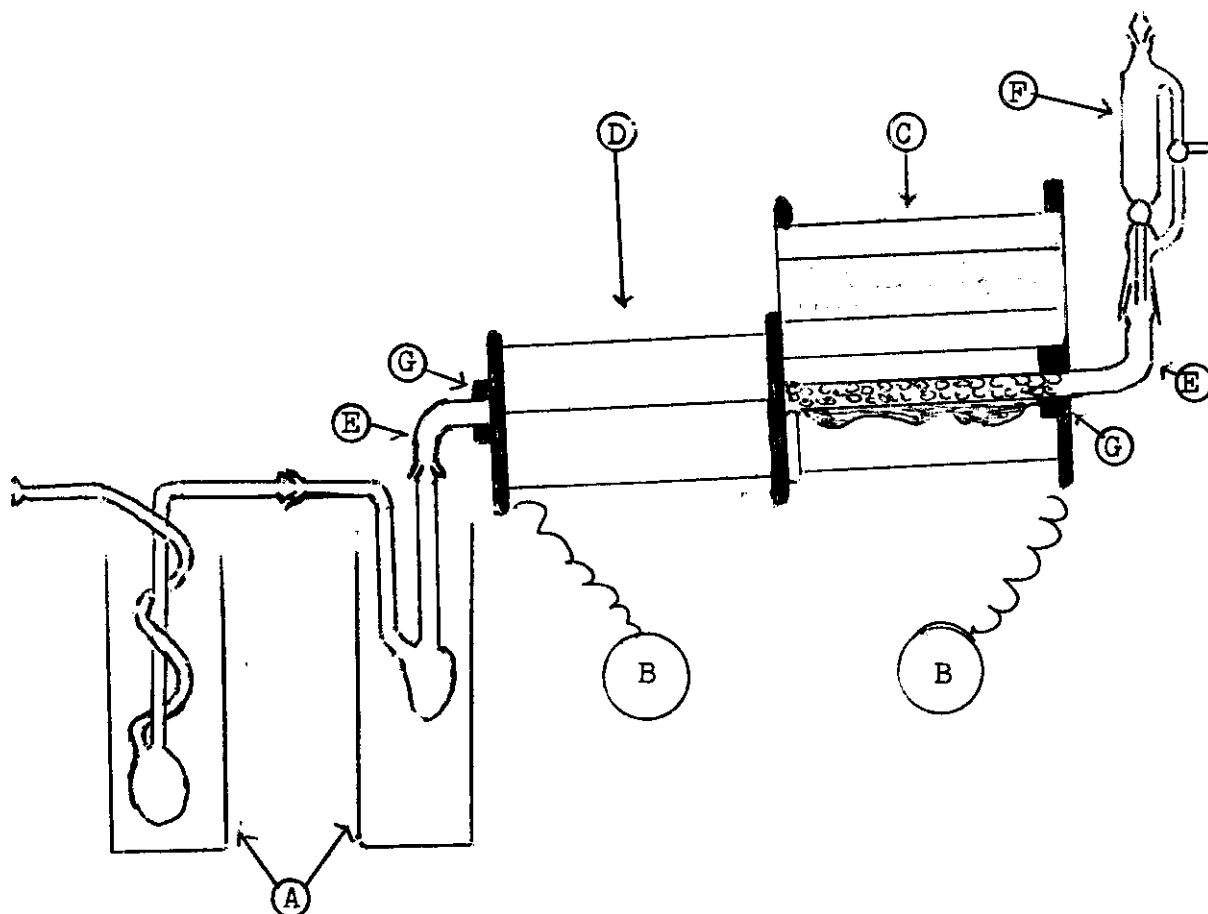
The temperature range of an electric furnace (see Figure 1, page 17) was determined in the following manner. Asbestos tape was wrapped around the ends of a straight pyrolysis tube 30 inches long and 3/4 inch in diameter. This tube was inserted in an electric furnace so that it was securely held in the center of the bore of the furnace and the asbestos tape sealed off the ends of the furnace bore. One end of the pyrolysis tube was plugged with a small cork. A wire was attached to a thermometer and placed in the pyrolysis tube. A glass-wool plug was used to seal the other end of the tube.

The temperature of the furnace was controlled by two Variacs, and the thermometer was moved to different positions in the tube. By adjusting the Variac readings and determining

the temperature at various points in the furnace, the Variac readings for temperature ranges were determined. When the Variac readings were 49 and 52 respectively, the temperature range of the furnace was 320-370°; for Variac readings of 42 and 43, the temperature range was 270-320°.

The straight pyrolysis tube was replaced by the curved reaction tube (see Figure 1, page 17, Item E). This reaction tube contained a 24/40 ground-glass joint on the upper end and a ground-glass ball joint on the lower. Asbestos tape (G) was used to hold the reaction tube firmly in the center of the furnace bore and to seal the ends of the furnace. The tube also contained a small glass grid 6 inches from the lower end. A small piece of glass wool was placed in the tube on the grid and the tube was filled to a height of 22 inches with alumina (ALCOA activated 8/14 mesh). A small dropping funnel (F), which contained a side-arm for pressure equalizing and a gas inlet tube, was fitted to the upper end of the reaction tube. Nitrogen gas, purified by bubbling through towers of pyrogallol-potassium hydroxide solution, concentrated sulfuric acid, and through several towers of Drierite, was slowly passed through the alumina-filled tube. The furnace was heated to 270-320° and a nitrogen flow of one bubble per six seconds was passed through the tube overnight.

The Variac readings were increased to 49 and 52 respectively and the nitrogen flow was increased to one bubble per second. Two hours were allowed for the furnace to warm to 320-370°.



- A Collecting flasks cooled in acetone-Dry Ice bath.
 B Variacs.
 C Furnace--open.
 D Furnace--closed.
 E Curved reaction tube with activated alumina.
 F Dropping funnel with side-arm for nitrogen inlet.
 G Asbestos tape.

FIGURE 1

ELECTRIC FURNACE FOR THE DEHYDRATION OF TETRAHYDROFURFURYL
 ALCOHOL TO Δ^2 -DIHYDROPYRAN

A total of 60 g. (0.59 mole) of tetrahydrofurfuryl alcohol, purified as previously described, was added to the hot alumina at the rate of one drop every six seconds. Two flasks (A) were attached to the lower end of the reaction tube to collect the reaction products. Each collecting flask was cooled in an acetone-Dry Ice bath. One gram of anhydrous potassium carbonate was added to the first collecting flask.

After all the tetrahydrofurfuryl alcohol was added, the nitrogen flow was increased to five bubbles per second for two hours. A green viscous liquid was observed in the first flask. The second flask contained no liquid. The flask which contained the green liquid and anhydrous potassium carbonate was allowed to warm to 0° in an ice-water bath. After thirty minutes two distinct layers were observed. The top layer was a deep-green organic liquid while the bottom layer was a colorless aqueous solution of potassium carbonate. A small amount of potassium carbonate remained undissolved in the aqueous solution.

The top organic-layer was removed from the flask with a 25 ml. pipet, and placed in a 50 ml. round-bottom flask. A small amount of lithium aluminum hydride was added and some foaming was noticed. After the foaming subsided the flask was fitted with a small ball-jointed distilling apparatus containing a 3 inch Vigreux column and a calcium chloride drying tube. The flask was heated by an electrically heated oil bath (bath temperature 125-140°). The fraction boiling

at 83-85 ° was collected; weight 31.0 g. (42%), n_D^{25} 1.4370.

McLeod⁽⁷⁾ reports b.p. 83.5-84 ° and n_D^{21} 1.4399.

B. Hydrolysis of Δ^2 -Dihydropyran to delta-Hydroxyvaleraldehyde and Preparation of the 2,4-Dinitrophenylhydrazone Derivative.

