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THE CHEMISTRY OF DI- AND TETRAHYDROPYRANS.

COMMUNICATION 3. ON THE ANOMALOUS BEHAVIOR OF 4-METHYL-5,6-DIHYDROPYRAN IN THE PRINS REACTIONS

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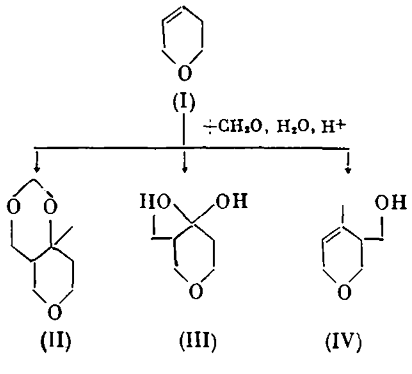
The condensation of olefins with formaldehyde under the conditions of acidic catalysis (the Prins reaction) results mainly in 1,3-dioxanes [1]. When dilute solutions of CH_2O (4-5%) are used [2], or acetic acid [3], the main products are a 1,3-diol or its diacetate. In the reaction of 4-methyl-5,6-dihydropyran (I) with a 30% aqueous solution of CH_2O, the yield of the expected dioxane in the form of a mixture of cis-trans-isomers of 10-methyl-1,3,7-trioxadecalin (II) was only 14%, while that of the diol — 3-hydroxymethyl-4-hydroxy-4-methyltetrahydropyran (III) — was 58% (cis- 5%, trans- 53%). Moreover, 3-hydroxymethyl-4-methyl-3,6-dihydropyran (IV) (5%) could also be isolated and identified



On the other hand, the condensation of CH_2O with other cyclic ethers (4-methylenetetrahydropyran and 4-phenyl-5,6-dihydropyran) leads to the corresponding dioxanes [4, 5]. The aim of the present work was to discover the reasons for the anomalous behavior of pyran (I) in the Prins reaction.

We found that in the reaction of 2-methyl-5,6-dihydropyran with formaldehyde, 6-methyl- and 9-methyl-1,3,7-trioxadecalins (V), (VI) are formed in an overall yield of 42% of theoretical

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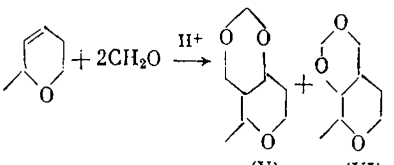
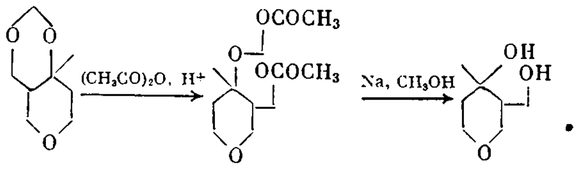


(V) (VI)

The PMR spectra of (V) and (VI) are similar, but the CH_3 group at the 9-position of the trioxadecalin ring of (VI) resonates in a weaker field due to a high degree of descreening by neighboring O atoms. When CH_2O is replaced by acetaldehyde in the reaction with (1), dioxanes – cis-trans-2,4,10-trimethyl-1,3,7-trioxadecalins (VII) – are also formed (48%). All these facts show that the anomalous behavior of (I) in the Prins reaction is due to the characteristic features of the pyran ring structure.

The accumulation of trans-(III) in the reaction mixture is in principle possible by three routes. First, due to the cis-trans-isomerism in the course of the dioxane–diol equilibrium transformations; second, as a result of a shift of the equilibrium in this system, but with trans-configuration products, in the direction of the diol; and, third, as a result of its preferential formation directly from the starting materials. The transformations of cis-(II) proceed strictly stereospecifically [6]

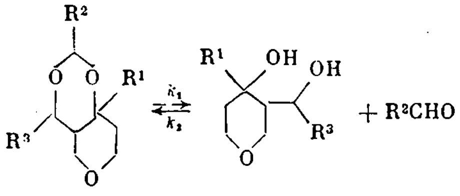


(II) (VIII) (III)

Taking into account the known generality of the principal elements of the hydrolysis and acetolysis reaction schemes, the possibility of the cis-trans-isomerization in the course of the reaction can thus be excluded unequivocally. Such a strict stereospecificity is characteristic of the hydrolysis of trans-(II) and acetylation of the isomers of (III).

