STUDY OF FURAN COMPOUNDS

XLIX. SOME PECULIARITIES OF THE ELECTROLYTIC ALKOXYLATION OF γ-CARBONYL-CONTAINING FURAN COMPOUNDS

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The electrolytic alkoxylation of several furan aldehydes and ketones was accomplished. It is shown that the electrolytic methoxylation of the aldehydes is an intramolecular reaction and leads to compounds of the 2,7-dimethoxy-1,6-dioxaspiro[4.4]-3-nonene series. Depending on the conditions, 2,7-dimethoxy-1,6-dioxaspiro[4.4]nonanes and 1,6-dioxaspiro[4.4]-nonanes were synthesized by the catalytic hydrogenation of the latter. The corresponding γ-carbonyl-containing 2,5-dimethoxy-2,5-dihydrofurans are formed in the case of the methoxylation of the furan ketones.

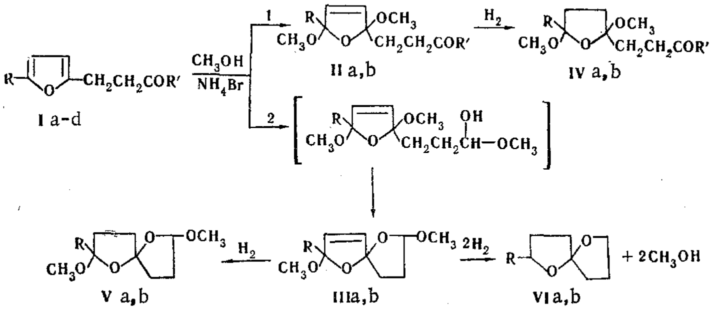
One of us has shown [2] that the product of the electrolytic methoxylation of 1-(2'-furyl)-3-butanone (Ia) is 2,5-dimethoxy-2,5-dihydrofuryl-3-butanone (IIa).

This paper is devoted to a further study of the electrolytic alkoxylation of γ-carbonyl-containing furan compounds.

We proceeded from the assumption that the methoxylation of aldehydes and ketones of the furan series can proceed in two directions:

1) methoxylation to form carbonyl-containing 2,5-dimethoxy-2,5-dihydrofurans;

2) methoxylation leading to spirocyclic compounds:



Ia, IIa, IVa R=H, R'=CH$_3$; Ib, IIb, IVb R=R'=CH$_3$; Ic, IIIa, Va, VIa R=R'=H;
Id, IIIb, Vb, VIb R=CH$_3$, R'=H

An experimental verification of this assumption demonstrated that the aldehydes and ketones of the furan series behave in different ways under the electrolysis conditions.

The subjects of the investigation were 1-(2'-furyl)-3-propanal (Ic) and Ia and their 5-methyl homologs (Id and Ib).

It turned out that the electrolytic methoxylation of furan aldehydes (Ic, d) leads to 72-75% yields of 2,7-dimethoxy-1,6-dioxaspiro[4.4]-3-nonenes (IIIa,b). The formation of spirocyclic compounds can ap-

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TABLE 1. 2,7-Dimethoxy-1,6-dioxaspiro[4.4]-3-nonenes and the Products of Their Catalytic Hydrogenation

Compound	R'	bp, °C (mm)	d_4^{20}	n_D^{20}	MR_D		Empirical formula	Found %		Calc. %		IR spectrum, cm^{-1}		Yield, %
					found	calc.		C	H	C	H	ν_{OCH_3}	$\nu_{C=C}$	
IIIa	H	88—90 (2)	1,1201	1,4550	45,29	45,47	$C_9H_{14}O_4$	58,18 58,39	7,58 7,78	58,05	7,58	2830	1630	74
IIIb	CH_3	96—98 (9)	1,0703	1,4530	50,42	50,09	$C_{10}H_{16}O_4$	60,36 60,38	8,40 8,38	59,98	8,07	2832	1635	72
Va	H	92—93 (10)	1,0816	1,4420	46,06	45,93	$C_9H_{16}O_4$	57,60 57,19	8,94 8,95	57,43	8,57	2828	—	89
Vb	CH_3	88—89 (9)	1,9360	1,4460	50,49	50,55	$C_{10}H_{18}O_4$	59,54 59,39	8,84 8,63	59,31	8,97	2830	—	89