To 0.50 g. (0.0060 mole) of Δ^2 -dihydropyran (prepared in the previous experiment) in a 100 ml. Erlenmeyer flask was added 2 ml. of distilled water and one drop of concentrated hydrochloric acid. The flask was stoppered and the solution was vigorously shaken until homogeneous. This required approximately thirty minutes. The solution was set aside for two hours.

A 2,4-dinitrophenylhydrazine solution was prepared according to the following procedure⁽¹⁶⁾. To a solution of 20 ml. of distilled water and 70 ml. of 95% ethanol in a 250 ml. Erlenmeyer flask was added a solution of 3.0 g. (0.015 mole) of 2,4-dinitrophenylhydrazine (Eastman White Label) in 15 ml. of concentrated sulfuric acid. The solution was thoroughly mixed, allowed to cool to room temperature, and filtered through a small Büchner funnel.

Fifty milliliters of the 2,4-dinitrophenylhydrazine solution was added to the delta-hydroxyvaleraldehyde solution. A copious yellow precipitate was observed after one minute. The solution was shaken and set aside for five hours. The yellow precipitate was collected by suction filtration, washed on the filter with a small amount of water, recrystallized from an alcohol-water mixture and dried for two days over

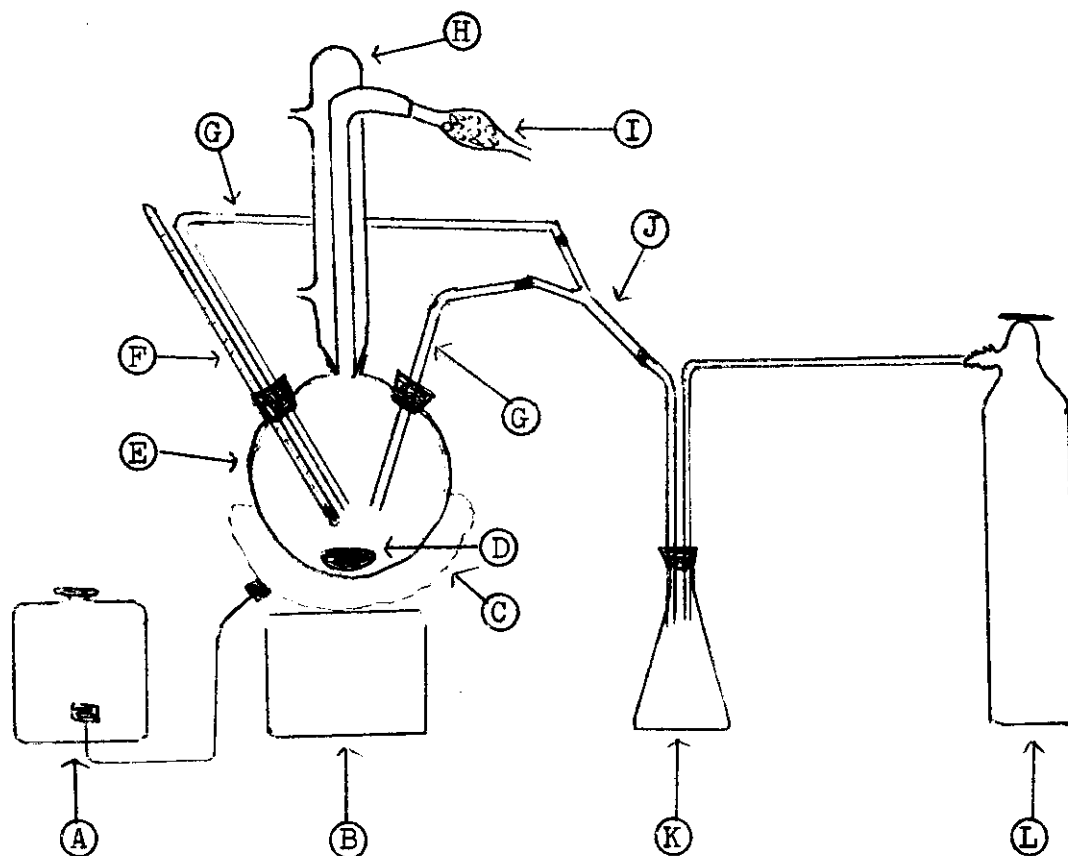
anhydrous calcium chloride. The resulting yellow crystals weighed 1.4 g. (84%) and melted at 112-113°. * Glacet⁽²⁾ reports melting point 113.2-113.5°.

C. Synthesis of Δ^3 -Dihydropyran.

The following procedure was adapted from Stouffer⁽¹⁹⁾.

In a 3-liter, 3-neck round-bottom flask were placed 2 l. of glacial acetic acid, 50 ml. of concentrated sulfuric acid, and 450 g. (15.0 moles) of paraformaldehyde (Baker and Adamson CP). A magnetic stirring egg was added and the flask and contents were carefully weighed. The mixture was heated to 90-95° by means of an electrically heated mantle until all of the paraformaldehyde had dissolved, and the solution was homogeneous. The flask was fitted with a magnetic stirrer, reflux condenser, and two gas inlet tubes. The internal temperature of the solution was maintained at 90-95° while propylene gas (Matheson Commercial Grade) was bubbled through the solution at a fairly rapid rate. During the reaction the solution turned deep brown. At intervals the reaction was stopped, the flask allowed to cool to room temperature, and the absorption of propylene gas determined by weighing the flask and contents. In seven hours, 150.0 g. of propylene had been absorbed, in fourteen hours 267.0 g. of gas absorbed, and after forty seven yours a total of 380.0 g. (9.05 moles) of

* All melting points in this report are uncorrected.



- A Variac
- B Magnetic stirrer
- C Heating mantle
- D Magnetic stirring egg
- E 3-Liter, 3-neck round-bottom flask
- F Thermometer
- G Gas inlet tube
- H Water condenser
- I Calcium chloride drying tube
- J "Y" tube
- K Gas trap
- L Compressed propylene gas

FIGURE 2

PROPYLENE-FORMALDEHYDE REACTION APPARATUS

propylene had been absorbed.

Upon cooling to room temperature, a large amount of white precipitate formed. Anhydrous sodium carbonate (100 g., 0.94 mole) was added to neutralize the sulfuric acid. The resulting metallic salts were removed by suction filtration through a large Büchner funnel and the dark brown filtrate was transferred to a 3-liter round-bottom flask. The flask was fitted with a one foot Vigreux column and a water condenser. Excess acetic acid, the bulk of which distilled at 34-37° (10 mm.) was removed. The fraction distilling at 65-89° (10 mm.) was collected. This fraction was distilled from a one liter round-bottom flask fitted with a one foot Vigreux column and a water condenser. The fraction boiling at 70-85° (10 mm.), which weighed 259 g., was collected. Redistillation of the liquid distilling below 70° (10 mm.) yielded 20 g. of distillate boiling at 70-85° (10 mm.). This fraction was added to the 259 g. of distillate described above to yield a total of 279 g. of liquid distilling over the range 70-85° (10 mm.), oil bath 115-125°.

The fraction boiling at 70-85° (279 g.) was redistilled in a 500 ml. round-bottom flask fitted with a one foot Vigreux column and a water condenser. Crude 4-acetoxytetrahydropyran (166 g.) was collected over the range 71-75° (10 mm.) with n_D^{25} 1.4353. Stouffer reports crude 4-acetoxytetrahydropyran boiling over the range 71-75° (10 mm.) with n_D^{25} 1.4350.

