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## Abstract

## Full Text

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# THERMAL DEHYDROGENATION OF 2,5-DIHYDROFURANS

Five-membered heterocyclic compounds—tetrahydrofuran, pyrrolidine, and thiophane—exhibit a profound difference with respect to the reaction of their dehydrogenation into the corresponding unsaturated heterocycles. Of these three compounds, pyrrolidine and thiophane can be dehydrogenated, respectively, to pyrrole and thiophene on platinum in the vapor phase at 300–400° ($^1$). Under the same conditions, tetrahydrofuran is not capable of undergoing dehydrogenation to furan ($^2$). However, tetrahydrofuran itself and its various homologues, on a platinum catalyst in the vapor phase, undergo isomerization with ring opening at one of the C—O bonds to form aliphatic ketones or aldehydes, the latter being completely decarbonylated to paraffin hydrocarbons ($^3$). In contrast to tetrahydrofurans, dihydrofurans show the ability to undergo interesting transformations under thermal conditions.

Using the transformation of 2,3-dihydrofuran into cyclopropanecarboxaldehyde as an example, Wilson ($^4$) demonstrated the possibility of a very peculiar transition from a five-membered oxygen-containing heterocycle to carbonyl compounds of the cyclopropane series. Recently we found that 2-methyl-4,5-dihydrofuran under thermal conditions undergoes an isomerization of the same type, being converted into methyl cyclopropyl ketone ($^5$):

$$\text{2-methyl-4,5-dihydrofuran} \xrightarrow{470\text{–}480^\circ} \text{methyl cyclopropyl ketone}$$

Between the transformations of 2,3-dihydrofurans into cyclopropane carbonyl compounds and the rearrangement of simple vinyl ethers into aliphatic aldehydes there is an obvious analogy. In connection with these experimental results, there arose the question, not without theoretical significance, of the behavior under thermal conditions of the isomeric 2,5-dihydrofurans. We obtained 2-methyl-, 2-ethyl-, and 2-isopropyl-2,5-dihydrofurans and investigated their transformations under the same conditions under which 2-methyl-4,5-dihydrofuran isomerizes to methyl cyclopropyl ketone, i.e., upon passing the vapors of these compounds over broken quartz or activated carbon at 470–480°. It turned out that under these conditions 2-alkyl-2,5-dihydrofurans dehydrogenate very smoothly to the corresponding furan homologues:

$$\text{2-alkyl-2,5-dihydrofuran} \longrightarrow \text{2-alkylfuran} + \mathrm{H_2}, \qquad R = \mathrm{CH_3},\ \mathrm{C_2H_5},\ \text{iso-}\mathrm{C_3H_7}.$$

This reaction proceeds with approximately equal ease both over quartz and over activated carbon (over quartz the degree of conversion is somewhat lower), and this leads to the conclusion that dehydrogenation of 2,5-dihydrofurans to the corresponding furans is not a catalytic reaction, but proceeds—

occurs only under the influence of temperature, which must be comparatively high. A temperature of 350° is still insufficient for the dehydrogenation of 2,5-dihydrofurans to furans.

The tetrahydrofuran ring at 470–480° undergoes no changes either over quartz or over charcoal. This fact indicates that formation of the second double (conjugated) bond takes place more readily than formation of the first (isolated) double bond—a phenomenon that is also observed in other cases.

One more circumstance should be noted: for formation of the furan nucleus, migration of the double bond from the 3,4-position to the 2,3- or 4,5-position is necessary. But such systems should isomerize to cyclopropane carbonyl compounds. Since this is not observed, it may be assumed that migration of the 3,4-double bond and elimination of two hydrogen atoms occur simultaneously, without intermediate formation of 2,3-dihydrofuran. Thus, investigation of the thermal transformations of 2,5-dihydrofurans leads to the following result: in contrast to 2,3-dihydrofurans, which isomerize to aldehydes or ketones of the cyclopropane series, 2,5-dihydrofurans undergo dehydrogenation to the corresponding furan compounds.

## Experimental Part

2,5-Dihydrofurans containing methyl, ethyl, and isopropyl groups in the $\alpha$-position were synthesized according to the scheme:

[structural scheme: furan-ring derivatives]

Addition of 2-alkyl-3-chlorotetrahydrofurans to caustic potash heated to 180–200°, with immediate distillation of the resulting product, gives only 2,5-dihydrofurans in yields up to 80%. The 2,5-dihydrofurans obtained had the following properties:

1) 2-methyl-2,5-dihydrofuran, b.p. 77–78° (750 mm); $n_D^{20}$ 1.4214; $d_4^{20}$ 0.8826;
2) 2-ethyl-2,5-dihydrofuran, b.p. 103.9–104.5° (750 mm); $n_D^{20}$ 1.4314; $d_4^{20}$ 0.8877;
3) 2-isopropyl-2,5-dihydrofuran, b.p. 122.7–122.9° (750 mm); $n_D^{20}$ 1.4345; $d_4^{20}$ 0.8793.

Vapors of the 2,5-dihydrofurans, together with nitrogen, were passed through a layer of broken quartz or activated birch charcoal heated to 470–480°. The liquid catalyzates, obtained in practically theoretical amount, were fractionated on a column. The yields of $\alpha$-alkylfurans were 90–95%. As a result of thermal dehydrogenation, the following were obtained in pure form:

1) $\alpha$-methylfuran, b.p. 62.5–64° (757 mm); $n_D^{20}$ 1.4320; $d_4^{20}$ 0.9118;

2) $\alpha$-ethylfuran, b.p. 91-91.5° (757 mm); $n_D^{20}$ 1.4404; $d_4^{20}$ 0.9018;

3) $\alpha$-isopropylfuran, b.p. 107.4–108.4° (745 mm); $n_D^{20}$ 1.4445; $d_4^{20}$ 0.8974.

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*Note: Figure translations are in progress. See original paper for figures.*

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