parently by explained by the fact that the hemiacetal of the furan aldehyde is obtained as an intermediate during the reaction, and favorable steric conditions for intermolecular cyclization are created. It is known [3-5] that intramolecular alkoxylation to form compounds of the 2-alkoxy-1,6-dioxaspiro[4.4]-3-nonene series occurs in the electrolysis of solutions of furan alcohols containing a hydroxyl group in the 3 position relative to the ring.

No absorption at 1680-1750 cm^{-1} is observed in the IR spectra of IIIa and IIIb, which indicates the absence of a carbonyl group. The spiran structure of IIIa and IIIb was confirmed by several intense bands at 980-1100 cm^{-1} associated with the stretching vibrations of the $-COC-$ bonds and characteristic for such spiroacetal structures [4-7]. The presence of a double bond is confirmed by a band of its stretching vibrations at 1630-1635 cm^{-1} and also by a band of stretching vibrations of the $CH=$ bond at 3095-3100 cm^{-1}. The stretching vibrations of the OCH_3 groups are displayed as a band at 2830-2832 cm^{-1}.

In addition to the results of elementary analysis and the IR spectra, the structures of IIIa and IIIb were experimentally confirmed by their transformations during catalytic hydrogenation. The hydrogenation of IIIa and IIIb under mild conditions (at room temperature in the presence of Raney nickel) results in the formation of the corresponding 2,7-dimethoxy-1,6-dioxaspiro[4.4]nonanes (Va and Vb), the physical constants and yields of which are presented in Table 1. The absorption bands at 1630 and 3095 cm^{-1} that characterize the presence of a $C=C$ bond are absent in the IR spectra of these compounds. When IIIa and IIIb are hydrogenated under more severe conditions (at 100-120 atm and 100° in the presence of Raney nickel), not only is the double bond in the ring hydrogenated, but both methoxy groups are cleaved to form 1,6-dioxaspiro[4.4]nonane (VIa) and its methyl homolog (VIb), which have physical constants and IR spectra that are identical to those of 1,6-dioxaspiro[4.4]nonanes obtained by the hydrogenation of γ-furylalkanols [8,9].

In the case of the electrolytic methoxylation of furan ketones (Ia and Ib), our investigations demonstrated that the reaction proceeds via route 1 to give 65-70% yields of 2,5-dimethoxy-2,5-dihydrofuryl-3-butanones (IIa, b). It is probable that this can be explained by the fact that the ketones, under these electrolysis conditions, are not converted in satisfactory yields to the hemiketals [10]. An intense band of carbonyl absorption at 1715-1720 cm^{-1} is observed in the IR spectra of IIa and IIb.

The corresponding 2,5-dimethoxytetrahydrofuryl-3-butanones (IVa, b) were obtained in quantitative yield by the catalytic hydrogenation of IIa and IIb.

The physical constants, analytical results, and some characteristic frequencies of the IR spectra of the previously undescribed IIb, IIIa, b, IVa, and Va, b are presented in Table 1 and in the experimental section of this paper.

EXPERIMENTAL*

The methods described in [11, 12] were used to obtain 1-(2'-furyl)-3-butanone (Ia), 1-(5'-methyl-2'-furyl)-3-butanone (Ib), 1-(2'-furyl)-3-propanol (Ic), and 1-(5'-methyl-2'-furyl)-3-propanol (Id).

The method typical for the electrolytic methoxylation is presented below.

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*With the participation of V. I. Pirozhkova.