The crude 4-acetoxytetrahydropyran (166 g.) was placed in a 300 ml. round-bottom flask containing 10.0 g. (0.053 mole) of p-toluenesulfonic acid monohydrate (Eastman). The flask was fitted with a one foot Vigreux column and a water condenser, and heated by means of a Wood's metal bath (bath temperature 230-245°). Distillation was at a rate of 15-20 drops per minute. The liquid in the flask turned dark brown and the distillate was slightly yellow. After the rate of distillation had diminished, the solution was allowed to cool to room temperature and an additional 10 g. of p-toluenesulfonic acid added. The solution was heated as described above and the distillation continued. The product which distilled over the range 92-119° weighed 137.1 g. A black tarry substance remained in the flask.

A few drops of the crude Δ^3 -dihydropyran was added to a solution of one milliliter of distilled water and two drops of concentrated hydrochloric acid. The mixture was vigorously shaken and set aside for one hour. The mixture was added to one milliliter of 2,4-dinitrophenylhydrazine solution (prepared as previously described on page 19). A very slightly cloudy solution was formed. After twenty four hours the appearance of the solution was unchanged.

The crude Δ^3 -dihydropyran (containing large amounts of acetic acid) was treated with 200 ml. of 0.1 N hydrochloric acid to destroy any Δ^2 -dihydropyran which might be present⁽¹¹⁾. The solution was shaken at intervals, and two layers formed on standing. The top organic layer was a yellow-orange liquid;

the bottom aqueous layer was slightly yellow. The mixture was transferred to a one liter Erlenmeyer flask and cooled in an ice-water bath. One hundred milliliters of cold ether was added and the mixture was vigorously shaken. A saturated aqueous solution (150 ml.) of sodium carbonate was slowly added to the mixture to neutralize the hydrochloric and acetic acids present. During this addition considerable foaming occurred. The mixture was shaken and additional sodium carbonate solution added until no foaming occurred and the mixture was slightly basic to pH paper. Two layers formed on standing. The upper ethereal-organic layer was separated from the lower aqueous layer by means of a large pipet and transferred to a 150 ml. Erlenmeyer flask. The aqueous layer was extracted with 50 ml. of ether and the ether layer was added to the previously separated ethereal-organic layer.

The ethereal-organic layer was dried briefly over anhydrous sodium carbonate and transferred to a 300 ml. round-bottom flask. Using a one foot Vigreux column and a water condenser, the bulk of the ether was distilled from the solution. The residue was transferred to a 150 ml. flask and the flask was fitted with a small ball-jointed distilling apparatus containing a 3 inch Vigreux column. A few granules of anhydrous calcium oxide was added to the solution. The fraction with b.p. 85-95° (52.4 g.) was collected (oil bath 130-150°).

The fraction boiling at 85-95° was placed in a 150 ml. flask and a small amount of calcium oxide added. The flask

was connected to the distilling apparatus described above and the distillate (37.1 g.) boiling over the range 92-93° was collected with n_D^{26} 1.4408. The oil bath temperature was 130°.

The fraction 92-93° (37.1 g.) was redistilled over a few granules of lithium aluminum hydride. The liquid distilling at 92-93° was collected and it weighed 29.0 g. (4% based on propylene absorbed). The index of refraction was n_D^{25} 1.4426. Olsen⁽⁹⁾ reports b.p. 92-93° and $n_D^{24.5}$ 1.4428. Hanschke⁽³⁾ reports b.p. 91.3-92.4° and n_D^{20} 1.4477. Paul⁽¹⁰⁾ reports b.p. 93-94° and n_D^{19} 1.4477.

A few drops of the Δ^3 -dihydropyran was added to a solution of one milliliter of distilled water and two drops of concentrated hydrochloric acid. The mixture was vigorously shaken and set aside for one hour. The solution was added to one milliliter of 2,4-dinitrophenylhydrazine solution (prepared as described on page 19). The solution remained clear. After twenty four hours the appearance of the solution was unchanged.

D. Infrared Spectra of Δ^2 -Dihydropyran and Δ^3 -Dihydropyran.

Infrared spectra of the solutions were taken using the same constant thickness liquid cell (0.5 mm.).

- (1) Carbon tetrachloride (Spectra Grade) - - neat.
- (2) Δ^2 -Dihydropyran - - 5%, 2%, 1%, and 0.1%
in carbon tetrachloride
- (3) Δ^2 -Dihydropyran - - neat.

(4) Δ^3 -Dihydropyran - - 5% in carbon tetrachloride.

(5) Δ^3 -Dihydropyran - - neat.

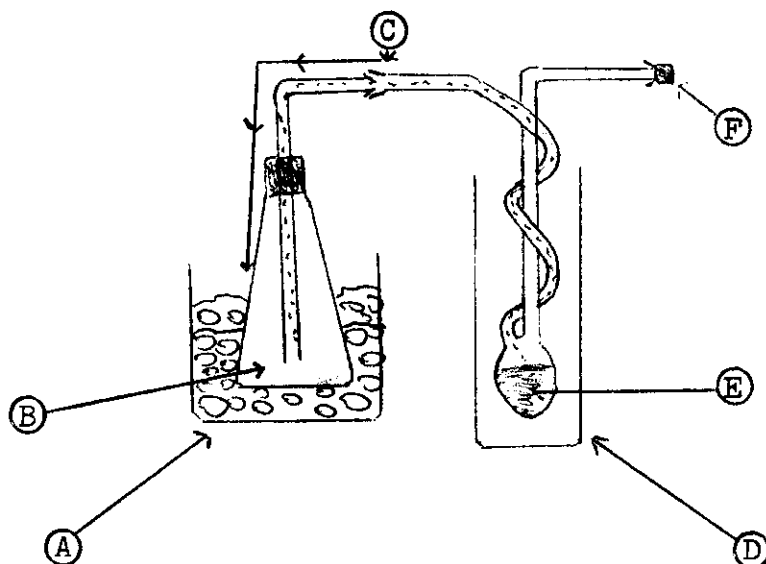
The spectra of the 5%, 2%, and 1% Δ^2 -dihydropyran solutions in carbon tetrachloride showed intense absorption at 6.08μ . The spectra of the 0.1% Δ^2 -dihydropyran in carbon tetrachloride showed weak absorption at 6.08μ . The spectra of neat Δ^3 -dihydropyran and of 5% Δ^3 -dihydropyran in carbon tetrachloride showed no absorption in the region $6.05-6.15\mu$. McLeod⁽⁷⁾ reports ~~a strong~~ a strong band at 6.09μ for the vinyl ether bond in Δ^2 -dihydropyran. It is therefore concluded from infrared spectra that there is less than 0.1 % Δ^2 -dihydropyran as impurity in the Δ^3 -dihydropyran used in the following pyrolysis experiments reported herein.

E. Preparation of dl-1,2,3,4-Tetrabromobutane.

The procedure in this experiment was adapted from Schubert and Lanka⁽¹⁵⁾.

In a 150 ml. flask was placed 50 ml. of chloroform (Matheson Reagent) and 25.0 g. (0.156 mole) of bromine. The flask and contents were carefully weighed and cooled in an ice-water bath. The flask was sealed with a tight fitting cork with one gas inlet opening. Butadiene*, which was stored as a liquid in a flask immersed in an acetone-Dry Ice bath,

* The author is indebted to Professor Arthur Cope, Massachusetts Institute of Technology for the supply of butadiene.



- A Ice-water bath
- B Reaction flask with chloroform-bromine solution
- C Gaseous butadiene *
- D Dewar flask with acetone-Dry Ice
- E Liquid butadiene
- F Cork plug --loose fit

* To generate gaseous butadiene, the acetone-Dry Ice bath was removed at intervals from the flask containing the liquid butadiene.

F I G U R E 3

BUTADIENE-BROMINE REACTION APPARATUS

was slightly warmed by removing the acetone-Dry Ice bath at intervals. The resulting gas was slowly bubbled through the chloroform-bromine solution. During the reaction a large amount of white crystals were formed in the flask. The butadiene inlet tube was removed and the flask was dried and weighed. After forty five minutes, 3.19 g. (0.059 mole) of butadiene had been absorbed.

