

FURAN COMPOUNDS.

XLIII[†]. SYNTHESIS OF 2-METHOXY-1,6,9-TRIOXASPIRO-[4,5]DEC-3-ENES

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Electrolysis of monofurfuryl ethers of ethylene glycol in methanolic solution results in intramolecular alkoxylation, with the formation of the hitherto undescribed 2-methoxy-1, 6, 9-trioxaspiro-[4, 5]dec-3-enes. Catalytic hydrogenation of the latter at room temperature in the presence of Raney nickel catalyst gives 70-90% yields of the 2-methoxy-1, 6, 9-trioxaspiro[4, 5]dec-3-enes.

Intramolecular electrolytic alkoxylation opens up wide possibilities for the preparation and thorough investigation of a range of spirocyclic compounds containing heteroatoms (oxygen and nitrogen), which are very promising in the search for biologically active compounds [2-7].

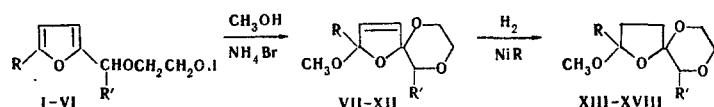
This reaction is known [2-4, 8] to take place on electrolysis of methanolic solutions of γ -furyl-3-alkanols, giving 2-methoxy-1, 6-dioxaspiro[4, 4]non-3-enes.

The present paper deals with the application of this electrolytic methoxylation for the preparation of a new spirane system, consisting of linked 5- and 6-membered rings, and containing three oxygen atoms.

The parent 1-(2'-furyl)- and 1-(5'-methyl-2'-furyl)-1-alkyl-2-oxa-4-alkanols (ethylene glycol monofurfuryl ethers) were obtained by condensing the sodium alkoxides from furyl- and 5-methylfurycarbinols with ethylene chlorohydrin.

Table 1 gives the physical constants, analyses, and some characteristic IR spectral frequencies of the ethylene glycol monofurfuryl ethers thus prepared.

The electrolytic alkoxylation of ethylene glycol monofurfuryl ether solutions in methanol gives the 2-methoxy-1, 6, 9-trioxaspiro[4, 5]dec-3-enes.



There were thus prepared, in yields of 60-77% the following: 2-methoxy- (VII), 2-methoxy-10-isopropyl- (VIII), 2-methoxy-10-n-butyl- (IX), 2-methoxy-2-methyl- (X), 2-methoxy-2-methyl-10-isopropyl- (XI), and 2-methoxy-2-methyl-10-n-butyl-1, 6, 9-trioxaspiro[4, 5]dec-3-enes (XII). The physical constants and analyses for these compounds are given in Table 2.

[†] For Part XLII, see [1].

[‡] Deceased.

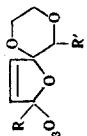
Chernyshevskii Saratov State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 9, pp. 1155-1159, September 1970. Original article submitted May 26, 1969.

TABLE 1. Ethylene Glycol Monofurfuryl Ethers 

Compound	R	R'	Bp, °C (press., mm)	n _D ²⁰	d ₄ ²⁰	MR _D		Molecular formula	Found, %		Calculated, %		IR Spectrum, cm ⁻¹		
						found	calculated		C	H	C	H	v _{C=C}	v _{OH}	Yield, %
I*	H	H	108—110 (9)	1.4840	1.1340	35.85	36.20	C ₇ H ₁₀ O ₃	59.13	7.07	59.15	7.10	1505 1595	3420	51
II	H	i-C ₃ H ₇	102—103 (3)	1.4710	1.0625	49.61	50.05	C ₁₀ H ₁₆ O ₃	65.07	8.83	65.19	8.75	1507 1599	3400	50
III	H	n-C ₄ H ₉	100—102 (2)	1.4711	1.0171	54.52	54.67	C ₁₁ H ₁₈ O ₃	66.51	8.96	66.64	9.15	1506 1595	3430	63
IV	CH ₃	H	113—114 (10)	1.4850	1.0942	40.82	40.91	C ₈ H ₁₂ O ₃	61.60	7.67	61.58	7.75	1565 1610	3440	61
V	CH ₃	i-C ₃ H ₇	113—115 (8)	1.4718	1.0175	54.54	54.68	C ₁₁ H ₁₈ O ₃	66.96	9.13	66.64	9.15	1562 1610	3440	48
VI	CH ₃	n-C ₄ H ₉	114—117 (3)	1.4720	0.9950	59.64	59.29	C ₁₂ H ₂₀ O ₃	67.55	9.56	67.89	9.50	1560 1610	3440	40

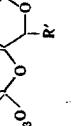
*Bp, 110°C (10 mm); nd²⁰ 1.4837; d₄²⁰ 1.1327 [11].

