FURAN ACETAL COMPOUNDS

IV.* SYNTHESIS OF AMINO DERIVATIVES OF 1,3-DIOXANES OF THE FURAN SERIES

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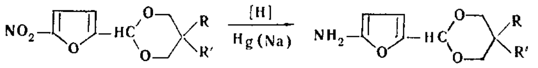
A method was developed for the preparation of amino derivatives of 1,3-dioxanes of the furan series by amalgam reduction of the corresponding nitro compounds. This method makes it possible to obtain amino compounds without destruction of the furan and dioxane rings. 2-α'-Aminofuryl-5-alkyl-5-methylol- and 5-α'-aminofuryl-5,5-bis(chloromethyl)-1,3-dioxanes and their azomethines were synthesized for the first time.

In a continuation of our studies [1, 2] to obtain new α'-substituted furan 1,3-dioxanes for biological tests we have synthesized the amino derivatives of this series of compounds.

Our attempts to synthesize aminoacetals by the direct reaction of hydroxy compounds with 5-aminofurfurals did not give positive results because of the sharply depressed electrophilicity of the carbon atom of the carbonyl group. It was recently [3] established that strictly selective reduction occurs in the amalgam reduction of carbonyl compounds of the furan series; the double bonds of the ring are not hydrogenated in the process. We therefore used an electrochemical method for the reduction of 5-α'-nitrofuryl-5-alkyl-5-methylol- and 5-α'-nitrofuryl-5,5-bis(chloromethyl)-1,3-dioxanes in sodium amalgam (the reaction was carried out in alcohol or aqueous alcohol containing no less than 30% lower aliphatic alcohols) to the amino derivatives of acetals via the scheme



$R = CH_3, C_2H_5, CH_2Cl$; $R' = CH_2OH, CH_2Cl$

The constants and yields of the synthesized compounds are presented in Table 1. The identification of the amino substituents in the 2-position of the furan 1,3-dioxanes was accomplished from qualitative reactions for the NH_2 group, the elementary composition, the molecular weight, and the UV and IR spectra. The latter made it possible to clearly reveal the vibrations of the furan (3110, 1600, 1512, 1470, 1006, 970, 880, and 740 cm^{-1}) and dioxane (1180, 1150, 1085, and 1040 cm^{-1}) rings and the band of the deformation vibrations of the NH_2 group of strong intensity at 1474 cm^{-1}. Since the valence vibrations of the OH of the C_5 methylol group at 3350-3500 cm^{-1} for I and II do not make it possible to trace the fine structure of the reduced group (amino or imino bands), the IR spectra of the reduced derivative of pentaerythritol dichlorohydrin (III) were obtained. The two bands at 3300 and 3420 cm^{-1}, in addition to the earlier noted ones, unambiguously indicate the presence of an NH_2 group in the synthesized furan 1,3-dioxanes [4].

The reaction of primary amines with carbonyl compounds to form azomethines (IV-VI) was used for additional identification of the synthesized products.

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*See [5] for communication III.

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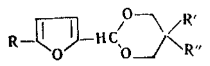
TABLE 1.



Comp.	R	R′	R″	Bp	Empirical formula	Found, %			Calculated, %			Yield, %
						C	H	N	C	H	N	
I	NH_2	CH_3	CH_2OH	102—103	$C_{10}H_{15}NO_4$	56,28	7,13	6,60	56,32	7,09	6,57	96
II	NH_2	C_2H_5	CH_2OH	110	$C_{11}H_{17}NO_4$	58,08	7,58	6,20	58,13	7,54	6,16	93
III	NH_2	CH_2Cl	CH_2Cl	96	$C_{10}H_{13}Cl_2NO_3$	45,07	4,95	5,31	45,13	4,92	5,26	92
IV	$\begin{array}{r}H_3C-C{=}N\\ \vert\quad\\ H_5C_2OOC-CH_2\end{array}$	CH_3	CH_2OH	89—90*	$C_{16}H_{23}NO_6$	59,20	7,13	4,51	59,06	7,12	4,30	98
V	$\begin{array}{r}H_3C-C{=}N\\ \vert\quad\\ H_5C_2OOC-CH_2\end{array}$	C_2H_5	CH_2OH	93*	$C_{17}H_{25}NO_6$	60,11	7,50	4,16	60,16	7,43	4,13	97
VI	$\begin{array}{r}H_3C-C{=}N\\ \vert\quad\\ H_5C_2OOC-CH_2\end{array}$	CH_2Cl	CH_2Cl	76*	$C_{16}H_{21}Cl_2NO_5$	50,72	5,59	3,71	50,79	5,56	3,69	96
VII	$C_6H_5-CH{=}N$	CH_2Cl	CH_2Cl	170*	$C_{17}H_{17}Cl_2NO_3$	57,58	4,82	3,92	57,62	4,80	3,95	97

*Mp.

EXPERIMENTAL

2-α′-Aminofuryl-5-methyl-5-methylol-1,3-dioxane (I). A total of 550 ml of a 2% solution in 70% ethanol was prepared from 11 g of 2-α′-nitrofuryl-5-methyl-5-methylol-1,3-dioxane [1] and fed from a buret at 10 ml/min into sodium amalgam (250 ml of sodium amalgam with a concentration of 1.7 g-equivalent Na per liter of mercury with a surface area of 140 cm²) with constant stirring of the amalgam and the solution being reduced. The completion of the reaction was recorded spectrophotometrically.

The product was isolated by prior vacuum distillation of a part of the solvent (70% of the total mass) at 30-40° (10-20 mm) with subsequent purification of the residual reaction mixture with a chromatographic column filled with aluminum oxide. Vacuum distillation of the solvent from the ethanol eluate yielded 9.2 g (96%) of a heavy viscous liquid with bp 102-103° and n_D^{20} 1.4255. Found %: N 6.60. $C_{10}H_{15}NO_4$. Calculated %: N 6.57.

Compounds II and III were obtained under similar conditions.

Azomethine IV. Compound I [2.25 g (0.0125 mole)] was stirred with 1.4 g (0.025 mole) of acetoacetic ester, and the resulting crystals were dried in a vacuum desiccator to give 4 g (98%) of a product with mp 89-90°. Found %: N 4.51. $C_{16}H_{23}NO_6$. Calculated %: N 4.30.

Compounds V-VII were obtained under similar conditions.

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