

CONJUGATED HYDROGENOLYSIS IN THE SYNTHESIS
OF TETRAHYDROFURAN HOMOLOGS

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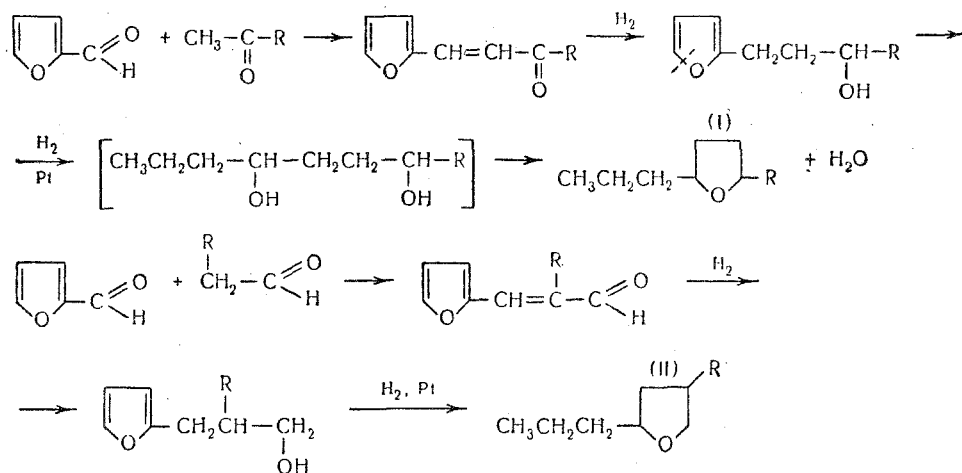
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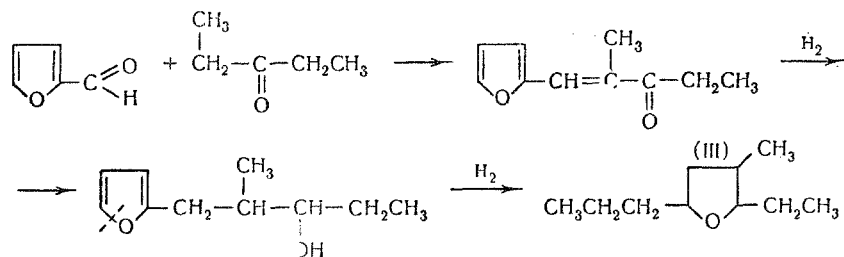
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A new method for the catalytic synthesis of tetrahydrofuran homologs was discovered recently [1,2]. This method is based on the possibility of the direct conversion of furan alcohols having the hydroxy group on the third carbon of the side chain into tetrahydrofuran homologs. Furan alcohols of such a structure may be obtained as a result of the condensation of furan carbonyl compounds with aliphatic carbonyl compounds and hydrogenation of the resulting furfurylidene ketones and 2-furanacroleins into furan alcohols. If the original furan carbonyl compound taken is 2-furaldehyde, then the structure of the resulting tetrahydrofuran homolog will be determined by the structure of the aliphatic carbonyl compound taken for condensation with 2-furaldehyde. From the scheme given below it will be seen that 2-furaldehyde and alkyl methyl ketones give 2-alkyltetrahydro-5-propylfurans (I) and 2-furaldehyde and aliphatic aldehydes give 4-alkyltetrahydro-2-propylfurans (II).



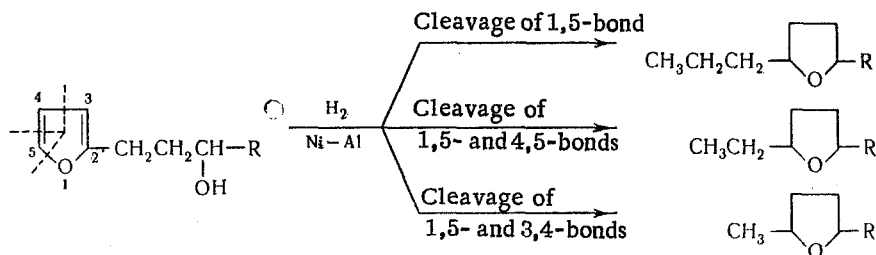
In the general case, from 2-furaldehyde and aliphatic ketones we obtain trialkyltetrahydrofurans. Thus, from 2-furaldehyde and 3-pentanone we obtain 2-ethyltetrahydro-3-methyl-5-propylfuran (III) [1].



