by bumping and spattering during evaporation and drying. If evaporation is conducted too slowly the mixture may form a crust over the surface or form a dense mass in the bottom of the weighing bottle which is very difficult to dry. The mean values are probably valid, however, to about 10 g. per 1000 g. of water.

The density determinations are summarized in Table II. In all four cases the density appears to be a linear function of concentration, in the case of the α-acids up to saturation, in the case of the β- and γ-acids up to about 0.8 $M$, the highest concentration measured. The densities were plotted against molarity and the best straight line was drawn through the experimental points for each case. The densities were expressed from these graphs by the equations

α-Amino-isobutyric acid $d^{25} = 0.9971 + 0.0257\ M$
α-Amino-*n*-butyric acid $d^{25} = 0.9971 + 0.0273\ M$
β-Amino-*n*-butyric acid $d^{25} = 0.9971 + 0.0263\ M$
γ-Aminobutyric acid $d^{25} = 0.9971 + 0.0294\ M$

In the third column of the table are shown the deviations of the values calculated by the equations from the measured values.

## Summary

The solubilities in water at 25° of glycine, α-amino-isobutyric acid, α-amino-*n*-butyric acid, β-amino-*n*-butyric acid and γ-aminobutyric acid have been measured. The solubilities remained essentially constant when successive saturated solutions were formed from the same portions of solid samples.

The densities of aqueous solutions of the four amino butyric acids at 25° were measured. Densities appear to be linear with respect to molarities in each case.

PITTSBURGH, PENNA. RECEIVED JUNE 17, 1947

---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

# Reactions of Furan Compounds. VII. Thermal Interconversion of 2,3-Dihydrofuran and Cyclopropane Aldehyde[1]

BY CHRISTOPHER L. WILSON

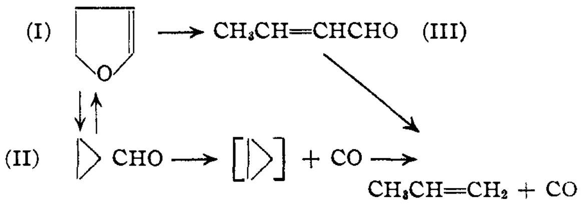
To explain the formation of cyclopropane aldehyde (II), in the pyrolytic decomposition of certain tetrahydrofuran compounds it was suggested in Part IV of this series[2] that the aldehyde resulted by rearrangement of 2,3-dihydrofuran (I). The rearrangement has now been established by experiments with pure 2,3-dihydrofuran made in quantity for the first time.

Cyclopropanealdehyde was just detectable after passing the dihydrofuran vapor through a tube filled with broken glass and heated to 375°. The contact time was 54 sec. The amount of aldehyde formed increased with temperature but the yield calculated on consumed dihydrofuran decreased and, instead, crotonaldehyde, carbon monoxide and propylene were formed. At 550° carbon monoxide and propylene constituted practically the entire product.

Contact materials of recognized catalytic activity had no appreciable accelerating influence on aldehyde formation. A nickel–copper catalyst, for example, gave no aldehyde at all but, instead, propane and carbon monoxide probably by ring fission first to *n*-butaldehyde. It is also possible that cyclopropanealdehyde and cyclopropane might have intervened. There was little, if any, reduction to tetrahydrofuran even when hydrogen was also admitted. An activated alumina which is effective in the rearrangement of ethylene oxides to aldehydes[3] caused complete destruction even at 200°. With aluminum silicate some cyclopropanealdehyde was obtained at 450° but the yield was lower than when only glass contact material was employed.

Using a glass filling for the reaction tube the effect of change of temperature on the formation of various products is given in the diagram. The increased formation of gases at the higher temperatures reduced the contact time which to some extent offset the effect of increased temperature.

The results are explained by supposing three consecutive reactions (I) → (II) → (III) → CO, $C_3H_6$. Attempts to establish this sequence further by experiments at 500° with (II) and (III) showed, however, that the true picture may not be so simple. Cyclopropanealdehyde (II) on heating gave a little 2,3-dihydrofuran in addition to crotonaldehyde, carbon monoxide and propylene, establishing the reversibility of the first step.



REACTION SCHEME AT 500°

Crotonaldehyde decomposed as expected into carbon monoxide and propylene. The ratio of these two gases by volume was 1.7:1 whereas from cyclopropane aldehyde the ratio was 1.1:1. It is not known why this ratio differs from unity

---

[1] This and the following paper were reported at the Atlantic City meeting of the American Chemical Society in April, 1947.

