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MECHANISM OF CYCLOALKYLATION OF ALLYLCARBINOLS WITH ALDEHYDES AND KETONES

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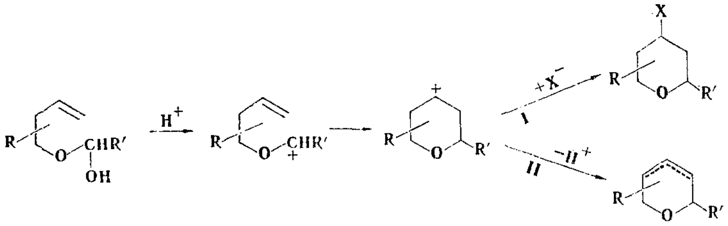
The reaction of methallylcarbinols with aldehydes and ketones in the presence of acidic catalysts, which leads to mixtures of dihydropyrans and tetrahydropyranols, was studied. It is shown that the formation of tetrahydropyranols occurs as a result of intramolecular bonding of the hydroxy group in the intermediate hemiacetal formed under the influence of the catalyst.

The reaction of allylcarbinols with aldehydes and ketones in the presence of acidic catalysts is a general method for the preparation of di- and tetrahydropyrans [1-5]. A number of new perfumes that are of practical interest have been found among them [6-8]. In this connection it has become necessary to improve the known methods for the synthesis of pyran derivatives and, in particular, to increase the yields and decrease the amount of waste waters.

According to the generally accepted opinion, the reaction of allylcarbinols with aldehydes and ketones as an intramolecular Prins reaction proceeds through an intermediate tetrahydropyranyl carbonium ion, which is stabilized either by deprotonation or by the addition of anions [9].



In conformity with these concepts, the reaction was carried out experimentally either in the presence of a large excess of anions (pathway I) or, on the other hand, in the absence of anions or in the presence of insufficient anions (pathway II). We obtained data that indi-

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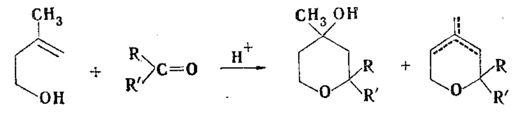
TABLE 1. Yields and Ratios of the Tetrahydro- and Dihydropyrans

Compound I and II	Overall yield of I and II, %	Ratio of I and II	Literature
a	97,6	68,9 : 31,1	[4, 10]
b	95,7	71,8 : 28,2	[4]
c	86,8	11,5 : 88,5	[4]
d	92	27,5 : 72,5	[10, 11]
e	95,5	34,7 : 65,3	[7]
f	80	55,7 : 44,3	[11]

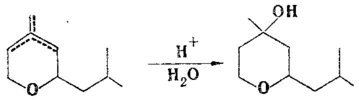
cate that the classical concepts [1–5, 9] far from completely (and inaccurately) reflect the nature of the intramolecular reaction in the intermediate unsaturated acetal. We noted that in order to obtain tetrahydropyranols it is not necessary to use a large excess of water, as is the practice of many researchers [1–5]. An exothermic reaction that leads to a mixture of tetrahydropyranol and dihydropyrans with preponderance of the former occurs when, for example, methyllylcarbinol and the aldehyde are mixed in the presence of catalytic amounts of acids (sulfuric, phosphoric, p-toluenesulfonic, etc.) (Table 1).



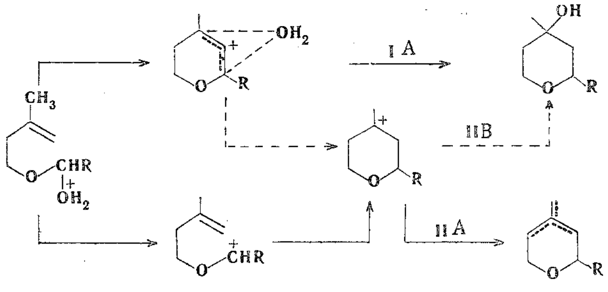
I a-f II a-f

I, II a $R=H$, $R=i\text{-}C_3H_7$; b $R=H$, $R'=CH_3{-}CH{=}CH$; c $R=H$, $R'=C_6H_{13}$; d $R=CH_3$, $R'=C_2H_5$; e $R=CH_3$, $R'=i\text{-}C_4H_9$; f $R=CH_3$, $R'=(CH_3)_2C{=}CH$