TABLE 2. 2-Methoxy-10-alkyl-1, 6, 9-trioxaspiro[4, 5]dec-3-enes



Compound	R	R'	Bp, °C (press., mm)	n _D ²⁰	d ₄ ²⁰	MR _D		Molecular formula	Found, %		Calculated, %		IR Spectrum, cm ⁻¹		
						found	calculated		C	H	C	H	v _{OCH₃}	v _{C=C}	Yield, %
VII	H	H	81—82 (2)	1.4710	1.1940	40.21	40.21	C ₈ H ₁₂ O ₄	56.09	7.13	55.80	7.03	2835 2830	1640	60
VIII	H	i-C ₃ H ₇	93—95 (1)	1.4560	1.0820	54.75	54.70	C ₁₁ H ₁₈ O ₄	61.83	8.87	61.66	8.44	2834 2834	1640 1630	73 76
IX	H	n-C ₄ H ₉	100—102 (1)	1.4629	1.0550	59.59	59.31	C ₁₂ H ₂₀ O ₄	63.11	9.01	63.15	8.83	2834 2834	1640	78
X	CH ₃	H	78—79 (2)	1.4641	1.1431	44.96	45.47	C ₉ H ₁₂ O ₄	57.88	7.44	58.05	7.58	2834 2834	1635	58
XI	CH ₃	i-C ₃ H ₇	74—78 (1)	1.4520	1.0400	59.21	59.32	C ₁₂ H ₂₀ O ₄	63.52	9.07	63.15	8.88	2830 2830	1635	58
XII	CH ₃	n-C ₄ H ₉	83—86 (1)	1.4500	1.0146	64.18	63.94	C ₁₃ H ₂₂ O ₄	64.45	9.55	64.43	9.15	2832 2832	1630	77

TABLE 3. 2-Methoxy-10-alkyl-1, 6, 9-trioxaspiro[4, 5]-decanes



Compound	R	R'	Bp, °C (press., mm)	n _D ²⁰	d ₄ ²⁰	MR _D		Molecular formula	Found, %		Calculated, %		IR Spectrum, cm ⁻¹	
						found	calculated		C	H	C	H	v _{OCH₃}	v _{OCH₃}
XIII	H	H	76—77 (2)	1.4560	1.1420	41.42	41.32	C ₈ H ₁₄ O ₄	55.08	8.27	55.16	8.10	2830 2830	91
XIV	H	i-C ₃ H ₇	73—75 (1)	1.4555	1.1210	55.00	55.17	C ₁₁ H ₂₀ O ₄	62.40	7.00	62.51	6.99	2832 2832	90
XV	H	n-C ₄ H ₉	110—114 (2)	1.4555	1.0526	59.42	59.77	C ₁₂ H ₂₂ O ₄	62.77	9.45	62.58	9.63	2834 2834	89
XVI	CH ₃	H	79—80 (4)	1.4550	1.1214	46.55	45.93	C ₉ H ₁₆ O ₄	57.45	8.46	57.43	8.29	2832 2832	78
XVII	CH ₃	i-C ₃ H ₇	67—68 (1)	1.4480	1.0336	59.65	59.79	C ₁₂ H ₂₂ O ₄	62.32	9.62	62.58	9.63	2830 2830	70
XVIII	CH ₃	n-C ₄ H ₉	76—77 (1)	1.4430	1.0030	64.58	64.41	C ₁₃ H ₂₄ O ₄	63.83	9.95	63.90	9.90	2830 2830	81

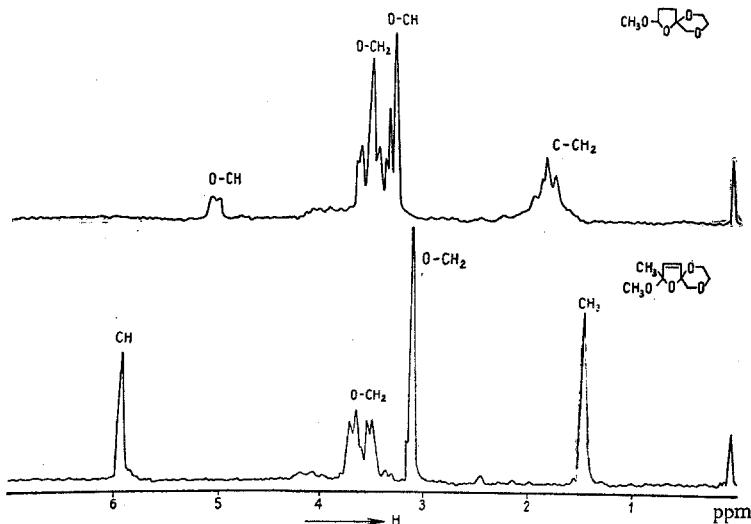


Fig. 1. NMR Spectra of 2-methoxy-2-methyl-1, 6, 9-trioxa-spiro[4, 5]dec-3-ene (X) and 2-methoxy-1, 6, 9-trioxaspiro[4, 5]decane (XIII).

Catalytic hydrogenation of VII-XII at room temperature in the presence of Raney nickel catalyst under pressure gave the following, in 70-90% yields: 2-methoxy-(XIII), 2-methoxy-10-isopropyl (XIV), 2-methoxy-10-n-butyl- (XV), 2-methoxy-2-methyl- (XVI), 2-methoxy-2-methyl-10-isopropyl-(XVII), and 2-methoxy-2-methyl-10-n-butyl-1, 6, 9-trioxaspiro[4, 5]decane (XVIII) (see Table 3).

