

## STUDY OF FURAN COMPOUNDS

## XXXII. New Polycyclic Spirans of the 1,6-Dioxaspiro[4,4]nonane Group\*

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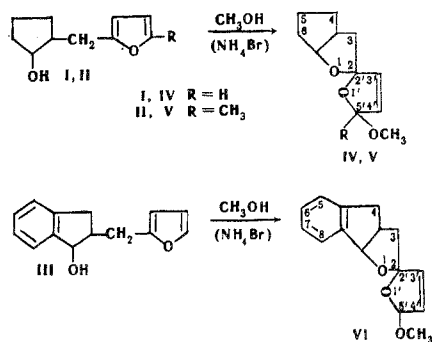
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Research on synthesis of polycyclic spirans of the 1,6-dioxaspiro[4,4]nonane group is continued. Electrolysis of methanol solutions of 2-furylecyclopentanol, 2-(5'-methyl-furfuryl)cyclopentanol, and 2-furfuryl-1-indanol, gives, by intramolecular alkoxylation, spiro{perhydrocyclopenta[b]furan-2, 2'-(5'-dihydrofuran)}, spiro{perhydrocyclopenta[b]furan-2, 2'-(5'-methoxy-5'-methyl-2', 5'-dihydrofuran)}, and spiro{2, 3, 3a, 8b-tetrahydro-4H-indeno[1, 2-b]furan-2, 2'-(5'-methoxy-2', 5'-dihydrofuran)}, hitherto undescribed in the literature. Depending on the conditions, catalytic hydrogenation of these gives: spiro{perhydrocyclopenta[b]furan-2, 2'-(5'-methoxytetrahydrofuran)}, spiro{2, 3a, 8b-tetrahydro-4H-indeno[1, 2-b]furan-2, 2'-(5'-methoxytetrahydrofuran)}, spiro{perhydrocyclopenta[b]furan-2, 2'-tetrahydrofuran}, and spiro{2, 3, 3a, 8b-tetrahydro-4H-indeno[1, 2-b]furan-2, 2'-tetrahydrofuran}.

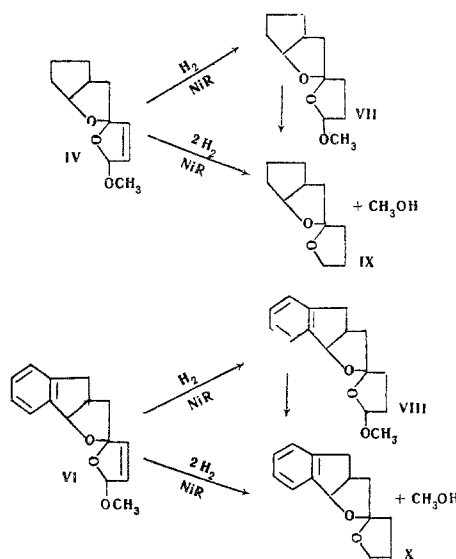
It was previously stated [2, 3], that under conditions where furan alcohols with a hydroxyl a position 3 in the side chain suffer alkoxylation, they cyclize intramolecularly to 2-alkoxy derivatives of 1,6-dioxaspiro[4,4]non-3-ene. The intramolecular alkoxylation reaction takes place generally, and can be extended to various compounds containing a furan ring and a similarly situated hydroxyl group [4, 5], among others, to furfuryl-substituted mono- and bicyclic alcohols of the cyclohexane series [5]. The present paper is concerned with further research in this field, as applied to cyclopentane derivatives.

Experiments using as model compounds 2-furfurylcyclopentanol (I), 2-(5'-methylfurfuryl)cyclopentanol (II), and 2-furfuryl-1-indanol (III) showed that when they were electrolyzed in methanol solution, reaction also took place intramolecularly, giving spiro{perhydrocyclopenta[b]-furan-2, 2'-(5'-methoxy-2', 5'-dihydrofuran)} (IV), spiro{perhydrocyclopenta[b]furan-2, 2'-(5'-methoxy-5'-methyl-2', 5'-dihydrofuran)} (V), and spiro{2, 3, 3a, 8b-tetrahydro-4H-indeno[1, 2-b]furan-2, 2'-(5'-methoxy-2', 5'-dihydrofuran)} (VI) (Table 1).



