RESEARCH ON FURAN ACETAL COMPOUNDS

X.* HYDROGENATION OF 2-FURYL-1,3-DIOXANES ON RANEY NICKEL

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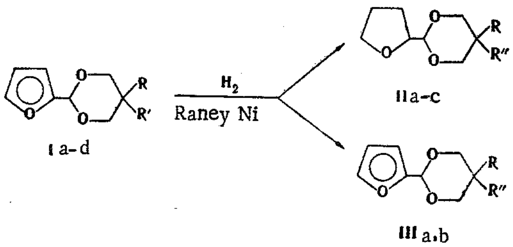
The possibility of the reduction of the furan ring to a tetrahydrofuran ring under the conditions of liquid-phase hydrogenation of 2-furyl-1,3-dioxanes on Raney nickel at atmospheric pressure is demonstrated. 2-Furyl or tetrahydro-2-furyl amino derivatives of 1,3-dioxane are formed in the case of 5-nitro-2-furyl-1,3-dioxanes as a function of the structure of the starting acetals. Data from the UV and IR spectra are presented.

Under the conditions of liquid-phase hydrogenation on nickel catalysts, furan compounds are, as a rule, reduced to tetrahydrofuran compounds; a pressure on the order of 150 atm and a high temperature (above 150°C) are required for this [2, 3]. Less study has been devoted to the behavior of substituted 1,3-dioxanes during hydrogenation on nickel catalysts; the only thing that is known is that either reduction of the substituents [4] or hydrogenolysis of the dioxane ring [5] occurs at 110-180 atm.

In the present research we investigated the possibility of hydrogenation of 2-furyl-1,3-dioxanes under mild conditions; from the point of view of the apparatus required, this may simplify the process design and make it possible to obtain tetrahydrofuran derivatives that are of promise as physiologically active compounds [6].

The following transformations occur in the case of hydrogenation of 5-substituted 2-(2-furyl)-1,3-dioxanes in a catalytic hydrogenating flask at atmospheric pressure on Raney nickel in ethanol:



Ia $R=R'=H$; Ib $R=R'=CH_3$; Ic $R=CH_3$, $R'=NO_2$; Id $R=C_2H_5$, $R'=NO_2$; IIa $R=R''=H$; IIb $R=R''=CH_3$; IIc, IIIb $R=C_2H_5$, $R''=NH_2$; IIIa $R=CH_3$, $R''=NH_2$

The hydrogenation of 2-furyl-1,3-dioxanes without substituents or those containing only alkyl substituents (Ia,b) leads to single transformation products – the corresponding tetrahydrofuran derivatives (IIa,b) (Table 1). The results of chromatographic analysis [gas–liquid chromatography (GLC) and thin-layer chromatography (TLC)] provide evidence for the high selectivity of the hydrogenation of dioxanes Ia,b on Raney nickel. The degree of purity of tetrahydrofuran acetals IIa,b ranged from 98.5 to 99.2%.

The hydrogenation of 5-alkyl-5-nitro-2-(2-furyl)-1,3-dioxanes (Ic,d) proceeds in two directions – reduction of the nitro group and reduction of the furan double bonds. Mainly 5-ethyl-5-amino-2-(tetrahydro-2-furyl)-1,3-dioxane (IIc) is formed in almost 99% yield in the hydrogenation of Id. Aminofuran dioxane IIIb is present in small amounts as an impurity.

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* See [1] for communication IX.

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TABLE 1. Comparison of the Properties of the Starting 1,3-Dioxanes (Ia-d) and Their Hydrogenation Products (IIa-c, IIIa,b)