[2] Wilson, *J. Chem. Soc.*, 58 (1945).

[3] Ipatiev and Leontovitch, *Ber.*, **36**, 2017 (1903).

but it is surprising that the two values are not the same if the cyclic aldehyde decomposed first to crotonaldehyde. It is possible, therefore, that crotonaldehyde does not intervene in the further decomposition of cyclopropane aldehyde and that some other reaction such as decomposition into cyclopropane and carbon monoxide may take place. Cyclopropane is known[4] to rearrange fairly rapidly into propylene at 500° particularly in the presence of certain radicals or atoms. In the experiments at 450° there was evidence for the production of a small amount of a gaseous hydrocarbon which did not react with bromine solution. Cyclopropane is stated[5] to react only slowly at ordinary temperature and could scarcely have been affected during the time taken for propylene absorption.

When dihydrofuran was heated the ratio of carbon monoxide to propylene was 1.45:1 between the figures for crotonaldehyde (1.7:1) and cyclopropane aldehyde (1.1:1). This result suggests that dihydrofuran was converted directly into both cyclopropane aldehyde and crotonaldehyde in approximately equal amounts depending perhaps on the particular atomic motions at the instant of breaking the carbon–oxygen bond. It is unlikely that the cyclic aldehyde was converted appreciably into crotonaldehyde other than by first forming dihydrofuran. Although the gas ratios were quite reproducible, it is realized that the deductions made from them are tentative and might, with further experiment, be explicable in a very different manner.

Vinyl ethers appear to rearrange irreversibly into aldehydes[2] and the same is true of ethylene oxides. Dihydrofuran may be considered as representing both classes of compound and the equilibrium between it and cyclopropane aldehyde seems to be the first one to be recorded although a good example of the conversion of a five into a three ring is the rearrangement of phenyl cyclopropyl ketimine into 2-phenyl-$\Delta^2$-pyrroline.[6]

## Experimental

Tetrahydrofurfuryl alcohol was passed over an activated Ferry alloy catalyst as described in Part III[7] and the product, b. p. 52–61°, containing 2,3-dihydrofuran (24.5%) was fractionated using a vacuum-jacketed 14-plate column incorporating a monel gauze spiral packing[8] to give 2,3-dihydrofuran, b. p. 54.6° (761 mm.), with an odor like tetrahydrofuran.

*Anal.* Calcd. for $C_4H_6O$: C, 68.5; H, 8.6. Found: C, 68.3; H, 8.8; purity by precipitation as γ-hydroxybutaldehyde-2,4-dinitrophenylhydrazone, 99.7%.

**Pyrolysis Technique.**—Dihydrofuran (20 g./hour) was dripped steadily into the reaction chamber along with hydrogen or carbon dioxide as carrier gas (2 liters/hour). Liquid products were caught in a trap at −78°. Propylene was absorbed in a solution of bromine in acetic acid. When gas analyses were to be performed carbon dioxide, instead of hydrogen, was used as carrier gas and the gasholder contained sodium hydroxide solution (15%). After an experiment the trap was removed from its cooling bath and allowed to warm to room temperature to expel dissolved gases.

**Identification and Analysis of Products.**—The liquid products from dihydrofuran, which had a pungent odor due to the presence of crotonaldehyde, were shaken with saturated aqueous sodium bisulfite until all the aldehyde was extracted. The upper layer was dried over potassium hydroxide and a weighed sample precipitated with dinitrophenylhydrazine solution, the derivative collected, washed with water, dried and weighed thus giving the total amount of aldehydes (cyclopropane aldehyde and crotonaldehyde) present. The melting point of the mixture was referred to a curve constructed from the melting points of mixtures of the authentic derivatives of cyclopropanealdehyde and crotonaldehyde precipitated in the same way from bisulfite solution. This gave the proportion of each aldehyde present.

