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The reaction of 3-methyl-3-buten-1-ol with acetophenone and benzalacetone affords a mixture of isomeric 2-methyl-2-aryldi- and tetrahydropyrans, the composition of which was ascertatined by chromatography-mass spectromety.

A number of papers [1-4] have been devoted to the condensation of γ -unsaturated alcohols with carbonyl compounds in an acid medium, which, depending on the conditions, affords isomeric dihydropyrans or tetrahydropyranols. In practically all cases, it was noted that aliphatic ketones have lower reactivity than aldehydes, and the possibility of using aliphatic-aromatic ketones was described with only one example in the reaction with 4-methyl-4-penten-2-o1 (I) [5]. However, this paper contains no data on the isomeric composition of the resulting dihydropyrans, and, in addition, the very fact of the existence of the isomers is only assumed.

In the present investigation, we consider the effect of the structure of the ketones on the course of the reaction with 3-methy1-3-buten-1-ol (II), and we studied the composition of the products in detail.

It was ascertained that at room temperature in an aqueous solution of sulfuric acid and with prolonged heating in hexane in the presence p-toluenesulfonic acid, the starting alcohol II and acetophenone III remain practically unchanged. It was only possible to carry out the reaction at a higher temperature in boiling octane (17%) and cumene (40%), although even in these cases a significant portion of the ketone remained unconverted:



Previously, in the alcohol I-p-toluenesulfonic acid-ketone III system in boiling benzene, Williams et al. [5] obtained 2,4,6-trimethyl-2-phenyl-3,6-dihydro-2H-pyran in ~18% yield on the basis of the starting ketone. According to the data of GLC analysis in our case, a mixture of three products (Va-c) was formed.

The low reactivity of the ketones could be explained by the electronic or steric effects of the substituents at the carbonyl group.

We synthesized derivatives of acetophenone III with electron-acceptor substituents, namely, α -bromoacetophenone VII and phenacylpyridinium bromide VIII. It was found that when they were heated with alcohol II in hexane the reaction did not proceed. Under more severe conditions (octane and toluene), there was significant resinification of the reaction material. These facts indicate the predominant effect of steric factors. To confirm the obtained results, we carried out experiments with anthraquinone and benzalacetone IV. In the first case, we observed a situation identical to the condensation of alcohol II with compounds VII and VIII, and when the phenyl substituent was removed from the reaction center (benzalacetone IV) we obtained the target product (VIa-c, also as a mixture of three isomers) in good yield

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TABLE 1. Chromatographic Mass Spectra of Compounds V-VI

Com- pound	Relative content,	Reten- tion time, sec	Value of m/z (relative intensity, %)*
Vc	8	1757	43 (100), 67 (47), 68 (17), 77 (16), 105 (25), 121 (49), 160 (34), 188 (6)
Va	14	1767	43 (46), 77 (14), 105 (17), 111 (24), 173 (100), 188 (5)
VЬ	78	1800	43 (22), 67 (32), 68 (100), 77 (17), 105 (48), 118 (16), 121 (37), 188 (3)
VIc	47	2289	41 (14), 43 (61), 53 (20), 67 (44), 77 (25), 91 (25), 103 (28), 115 (11), 123 (17), 128 (25), 129 (38), 131 (94), 145 (71), 146
'VIa VIb	15 38	2304 2340	(13), 147 (46), 186 (47), 199 (100), 200 (12), 214 (63) 43 (21), 91 (15), 199 (100), 200 (14), 214 (16) 43 (14), 68 (19), 91 (13), 103 (14), 118 (15), 131 (100), 145 (62) 146 (33) 171 (12) 214 (3)
			(02); 110 (00); 111 (12); 214 (0)

*With the exception of molecular ions, the peaks of ions, the peaks of ions with intensity $\geq 10\%$ are given.

(37%) with heating in benzene.

Since the components of the mixtures V and VI could not be separated by the usual methods, chromatography-mass spectrometry was used to identify them. The behavior of the cyclic ethers isomeric with respect to the position of the double bond under the effect of electron impact was specific. Previously this was shown for the case 2-alkyl (aryl)-4-methyl-5,6- and -3,6- dihydro-2H- and 4-methylenetetrahydropyrans [6].