The contents of the flask were transferred to a 200 ml. beaker and the chloroform and excess bromine allowed to evaporate at room temperature. Three hundred milliliters of ligroin was added to the resulting white crystals and the solution was warmed on a steam bath until all the crystals went into solution. The beaker was removed from the steam bath and cooled in an ice-water bath. A large quantity of white, needle-like crystals precipitated from the cold ligroin solution. The crystals were collected by suction filtration and recrystallized from 300 ml. of 85% ethanol. After drying for two days over anhydrous calcium chloride, the white crystals weighed 13.0 g. and melted at 115.5-116.5°. Based on 3.19 g. of butadiene absorbed, the yield of the high melting racemic isomer of 1,2,3,4-tetrabromobutane was 59%. Slobodin and Zaboev⁽¹⁷⁾ have identified the high melting 1,2,3,4-tetrabromobutane (m.p. 116-117 °) as the racemic isomer.

F. Identification of Butadiene, Formaldehyde, and Δ^2 -Dihydropyran under Various Conditions.

1. Identification of butadiene in the presence of formaldehyde, tetrahydrofurfuryl alcohol, Δ^2 -dihydropyran, Δ^3 -dihydropyran, green product of unknown composition from the rearrangement of tetrahydrofurfuryl alcohol over hot alumina, and water.

In a 150 ml. Erlenmeyer flask were placed 100 ml. of distilled water, 1.00 g. of Δ^2 -dihydropyran, 0.5 g. of Δ^3 -dihydropyran, 5.41 g. of 37% formaldehyde solution, 1.0 g. of tetrahydrofurfuryl alcohol, and 0.5 g. of green product as described above. Connected to this flask by glass tubing was a second 150 ml. Erlenmeyer flask which contained chloroform and bromine cooled in an ice-water bath. Butadiene gas (generated as described in the preceding experiment) was bubbled through the first flask and absorbed in the second flask. During the reaction white crystals appeared in the second flask. The reaction was stopped and the chloroform and excess bromine in the second flask allowed to evaporate. Fifty milliliters of ligroin was added to the second flask containing the white crystals, and the mixture was warmed on a steam bath until the solution was homogeneous. The solution was removed from the steam bath and cooled in an ice-water bath. White needles immediately precipitated. The white crystals, which were recrystallized from 75 ml. of 85% ethanol and dried for two days over anhydrous calcium chloride, melted at 115.5-116.5°. The mixed melting point with authentic dl-1,2,3,4-tetrabromobutane prepared in the previous experiment was 115.5-116.5°.

2. Quantitative identification of formaldehyde in the presence of butadiene, tetrahydrofurfuryl alcohol, Δ^2 -dihydropyran, Δ^3 -dihydropyran, green product of unknown composition from the rearrangement of tetrahydrofurfuryl alcohol over hot alumina, and water.

To the aqueous, heterogeneous mixture in the first flask from the preceding experiment (Experiment F 1) was added 50.0 ml. of benzene. The heterogeneous solution was vigorously mixed. The mixture formed two distinct layers on standing, a top greenish benzene layer and a bottom aqueous layer. The benzene layer was separated with a small pipet and washed with 10 ml. of distilled water. These washings were added to the aqueous layer.

The aqueous layer was diluted to 200 ml. with distilled water and a 25 ml. aliquot was added to a 100 ml. beaker. Twenty five milliliters of a 10% alcoholic dimedone solution was added and the mixture was heated on a steam bath for five minutes. A copious white precipitate formed during the warming. The beaker was removed from the steam bath and cooled in an ice-water bath. The resulting white crystals were collected by suction filtration and recrystallized from 95% ethanol. The white crystals, which were dried for two days over anhydrous calcium chloride, weighed 2.24 g. (92% recovery) and melted at 188.5-189°. Vogel⁽²⁰⁾ reports the dimedone derivative of formaldehyde with m.p. 189°.

3. Qualitative identification of formaldehyde in an aqueous solution.

One gram of 37% formaldehyde solution was diluted with various quantities of distilled water. When treated with a few drops of 2,4-dinitrophenylhydrazine solution (prepared as described on page 19), one milliliter of this diluted aqueous formaldehyde solution gave an immediately distinct yellow precipitate with a solution of 0.37 g. (0.012 mole) of formaldehyde in 64 l. of solution. This is a sensitivity of 0.0006 g. of formaldehyde in 100 ml. of water.

4. Quantitative identification of Δ^2 -dihydropyran in an aqueous solution.

In a 250 ml. Erlenmeyer flask was placed 0.12 g. (0.0014 mole) of Δ^2 -dihydropyran and 100 ml. of distilled water. Five drops of concentrated hydrochloric acid was added, the solution was thoroughly mixed and set aside for one hour. A 50.0 ml. aliquot was placed in a 100 ml. Erlenmeyer flask. Ten milliliters of a 2,4-dinitrophenylhydrazine solution (prepared as described on page 19) was added. A yellow precipitate appeared in one minute. The solution was set aside for five hours, the resulting yellow precipitate collected, and the crystals were recrystallized from an ethanol-water solution. The resulting yellow crystals weighed 0.14 g. (70% recovery) and melted at 112-113°. Glacet⁽²⁾ reports m.p. as 113.2-113.5°.

5. Qualitative identification of Δ^2 -dihydropyran in an aqueous solution.

To 0.33 g. (0.0038 mole) of Δ^2 -dihydropyran was added a solution of 100 ml. of distilled water and 10 drops of concentrated hydrochloric acid. The mixture was vigorously mixed and set aside for five hours. When treated with a few drops of 2,4-dinitrophenylhydrazine solution (prepared as described on page 19), one milliliter of diluted Δ^2 -dihydropyran solution gave a distinct yellow precipitate with a solution equivalent to 0.33 g. of Δ^2 -dihydropyran in 2 l. of solution. This is a sensitivity of 0.017 g. of Δ^2 -dihydropyran in 100 ml. of solution.

G. Tetrahydrofurfuryl Alcohol over Activated Alumina at 320-370°.

The apparatus used was similar to that described in Experiment A, page 15 (see Figure 1, page 17) except for the collecting system which is described below. The Variac readings for warming the electric furnace were 49 and 52 respectively for a temperature range of 320-370°. The reaction tube was filled with fresh alumina to a height of 22 inches. Five grams of distilled tetrahydrofurfuryl alcohol (see page 15) was added to the dropping funnel. Nitrogen, which had been passed through the alumina-filled tube at a rate of one bubble per six seconds for three hours while the furnace was being warmed, was passed through at a rate of one bubble per second. The tetrahydrofurfuryl alcohol was added to the alumina at a

rate of one drop every six seconds.

The reaction products were bubbled through a collecting flask containing 100 ml. of distilled water in an ice-water bath, and a second flask containing 5.0 g. (0.031 mole) of bromine in 20 ml. of chloroform, also immersed in an ice-water bath. After all the tetrahydrofurfuryl alcohol was added, the flow of nitrogen was increased to five bubbles per second for two hours.

The bromine and chloroform in the second flask were allowed to evaporate at room temperature. There was no visible residue.

The first flask, which contained a small amount of green organic material floating on top of the aqueous layer, was treated with 10 ml. of 5% hydrochloric acid solution. After stirring for one hour, this heterogeneous mixture was treated with 75 ml. of a 2,4-dinitrophenylhydrazine solution (prepared as described on page 19). A yellow-orange precipitate formed immediately. This precipitate was collected by suction filtration and recrystallized from an alcohol-water mixture. The resulting yellow-orange crystals of 2,4-dinitrophenylhydrazone of delta-hydroxyvaleraldehyde weighed 1.9 g (14%) and melted at 112-113 °. Glacet⁽²⁾ reports m.p. 113.2-113.5 °.

