ELECTROLYTIC ETHOXYLATION OF SEVERAL γ-FURYLALKANOLS

I. A. Markushina and N. V. Shulyakovskaya

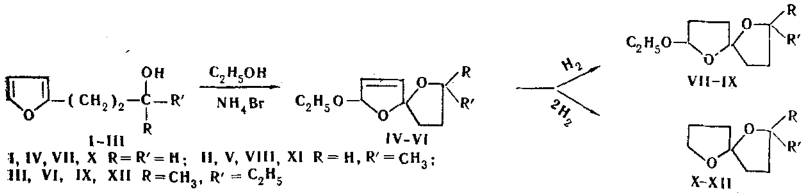
UDC 547.727:542.941.7

Compounds of the 2-ethoxy-1,6-dioxaspiro[4.4]-3-nonene series were obtained during the electrolysis of solutions of primary, secondary, and tertiary γ-furylalkanols in ethanol as a result of intramolecular alkoxylation. Depending on the conditions, catalytic hydrogenation of the products leads to the formation of 2-ethoxy-1,6-dioxaspiro[4.4]nonanes or 1,6-dioxaspiro[4.4]nonanes.

One of us, together with Ponomarev [1,2], has previously established that the electrolytic methoxylation of γ-furylalkanols proceeds intramolecularly and leads to the formation of methoxy derivatives of 1,6-dioxaspiro[4.4]-3-nonene.

In order to study the interrelationship between the chemical structure and the biological activity of the spirans, we have synthesized compounds of the 2-ethoxy-1,6-dioxaspiro[4.4]-3-nonene series from 1-(α-furyl)-3-propanol (I), 1-(α-furyl)-3-butanol (II), and 1-(α-furyl)-3-methyl-3-pentanol (III).

Our investigations indicated that the reaction also proceeds intramolecularly during the electrolysis of solutions of I-III in ethanol leading to the formation of 2-ethoxy- (IV), 2-ethoxy-7-methyl- (V), and 2-ethoxy-7-methyl-7-ethyl-1,6-dioxaspiro[4.4]-3-nonenes (VI) in yields of 76-83%.



I-III

IV-VI

VII-IX

X-XII

I, IV, VII, X $R = R' = H$; II, V, VIII, XI $R = H, R' = CH_3$; III, VI, IX, XII $R = CH_3, R' = C_2H_5$

The corresponding 2-ethoxy-1,6-dioxaspiro[4.4]nonanes (VII-IX) were obtained by catalytic hydrogenation of compounds IV-VI at room temperature in the presence of a Raney nickel catalyst.

Cleavage of the ethoxy group occurs in addition to reduction of the double bond in the ring during hydrogenation under more severe conditions (hydrogen pressure of 120 atm at 100-120°), and the well-known 1,6-dioxaspiro[4.4]nonane and its homologs are formed.

The IR spectra, in which one should note the presence of a large number of bands of high intensity characteristic for similar spiroacetal structures [2-4], are a partial confirmation of the structures of IV-IX. The intense bands at 980-1160 cm^{-1} are associated with the stretching vibrations of the $-C-O-C-$ and $-C-O-C-O-C-$ groups. The absorption band at 2872-2885 cm^{-1} corresponds to the valence vibrations of the $-OC_2H_5$ group [5]. The presence of a double bond in IV-VI is confirmed by the band at 1260-1635 cm^{-1}.

The IR spectra of X-XII are identical to the spectra of the spirans obtained during hydrogenation of the corresponding γ-furylalkanols or 2-methoxy-1,6-dioxaspiro[4.4]-3-nonenes.

The physical constants, analyses, and several characteristic frequencies of the IR spectra of compounds IV-IX, which have not previously been described, are presented in Table 1.

N. G. Chernyshevskii Saratov State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 10, pp. 1303-1305, October, 1970. Original article submitted August 10, 1969.