To verify the correctness of the second supposition, we studied the kinetics of the equilibrium transformations in the dioxane–diol system, using the model of trans-isomers of (II), (III), and trans-(VII), (IX) (Table 1).

The data obtained show that the hydrolysis of trans-(II) proceeds at the highest rate, while judging from the value of K_e, the equilibrium is shifted in the direction of the formation of a diol



$R^1 = CH_3$, $R^2 = R^3 = H$ (II), (III); $R^1 = R^2 = R^3 = CH_3$ (VII), (IX).

In the case when acetaldehyde is used, when the main reaction product is a compound with a dioxane structure (VII), the equilibrium is shifted in the opposite direction. Similar results were obtained by various authors who studied the hydrolysis of several other dioxane structures, which are the main products of the reaction of olefins with CH_2O under the Prins reaction conditions [3, 7].

The cis-(II) forming in parallel with the trans-isomer does not undergo hydrolysis to such a considerable extent. This is probably due to the lower strain of the cis-decalin ring, as noted in [3].

trans-Trioxadecalin (VII) also hydrolyzes inappreciably, since in contrast to isomers of (VII), which are readily soluble in water, compound trans-(IX), formed as a result of its hydrolysis, is practically insoluble in water.

TABLE 1. Results of Kinetic Studies in the Dioxane–Diol System in Aqueous Solution ($[H_2SO_4]$ = 0.97 mole/liter; 75°C)

Dioxane	Hydrolysis		Diol	Acetylation		K_e
	$k_1 \cdot 10^3$, min^{-1}	E, kJ/mole		$k_2 \cdot 10^2$, liter/mole·min	E, kJ/mole	
cis-(II)	4,56	70,2	cis-(III)	3.05	121,2	0,150
trans-(II)	33,1	61,0	trans-(III)	3,25	115.4	1,02
trans-(VII)*	33,5	79,4	trans-(IX)	23,5	64,0	0,143

*The kinetics of hydrolysis were studied at 68.5°C.

Thus, since in fairly concentrated formaldehyde solutions the diol cannot be the main reaction product, its preferential formation is explained by a shift of the equilibrium in the trans-trioxadecalin–trans-diol system in the direction of the latter, due to its higher thermodynamic stability.

EXPERIMENTAL

The PMR spectra of the synthesized compounds were recorded on a Tesla BS-487C apparatus with a working frequency of 80 MHz in a CCl_4 solution, using HMDS as the internal standard. The values of the chemical shifts of protons are given in ppm.

The equilibrium hydrolysis of the dioxane structures was studied in a glass reactor equipped with a reflux condenser, thermometer, a sampler, and a thermostating jacket. The stirring was carried out by using a magnetic stirrer. The products were analyzed by the GLC method after a preliminary neutralization of the catalyst and removal of CH_2O in the form of urotropine by gaseous ammonia (LKhM-8MD chromatograph, catharometer, 5% SE-30 on chromatone N-AW-HMDS, helium – 30 ml/min, temperature programming (6 deg/min) from 100-200°C, a 2000 × 3 mm stainless steel column, internal standard – cyclohexanol). The concentration of formaldehyde was determined by the sulfite method [8].

The reaction of (I) with formaldehyde was carried out under conditions similar to those described in [4]. The isomers of (II) and (III) were separated by column chromatography on Al_2O_3. The physicochemical constants of trans-(III) and the isomers of (II) corresponded to the data given in [4]. Cis-(III) (5%) – bp 141-142°C (14 mm); n_D^{20} 1.4859. 3-Hydroxymethyl-4-methyl-3,6-dihydropyran (IV) (5%) – bp 71-73°C (14 mm); n_D^{20} 1.4838. PMR spectrum of (IV) (δ, ppm): 1.65 s (CH_3), 1.81-2.23 m (CH, CH_2OH), 2.94 s (OH), 3.56-3.92 m (CH_2O), 5.40 m (CH=C).