H. Δ^3 -Dihydropyran over Activated Alumina at 270-320 °.

The apparatus used was similar to that described in Experiment A, page 15 (see Figure 1, page 17) except for the collecting system which is described below. The Variac readings for heating the electric furnace were 42 and 43 respectively for a temperature range of 270-320 °. The reaction tube was filled with fresh alumina to a height of 22 inches. Nitrogen, which had been passed through the alumina-filled tube at a rate of one bubble per six seconds for three hours while the furnace was being warmed, was passed through at a rate of one bubble per second. The Δ^3 -dihydropyran (5.41 g.) was added to the alumina at a rate of one drop per seven seconds. After all the Δ^3 -dihydropyran was added, the nitrogen was increased to five bubbles per second for two hours.

The reaction products were bubbled through a series of four 150 ml. flasks connected by glass tubing (see Figure 4, page 35).

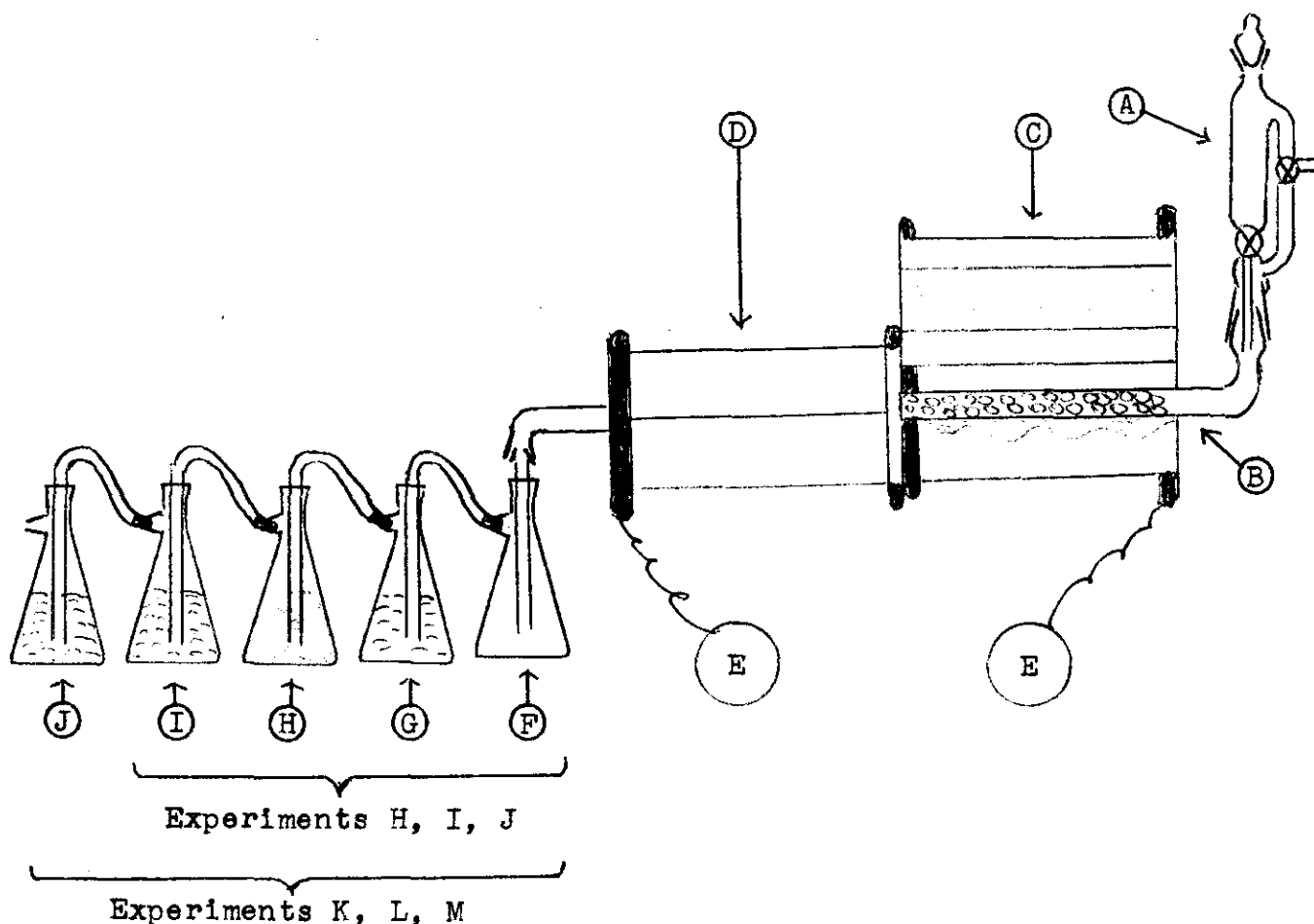
Trap 1- empty and cooled in an ice-water bath.

Trap 2- contained 100 ml. of distilled water.

Trap 3- contained 50 ml. of chloroform and 24 g. (0.150 mole) of bromine; cooled in an ice-water bath.

Trap 4- contained 100 ml. of 95% ethanol.

The first trap contained a small amount of green liquid after completion of the reaction. This liquid was treated with a solution of 3 ml. of distilled water and 3 drops of



- A Dropping funnel with side-arm for nitrogen inlet.
- B Curved reaction tube with activated alumina.
- C Furnace--open.
- D Furnace--closed.
- E Variacs.
- F Trap 1--empty and cooled in an ice-water bath.
- G Trap 2--contained 100 ml. of distilled water.
- H Trap 3--contained chloroform and bromine cooled in an ice-water bath.
- I Trap 4--contained 100 ml. of 95% ethanol.
- J Trap 5--contained 100 ml. of a clear, saturated calcium hydroxide solution.

F I G U R E 4

APPARATUS FOR PYROLYSIS EXPERIMENTS

concentrated hydrochloric acid. The mixture was stirred for one hour and 5 ml. of a 2,4-dinitrophenylhydrazine solution (prepared as described on page 19) was added. The mixture remained clear except for a small amount of green liquid which was insoluble in the aqueous solution. The contents were thoroughly mixed, added to a 25 ml. Erlenmeyer flask and stoppered. After twenty four hours the appearance of the mixture was unchanged.

One milliliter of the aqueous solution in the second trap was treated with two drops of concentrated hydrochloric acid and the solution was set aside for one hour. Two milliliters of a 2,4-dinitrophenylhydrazine solution was added. No precipitate was formed. The flask was stoppered and set aside for twenty four hours. The appearance of the solution was unchanged.

Twenty five milliliters of the aqueous solution in the second trap was placed in a 100 ml. Erlenmeyer flask. Twenty five milliliters of a 10% dimedone solution in absolute ethanol was added and the mixture was warmed on a steam bath for five minutes until the solution was clear. The clear solution was cooled to 5° and a small quantity of white crystals formed. The white precipitate, which was recrystallized from an aqueous alcohol solution, weighed 1.0 g. and melted at 143.5-146.5°. An additional recrystallization from 95% ethanol raised the melting point to 146-147°. A mixed melting point of the above white crystals and authentic dimedone derivative of formaldehyde (m.p. 188.5-189°) had a melting point of

134-139°. A mixed melting point of the above crystals and authentic dimedone reagent (m.p. 146.5-147°) had a melting point of 146-147°.

