REACTION OF VINYL ETHERS WITH FURAN AND
WITH 2-METHYLFURAN

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Translated from Izvestiya Akademii Nauk SSSR, No. 12, pp. 2224-2226, December, 1962
Original article submitted April 18, 1962

We have previously reported [1] the ability of vinyl ethers to undergo diene condensation with some acyclic, cyclic, and polycyclic dienes. It was of interest to study the diene condensation of vinyl ethers with heterocyclic dienes, in particular furan and its homologs. There is a reference in the literature [2] to the reaction of furan, as a diene, with maleic anhydride with formation of 7-oxabicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride. In subsequent investigations it was shown that furan derivatives having electron-donating substituents in the ring are more active as dienes than furan itself. As well as diene condensation, in some cases "substitutive addition" [3] occurs in the α-position of the furan ring. Later, Alder and Schmidt [4] showed that in presence of acid catalysts furan and its homologs take part in substitutive addition with 2-methyl vinyl ketone, phenyl vinyl ketone, and crotonaldehyde. Naazarov and Nagibina [5] carried out the substitutive-addition reaction of 2-methylpropenyl vinyl ketone with furan and with 2-methylfuran. Yur'ev and co-workers [6, 7] extended this reaction and showed that substitutive addition to a,β-unsaturated ketones and aldehydes has a general character and can serve as a convenient method of synthesizing ketones of the furan series.

The object of the present work was the study of the conditions under which vinyl ethers react with furan and with 2-methylfuran and the elucidation of the character of this reaction both under the conditions of the diene synthesis, and under the conditions of substitutive-addition reactions with furans. Diene-synthesis experiments were carried out with furan, 2-methylfuran, and 2-ethyl-5-methylfuran, using butyl vinyl, phenyl vinyl, and divinyl ethers in the temperature range 100-280° with reaction times of 10-22 hours. However, in all cases we did not succeed in isolating the condensation product, and the starting materials were recovered unchanged. The substitutive-addition reaction was carried out with furan and 2-methylfuran, on the one hand, and butyl vinyl and phenyl vinyl ethers, on the other, in presence of sulfuric acid, hydrochloric acid, aluminum chloride, boron trifluoride etherate, or a butyl alcohol solution of ferric chloride (see table). On analogy with the reaction between 2-methylfuran and a,β-unsaturated ketones and aldehydes, it may be expected that in our case reaction will proceed as follows:

\[ \text{CH}_2=\text{CH} - \text{OR} \xrightarrow{\text{H}_2\text{SO}_4} \left( \begin{array}{c} \text{CH}_3 - \text{CH} - \text{OR} \\ \text{RO} \end{array} \right) \]

in which \( R = \text{C}_4\text{H}_9 \) and \( \text{C}_6\text{H}_5 \).

However, we did not succeed in isolating the 2-(1-alkoxyethyl)- or 2-(1-aryloxyethyl)-5-methylfuran (I). Instead, we obtained 2,2'-ethylidenebis(5-methylfuran) (II), the formation of which could occur by the replacement of the butoxy or phenoxy group of (I) by a methylfuryl group:

\[ \text{CH}_3 - \text{CH} - \text{OR} \xrightarrow{\text{H}_2\text{SO}_4} \left( \begin{array}{c} \text{CH}_3 - \text{CH} - \text{CH}_2 \\ \text{CH}_3 \end{array} + \text{ROH} \right) \]
which indicates the instability of (I) under the conditions of reaction. Confirmation of this course of reaction is provided by the fact that in the reaction of 2-methylfuran with butyl vinyl ether we isolated butyl alcohol and acetaldehyde dibutyl acetal, formed by reaction of the original butyl vinyl ether with butyl alcohol. Study of the conditions for substitutive addition with 2-methylfuran showed that reaction with phenyl vinyl ether requires more severe conditions than reaction with butyl vinyl ether, which is in accord with the behavior of this ether in other reactions proceeding by the ionic mechanism.