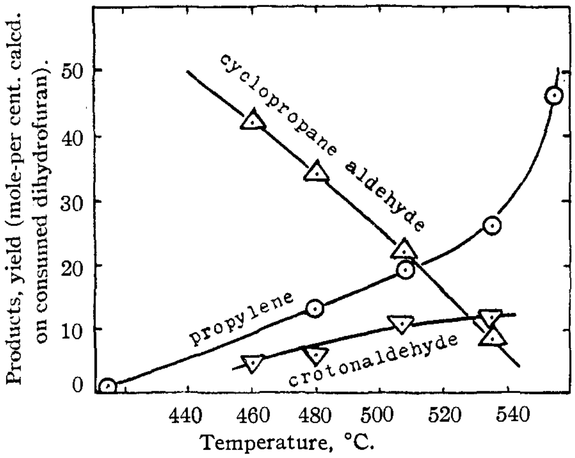


Fig. 1.—Pyrolysis of 2,3-dihydrofuran.

The reference melting point curve was constructed from the following figures. The amount (%) of the crotonaldehyde derivative is given in parentheses 178.5° (0), 173.4° (9.95), 166.0° (23.2), 160.5° (33.6), 148.2° (47.6), 156.0° (56.6), 161.7° (63.7) and 182° (100%). All melting points were uncorrected but were determined with the same thermometer in the same apparatus. The eutectic melted at 144° and contained 50.0% of each derivative.

Repeated crystallization from ethyl acetate–ethyl alcohol of the mixed dinitrophenylhydrazones obtained from an experiment with dihydrofuran at 500° gave the red crotonaldehyde derivative m. p. 184–185° identified by m. p., 189–191°, with an authentic specimen (m. p. 190–191°). The more soluble cyclopropane compound which separated from the mother liquor had m. p. 175°. The dinitrophenylhydrazone from pure cyclopropane aldehyde (see below) had m. p. 186–187.5°. That described in Part IV[1] contained 5% of the crotonaldehyde derivative.

Propylene was estimated as dibromide, b. p. 140–141°, obtained by neutralizing the contents of the bromine trap. A quantity of the crude bromides was distilled giving 80%, b. p. 140–141°; there was no indication of any 1,3-dibromide b. p. 161°.

Gas analyses were carried out using an Orsat apparatus, propylene being absorbed in a 50% aqueous acetic acid solution of bromine and carbon monoxide in a hydrochloric acid solution of cuprous chloride.

Using carbon dioxide as carrier gas the gaseous products consisted of carbon monoxide and propylene in the following ratio at various temperatures: 1.43 (455°), 1.45 (540°) and 1.45 (550°). At 455° the gases also contained

---

[4] Corner and Pease, THIS JOURNAL, **67**, 2067 (1945); Ogg and Priest, *J. Chem. Phys.*, **7**, 736 (1939).

[5] Kharasch, Fineman and Mayo, THIS JOURNAL, **61**, 2139 (1939).

[6] Murray and Cloke, *ibid.*, **68**, 126 (1946).

[7] Wilson, *J. Chem. Soc.*, 53 (1945).

[8] Bower and Cooke, *Ind. Eng. Chem.*, *Anal. Ed.*, **15**, 290 (1943).

about 9% by volume of a saturated gas which burnt with a luminous flame, this may have been cyclopropane. At 540° the amount was only 2.8%.

**Cyclopropanealdehyde.**—The bisulfite extract of the product from the pyrolysis of dihydrofuran at 480° was neutralized (phenolphthalein) with sodium hydroxide (33%). The upper layer was separated and the aqueous layer extracted seven times with ether. The extract was dried over anhydrous magnesium sulfate, the ether separated under a column and the residue distilled. The aldehyde, b. p. 99.3–99.5° (771 mm.), did not solidify at −78°.

*Anal.* Calcd. for $C_4H_6O$: C, 68.5; H, 8.6. Found: C, 68.4; H, 8.8.

The yield was 24% calculated on dihydrofuran consumed. Recovery of the aldehyde was 75% of that estimated in the bisulfite. The dinitrophenylhydrazone formed orange red prisms, m. p. 186–187.5°, after recrystallization from ethyl acetate.

**Pyrolysis of Cyclopropanealdehyde.**—The aldehyde (10 g.) was dripped into the furnace tube at 500° during thirty minutes together with carbon dioxide (2 liters/hour). An upper layer remained after the liquid product had been shaken with bisulfite. This was separated by evacuation through a cooled trap and proved to be 2,3-dihydrofuran (0.7 g.) identified as γ-hydroxybutaldehyde 2,4-dinitrophenylhydrazone. The aldehydes (4.8 g.) in the bisulfite consisted of 4% crotonaldehyde and the rest cyclopropanealdehyde. Gaseous products after removing carbon dioxide measured 700 cc. (770 mm., 20°) and consisted of carbon monoxide and propylene in a ratio 1.08:1.