While the Δ^3 -dihydropyran was being passed over the hot alumina, a white precipitate formed in the third trap. The contents of this trap were placed in a 150 ml. beaker and the chloroform and excess bromine allowed to evaporate at room temperature. One hundred milliliters of ligroin was added to the resulting white crystals and the mixture was warmed on a steam bath until the solution was clear. The solution was cooled and a copious white precipitate formed. Recrystallization from 85% ethanol and drying for two days over anhydrous calcium chloride gave 5.73 g. of product which melted at 115.5-116.5°. A mixed melting point with authentic dl-1,2,3,4-tetrabromobutane prepared from butadiene gave a melting point of 115.5-116.5°. The yield of dl-1,2,3,4-tetrabromobutane from this reaction was 23.7%. Based on a yield of 59% of dl-1,2,3,4-tetrabromobutane from pure butadiene, the yield of butadiene from Δ^3 -dihydropyran is estimated at 40%.

In a small test tube, 2 ml. of 2,4-dinitrophenylhydrazine solution (prepared as described on page 19) was added to one milliliter of the alcoholic solution in the fourth trap. The solution remained clear. The test tube was stoppered and set aside. After twenty four hours the appearance of the solution was unchanged.

I. Δ^3 -Dihydropyran over Activated Alumina at 320-370°.

This experiment was similar to the previous experiment (Experiment H) except that it was performed at a higher temperature. For a temperature range of 320-370°, the Variac readings were 49 and 52 respectively. The flow rate of nitrogen and the rate of addition of Δ^3 -dihydropyran to the alumina were the same as in the previous experiment. The alumina was also the very same alumina used in the previous experiment.

In this pyrolysis experiment 5.94 g. (0.0707 mole) of Δ^3 -dihydropyran was passed over the hot alumina. As in the previous experiment, the reaction products were bubbled through a series of four 150 ml. flasks which were connected by glass tubing (see Figure 4, page 35).

Trap 1- empty and cooled in an ice-water bath.

Trap 2- contained 100 ml. of distilled water.

Trap 3- contained 50 ml. of chloroform and 24 g. (0.15 mole) of bromine; cooled in an ice-water bath.

Trap 4- contained 100 ml. of 95% ethanol.

The first trap contained a small amount of green liquid after completion of the reaction. This liquid was treated with a solution of 3 ml. of distilled water and 3 drops of concentrated hydrochloric acid. The mixture was stirred for one hour and 5 ml. of 2,4-dinitrophenylhydrazine solution (prepared as described on page 19) was added. The mixture remained clear except for a small amount of green liquid

which was insoluble in the aqueous solution. The contents were thoroughly mixed, added to a 25 ml. Erlenmeyer flask and stoppered. After twenty four hours the appearance of the mixture was unchanged.

One milliliter of the aqueous solution in the second trap was treated with two drops of concentrated hydrochloric acid and set aside for one hour. Two milliliters of 2,4-dinitrophenylhydrazine solution (prepared as described on page 19) was added. No precipitate was formed. The flask was stoppered and set aside for twenty four hours. The appearance of the solution was unchanged.

As in the previous experiment, an attempt was made to prepare a dimedone derivative from the aqueous solution in the second trap. The results were the same as in the previous experiment. No dimedone derivative was formed.

The contents of the third trap, which contained a large amount of white crystals, were placed in a 150 ml. beaker and the chloroform and excess bromine allowed to evaporate at room temperature. One hundred fifty milliliters of ligroin was added to the resulting white crystals and the mixture was heated on a steam bath until the solution was clear. The beaker was cooled in an ice-water bath and a copious white precipitate formed. Recrystallization from 85% ethanol and drying for two days over anhydrous calcium chloride gave 10.3 g. of product which melted at 115.5-116.5°. A mixed melting point with authentic dl-1,2,3,4-tetrabromobutane prepared from butadiene

had melting point 115.5-116.5°. The yield of dl-1,2,3,4-tetrabromobutane from this reaction was 38.5%. From the yield of 59% of dl-1,2,3,4-tetrabromobutane from pure butadiene, the yield of butadiene from Δ^3 -dihydropyran is estimated at 65%.

In a small test tube, 2 ml. of 2,4-dinitrophenylhydrazine solution was added to one milliliter of the alcoholic solution in the fourth trap. The solution remained clear. The test tube was stoppered and set aside. After twenty four hours the appearance of the solution was unchanged.

J. Δ^3 -Dihydropyran over Activated Alumina at 320-370° in the Absence of Nitrogen.

This experiment was similar to the previous experiment (Experiment I) except that no nitrogen as a carrier gas was used during the pyrolysis of the Δ^3 -dihydropyran.

Nitrogen was allowed to flow at a rate of two bubbles per second for five hours through the cold reaction tube containing the very same alumina used in the previous experiment. The alumina was allowed to warm to 320-370° for two hours while the flow of nitrogen was continued. The nitrogen inlet tube was sealed off close to the dropping funnel gas inlet arm during the addition of 5.00 g. (0.0600 mole) of Δ^3 -dihydropyran which was added at the rate of one drop every six seconds. Twenty minutes after all the Δ^3 -dihydropyran was added to the hot alumina, nitrogen was passed through the hot alumina with a flow of five bubbles per second for two hours.

The reaction products were collected and tested as in the previous experiment. The qualitative results were the same as in the previous experiment. No formaldehyde or Δ^2 -dihydropyran were detected either as the dimedone, or as the 2,4-dinitrophenylhydrazone derivatives. The yield of dl-1,2,3,4-tetrabromobutane, m.p. 115.5-116.5°, mixed melting point with authentic dl-1,2,3,4-tetrabromobutane 115.5-116.5°, which was isolated in the same manner as in the previous experiment, was 5.10 g. (22.3%). From the yield of 59% of dl-1,2,3,4-tetrabromobutane from pure butadiene, the yield of butadiene from Δ^3 -dihydropyran is estimated at 39%.

K. Aqueous Formaldehyde over Activated Alumina at 320-370°.

The apparatus used in this experiment was the same as in the preceding experiment except for the collecting system which is described below. The reaction tube was filled to a height of 22 inches with fresh alumina. Nitrogen, at a rate of one one bubble per second, was allowed to pass through the reaction tube while the alumina was being warmed to 320-370° (Variac readings 49 and 51 respectively).

A 37% aqueous formaldehyde solution (5.0 g.), which contained 1.9 g. (0.062 mole) of formaldehyde, was diluted to 10 ml. with distilled water. The diluted formaldehyde solution was added to the fresh, hot alumina at a rate of one drop per six seconds. Nitrogen flow was continued at the rate of one bubble per second while the formaldehyde solution was added.

The reaction products were collected in a series of five collecting flasks (see Figure 4, page 35).

Trap 1- empty and cooled in an ice-water bath.

Trap 2- contained 100 ml. of distilled water.

Trap 3- contained 50 ml. of chloroform and 10 g. (0.062 mole) of bromine; cooled in an ice-water bath.

Trap 4- contained 100 ml. of 95% ethanol.

Trap 5- contained 100 ml. of a clear, saturated calcium hydroxide solution.

After all the formaldehyde solution was added, nitrogen was passed over the hot alumina for two hours. The appearance of the first four collecting flasks did not change during the reaction. A milky white precipitate was formed in the fifth trap.

Two milliliters of the solution in Traps 2-5 were placed in four separate test tubes. Two milliliters of a 2,4-dinitrophenylhydrazine solution (prepared as described on page 19) was added to each test tube. The solutions remained clear. Each test tube was stoppered and set aside. After twenty four hours their appearance had not changed.

The aqueous solution in the second trap was slightly acidic towards litmus. When a drop of concentrated hydrochloric acid was added to 5 ml. of this solution in a test tube, a colorless gas was released. A clear, saturated calcium hydroxide solution (2 ml.) was added to another 5 ml. of this aqueous solution. A milky white precipitate was formed which immediately dis-

sappeared with the evolution of a colorless gas when a few drops of concentrated hydrochloric acid was added.

Concentrated hydrochloric acid (0.5 ml.) was added to the fifth trap which contained the milky white precipitate. A colorless gas was evolved and the contents of the flask turned clear.