Compound	R	R′	R″	mp, °C	n_D^{20}	d_4^{20}	R_f[a]	Found				Empirical formula	Calculated				UV spec.		Yield, %
								C, %	H, %	N, %	MR_D		C, %	H, %	N, %	MR_D	λ_{max}, nm	lg ε	
Ia	H	H	—	139 (6)[b]	1,4913	1,2002	0,75	62,17	6,52	—	39,20	$C_8H_{10}O_3$	62,32	6,49	—	39,06	208	3,95	87,0
IIa	H	—	H	116 (10)[b]	1,4684	1,1498	0,64	60,20	8,85	—	40,89	$C_8H_{14}O_3$	60,76	8,86	—	40,33	—	—	99,8
Ib	CH_3	CH_3	—	29	—	—	0,82	65,81	7,74	—	—	$C_{10}H_{14}O_3$	65,93	7,70	—	—	210	3,95	90,0
IIb	CH_3	—	CH_3	126[c]	1,4574	1,0262	0,69	65,50	10,40	—	49,40	$C_{10}H_{18}O_3$	64,52	9,68	—	49,50	—	—	99,2
Ic	CH_3	NO_2	—	83	—	—	0,72	50,20	5,00	6,10	—	$C_9H_{11}NO_5$	50,70	5,17	6,56	—	211	4,05	72,5
IIIa	CH_3	—	NH_2	43—45	—	—	0,29	59,20	6,95	7,40	—	$C_9H_{13}NO_3$	59,00	7,10	7,65	—	213	3,85	99,0
Id	C_2H_5	NO_2	—	57	—	—	0,78	52,77	6,00	6,50	—	$C_{10}H_{13}NO_5$	52,86	5,73	6,17	—	212	3,95	66,0
IIc[d]	C_2H_5	—	NH_2	135[c]	1,4912	1,1276	0,26	60,20	9,28	7,45	51,62	$C_{10}H_{19}NO_3$	59,70	9,45	6,97	51,48	—	—	98,7

[a] From the results of thin-layer chromatography on Silfuol [elution with benzene–acetone (2 : 1)].

[b] These are the boiling points in degrees Centigrade [pressure in millimeters (mercury column)].

[c] These are the boiling points in degrees Centigrade by the Emich method.

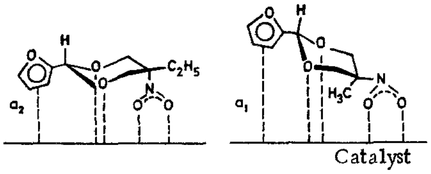
[d] For IIIb, R= C_2H_5, R″ = NO_2, λ_{max} 216 nm, and R_f 0.39; the product was obtained in 0.5% yield.

Under the same conditions, 5-methyl-5-nitro-2-(2-furyl)-1,3-dioxane Ic is converted quantitatively to amino derivative IIIa. This difference in the results is evidently due to the difference in the adsorption of the molecules of the reacting substances on the catalyst surface because of their structures.

1,3-Dioxane exists in two energetically equivalent chair conformations that are rapidly interconverted (E_{act} = 10.1 kcal/mole). The mobility of the dioxane ring is reduced in 5,5-dimethyldioxane (E_{act} = 11.2 kcal/mole) [7]. Compounds Id and Ic, which contain alkyl and nitro groups in the 5 position and a conformation-fixing group in the 2 position, should have considerably lower mobility and should exist in one of two primary chair or somewhat distorted chair conformations.

The ring is more convex for 5,5-disubstituted 1,3-dioxanes, since in the case of a quaternary carbon atom in the 5 position the angle in the ring changes from 111 to 109.5°. This convexity increases the compression of the axial substituent, and the resulting increase in the effective conformational energy of the substituent is more important for a larger group, which therefore has less likelihood of being found in an axial orientation [8]. We have previously shown by PMR spectroscopy [9] that 5-ethyl-5-nitro-2-(5-X-fur-2-yl)-1,3-dioxanes have a primary chair conformation with a cis orientation of the equatorial furyl group and an axial nitro group relative to the dioxane ring. However, whereas Id has ethyl and nitro groups of comparable volume, in the case of Ic the volume of the nitro group considerably exceeds the volume of the methyl group. It is therefore natural that a primary chair conformation with a trans orientation of the nitro group is realized for Ic. The existence of Id and Ic in the cis and trans forms, respectively, also explains the difference in their behavior during hydrogenation.

Even in the starting molecule of Ic the conformation ensures an orientation on the catalyst for which the furan ring is inaccessible to hydrogenation, in contrast to Id ($a_1 > a_2$). This effect is reinforced even more by deformation of the molecule, which leads to its compression, during sorption on the active centers of the catalyst.



It is possible that it is precisely the presence of a small amount of the trans isomer in starting Id that is responsible for the admixture of aminodioxane IIIb in the catalysate.