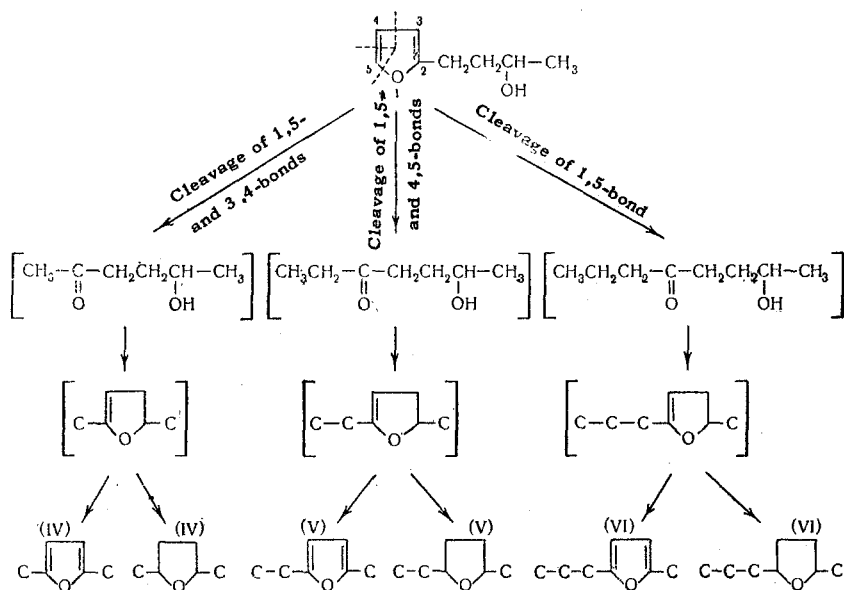
It is not difficult to see the limited character of this method of synthesizing tetrahydrofuran homologs, namely that in all cases tetrahydrofuran homologs containing an α -propyl group is formed. This is obvious from the mechanism of the formation of tetrahydrofurans: the α -propyl group is formed from the carbon atoms that form the furan ring

in the furan alcohol, so that, as a result of the hydrogenolysis of the latter, a propyl group is bound to be formed in the resulting tetrahydrofuran homolog.

However, there is the possibility of developing this method further in the direction of increasing its generality. It is possible to form other alkyl groups instead of the propyl group in the α -position of the tetrahydrofuran ring; in the first place, those with a shorter carbon chain. The propyl group is formed by hydrogenolysis of the furan ring in furan alcohols at the ether linkage not adjacent to the side group. However, it is known that the furan ring is capable of undergoing conjugated hydrogenolysis on hydrogenation in the vapor phase over a skeletal nickel-aluminum catalyst [3]. In this case, the furan nucleus undergoes cleavage in three directions: 1) at the 1,5-bond; 2) at the 1,5- and 4,5-bonds; and, 3) at the 1,5- and 3,4-bonds (see scheme). Hydrogenolysis of the furan ring at the 1,5-bond gives a propyl group; cleavage of the 1,5- and 4,5-bonds gives an ethyl group; and cleavage of the ring at the 1,5- and 3,4-bonds leads to the formation of a methyl group. Hence, as a result of conjugated hydrogenolysis, furan alcohols can form tetrahydrofurans of three series: α -methyl-, α -ethyl-, and α -propyl tetrahydrofurans.

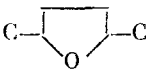
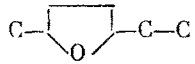
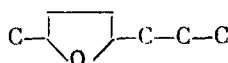
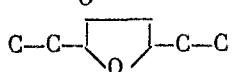
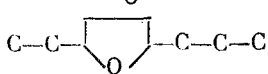


In the present work we investigated the hydrogenation of two furan alcohols in which R is methyl and ethyl, respectively. α -Methyl-2-furanpropanol ($\text{R} = \text{CH}_3$) and α -ethyl-2-furanpropanol ($\text{R} = \text{C}_2\text{H}_5$) were passed as mixtures with hydrogen over a skeletal nickel-aluminum catalyst at 220-230°. From the catalyzates of these furan alcohols by fractionation through a column we isolated fractions corresponding in each case to three tetrahydrofuran homologs. However, these fractions were not pure tetrahydrofurans, but contained an admixture (20-40%) of the corresponding furan homologs, whose boiling points were close to those of the tetrahydrofuran derivatives. The probable scheme of the formation of furan and tetrahydrofuran homologs in the hydrogenation of furan alcohols over a skeletal nickel-aluminum catalyst may be the following: as a result of conjugated hydrogenolysis of the furan ring, the furan alcohols give 1,4 keto alcohols, which are cyclized with liberation of water into dihydrofurans; the latter are either hydrogenated into tetrahydrofurans or dehydrogenated into furans.



The dehydrogenation of the dihydrofuran ring into the furan ring proceeds very readily over various catalysts containing Group VIII metals [4], and the hydrogenation of the dihydrofuran ring into the tetrahydrofuran ring proceeds more readily than the hydrogenation of furans into tetrahydrofurans.

Properties of Tetrahydrofuran Homologs

Tetrahydrofuran homolog	B.p. (°C at 760 mm)	n_D^{20}	d_4^{20}	MR	
				found	calculated
	92—94	1,4050	0,8305	29,55	29,35
	115—117	1,4147	0,8358	34,19	33,97
	140—142	1,4200	0,8380	38,72	38,59
	138—140	1,4230	0,8421	33,77	38,59
	157—159	1,4301	0,8482	43,33	43,21

In order to determine the relative amounts of the homologs of furan and tetrahydrofuran formed as a result of the conjugated hydrogenolysis of furan alcohols, fractions containing mixtures of furans and tetrahydrofurans were hydrogenated in the liquid phase over a skeletal nickel-aluminum catalyst. After this, the catalyzate contained only tetrahydrofuran homologs, which were separated by fractionation through an efficient column. In the products of the hydrogenation of furan alcohols, the content of furans and tetrahydrofurans amounted to 80-90% on the average; of this, about 35% consisted of α -methyl homologs (IV), about 20% of α -ethyl homologs (V), and about 45% of α -propyl homologs (VI).