The 37% aqueous formaldehyde solution was neutral to litmus paper. No gas was released when this formaldehyde solution was treated with a drop of concentrated hydrochloric acid. When 5 ml. of this formaldehyde solution was treated with 2 ml. of a clear, saturated calcium hydroxide solution, no precipitate formed.

The above experiment was repeated in the absence of nitrogen as a carrier gas. Identical tests were made for the identification of formaldehyde in the reaction products. The results were negative; no formaldehyde survived the reaction. The tests for carbon dioxide in the reaction products were, as in the above experiment, positive. A colorless gas was observed in this experiment which was not soluble in any of the solutions in the collecting flasks and which escaped from the fifth trap. This gas was not identified.

Fresh alumina was added to the reaction tube to a height of 22 inches. The furnace was heated as before to 320-370° while a slow stream of nitrogen was passed through the tube for three hours. Ten milliliters of distilled water was added to the hot alumina at a rate of one drop every six seconds.

The nitrogen flow was adjusted to one bubble per second and the reactions products were collected in a series of five traps as previously described. On completion of the reaction, nitrogen was passed over the alumina for two hours. The solutions in the collecting flasks were tested for formaldehyde and carbon dioxide in the same manner as previously described. The results were negative; no formaldehyde or carbon dioxide was detected.

L. Δ^3 -Dihydropyran over Activated Alumina at 320-370° in the Presence of Tetrahydrofurfuryl Alcohol.

The apparatus used in this experiment was the same as in the preceding experiment (see Figure 4, page 35). The reaction tube was filled to a height of 22 inches with fresh alumina. Nitrogen at a rate of one bubble per second was passed through the reaction tube for three hours while the alumina was being warmed to 320-370°.

In a 25 ml. Erlenmeyer flask was placed 5.00 g. (0.0600 mole) of Δ^3 -dihydropyran and 5.00 g. (0.044 mole) of tetrahydrofurfuryl alcohol (purified as described on page 15). The contents were thoroughly mixed and the homogeneous solution was added to the hot alumina at a rate of one drop every eight seconds. After all the Δ^3 -dihydropyran-tetrahydrofurfuryl alcohol solution was added, nitrogen flow was increased to five bubbles per second for two hours.

The reaction products were collected in a series of five collecting flasks (see Figure 4, page 35).

Trap 1- empty and cooled in an ice-water bath.

Trap 2- contained 100 ml. of distilled water.

Trap 3- contained 50 ml. of chloroform and 24 g. (0.15 mole) of bromine; cooled in an ice-water bath.

Trap 4- contained 100 ml. of 95% ethanol.

Trap 5- contained 100 ml. of a clear, saturated calcium hydroxide solution.

During the reaction, a relatively large amount of green organic layer and a small amount of aqueous layer was formed in the first trap. White crystals were observed in the third trap. Trap five contained a fairly large amount of milky white precipitate.

The contents of the first trap were placed in a 25 ml. Erlenmeyer flask and 10 ml. of a 2,4-dinitrophenylhydrazine solution (prepared as described on page 19) was added. A small amount of redish-orange precipitate was formed. The flask was stoppered and the contents thoroughly mixed and set aside for twenty four hours. A small amount of redish-orange precipitate was observed in the bottom of the flask and a green organic liquid was floating on top of the aqueous solution. The green organic layer was removed by a small pipet and discarded. The redish-orange precipitate was collected by suction filtration and recrystallized twice from 95% ethanol. The precipitate, which was dried for two days over anhydrous

calcium chloride, weighed 0.08 g. and melted over the range 145-195°. The precipitate was dissolved in one milliliter of benzene and precipitated with 7 ml. of petroleum ether. The resulting red precipitate was collected by suction filtration, washed on the filter with a small amount of petroleum ether, and dried for two days over anhydrous calcium chloride. The red precipitate melted over the range 188-220°. There was not sufficient precipitate for a further attempt at purification.

Twenty milliliters of the aqueous solution in the second trap were placed in a 50 ml. Erlenmeyer flask and 20 ml. of a 2,4-dinitrophenylhydrazine solution (prepared as described on page 19) was added. A small amount of orange-yellow precipitate was formed. The flask was stoppered and set aside for five hours. The precipitate, which was collected by suction filtration and recrystallized from 95% ethanol weighed 0.03 g. (1.3%) and melted at 112-116°. Recrystallization from benzene-petroleum ether solution and drying for two days over anhydrous calcium chloride gave 0.02 g. of orange-yellow crystals which melted at 112-114°. The mixed melting point of the above crystals and authentic 2,4-dinitrophenylhydrazone of delta-hydroxyvaleraldehyde was 112-114°.

A 20.0 ml. aliquot of the aqueous solution in the second trap was placed in a 50 ml. Erlenmeyer flask and 5 ml. of a 10% alcoholic dimedone solution was added. The clear solution was heated on a steam bath for ten minutes. The flask was

stoppered and set aside for twenty four hours. No precipitate was formed. Upon cooling in an ice-water bath to 4° , a small amount of white crystals formed. After drying for two days over anhydrous calcium chloride, the crystals melted at $147-149^{\circ}$. The mixed melting point of the above crystals and authentic dimedone reagent (m.p. $146.5-147^{\circ}$) had m.p. $147-149^{\circ}$.

The contents of the third trap (containing white crystals) were placed in a 150 ml. beaker and the chloroform and excess bromine allowed to evaporate at room temperature. One hundred and fifty milliliters of ligroin was added to the resulting white crystals and the mixture was heated on a steam bath until the solution was clear. The beaker was removed from the steam bath and cooled in an ice-water bath. A copious white precipitate formed. Recrystallization from 85% ethanol and drying for two days over anhydrous calcium chloride yielded 7.50 g. (33.7%) of dl-1,2,3,4-tetrabromobutane, m.p. $115.5-116.5^{\circ}$. A mixed melting point of the above crystals and authentic dl-1,2,3,4-tetrabromobutane from butadiene was $115.5-116.5^{\circ}$. From a yield of 59% of dl-1,2,3,4-tetrabromobutane from pure butadiene, the yield of butadiene from Δ^3 -dihydropyran is estimated at 57%.

In a small test tube 2 ml. of 2,4-dinitrophenylhydrazine solution was added to one milliliter of the alcoholic solution from the fourth trap. The solution remained clear. The test tube was stoppered and set aside. After twenty four hours the appearance of the solution was unchanged.

Concentrated hydrochloric acid (0.5 ml.) was added to the aqueous solution (containing a milky white precipitate) in the fifth trap. A colorless gas was released and the contents of the flask turned clear.

M. Δ^3 -Dihydropyran over Activated Alumina at 320-370° in the Presence of Δ^2 -Dihydropyran.

The apparatus used in this experiment was the same as in the previous pyrolysis experiment. The reaction tube was filled to a height of 22 inches with fresh alumina. Nitrogen at a rate of one bubble per second was passed through the reaction tube for three hours while the alumina was being warmed to 320-370°.

In a 25 ml. Erlenmeyer flask was placed 5.50 g. (0.0655 mole) of Δ^3 -dihydropyran and 9.00 g. (0.108 mole) of Δ^2 -dihydropyran. The contents were thoroughly mixed and the homogeneous solution was added to the dropping funnel. The nitrogen flow was continued at a rate of one bubble per second as the solution was added to the hot alumina at a rate of one drop every eight seconds. After all the Δ^3 -dihydropyran- Δ^2 -dihydropyran solution was added, the nitrogen flow was increased to five bubbles per second for two hours.

The reaction products were collected in a series of five collecting flasks (see Figure 4, page 35).

Trap 1- empty and cooled in an ice-water bath.

Trap 2- contained 100 ml. of distilled water.

Trap 3- contained 50 ml. of chloroform and 24 g. (0.15 mole) of bromine; cooled in an ice-water bath.