**Pyrolysis of Crotonaldehyde.**—Redistilled crotonaldehyde (4.22 g.) was passed with 2 liter/hour of hydrogen into the glass furnace tube at 550°. Consumption was 86% and the yield of propylene 52%. Using carbon dioxide instead of hydrogen gave a $CO/C_3H_6$ ratio of 1.74 (500°) and 1.68 (550°), these gases accounting for 96% of the total gaseous product.

## Summary

1. 2,3-Dihydrofuran has been shown to rearrange on heating to above 375° reversibly to cyclopropane aldehyde.

2. Crotonaldehyde, propylene and carbon monoxide are also present in the reaction product and the formation of these is discussed.

NOTRE DAME, INDIANA RECEIVED JULY 9, 1947

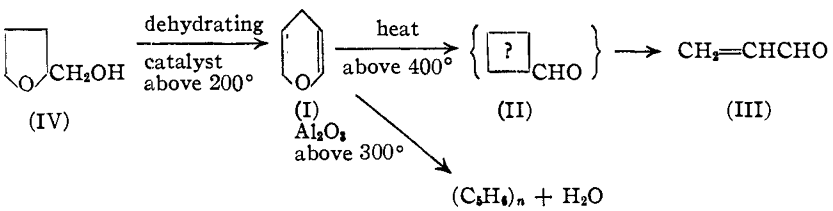
---

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

# Reactions of Furan Compounds. VIII. Dehydration of Tetrahydrofurfuryl Alcohol to 2,3-Dihydropyran and Subsequent Formation of Acrolein and Ethylene[1]

BY CHRISTOPHER L. WILSON

After 2,3-dihydrofuran had been shown to rearrange on heating into cyclopropane aldehyde,[2] it became of interest to study the behavior of the homolog, 2,3-dihydropyran (I) which by an analogous reaction should give cyclobutanealdehyde (II). Dihydropyran on heating above 400°, however, gave no cyclobutanealdehyde (II) but acrolein (III) and ethylene instead. Whilst it is still possible that cyclobutanealdehyde (II) intervened and proved to be very unstable, the process could proceed in other ways. For example, the fission is analogous to a reverse diene addition like the splitting of cyclohexene into butadiene and ethylene and there is no evidence that cyclobutane compounds intervene here.



It is surprising, in view of the fission reaction, that acrolein has not been detected before in the products of catalytic dehydration of tetrahydrofurfuryl alcohol (IV) to dihydropyran[3] when the temperature is 400° or higher. Kline and Turkevich[4] using a thoria catalyst at 550° referred to the formation of low-boiling material which "polymerized on standing and had a sharp odor" but they failed to identify acrolein. Paul's experience was similar.[5]

The reason for the anomaly has now become apparent. If the catalyst used for dehydrating tetrahydrofurfuryl alcohol to dihydropyran is too active, as is alumina, the dihydropyran molecule first produced is further dehydrated to hydrocarbon material (given as $(C_5H_6)_n$ in Table I) before it has a chance to split into acrolein and ethylene. It is possible using a less active catalyst to get high yields of acrolein in one step from tetrahydrofurfuryl alcohol. Such a catalyst has been found to be an alumina–silica combination in the mole ratio 1:2 employed at 450–500° at which temperature dihydropyran splits rapidly.

Data illustrating the behavior of alumina and alumina–silica are given in Tables I and II. The

---

[1] A preliminary announcement of this work has already been made (Wilson, *Nature*, **157**, 846 (1946)). Subsequently an independent publication appeared describing the thermal fission of dihydropyran (Bremner, Jones and Beaumont, *J. Chem. Soc.*, 1018 (1946)).

[2] Wilson, THIS JOURNAL, **69**, 3002 (1947).

[3] "Organic Syntheses," **23**, 25 (1943); Paul, *Compt. rend.*, **96**, 1409 (1933); *Bull. Soc. Chim.*, **53**, 1489 (1933).

[4] Kline and Turkevich, THIS JOURNAL, **67**, 498 (1945).

[5] R. Paul, private communication, *Bull. Soc. Chim.*, **14**, 167 (1947).