These data indicate that the hydroxy group upon protonation does not lead to the formation of a carbonium ion and water but rather reacts via some other pathway. It is most likely that attack of the hemiacetal carbon on the multiple bond and the formation of a heteroring commence with protonation and stretching of the C–$\overset{+}{O}H_2$ bond and prior to the liberation of water. Intramolecular bonding of the hydroxy group occurs subsequently with the generation of a new C–C bond and an increase in the positive charge on the γ-carbon atom of the future pyran derivative, for otherwise it is difficult to imagine that at such a very low concentration of liberated water its molecules could so easily again encounter "its own" carbonium ion or the already cyclized (tetrahydropyranyl) carbonium ion. In addition, it turns out that such ions are deprotonated much more readily than they add anions even at very high concentrations of the latter. Thus Ia [10] is formed in only 23% yield at 40–50°C when a mixture of isomers IIa is stirred with a large excess of 20% sulfuric acid for 50–60 h.



Since the corresponding tetrahydropyranols are not deprotonated at 20–25°C, over which range the reaction of methyllylcarbinol with aldehydes leads to dihydropyrans in high yields, it may be assumed that the amount of dihydropyrans obtained in the course of this reaction corresponds to that fraction of the molecules in the hemiacetal of which cleavage of the C–$\overset{+}{O}H_2$ bond has time to occur.



If the indicated assumptions really do hold true, one should observe a correlation between the structure and the reactivity of the intermediate particles. In particular, the hemiketals of aliphatic ketones, owing to the effect of two electron-donor groupings, should form carbonium ions more readily than the hemiacetals and should lead to an increase in the fraction of the reaction via Scheme II, i.e., to the primary formation of dihydropyrans. It follows from Table 1 that the experimental data confirm the assumptions made above: Ketones primarily form dihydropyrans, whereas aldehydes primarily form tetrahydropyranols.

EXPERIMENTAL

The identical character of the reaction products and genuine samples was determined with a Khrom-4 chromatograph with a catharometer and 25 by 2000 and 25 by 3000 mm columns packed with Chromaton applied to 7% PEG-20M and Apiezon-M; the carrier gas (helium) flow rate was 20-60 ml/min and the temperature was 80-150°C. The yields and ratios of the dihydropyrans and tetrahydropyranols were determined gravimetrically.

Reaction of Methallylcarbinol with Aldehydes and Ketones. A catalytic amount of p-toluenesulfonic acid was added at 20-25°C to a stirred mixture of equimolar amounts of methallylcarbinol, the carbonyl compound, and an equal volume of benzene or ether, and the course of the reaction was monitored by gas–liquid chromatography (GLC). The reaction with aldehydes was complete after 3-6 h, while the reaction with ketones was complete after 15-20 h. The reaction mixture was neutralized and filtered, the solvent was removed, and the residue was distilled. The conversion of methallylcarbinol was 60-90%, the selectivity was greater than 95%, and the overall yields of di- and tetrahydropyrans were 70-95% (Table 1).

4-Methyl-2-isobutyltetrahydropyran-4-ol. A mixture of 9 g (58 mmole) of "izookisi rozy"* and 2 ml of 30% sulfuric acid was stirred at 40-50°C for 45 h, after which it was made alkaline and extracted thoroughly to give 3 g (30.1%) of 2-isobutyl-4-methyltetrahydropyran-4-ol, the physicochemical constants of which were identical to those of a genuine sample [10].

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*Transliterated from Russian original; meaning unknown — Consultants Bureau.