As is evident from the data of Table 1, all the synthesized compounds had distinct molecular ions with relative intensities from 3 to 65%. The most unambiguous spectra were characteristic of isomers of type a, in which the main direction of fragmentation was determined by elimination of the substituent from the 2 position of the ring, with the methyl group being abstracted preferentially. To a lesser degree and only in the case of compound VIa we observed the formation of a fragment with $m/z 111 [M-R]^+$. The isomers of type b underwent cleavage by the mechanism of retro Diels-Alder decomposition (RDD). The most complex spectra were observed in the fragmentation of compounds of type c, when several variants of the decomposition occurred in parallel: at the $0-C_{(6)}$ and $C_{(5)}-C_{(4)}([M-C_2H_4]^+)$ bonds in the fragmentation of compounds of type c, when $C_{3H_7}^+$ was also formed in parallel:





From what has been described above, it follows that in the reaction of alcohol II with ketones III and IV di- and methylenetetrahydropyrans isomeric with respect to the position of the double bond were formed and could be identified unambiguously according to the mass spectra.

EXPERIMENTAL

Chromatographic-mass-spectrometric analysis was carried out with a Finnigan-4021 instrument with a glass capillary column (30 m \times 0.25 mm). He carrier gas (1 ml/min), SE-30 phase, temperature-programming conditions (5°C/min) from 50 to 180°C (further in the isotherm), and ionization energy of 70 eV.

Proton NMR spectra were recorded on a Tesla BS-487-C instrument (80 MHz) in CCl4.

The reaction of alcohol II with the carbonyl compounds was carried out by the procedure of [3].

We obtained compounds V [17% yield (octane, 10 h) and 40% yield (cumene, 8 h); bp 120-126°C (5 gPa); n_D^{∞} 1.5352; proton NMR spectrum (CCl₄): 6.9-7.2 (C₆H₅), 5.7 (CH=C), 5.2 (CH₂=C), 3.9-3.2 (CH₂-O), 2.5-1.9 (CH₂), 1.6 (CH₃), 1.25 ppm (CH₃). Found: C 82.71; H 8.22%. C₁₃H₁₆O Calculated: C 82.98; H 8.51%] and VI [38% yield (benzene, 10 h); n_D^{∞} 1.5655 ; proton NMR spectrum (CCl₄): 6.9 (C₆H₅), 5.9 (CH=C), 4.6 (CH₂=C). 3.8-3.3 (CH₂-O). 2.3-1.9 (CH₂). 1.6 (CH₃), 1.2 ppm (CH₃) (the number of

protons is not indicated because the spectrum was recorded for a mixture of isomers). Found: C 83.95; H 8.01%. C₁₅H₁₈O. Calculated: C 84.11; H 3.41%]

Compound VII was synthesized by the method of [7], and VIII was synthesized by the procedure of [8].

The reaction with alcohol II was carried out by the method of [3], but products of pyran structure were not obtained.

LITERATURE CITED

- 1. E. Hanshke, Chem. Ber., 88, 1053 (1955).
- 2. R. Helin, R. Henry, and S. Gelin, C. R. Acad. Sci., 273, 254 (1971).
- 3. A. A. Gevorkyan, A. S. Arakelyan, and P. I. Kazaryan, Khim. Geterotsikl. Soedin., No. 12, 1611 (1982).
- 4. A. A. Gevorkyan, A. S. Arakelyan, and N. M. Khizyantsyan, Arm. Khim. Zh., No. 9, 743 (1977).
- 5. P. H. Williams, G. G. Ecke, and S. A. Ballard, J. Am. Chem. Soc., 72, 5738 (1950).
- U. G. Ibatullin, Yu. N. Popov, I. R. Kleinos, and M. G. Safarov, Manuscript Deposited at the Branch of the Scientific-Research Institute of Technicoeconomic Research of the Ministry of the Chemical Industry of the USSR, July 24, 1984 [in Russian], No. 701 khp-D 84.
- 7. Weygand-Hilgetag, Experimental Methods in Organic Chemistry [Russian translation], Khimiya, Moscow (1969), p. 183.
- 8. N. A. Akmanova, R. F. Sagitdinova, R. F. Taipov, and V. P. Yur'ev, Zh. Org. Khim., <u>16</u>, 2309 (1980).