Hydrogenation of compounds IV and VI under mild conditions (room temperature, over Raney nickel, and under pressure) gave good yields of spiro{perhydrocyclopenta[b]furan-2, 2'-(5'-methoxytetrahydrofuran)} (VII) and spiro{2, 3, 3a, 8b-tetrahydro-4H-indeno[1, 2-b]furan-2, 2'-(5'-methoxytetrahydrofuran)} (VIII) (Table 1).

Hydrogenation under more drastic conditions (over Raney nickel, pressure 100-200 atm, temperature 100°-120° C) led to reduction of the double bond in the 5-membered ring being accompanied by splitting off of the methoxyl group, and formation of spiro{perhydrocyclopenta[b]furan-2, 2'-tetrahydrofuran} (IX), and spiro{2, 3, 3a, 8b}tetrahydro-4H-indeno[1, 2-b]furan-2, 2'-tetrahydrofuran} (X) (Table 1).



The IR spectra of polycyclic spirans IV-X, determined in the region 700-1800  $\text{cm}^{-1}$ , are characterized by a large number of high-intensity lines, which are also characteristic of similar spiroacetal structures [3, 4, 6-8]. (Figs. 1-3). Noteworthy for all the spirans are intense bands in the 1000-1100  $\text{cm}^{-1}$  region, connected with valence vibrations of the C—O—C group.

Deformation vibration bands of methyl and methylene groups are found at 1380 and 1460  $\text{cm}^{-1}$ . The presence of a double bond in compounds IV, V, and VI is confirmed by a band of valence vibrations of the C=C bond at 1650  $\text{cm}^{-1}$ . The spectra of spirans VI, VIII, and X have absorption bands at 1510 and 1630  $\text{cm}^{-1}$ , characteristic of the aromatic ring.

\*For Part XXXI see [1].

Table 1  
Polycyclic Methoxy-1,6-dioxaspiro[4,4]nonanes and their Catalytic Hydrogenation Products

Compound	Bp, ° C (pressure mm)	$d_4^{20}$	$n_D^{20}$	$MR_D$			C, %		H, %		Yield, %
				Found	Calculated		Found	Calculated	Found	Calculated	
IV	84—85 (3)	1.108	1.4870	51.03	50.76	$C_{11}H_{16}O_3$	66.65	67.32	8.08	8.22	72.5
V	99—100 (5)	1.067	1.4761	55.17	55.47	$C_{12}H_{18}O_3$	66.98		8.50		68
							68.49	68.54	8.45	8.62	
VI	129—132 (1)	1.1784	1.5550	66.53	65.73	$C_{15}H_{16}O_3$	69.04		8.49		72
							73.94	73.75	6.70	6.60	
VII	85—86 (5)	1.071	1.4695	51.60	51.33	$C_{11}H_{18}O_3$	73.56		6.82		83
							66.36	66.64	9.50	9.15	
VIII	118—120 (1)	1.1531	1.5366	66.66	66.19	$C_{15}H_{18}O_3$	66.87		9.32		68
							72.63	73.15	7.46	7.36	
IX	85—86 (10)	1.052	1.4742	44.96	45.07	$C_{10}H_{16}O_2$	72.79		7.31		78.5
							71.91	71.39	9.37	9.59	
X	141—144 (3)	1.1352	1.5411	59.87	59.93	$C_{14}H_{16}O_2$	70.99		9.58		71
							77.79	77.75	8.14	7.46	
							77.94		8.19		

Table 2  
Electrolysis Conditions for Compounds II and III

Compound	Quantity of starting material, mole	Current, a	Voltage, V	Temperature in the electrolysis cell, °C
II	0.36	5.0—4.0	9—20	—12
III	0.15	4.0—3.0	8—18	—16

