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Abstract

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ALKYLATION OF TETRAHYDROFURAN WITH ETHYLENE

The attention of many investigators is currently attracted to the problem of the alkylation of alkanes. After the possibility of alkylating paraffin hydrocarbons had been established, it was natural to expect that an analogous reaction could be carried out with saturated cyclic compounds. The alkylation of cyclanes has been little studied. The alkylation reaction of saturated oxygen-containing rings has not been investigated at all. An approximate calculation carried out by us showed that this reaction is thermodynamically possible.

In the present article, the possibility of alkylating tetrahydrofuran with ethylene at elevated temperatures and pressures is shown for the first time. The influence of temperature, duration of the experiment, and component ratio on the direction of the reaction and the yield of α-ethyltetrahydrofuran was also studied.

Experimental Part

The alkylation was carried out in a rotating autoclave of 250 ml capacity. Into it were charged 0.75 g-mole of tetrahydrofuran; the air was then displaced with ethylene, the necessary pressure was established, and heating was switched on. Upon completion of the experiment, the autoclave was cooled, the excess pressure was released, and the obtained catalyzate was dried over potash. The catalyzate was distilled from a Favorskii flask into three fractions: I—up to 64°; II—64-70°; III—70-120°, and a residue boiling above 120°. The separated fractions were analyzed by the method of gas-liquid chromatography (^{1}) on a 2-meter column packed with diatomite impregnated with tricresyl phosphate. Hydrogen, passed through the column at a rate of 40 ml/hr, was used as the carrier gas. At the same time, the structure of alkyltetrahydrofurans was determined from the number of CH_2 and CH_3 groups by infrared spectroscopy (^{2}). The spectra of the narrow fractions were recorded on a UR-10 instrument in a CCl_4 solution, with an LiF prism, in the region 2800-3100 cm^{-1}, at a concentration of 0.1-0.03 g-mole/l. The thickness of the absorbing layer was 0.25 mm. The cell of constant volume was 1 ml. The intensities of the bands corresponding to the asymmetric stretching vibrations of the CH_2 and CH_3 groups were measured.

We also determined the elemental composition of the alkyltetrahydrofurans.

Into the autoclave were placed 2 g-moles of tetrahydrofuran, and alkylation was carried out at 325° and an initial ethylene pressure of 25 atm. for one hour; after ethylene had been pumped in, the autoclave was heated at the same temperature for one more hour. Distillation of the catalyzate on an efficient column gave an individual substance with b.p. 105-106° at 751 mm Hg, n_D^{20} 1.4151 and d_4^{20} 0.8542.

Measurement of the intensities of the bands at 2937 and 2967 cm^{-1} showed that this compound contains one CH_3 and four CH_2 groups, which corresponds to the structure of ethyltetrahydrofuran.*

* The authors express their gratitude to B. V. Lopatin for recording the spectra.

The elemental composition of the substance obtained agrees with that theoretically calculated for ethyltetrahydrofuran.

Found, %: C 72.30; 72.34; H 12.17; 12.23
$C_6H_{12}O$. Calculated, %: C 71.94; H 12.08

The literature data for α-ethyltetrahydrofuran: b.p. 105-106°, n_D^{20} 1.4165; d_4^{20} 0.8553 (^{3}), and for β-ethyltetrahydrofuran: b.p. 115.5-116.5°, n_D^{20} 1.4204; d_4^{20} 0.8601 (^{4})—indicate that, under the conditions described, alkylation of tetrahydrofuran proceeds in the α-position. In chromatographic analysis, the peaks of the ethyltetrahydrofuran obtained and of the reference α-ethyltetrahydrofuran coincided.

Apparently, the reaction of thermal alkylation of tetrahydrofuran proceeds by a mechanism analogous to that for the reaction of thermal alkylation of alkanes (^{5}):

$$\mathrm{THF} \rightleftharpoons \mathrm{THF}^{\bullet} + \mathrm{H}^{\bullet}$$

$$\mathrm{THF}^{\bullet} + \mathrm{CH_2{=}CH_2} \rightleftharpoons \mathrm{THF\text{-}CH_2\text{-}\dot{C}H_2}$$

$$\mathrm{THF\text{-}CH_2\text{-}\dot{C}H_2} + \mathrm{THF} \rightleftharpoons \mathrm{THF\text{-}CH_2\text{-}CH_3} + \mathrm{THF}^{\bullet}$$

In the present work the results are given of a study of the effect of temperature, duration of the experiment, and ratio of the components on the degree of conversion of tetrahydrofuran, and on the yields of α-ethyltetrahydrofuran and polyalkylate*.

