# CHEMISTRY

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1962

SovietRxiv

## Abstract

## Full Text

*CHEMISTRY*

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# CATALYTIC DEHYDROGENATION OF DIHYDROFURANS

## SYNTHESIS OF 2,4-DIALKYLFURANS

Our studies have established that dihydro- and tetrahydrofuran rings are capable of undergoing dehydrogenation in the vapor phase over catalysts—metals of Group VIII of the periodic system ([1],[2]). This reaction is less characteristic of the tetrahydrofuran ring, since the latter reacts to a considerably greater extent as a cyclic ether, i.e., isomerizes with cleavage of one of the C—O bonds to aliphatic oxo compounds ([3]). 2,3- and 2,5-dihydrofurans are readily dehydrogenated to the corresponding furans over metallic catalysts (Pt, Pd, Rh, etc.) at relatively low temperatures of the order of 200-300° (reaction 1). Side reactions occur at the same time. The hydrogen evolved hydrogenates dihydrofurans to tetrahydrofurans (reaction 2) or brings about hydrogenolysis of the furans formed (reaction 3). On the other hand, tetrahydrofurans isomerize, especially readily on platinum, to aliphatic ketones (reaction 4). All these transformations are explained by the following scheme:

$$\text{dihydrofuran-}R \longrightarrow \text{furan-}R + H_2 \tag{1}$$

$$\text{dihydrofuran-}R + H_2 \longrightarrow \text{tetrahydrofuran-}R \tag{2}$$

$$\text{furan-}R + H_2 \longrightarrow \text{C—C—C—C(= O)—R} \tag{3}$$

$$\text{tetrahydrofuran-}R \xrightarrow{\text{isomerization}} \text{C—C—C—C(= O)—R} \tag{4}$$

As a consequence of these side reactions, the catalytic dehydrogenation of 2,3- and 2,5-dihydrofurans gives furans in an average yield of 50%. However, in the case of 3,5-dihydrofurans it is possible to carry out dehydrogenation in the presence of such inert contacts as charcoal or quartz at 470-500°. Under these conditions side reactions 2-4, since they are catalytic, do not occur, and therefore the yields of furans reach 95% ([4]). By this route, however, it is impossible to dehydrogenate 2,3-dihydrofurans, since under the action of temperature (470–500°) they isomerize to carbonyl compounds of the cyclopropane series ([5]).

In the present work, the synthesis of 2,4-dialkylfurans was carried out by catalytic dehydrogenation of the corresponding homologs of 2,3-dihydrofuran. To obtain the latter, a modified method was used for the synthesis of tetrahydrofuran homologs from 1-furylalkanols-3 ([6]). The hydrogenolysis was applied not to the furan alcohols themselves, but to their acetates (I), which made it possible

**Table 1**

**Products of the transformations of dihydrofurans on Pt–C at 300°**

| Starting substance | Catalyst composition | Yield, % | B.p., °C/mm | $n_D^{20}$ | $d_4^{20}$ | M.p. of semicarbazone, °C | $MR_D$, found | $MR_D$, calculated | Found, %, C | Found, %, H | Calculated, %, C | Calculated, %, H |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| [[structural formula: dihydrofuran ring bearing a propyl substituent]] | Heptan-4-one | 38–40 | 142–143/740 | 1.4085 | 0.8180 | 131–132 | 34.47 | 34.53 | – | – | – | – |

| Starting substance | Catalyst composition | Yield, % | B.p., °C/mm | $n_D^{20}$ | $d_4^{20}$ | M.p. of semicarbazone, °C | $MR_D$, found | $MR_D$, calculated | Found, %, C | Found, %, H | Calculated, %, C | Calculated, %, H |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| [[structural formula: dihydrofuran ring bearing a propyl substituent]] | [[structural formula: furan ring bearing a propyl substituent]] | 50 | 114–114.5/740 | 1.4400 | 0.8880 | — | 32.69 | 33.03 | — | — | — | — |
| [[structural formula: 4-methyl-substituted dihydrofuran ring bearing a propyl substituent]] | 2-Methylheptan-4-one | 36–38 | 154–156/754 | 1.4108 | 0.8125 | 123–124 | 39.16 | 39.15 | — | — | — | — |