The results of the present investigation have two-fold significance: 1) the conjugated hydrogenolysis of furan alcohols considerably extends the scope of the synthesis of tetrahydrofuran homologs because it makes it possible to obtain three series of tetrahydrofurans, namely the α -methyl, α -ethyl, and α -propyl homologs; 2) on hydrogenation over a skeletal Ni - Al catalyst, furan alcohols are converted not only into tetrahydrofuran homologs, but also into furan homologs. It is possible that change of some of the reaction conditions in the hydrogenation of furan alcohols will enable us to obtain furan homologs in higher yield. In that case it would be of practical importance to find methods for the effective separation of furan and tetrahydrofuran homologs, which often do not show significant differences in boiling point.

EXPERIMENTAL

α -Alkyl-2-furanpropanols were prepared from 2-furaldehyde and alkyl methyl ketones in two stages: condensation of 2-furaldehyde with the ketone, and catalytic reduction of the condensation product (furfurylidene ketone) to give the corresponding furan alcohol. The condensation of 2-furaldehyde with acetone and with butanone was carried out by the method described by Hinz and co-workers [5]. The resulting furfurylidene ketones were vacuum-distilled: furfurylideneacetone had b.p. 90-93° (5 mm); 1-furfurylidene-2-butanone had b.p. 100-102° (5 mm). The hydrogenation of the furfurylidene ketones into α -alkyl-2-furanpropanols was carried out in a rotating autoclave in presence of a skeletal copper-aluminum catalyst at 100-130° under an initial hydrogen pressure of 100-120 atm. Under these conditions, only the double bond and carbonyl group in the side chain were hydrogenated; hydrogenolysis of the furan ring occurred to an extremely small extent. The yields of α -alkyl-2-furanpropanols averaged at 95%. The furan alcohols were distilled at reduced pressure. α -Methyl-2-furanpropanol had: b.p. 67-69° (4 mm); d_4^{20} 1.0202; n_D^{20} 1.4754. 2-Ethyl-2-furanpropanol had: b.p. 77-78° (4 mm); d_4^{20} 1.0023; n_D^{20} 1.4745.

Both stages in the synthesis of tetrahydrofuran homologs were catalytic: the hydrogenation of furfurylidene ketones into furan alcohols, and the conversion of the latter into tetrahydrofuran homologs by conjugated hydrogenolysis. For the first of these stages we used a skeletal copper-aluminum catalyst (previously, mainly copper chromite had been used for this purpose), and for the second we used a skeletal nickel-aluminum catalyst. These catalysts were prepared by analogous methods: pieces of copper- or nickel-aluminum alloy were placed in a porcelain beaker cooled externally with ice, and 10% sodium hydroxide solution was added dropwise in such an amount that about one-half of the aluminum present in the alloy was removed. After the addition of all the alkali, the catalyst was left for several hours at room temperature, and then it was washed free from alkali with water (test with phenolphthalein). The catalysts were preserved under a layer of water.

Conversion of the Furan Alcohols into Tetrahydrofuran Homologs. α -Alkyl-2-furanpropanols were converted into furan and tetrahydrofuran homologs by hydrogenation by the flow method over a skeletal nickel-aluminum catalyst at 220-230° and ordinary pressure. The reactor was a quartz tube, in which 100 ml of catalyst was placed. The temperature was measured with a chromel-alumel thermocouple, which was placed in the middle of the catalyst layer. In each experiment we took 150 g of the furan alcohol. Hydrogen was passed in from an electrolyzer. The starting material was fed to the catalyst from an automatic buret at a space velocity of 0.1 hr⁻¹. After being separated from water and dried with calcium chloride, the catalyzates were fractionated through a column of about 30-plate efficiency. Fractions corresponding to furan and tetrahydrofuran homologs were hydrogenated in the liquid phase over a skeletal nickel-aluminum catalyst at 100-130° with the object of converting furan homologs into the corresponding tetrahydrofurans. The hydrogenation products were then fractionated through a column. From α -methyl-2-furanpropanol we obtained tetrahydro-2,5-dimethylfuran, 2-ethyltetrahydro-5-methylfuran, and tetrahydro-2-methyl-5-propylfuran; from α -ethyl-2-furanpropanol we obtained 2-ethyltetrahydro-5-methylfuran, 2,5-diethyltetrahydrofuran, and 2-ethyltetrahydro-5-propylfuran. The properties of the tetrahydrofuran homologs are given in the table.

SUMMARY

As a result of conjugated hydrogenolysis, over a skeletal Ni - Al catalyst at 220-230°, α -alkyl-2-furanpropanols were converted into furan and tetrahydrofuran homologs with a predominance of the latter. About 35% of α -methyl homologs, about 20% of α -ethyl homologs, and about 45% of α -propyl homologs were formed.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.