TABLE 2. Conditions for the Electrolysis of Ia, b, d

Compound	Amt. of starting compound, mole	Current strength, A	Voltage, V	Electrolyzer temp., °C
Ia	0,30	4,0—3,5	7—12	−10
Ib	0,31	4,0—3,5	5—14	−13
Id	0,50	4,5—4,0	8—10	−20

2,7-Dimethoxy-1,6-dioxaspiro[4.4]-3-nonene (IIIa). A mixture of 63 g (0.5 mole) of Ic and 10 g of ammonium bromide was dissolved in 350 ml of methanol and placed in an electrolyzer [2]. The reaction mixture was cooled to −20°, and this temperature was maintained during the experiment. The current strength was 4-4.5 A, and the voltage was 8-10 V. At the end of the electrolysis, the solution was treated with sodium methoxide (2.4 g of sodium metal in 40 ml of methanol). The methanol and ammonia were removed by distillation on a water bath at reduced pressure, and the precipitate of sodium bromide was removed by filtration and washed several times with ether. The ether was evaporated, and the residue was vacuum distilled to give 66 g (74%) of IIIa.

The data for the conditions of the electrolysis of Ia,b,d are presented in Table 2.

2,5-Dimethoxy-2,5-dihydrofuryl-3-butanone (IIa). This compound had bp 102-105° (2 mm) and n_D^{20} 1.4565 [bp 102-104° (2 mm) and n_D^{20} 1.4568 [2, 11]].

2-Methyl-2,5-dimethoxy-2,5-dihydrofuryl-3-butanone (IIb). This was obtained in 71% yield and had bp 93-95° (2 mm), d_4^{20} 1.1156, and n_D^{20} 1.4640. Found %: C 61.64, 62.34; H 8.37, 8.33. MR_D 55.49. $C_{11}H_{18}O_4$. Calculated %: C 61.66; H 8.47; MR_D 55.31.

The catalytic hydrogenation was accomplished in a 250 ml rotating steel autoclave.

2,7-Dimethoxy-1,6-dioxaspiro[4.4]nonane (Va). A mixture of 8 g (0.04 mole) of IIIa, 90 ml of absolute alcohol, and 1 g of Raney nickel was placed in an autoclave. The initial pressure was 100 atm at room temperature. The hydrogenation was complete after the absorption of 0.53 liter of hydrogen. The catalyzate was extracted from the autoclave, and the catalyst was removed by filtration. The alcohol was removed by distillation at reduced pressure, and the residue was vacuum distilled to give 7.1 g (89%) of Va.

2,7-Dimethoxy-2-methyl-1,6-dioxaspiro[4.4]nonane (Vb). This compound was similarly obtained.

1,6-Dioxaspiro[4.4]nonane (VIa). An autoclave was charged with 8 g (0.04 mole) of IIIa, 80 ml of absolute alcohol, and 1 g of Raney nickel. The initial hydrogen pressure was 120 atm at 120°. The reaction was complete after the absorption of 3.15 liter of hydrogen. The catalyst was worked up as indicated above. The residue was vacuum distilled to give 3.6 g (69%) of a product with bp 80-83° (60 mm) and n_D^{20} 1.4468 [bp 81-82° (60 mm) and n_D^{20} 1.4460 [8]].

2-Methyl-1,6-dioxaspiro[4.4]nonane (VIb). This compound was obtained in 70% yield by hydrogenation under these conditions and had bp 162-165° (760 mm) and n_D^{20} 1.4427 (bp 162-164° (760 mm) and n_D^{20} 1.4429 [9]).

2,5-Dimethoxytetrahydrofuryl-3-butanone (IVa). This compound had bp 124-126° (4 mm) and n_D^{20} 1.4435 [bp 124.5-126.5° (4 mm) and n_D^{20} 1.4432 [2, 11]].

2-Methyl-2,5-dimethoxytetrahydrofuryl-3-butanone (IVb). This was obtained in 97% yield and had bp 93-95° (9 mm), d_4^{20} 1.0354, and n_D^{20} 1.4440. Found %: C 61.20, 61.35; H 9.20, 9.28; MR_D 55.51. $C_{11}H_{20}O_4$. Calculated %: C 61.08; H 9.32; MR_D 55.78.

The IR spectra of capillary-thin layers of the compounds between potassium bromide plates were recorded with a UR-10 double-beam spectrophotometer at 400-4000 cm^{-1}.

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