Fig. 1. Effect of temperature (A) and duration of the experiment (B) on the degree of conversion of tetrahydrofuran (a), and on the yield of α-ethyltetrahydrofuran (b) and polyalkylate (c). For A: 1—duration of experiment 45 min, 2—90 min, 3—200 min. For B: 1—temperature 325°, 2—350°, 3—375°

Fig. 1. Effect of temperature (**A**) and duration of the experiment (**B**) on the degree of conversion of tetrahydrofuran (*a*), and on the yield of α-ethyltetrahydrofuran (*b*) and polyalkylate (*c*). For **A**: 1—duration of experiment 45 min, 2—90 min, 3—200 min. For **B**: 1—temperature 325°, 2—350°, 3—375°.

For this purpose, three series of experiments on alkylation were carried out—alkylation of tetrahydrofuran for durations of 45, 90, and 200 min. Preliminary experiments established that below 300° the alkylation reaction practically does not proceed, while at temperatures above 400° side processes proceed at a high rate. Therefore each series of experiments was carried out at temperatures of 325, 350, and 375°.

Figure 1A presents the curves obtained in studying the dependence of the degree of conversion of tetrahydrofuran and the yields of α-ethyltetrahydrofuran and polyalkylate on temperature. In studying the influence of the duration of the experiment on the degree of conversion of tetrahydrofuran and the yields of α-ethyltetrahydrofuran and polyalkylate, the curves shown in Fig. 1B were obtained.

Analysis of Fig. 1 shows that the optimum conditions for the alkylation of tetrahydrofuran are a temperature of 350° and an experiment duration of 90 min. With increasing temperature, the degree of conversion of tetrahydrofuran rises sharply as a result of considerable formation of low-boiling products due to side reactions.

Table 1

Influence of the tetrahydrofuran : ethylene ratio on the composition of the catalyzate

Experiment No.	Ethylene pressure, atm	Degree of conversion of tetrahydrofuran, g	Degree of conversion of tetrahydrofuran, % of amount taken	Degree of conversion of tetrahydrofuran, % on catalyzate	Yield of α-ethyltetrahydrofuran, g	Yield of α-ethyltetrahydrofuran, % of starting material	Yield of α-ethyltetrahydrofuran, % of reacted material	Yield of α-ethyltetrahydrofuran, % on catalyzate	Yield of polyalkylate, g	Yield of polyalkylate, % on catalyzate	Weight of catalyzate, g
1	50	10.4	19.2	19	3	4	20.8	5.5	7.1	13	54.6
2	10*	3.9	7.2	7.4	0.6	0.8	11.1	1.1	1.7	3.4	52.4

* Plus 40 atm nitrogen.

* By polyalkylate we conventionally mean the residue boiling higher than α-ethyltetrahydrofuran.

The influence of the ratio of the components tetrahydrofuran : ethylene on the degree of conversion of tetrahydrofuran and the yields of α-ethyltetrahydrofuran and polyalkylate was studied with 0.75 g-mole of tetrahydrofuran at 350° and an experiment duration of 90 min. As can be seen from Table 1, an increase in ethylene pressure leads to a substantial increase in the yields both of α-ethyltetrahydrofuran and of products of deeper alkylation.

The results of our work have demonstrated the possibility of thermal alkylation of saturated oxygen-containing cyclic compounds.

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1. N. I. Shuikin, V. V. An, B. L. Lebedev, *Zav. lab.*, No. 6, (1961).
2. N. I. Shuikin, B. V. Lopatin, B. L. Lebedev, *ZhAKh*, **16** (1961)—in press.
3. Yu. K. Yur' ev, I. P. Tragerov, *ZhOKh*, **19**, 724 (1949).
4. Yu. K. Yur' ev, I. P. Tragerov, *ZhOKh*, **18**, 1811 (1948).
5. E. E. Frey, H. J. Hepp, *Ind. and Eng. Chem.*, **28**, 1439 (1936).

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