THERMAL ALKYLLATION OF TETRAHYDRO-2-METHYL-
FURAN WITH ETHYLENE

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Translated from Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk,
No. 12, pp. 2195-2198, December, 1961
Original article submitted June 16, 1961

We recently showed that tetrahydrofuran can be thermally alkylated with ethylene [1]. It was of interest in this
connection to determine the effect of the presence of a methyl group at the position at which ethylene enters the
tetrahydrofuran ring. With this object we investigated the reaction between tetrahydro-2-methylfuran and ethylene
under various conditions (variation of temperature, reaction time, and proportions of reactants). We showed that in
the reaction of tetrahydro-2-methylfuran with ethylene in the range 325-375° two main reactions were observed: the
alkylation and the isomerization of the tetrahydro-2-methylfuran. It was found that ethylene attacks the tetrahydro-
furan ring in the 5-position. Earlier, one of us in collaboration with Bel'skii [2] discovered the isomerization of the
tetrahydrofuran ring at 250° over platinized charcoal with formation of aliphatic ketones. In the present work we
showed that similar isomerization of tetrahydro-2-methylfuran occurs at 325-375° in absence of catalysts. The alkyla-
tion of tetrahydro-2-methylfuran was carried out by the procedure that we described previously [1]. In all experiments
we took 0.75 mole of tetrahydro-2-methylfuran for reaction. The reaction products were analyzed by the methods of
gas-liquid chromatography and infrared spectroscopy [3, 4]. Fractionation of the products of the alkylation of tetra-
hydro-2-methylfuran with ethylene through a column of 40-plate efficiency gave ethyltetrahydromethylfuran of
b.p. 117.5-118°; n₂₀ 1.4168; d₀⁴ 0.8440. Measurements of the intensities of the absorption bands of the C–H valence
vibrations of the CH₃ and CH₂ groups (at 2965 and 2926 cm⁻¹) showed that the substance isolated had two CH₃ groups
and three CH₂ groups and was indeed ethyltetrahydromethylfuran. Found: C 73.33; 73.20; H 12.43; 12.44%. C₁₇H₁₄O. Cal-
culated: C 73.62; H 12.36%.

On investigation of the composition of the alkylation products in the combined catalyze from all experi-
ments were found 2-pentanone; b.p. 99-100°; n₂₀ 1.3910; d₀⁴ 0.8130. A special experiment showed that at 350° in

Effect of Pressure on the Rate and Course of the Reaction at 350°

| Duration of expt. (min) | Pressure (atm) | Amt of catalyze (g) | Amt. of tetrahydro-
methylfuran that acts | Yield of 2-
pentanone | Yield of ethyltetra-
hydromethylfuran | Yield of polyalkyl product |
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<tbody>
<tr>
<td></td>
<td>ethyl–nitro-</td>
<td></td>
<td>% in catalyzate</td>
<td>% of theor.</td>
<td>% in catalyzate</td>
<td>% on amt.</td>
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<tr>
<td></td>
<td>ene</td>
<td></td>
<td>% in catalyzate</td>
<td>% of theor.</td>
<td>% in catalyzate</td>
<td>% on amt.</td>
</tr>
<tr>
<td>90</td>
<td>50</td>
<td>69.9</td>
<td>17.8</td>
<td>16.5</td>
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<td>3.7</td>
</tr>
<tr>
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<td>40</td>
<td>63.4</td>
<td>17.4</td>
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<tr>
<td>90</td>
<td>60</td>
<td>62.4</td>
<td>83</td>
<td>85.9</td>
<td>13.6</td>
<td>14.1</td>
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presence of nitrogen at 50 atm the isomerization of tetrahydro-2-methylfuran into 2-pentanone did indeed occur
(table). This is confirmed by spectroscopic analysis. The spectrum of the fraction of b.p. 98-104° was determined
in the range 1600-1800 cm⁻¹. It contained C=O absorption bands at 1715 cm⁻¹ (strong) and 1735 cm⁻¹ (weak). The
first is due to the $C=O$ valence vibrations in a ketone group, and the second to these vibrations in an aldehyde group [5]. Comparison of the 2-pentanone isolated with the standard by chromatographic analysis gave satisfactory results.

The establishment of the fact of the thermal isomerization of tetrahydro-2-methylfuran into 2-pentanone under our conditions considerably facilitates the resolution of the question of the possible place of the introduction of the ethylene into the tetrahydromethylfuran molecule. It would appear that the alkylation of the CH$_3$ group and of the tetrahydrofuran ring in the 2-position cannot occur, for the 2-ethyltetrahydro-2-methylfuran which would then be formed has two CH$_3$ and four CH$_2$ groups, and tetrahydropentylfuran has one CH$_3$ and five CH$_2$ groups, which is not in accord with the results obtained.

There is no information in the literature on the physical properties of 3-ethyltetrahydro-2-methylfuran and 4-ethyltetrahydro-2-methylfuran, but it is known that the ketones and aldehydes formed by their isomerization have b.p. about 140°. The isomerization of 2-ethyltetrahydro-5-methylfuran gives 2- and 3-heptanones, b.p. 147-150°. By fractionation through a column, from the combined catalyzate we isolated a ketone of b.p. 147.5-149°, $n D^20$ 1.4143; and $d^20$ 0.8205, with a semicarbazone of m.p. 104.5-105.5°, which corresponds to the melting point of the semicarbazone of 3-heptanone.

Hence, at 325-375° and 10-50 atm of ethylene, the tetrahydromethylfuran ring is alkylated in the 5-position with formation of 2-ethyltetrahydro-5-methylfuran. This probably indicates the enhanced reactivity of the $\alpha$-hydrogen atoms. In the isomerization of tetrahydro-2-methylfuran ring opening occurs at the C-O bond most remote from the methyl group, whereas the isomerization of the 2-ethyltetrahydro-5-methylfuran formed occurs with ring opening mainly at the C-O bond adjacent to the methyl group.

We studied the effect of temperature, reaction time, and proportions of reactants on the conversion of tetrahydro-2-methylfuran, its isomerization, and the yield of alkylation products.

Figure 1 shows the results of investigations to determine the effect of temperature at a reaction time of 90 minutes and an ethylene pressure of 50 atm. With rise in temperature the amount of unchanged tetrahydro-2-methyl-