TABLE 1. 2-Ethoxy-1,6-dioxaspiro[4.4]-3-nonenes and Their Catalytic Hydrogenation Products

Comp.	bp, °C (mm)	n_D^{20}	d_4^{20}	MR_D		IR spectrum, cm⁻¹		Empirical formula	Found %		Calc. %		Yield, %
				found	calc.	$\nu_{-OC_2H_5}$	$\nu_{C=C}$		C	H	C	H	
IV	89—92 (10)	1,4600	1,0718	43,50	43,82	2885	1635	$C_9H_{14}O_3$	63,57 63,53	8,79 8,52	63,54	8,30	83
V	81—83 (6)	1,4550	1,0296	48,52	48,44	2882	1630	$C_{10}H_{16}O_3$	65,01 65,11	8,79 8,76	65,20	8,76	76
VI	101—103 (10)	1,4540	1,0017	57,39	57,63	2883	1630	$C_{12}H_{20}O_3$	67,80 67,78	9,60 9,62	67,89	9,50	80
VII	69—71 (10)	1,4449	1,0374	44,17	44,29	2885	—	$C_9H_{16}O_3$	62,82 62,65	9,14 9,26	62,77	9,37	82
VIII	83—85 (10)	1,4410	1,0031	48,98	49,01	2872	—	$C_{10}H_{18}O_3$	64,90 64,81	10,02 10,00	64,49	9,74	81
IX	102—105 (10)	1,4440	0,9782	58,19	58,15	2883	—	$C_{12}H_{22}O_3$	67,22 66,85	10,52 10,44	67,25	10,35	81

EXPERIMENTAL

γ-Furylalkanols (I-III). These were prepared in accordance with [6]. The electrolysis was carried out in an electrolyzer with a carbon anode and a nickel cathode [7,8]. The electrolyte was ammonium bromide. A typical method used for the electrolysis of the solutions of γ-furylalkanols is presented below.

2-Ethoxy-1,6-dioxaspiro[4.4]-3-nonene (IV). Compound I [33 g (0.262 mole)] and 5 g of ammonium bromide were dissolved in 250 ml of absolute ethanol, and the solution was placed in an electrolyzer. The reaction mixture was cooled to −10° and kept at this temperature during the experiment. The current strength was 2.5-3.5 A, and the voltage was 24-26 V. At the end of the electrolysis the solution was treated with sodium ethoxide (1.2 g of sodium in 20 ml of ethanol). The ethanol and ammonia were removed on a water bath at reduced pressure, and the precipitate of sodium bromide was filtered off and washed several times with ether. The residue after removal of ether was distilled in vacuo to give 35.8 g (83%) of product.

Compounds V and VI were similarly obtained.

The 2-ethoxy-1,6-dioxaspiro[4.4]-3-nonenes were catalytically hydrogenated in a 250-ml rotating steel autoclave.

2-Ethoxy-1,6-dioxaspiro[4.4]nonane (VII). A mixture of 10 g (0.06 mole) of IV, 60 ml of absolute alcohol, and 1 g of Raney nickel was placed in an autoclave. The initial hydrogen pressure was 100 atm at room temperature. The hydrogenation was complete on absorption of 1.5 liter of hydrogen. The catalyst was filtered off, the ethanol was removed at reduced pressure, and the residue was distilled in vacuo to give 8.45 g (83%) of product.

Compounds VIII and IX were similarly obtained.

1,6-Dioxaspiro[4.4]nonane (X). A mixture of 10 g (0.06 mole) of IV, 60 ml of absolute alcohol, and 1 g of Raney nickel was placed in an autoclave. The initial hydrogen pressure was 120 atm at 120°. The reaction was complete when 2.9 liter of hydrogen had been absorbed. The catalysate was treated as indicated above. The residue was distilled in vacuo to give 6.4 g (59%) of product with bp 83-85° (61 mm), n_D^{20} 1.4480, and d_4^{20} 1.0320 [9].

2-Methyl-1,6-dioxaspiro[4.4]nonane (XI). This compound was obtained in 49% yield by hydrogenation, under the same conditions of V, and had bp 162-165° (760 mm), n_D^{20} 1.4428, and d_4^{20} 0.9920 [10].

2-Methyl-2-ethyl-1,6-dioxaspiro[4.4]nonane (XII). This compound was obtained from VI in 46% yield and had bp 102-105° (45 mm), n_D^{20} 1.4440, and d_4^{20} 0.9622 [11].

The IR spectra were recorded with a UR-10 double-beam spectrophotometer from 400 to 4000 cm^{-1}. All of the compounds were investigated in a capillary-thin layer between potassium bromide plates.

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