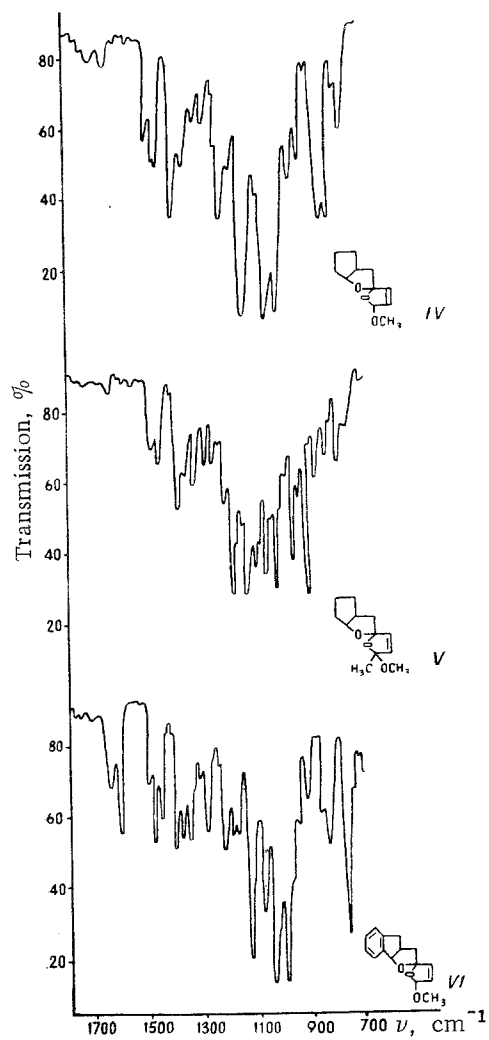


Fig. 1. IR spectra of compounds IV-VI.

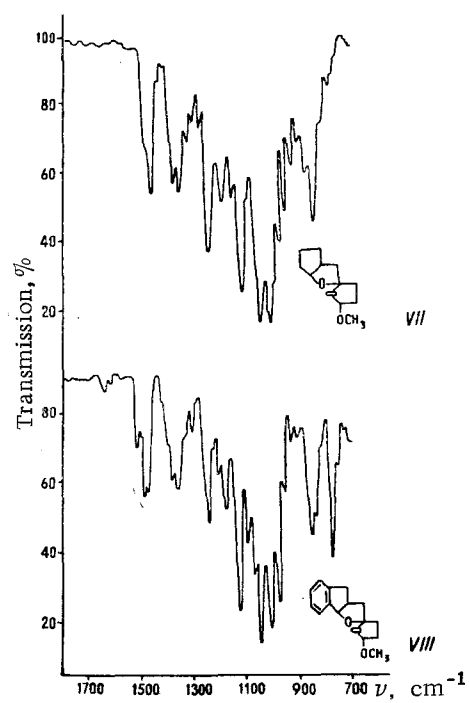


Fig. 2. IR spectra of compounds VII and VIII.

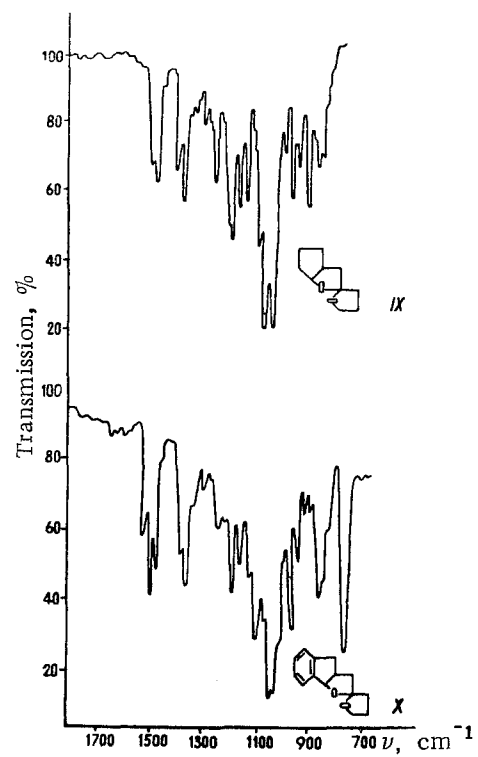


Fig. 3. IR spectra of compounds IX and X.

## EXPERIMENTAL\*

2-Furfurylidene-cyclopentanone (XI) was prepared as per the literature [9].