Substitutive-addition Reaction between Butyl Vinyl Ether and 2-Methylfuran

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Amount of catalyst for 0.1 mole of butyl vinyl ether (ml)</th>
<th>Reaction time (h)</th>
<th>Reaction temp. (°C)</th>
<th>Yield of 2,2'-ethylidenebis(5-methylfuran) (II) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>96% H₂SO₄</td>
<td>0.1</td>
<td>3.5</td>
<td>5-7</td>
<td>46.8</td>
</tr>
<tr>
<td>35% HCl</td>
<td>0.5</td>
<td>2.5</td>
<td>25-30</td>
<td>58.3</td>
</tr>
<tr>
<td>60% BF₃(C₂H₅)OH</td>
<td>0.1</td>
<td>2</td>
<td>5-7</td>
<td>18.2</td>
</tr>
<tr>
<td>FeCl₃(C₄H₅OH)</td>
<td>0.2</td>
<td>1.3</td>
<td></td>
<td>12</td>
</tr>
<tr>
<td>AlCl₃</td>
<td>0.5 g</td>
<td>2.5</td>
<td></td>
<td>26.1</td>
</tr>
</tbody>
</table>

**EXPERIMENTAL**

**Reaction of Butyl Vinyl Ether with 2-Methylfuran in Presence of HCl.** A three-necked flask fitted with stirrer, thermometer, reflux condenser, and dropping funnel was charged with 24.6 g of dry 2-methylfuran and 0.5 ml of concentrated hydrochloric acid. 10 g of dry butyl vinyl ether was added dropwise to the mixture at 25-30° over a period of 90 minutes, after which the mixture was stirred further at this temperature for one hour. The mixture was then diluted with 40 ml of ether, washed with sodium bicarbonate solution and with water, dried over magnesium sulfate, and fractionated. After the removal of ether we isolated the following fractions: I (3.5 g), b.p. 63-75°; II (5.7 g), b.p. 75-125°; III (2.8 g), b.p. 70-100° (15 mm); IV (11 g), b.p. 105-117° (15 mm); residue (1.5 g). From Fraction II we isolated butyl alcohol, b.p. 118-119° (760.5 mm) and nᵣ 1.3988; from Fraction III we isolated acetaldehyde dibutyl acetal, b.p. 73.5-74° (12 mm), nᵣ 1.4083; dᵣ 0.8304 (the literature [8] gives: b.p. 184-185°; nᵣ 1.4991; dᵣ 1.0282. Found: C 75.62; 75.85; H 7.46; 7.40%. Cl₈H₄O₂. Calculated: C 75.78; H 7.36%. The literature [9] gives: b.p. 113° (12 mm); nᵣ 1.4993; dᵣ 1.027.

**Reaction of Butyl Vinyl Ether with Furan in Presence of HCl.** In the reaction of 20.4 g of furan with 10 g of butyl vinyl ether in presence of 0.5 ml of concentrated hydrochloric acid under similar conditions we isolated 4.5 g (27.7%) of 2,2'-ethylidenedifuran; b.p. 83-84° (12 mm); nᵣ 1.4986; dᵣ 1.0695. The literature [9] gives: b.p. 86-87° (15 mm); nᵣ 1.4993; dᵣ 1.073.

**Reaction of Phenyl Vinyl Ether with 2-Methylfuran in Presence of HCl.** A mixture of 36.9 g of 2-methylfuran, 18 g of phenyl vinyl ether, and 0.5 ml of concentrated hydrochloric acid was heated at 90° in a rotating autoclave for four hours. After treatment as described above, fractionation gave 7 g of a fraction of b.p. 107-115° (13 mm), which after redistillation was found to be 2,2'-ethylidenebis(5-methylfuran) (II); b.p. 109° (12 mm); nᵣ 1.4991; dᵣ 1.0285; yield 24.1%.

**SUMMARY**

1. The reaction of vinyl ethers with furan and with 2-methylfuran was studied under conditions under which vinyl ethers undergo diene condensation and also in presence of acid catalysts.

2. Under diene-synthesis conditions vinyl ethers do not react with furan and with 2-methylfuran, but in presence of acid catalysts substitutive addition occurs, leading to the addition of two molecules of 2-methylfuran or furan to the vinyl ether molecule and formation of 2,2'-ethylidenebis(5-methylfuran) and 2,2'-ethylidenedifuran.

**LITERATURE CITED**