| Starting substance | Catalyst composition | Yield, % | B.p., °C/mm | $n_D^{20}$ | $d_4^{20}$ | M.p. of semicarbazone, °C | $MR_D$, found | $MR_D$, calculated | Found, %, C | Found, %, H | Calculated, %, C | Calculated, %, H |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| [[structural formula: methyl-substituted dihydrofuran ring bearing a propyl substituent]] | [[structural formula: methyl-substituted furan ring bearing a propyl substituent]] | 50 | 142–144/754 | 1.4435 | 0.8832 | – | 37.31 | 37.65 | 77.20 | 9.88 | 77.37 | 9.74 |
| [[structural formula: methyl-substituted dihydrofuran ring bearing a propyl substituent]] | 3-Methyloctan-5-one | 36–38 | 60–62/11 | 1.4212 | 0.8236 | 61–62 | 43.81 | 43.77 | – | – | – | – |

| Starting substance | Catalyst composition | Yield, % | B.p., °C/mm | $n_D^{20}$ | $d_4^{20}$ | M.p. of semicarbazone, °C | $MR_D$, found | $MR_D$, calculated | Found, %, C | Found, %, H | Calculated, %, C | Calculated, %, H |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| [[structural formula: methyl-substituted dihydrofuran ring bearing a propyl substituent]] | [[structural formula: ethyl- and propyl-substituted furan ring]] | 50 | 48.5–49.5/11 | 1.4461 | 0.8776 | — | 42.00 | 42.27 | 78.12 | 10.30 | 78.21 | 10.21 |

to obtain acetates of $\gamma$-keto alcohols (II), and from them the corresponding keto alcohols (III) and dihydrofurans (IV).

$$(I) \xrightarrow[220^\circ]{H_2,\ Pt-C} (II)$$

$$\xrightarrow[H^+]{CH_3OH} (III) \xrightarrow{-H_2O} (IV) \xrightarrow[300^\circ]{Pt-C,\ -H_2} (V)$$

$$R = H,\ CH_3,\ C_2H_5$$

Dehydrogenation of the dihydrofurans (IV) to the corresponding furans (V) was carried out over platinized charcoal at 300°. The 2,4-dialkylfurans were obtained in 50% yield. As a result of side reactions (2) and (4), aliphatic ketones (35-40%) and paraffin hydrocarbons were formed (Table 1).

## Experimental Part

**2,3-Dihydrofurans** were obtained according to the following scheme:

$$\text{furfural} + \text{aldehyde} \longrightarrow \alpha\text{-alkyl-}\beta\text{-furylacrolein} \xrightarrow[130^\circ]{H_2,\ Cu-Al} \text{furyl alcohol}$$

$$\xrightarrow{Ac_2O} \text{acetate} \xrightarrow[220^\circ]{H_2,\ Pt-C} \gamma\text{-keto acetate} \xrightarrow[H^+]{CH_3OH} \text{2,3-dihydrofuran}$$

The condensation of furfural with aldehydes, the hydrogenation of $\alpha$-alkyl-$\beta$-furylacroleins to furan alcohols, and the acetylation of the latter have been described in ([7] [9]).

The properties of the obtained homologs of 2,3-dihydrofuran are given in Table 2.

**Table 2**

**Properties of 2,3-dihydrofurans**

| Dihydrofurans | B.p., °C/mm | $n_D^{20}$ | $d_4^{20}$ | $MR_D$, found | $MR_D$, calculated |
|---|---|---|---|---|---|
| 2-propyl-2,3-dihydrofuran | 129–131/741 | 1.4345 | 0.8791 | 33.26 | 33.50 |
| 2-propyl-4-methyl-2,3-dihydrofuran | 150–152/756 | 1.4380 | 0.8734 | 37.91 | 38.12 |
| 2-propyl-4-ethyl-2,3-dihydrofuran | 61–62/1178–80/22 | 1.4401 | 0.8713 | 42.42 | 42.73 |

**Catalyst**—platinized charcoal (10% Pt) was prepared by impregnating activated birch charcoal with a solution of chloroplatinic acid, which was then reduced with formalin in the presence of caustic alkali.

The starting dihydrofurans were passed over the catalyst at a space velocity of 0.1 $h^{-1}$. The liquid catalyzates, obtained in yields of more than 95%, were distilled on a column. The results of the experiments are presented in Table 1.

Thus, it has been established that by catalytic dehydrogenation in the vapor phase over Pt–C at 300° from homologs of 2,3-dihydrofuran, 2,4-dialkylfurans are obtained in 50% yield.

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Received
10 VII 1962

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