2-(5'-Methylfurfurylidene)cyclopentanone (XII) was prepared similarly, by condensing 5-methylfurfural with cyclopentanone in the presence of 0.1 N NaOH. Yield 63.6%, bp 151°–153° C (11 mm); 62°–63° C. Found: C 74.55; 74.43; H 6.80; 6.67%. Calculated for  $C_{11}H_{12}O_2$ : C 74.98; H 6.86%.

2-Furfurylidene-1-indanone (XIII) was prepared by condensing furfural with 1-indanone in ethanol solution, with cooling, and in the presence of 20% NaOH solution. Yield 93%, bp 115.5°–116.5° C. Found: C 79.61; 79.58; H 4.90; 5.01%. Calculated for  $C_{14}H_{10}O_2$ : C 79.98; H 4.79%.

2-Furfurylcyclopentanol (I), 2-(5'-methylfurfuryl)-cyclopentanol (II), and 2-furfuryl-1-indanol (III) were prepared by hydrogenating XI, XII, and XIII at 120° C 100–120 atm over Cu chromite catalyst.

2-Furfurylcyclopentanol: yield 70%, bp 110°–111° C (9 mm);  $d_4^{20}$  1.042;  $n_D^{20}$  1.5043. Found: C 71.88; 72.42; H 8.56; 8.60%;  $MR_D$  46.22. Calculated for  $C_{10}H_{14}O_2$ : C 72.26; H 8.49%;  $MR_D$  46.50.

2-(5'-Methylfurfuryl)cyclopentanol: yield 67%, bp 123°–126° C (10 mm);  $d_4^{20}$  1.056;  $n_D^{20}$  1.5030. Found: C 73.35; 73.45; H 9.23; 9.11%;  $MR_D$  50.43. Calculated for  $C_{11}H_{16}O_2$ : C 73.29; H 8.95%;  $MR_D$  50.81.

2-Furfuryl-1-indanol: yield 82%, bp 165°–167° C (5 mm);  $d_4^{20}$  1.1472;  $n_D^{20}$  1.5668. Calculated for  $C_{14}H_{14}O_2$ : C 78.48; H 6.59%;  $MR_D$  61.08.

Spiro[perhydrocyclopenta[b]furan-2, 2'-(5'-methoxy-2', 5'-dihydrofuran)] (IV). 58.2 g (0.35 mole) freshly-distilled 2-furfurylcyclopentanol and 5 g (0.051 mole)  $NH_4Br$  in 220 ml MeOH were placed in an electrolysis cell with a Ni cathode and a carbon anode [10, 11]. The solution was cooled to  $-12^\circ$ , and kept there during the entire run. Current 4–5 A, voltage 9–20 V. At the end of the electrolysis, the solution was treated with NaOMe (1.2 g Na in 20 ml MeOH). MeOH and  $NH_3$  were vacuum-distilled off on a water-bath. The precipitate of NaBr was filtered off and washed on the filter with ether a few times. The ether was taken off, and the residue vacuum-distilled, yield 49.5 g (72.5%).

Table 2 gives the electrolysis conditions for compounds II and III.

Spiro[perhydrocyclopenta[b]furan-2, 2'-(5'-methoxy-tetrahydrofuran)] (VII). 30.0 g compound IV, 35 ml

dry EtOH, and 3 g Raney Ni were charged into a 250 ml rotating steel autoclave. Initial hydrogen pressure 80 atm, room temperature. Hydrogenation was complete when 3.8 l hydrogen had been absorbed. The catalyst was filtered off, the solvent distilled off on a water-bath, and the residue then vacuum-distilled.

Compound VI was hydrogenated similarly.

Spiro[perhydrocyclopenta[b]furan-2, 2'-tetrahydrofuran] (IX). 20.0 g compound VII, 45 ml dry EtOH, and 2 g Raney Ni were charged into a 250 ml rotating steel autoclave. Initial hydrogen pressure 120 atm, temperature 100° C. Hydrogenation was complete when 5 l hydrogen had been absorbed. The product was worked up in the way described above. The residue was vacuum-distilled.

The IR spectra were determined with a H-800 (Hilger) spectrophotometer, over the range 700–1800  $cm^{-1}$ , using a NaCl prism. Two compounds were investigated in the liquid state, in the form of capillary films between NaCl plates. \*\*

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