Trap 4- contained 100 ml. of 95% ethanol.

Trap 5- contained 100 ml. of a clear, saturated calcium hydroxide solution.

During the reaction a relatively large amount of aqueous-insoluble green organic liquid and a small amount of water were collected in the first trap. White crystals were observed in the third trap. The fifth trap contained a fairly large amount of milky white precipitate.

The contents of the first trap were placed in a 25 ml. Erlenmeyer flask and 10 ml. of a 2,4-dinitrophenylhydrazine solution (prepared as described on page 19) was added. A small amount of orange-yellow precipitate was formed. The flask was stoppered and the contents thoroughly mixed and set aside for twenty four hours. The top aqueous-insoluble green organic liquid was removed by a small pipet and discarded. The orange-yellow precipitate was separated from the solution by suction filtration but there was insufficient material to determine a melting point.

Twenty five milliliters of the aqueous solution from the second trap was placed in a 50 ml. Erlenmeyer flask and 20 ml. of a 2,4-dinitrophenylhydrazine solution was added. An orange-yellow precipitate formed immediately. The flask was stoppered and set aside for five hours. The precipitate was collected by suction filtration. Recrystallization from a benzene-

petroleum ether solution gave 0.20 g. (3%) of yellow crystals which melted at 111.5-116°. The mixed melting point of the above crystals and authentic 2,4-dinitrophenylhydrazine of delta-hydroxyvaleraldehyde (m.p. 112-113°) had m.p. 112-116°.

The contents of the third trap (containing white crystals) were placed in a 150 ml. beaker and the chloroform and excess bromine allowed to evaporate at room temperature. One hundred and fifty milliliters of ligroin was added to the resulting white crystals and the mixture was heated on a steam bath until the solution was clear. The beaker was removed from the steam bath and cooled in an ice-water bath. A copious white precipitate formed. Recrystallization from 85% ethanol and drying for two days over anhydrous calcium chloride gave 7.48 g. of product which melted at 113.5-115.5°. An additional recrystallization gave 7.08 g. (28.9%) of dl-1,2,3,4-tetrabromobutane, m.p. 114.5-116.5°. The mixed melting point of the above crystals and authentic dl-1,2,3,4-tetrabromobutane from pure butadiene was 114.5-116.5°. From the yield of 59% of dl-1,2,3,4-tetrabromobutane from pure butadiene, the yield of butadiene from Δ^3 -dihydropyran is estimated at 49%.

In a small test tube, 2 ml. of a 2,4-dinitrophenylhydrazine solution was added to one milliliter of the alcoholic solution in the fourth trap. The solution remained clear. The test tube was stoppered and set aside. After twenty four hours the appearance of the solution was unchanged.

Concentrated hydrochloric acid (0.5 ml) was added to the contents of the fifth trap which contained a milky white precipitate. A colorless gas was released and the contents of the flask turned clear.

IV. TABULATED RESULTS

Conditions	Δ^2 -Dihydropyran	Butadiene	Formaldehyde	Carbon Dioxide
Tetrahydrofurfuryl Alcohol at 320-370°.	14%	Negative	-	-
Δ^3 -Dihydropyran at 270-320°.	Negative	40%	Negative	-
Δ^3 -Dihydropyran at 320-370°.	Negative	65%	Negative	-
Δ^3 -Dihydropyran at 320-370° without a carrier gas.	Negative	39%	Negative	-
Aqueous Formaldehyde at 320-370°.	Negative	Negative	Negative	Positive
Aqueous Formaldehyde at 320-370° without a carrier gas.	Negative	Negative	Negative	Positive
Water at 320-370°.	Negative	Negative	Negative	Negative
Δ^3 -Dihydropyran in the presence of Tetrahydrofurfuryl Alcohol at 320-370°.	1.3%	57%	-	Positive
Δ^3 -Dihydropyran in the presence of Δ^2 -Dihydropyran at 320-370°.	3%	49%	-	Positive

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VI ABSTRACT

In previous work it was found that tetrahydrofurfuryl alcohol dehydrates, with a corresponding ring expansion, to Δ^2 -dihydropyran. If the tetrahydrofurfuryl alcohol is labeled with carbon-14 on the external methylene carbon atom, the resulting Δ^2 -dihydropyran is labeled in approximately equal proportions on position 2 and on position 6.

In addition Δ^2 -dihydropyran labeled with carbon-14 on position 3 rearranges when passed over hot alumina. The resulting Δ^2 -dihydropyran was labeled approximately equally on position 2 and 6.

One way to account for the above rearrangement is to postulate double bond migration around the carbon ring from one side to the other. If this process is operating, Δ^3 -dihydropyran when passed over hot alumina should lead to Δ^2 -dihydropyran. To preclude the possibility that this process is operating, Δ^3 -dihydropyran was synthesized and tested in this manner.

The pyrolysis of Δ^3 -dihydropyran at 600° has been observed before in which butadiene and formaldehyde were isolated. This behavior of Δ^3 -dihydropyran has been compared to the reverse Diels-Alder reaction of cyclohexene at elevated temperature which yields butadiene and ethylene. In anticipation of butadiene from Δ^3 -dihydropyran in the

presence of hot alumina, a suitable means of identification was sought. Bromination of butadiene in cold chloroform containing excess bromine gives two isomeric 1,2,3,4-tetrabromobutanes which can be readily separated by crystallization from ligroin. Butadiene was brominated and the two isomeric tetrabromobutanes isolated in this manner. The yield (59%) of the high melting (117°) racemic isomer was used to estimate the amount of butadiene from Δ^3 -dihydropyran in the present work. Controlled experiments also established that aqueous formaldehyde does not survive when passed over hot alumina. The products of this reaction were carbon dioxide which was absorbed in a saturated calcium hydroxide solution, and an unidentified gas.

In preliminary work, a series of experiments were carried out in which Δ^2 -dihydropyran, butadiene, and formaldehyde were isolated and identified with high precision under the same conditions used in the pyrolysis experiments in the present work. The problem of detecting and distinguishing Δ^2 -dihydropyran in the presence of Δ^3 -dihydropyran was straight forward and made use of the difference in the behavior of the two compounds to dilute aqueous acid. Whereas Δ^2 -dihydropyran is readily hydrolyzed to delta-hydroxyvaleraldehyde which is easily identified as its 2,4-dinitrophenylhydrazone, Δ^3 -dihydropyran is inert under the same conditions. Formaldehyde is easily identified in an aqueous

solution as either the 2,4-dinitrophenylhydrazone or as the dimedone derivative.

In the present work when neat Δ^3 -dihydropyran was passed over hot (270-320° and 320-370°) alumina, butadiene as the racemic 1,2,3,4-tetrabromobutane was isolated in yields varying from 39% to 65%. Carbon dioxide, which was collected in a saturated calcium hydroxide solution, was also detected. No Δ^2 -dihydropyran or formaldehyde were detected as either the 2,4-dinitrophenylhydrazone or as the dimedone derivative.

When Δ^3 -dihydropyran was passed over hot (320-370°) alumina in the presence of tetrahydrofurfuryl alcohol, and in the presence of Δ^2 -dihydropyran, butadiene as the racemic 1,2,3,4-tetrabromobutane was isolated in yields of 57% and 49% respectively. Carbon dioxide, and Δ^2 -dihydropyran as the 2,4-dinitrophenylhydrazone of delta-hydroxyvaleraldehyde, were also detected.

Other experiments established that no butadiene is formed when tetrahydrofurfuryl alcohol dehydrates to Δ^2 -dihydropyran and therefore renders highly unlikely the possibility that Δ^3 -dihydropyran is involved in the alumina transformation of tetrahydrofurfuryl alcohol to Δ^2 -dihydropyran or in the subsequent rearrangement of Δ^2 -dihydropyran.