Trans-2,4,10-trimethyl-1,3,7-trioxadecalin (VII). A mixture of 127.9 g (1.3 mole) of (I), 264 g (2.0 moles) of paraldehyde, and 18 g (0.19 mole) of H_2SO_4 was heated with stirring for 3 h, maintaining the temperature at 57-60°C. After cooling, the organic layer was separated from the aqueous layer, and the two layers were purged with gaseous ammonia for 20 min. The aqueous layer was extracted by 3 × 100 ml of ether and dried over $MgSO_4$. The yield was 371 g of reaction mixture. A fraction with bp 90-100°C (4 mm) contained mainly a mixture of cis-trans-isomers of (VII) in a ratio of 1:11. The yield of the fraction was 48% at an 80% conversion of (I). The pure trans-(VII) was characterized by bp 103°C (4 mm); n_D^{20} 1.4656. PMR spectrum of trans-(VII) (δ, ppm): 1.11 t (2, $4CH_3$), 1.30 s ($10CH_3$), 1.30-1.59 m (CH_2, CH), 2.90 t ($8CH_a$), 3.40-3.83 m (CH_2O, CHO), 4.76 d (OCHO).

6-Methyl- and 9-Methyl-1,3,7-trioxadecalin. The charging of 2-methyl-5,6-dihydropyran, formalin, and H_2SO_4 and also the isolation of the products were carried out as in [4]. The reaction was carried out at 80°C, and its duration was controlled by periodic withdrawal of probes and analysis for the content of formaldehyde. In the course of 24 h, 1.2 mole of CH_2O enters the reaction. The fraction bp 94-96°C (2 mm), n_D^{20} 1.4680 is a mixture of isomers (V) and (VI). The yield of the isomers was 42%. The mixture was separated by the TLC method on Al_2O_3. PMR spectrum of (V) (δ, ppm): 1.06 (CH_3), 1.21-1.82 m (CH, CH_2); 2.67-4.19 m (CHO, CH_2O), 4.42-4.90 m (OCH_2O).

CONCLUSIONS

1. In the reaction of formaldehyde with 2-methyl-5,6-dihydropyran and of acetaldehyde with 4-methyl-5,6-dihydropyran under Prins reaction conditions, compounds with 1,3-dioxane structure, the corresponding trioxadecalins, are formed as the main products.

2. 4-Methyl-5,6-dihydropyran reacts with CH_2O anomalously with the preferential formation of diols, cis- and trans-3-hydroxymethyl-4-hydroxy-4-methyltetrahydropyrans (1:10). This is explained by a shift of the equilibrium in the trans-trioxadecalin—trans-diol system in the direction of the latter due to its higher thermodynamic stability.

3. The acetylation of cis- and trans-diols and also the hydrolysis and acetolysis of cis- and trans-trioxadecalins proceeds with a complete retention of the configuration.

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THE CHEMISTRY OF DI- AND TETRAHYDROPYRANS.

COMMUNICATION 4. REACTION OF 4-METHYLENETETRAHYDROPYRAN WITH FORMALDEHYDE AND ACETALDEHYDE

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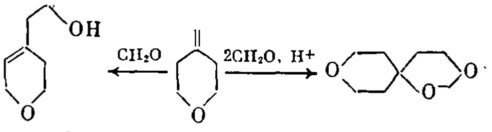
4-Methylenetetrahydropyran (I) is a large-scale side product in the synthesis of isoprene from isobutylene and formaldehyde [1], but its chemical properties have almost not been studied as yet. In the present work we study the reactions of (I) with CH_2O and MeCHO.

The condensation of (I) with CH_2O in the presence of H_2SO_4 leads mainly to 1,3,9-trioxaspiro[5.5]undecane (II) (62%), while its heating to 180°C without a catalyst gives 4-(2'-hydroxyethyl)-5,6-dihydropyran (III) (16%)



(III) (I) (II)

The PMR spectrum of physicochemical properties of (II) (Table 1) correspond to the known data [2]. In the mass spectrum of (II) there is observed not only the fragment resulting from the elimination of the CH_2O group, usually for the dioxane structures, but also a product of splitting H_2O with m/z 140 (53%).* The high intensity of the fragment formed indicates its stability. One of the probable structures of this type can be obtained when protons are shifted from C^2 and C^4 to the O atom

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*Here and below, the intensity is given in percent of maximal peak.

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