A peculiarity of the IR spectra of these compounds is the presence of a band of medium intensity at 918-920 cm^{-1}, which is characteristic for the tetrahydrofuran ring [10]. The remaining absorption bands of the tetrahydrofuran ring are masked by the acetal bands.

The UV spectra of the reaction products were recorded after separation of the catalysates by preparative thin-layer chromatography (TLC). The UV spectra of IIa-c are descending curves with λ_{max} at 200 nm, i.e., the absorption maxima are found in the vacuum UV region (180-190 nm). The dioxanes of the aminofuran series (IIIa,b) have distinct maxima in the UV region with a slight bathochromic shift with respect to the starting compounds Ic,d (Table 1).

A comparison of the IR spectra of acetals Ic,d and IIc, IIIa showed that the nitro group in the 5 position of the dioxane ring is completely reduced during hydrogenation. The spectra of IIc and IIIa do not contain the characteristic ν_{NO_2} bands at 1540-1550 and 1350-1380 cm^{-1}. Broad absorption bands of an amino group appear at 3370, 3300, and 1600 cm^{-1}. The furan $\nu_{C=C}$ bands are distinctly visible in the spectra of the starting dioxanes and IIIa, and this indicates that they contain an unhydrogenated furan ring. The presence in IIa-c of a tetrahydrofuran ring is confirmed by the band at 918-920 cm^{-1} and the absence of a $\nu_{C=C}$ band at 1560 cm^{-1}. Acetal bands at 1010-1200 cm^{-1} are observed in the spectra of both the starting compounds and the hydrogenation products.

Thus the spectra and chromatographic data confirm the presence of tetrahydrofuran and amino derivatives and the absence of hydrogenolysis products under the indicated conditions.

EXPERIMENTAL

The gas–liquid chromatograms were obtained with an LKhM-7A chromatograph with a flame-ionization detector and a 2-m by 4-mm column with 15% Apiezon L on Chromaton N-AW as the stationary phase. The

IR spectra of the compounds were obtained with Specord and UR-20 spectrometers. The UV spectra of aqueous ethanol solutions of the compounds were recorded with a Specord spectrophotometer.

The 2-furyl-1,3-dioxanes (Ia-d) were synthesized by the method in [11]. The Raney nickel catalyst was prepared by the method in [12].

Hydrogenation. A catalytic hydrogenating flask was charged with 1-2 g of the catalyst, 0.01 mole of the starting dioxane, and 40 ml of ethanol, and the reaction was carried out at 60° in a stream of hydrogen with vigorous stirring for 5-8 h. Electrolytic hydrogen was used without additional purification.

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RING OPENING IN 5-ARYL-2,3-FURANDIONES

SYNTHESIS OF AROYLPYRUVIC ACID ESTERS*

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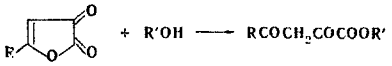
Aroylpyruvic acid esters are formed by the action of alcohols and phenol on 5-aryl-2,3-furandiones.

5-Aryl-2,3-furandiones (I) are unusually easily decyclized under the influence of nucleophilic reagents [2]. The rings of I are also opened by alcohols to give aroylpyruvic acid esters (II) (Table 1).



I

II

I a $R=C_6H_5$; b $R=p\text{-}CH_3C_6H_4$; c $R=p\text{-}CH_3OC_6H_4$; d $R=p\text{-}BrC_6H_4$; II a $R=C_6H_5$, $R'=CH_3$; b $R=p\text{-}CH_3=$ $=C_6H_4$, $R'=CH_3$; c $R=p\text{-}CH_3OC_6H_4$, $R'=CH_3$; d $R=p\text{-}BrC_6H_4$, $R'=CH_3$; e $R=C_6H_5$, $R'=C_2H_5$; f $R=C_6H_5$, $R'=CH(CH_3)_2$; g $R=C_6H_5$, $R'=n\text{-}C_4H_9$; h $R=C_6H_5$, $R'=CH_2C\equiv CH$; i $R=C_6H_5$, $R'=C_6H_5$

Of the aroylpyruvic acid esters, only the methyl and ethyl esters, obtained by Claisen reaction [3] in methanol or ethanol, have been accessible, regardless of the character of the alkyl group in the oxalic acid

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