The structure of VII-XVIII was confirmed by their IR and NMR spectra. The IR spectra were characterized by the presence of a large number of bands of high intensity, typical of the spiroacetal structure [3, 4, 8-10]. It is important to note that all the spirans exhibit intense bands in the 980-1160 cm^{-1} range, due to stretching of the C-O-C and C-O-C-O-C groups, and also a band at 2830-2834 cm^{-1} due to the OCH_3 group. The presence of a double bond in VII-XII was confirmed by the stretching band at 1630-1640 cm^{-1} .

The NMR spectrum of X (see Fig. 1) showed signals (δ -scale) at 1.49 and 3.14 ppm, attributed to the protons in the CH_3 and OCH_3 groups, respectively. The broad signal at 3.41-3.63 ppm corresponds to the 6 protons of the O-CH_2 groups. The signal at 5.87 ppm arises from the protons of the C-CH groups. In XIII, in addition to the signals due to the O-CH_3 and O-CH_2 groups (3.25-3.32, 3.41-3.60 ppm), a wide signal appears with peaks at 1.71 and 1.80 ppm, corresponding to the 4 protons of the C-CH_2 groups, and also a signal at 5.00 and 5.05 ppm, arising from the proton of the O-CH group. The authors express their sincere thanks to G. V. Lagodzinskoi for obtaining and helping to interpret the NMR spectra.

EXPERIMENTAL*

1-Isopropyl-(5'-methyl-2'-furyl)carbinol was obtained by the Grignard reaction, starting from equimolecular amounts of magnesium and isopropyl bromide (1.1 mole), and 1 mole of 5-methylfurfural, in 65% yield. $\text{Bp } 83-85^\circ$ (9 mm); $n_D^{20} 1.4740$; $d_4^{20} 0.9970$. Found: C 69.62; 69.66; H 8.99; 8.95%. $\text{MR}_D 43.54$. $\text{C}_9\text{H}_{14}\text{O}_2$. Calculated: C 70.10; H 9.15%; $\text{MR}_D 43.80$.

1-(α -furyl)- (I), 1-(α -furyl)-1-isopropyl- (II), 1-(α -furyl)-n-butyl- (III), 1-(5'-methyl-2'-furyl)- (IV), 1-(5'-methyl-2'-furyl)-1-isopropyl- (V), and 1-(5'-methyl-2'-furyl)-1-n-butyl-2-oxabutan-4-ol (VI) were obtained by the condensation of the sodium alkoxides of the appropriate furylcarbinols with ethylene chlorohydrin in dry toluene at $\sim 100^\circ$ [11].

2-Methoxy-1, 6, 9-trioxaspiro[4,5] dec-3-ene (VII). 106.5 g (0.75 mole) of freshly-distilled I and 13 g (0.133 mole) of ammonium bromide were dissolved in 250 ml of methanol, and placed in an electrolyzer with a carbon anode and a nickel cathode, as described previously [12, 13]. The solution was cooled to -12° , and kept at this temperature throughout the experiment. The current strength was 5-6 A, at a voltage of 8-14 V. When the electrolysis was complete, the solution was treated with sodium methoxide (3.12 g of sodium in 30 ml of methanol). The methanol and ammonia were distilled from the water bath under

*With the participation of A. Novikova.

TABLE 4. Conditions for the Electrolysis of II-VI

Compound	Amount of starting material, moles	Current, A	Voltage, V	Temp. of Electrolysis, °C
II	0,30	6,0-5,0	9-12	-12
III	0,33	5,0-4,0	8-12	-12
IV	0,53	5,0-4,0	8-13	-12
V	0,30	5,0-4,0	9-15	-14
VI	0,25	6,0-4,0	8-14	-14

reduced pressure, and the precipitate of sodium bromide which separated was filtered off and washed several times on the filter with ether. The ether was evaporated, and the residue was distilled in *vacuo* to give 74.5 g (60%) of product. The conditions for the electrolysis of II-VI are given in Table 4.

2-Methoxy-1, 6, 9-trioxaspiro[4, 5] decane (XIII). Eleven grams of VII, 60 ml of absolute methanol, and 2 g of Raney nickel were placed in a rotating steel autoclave of 250 ml capacity. The initial hydrogen pressure was 100 atm, at room temperature. The hydrogenation was terminated when the calculated amount of hydrogen had been absorbed. The catalyst was filtered off, the methanol removed under reduced pressure, and the residue was distilled in *vacuo* to give a yield of 10 g (91%). Compounds VIII-XII were hydrogenated similarly.

IR spectra were recorded on a split-beam UR-10 spectrophotometer in the 400-4000 cm^{-1} range. All compounds were examined as capillary thin layers between potassium bromide disks.

NMR spectra were taken in carbon tetrachloride on a JNM-C-60 apparatus with a working frequency of 60 MHz, using tetramethylsilane as internal standard.

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