A STUDY OF FURAN COMPOUNDS

XXXVI. Formation and Hydrogenation of Polyalkyl Substituted 2-Methoxy-1, 6-dioxaspiro [4.4]nonenes-3*

A. A. Ponomarev, A. D. Peshekhonova, and I. A. Markushina

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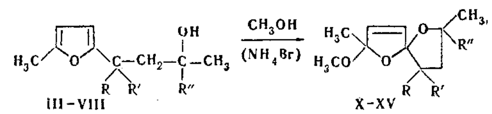
This communication describes the electrolytic methoxylation of secondary and tertiary γ-furylalkanoles containing a methyl group in position 5 of the furan ring and also in certain cases the gem-dimethyl group at the first carbon atom from the ring in the side chain. During this process previously unknown derivations of 2-methyl-2-methoxy spirononenes were obtained. Catalytic hydrogenation of the latter at room temperature leads mainly to the formation of the corresponding spirononane and the tetrahydrofuranic ketone, which indicates that hydrogenolysis readily proceeds at the carbon-oxygen bonds.

The reaction of intramolecular electrolytic alkoxylation of the 1-(α-furyl) 3-alkanols leads to the formation of 2-methoxy-1, 6-dioxaspiro[4.4]non-3-ene and its homologs [2, 3]. More complex systems of a similar type may also be obtained [4–7]. It has been eslished [2, 3, 5, 6] that 2-methoxy-1, 6-dioxaspiro [4.4]-non-3-ene, and its homologs containing alkyl radicals in position 7 of the spirane ring, incorporate hydrogen at the double bond during catalytic hydrogenation over Raney nickel at room temperature and are converted into the corresponding 2-methoxy-1, 6 dioxaspiro[4.4]nonanes with yields of 80–90%, and at 120° C undergo hydrogenolysis at the CH_3O—C bond to form the corresponding 1, 6-dioxaspiro[4.4]nonanes. Other methods for obtaining the latter compounds have been described [8–13].

Synthesis of the polyalkyl-substituted spiranes of the 2-methoxy-1, 6-dioxaspiro[4.4]non-3-ene group, described in this report was used for further study of the substitution reaction in this series. In addition, in relation to the well-known factors concerning the effect of the accumulation of alkyl radicals in the aliphatic chain on the processes of ring formation [12-15, 23], it was of great interest to determine to what extent these structural characteristics affect the electrochemical process of the formation of 2-methoxy-1, 6-dioxaspiro[4.4]non-3-ene, and also to what extent they affect properties of the latter

1-(5-Methyl-2'furyl)-3-butanone (I), 2-(5'-methyl-2'-furyl)-2-methyl-4-pentanone (II), 1-(5'-methyl-2'-furyl-3-butanol (III), 2-(5'-methyl-2'-furyl)-2-methyl-3-pentanol (IV), 2-(5'-methyl-2'-furyl)-2, 4-dimethyl-4-hexanol (V), 1-(5'-methyl-2'-furyl)-3-methyl-3-butanol (VI), 1-(5'-methyl-2'-furyl)-3-methyl-3-pentanol (VII), 2-(5'-methyl-2'-furyl)-2, 4-dimethyl-4-pentanol (VIII), and 2-(5'-methyl-2'-furfuryl)-cyclopentanol (IX) were obtained for the above-mentioned synthesis by methods described in the experimental part of the report. By electrolytic alkoxylation of the above alcohols in methanol, it was possible to synthesize the polyalkyl-substituted 2-methoxy-1, 6-dioxaspiro[4.4]non-3-enes according to the scheme:



By this method 2-methoxy-2, 7-dimethyl-(X), 2-methoxy-2, 7, 7-trimethyl-(XI), 2-methoxy-2, 7-dimethyl-7-ethyl-(XII), 2-methoxy-2, 7, 9, 9-tetramethyl-(XIII), 2-methoxy-2, 7, 7, 9, 9-pentamethyl-(XIV) and 2-methoxy-2, 7, 9, 9-tetramethyl-7-ethyl-1, 6-dioxaspiro[4.4]non-3-ene (XV) were obtained (Table 1). Spiro[3H-cyclopentafuran-2, 2'-(5'-methoxy-5'-methyl) furan] (XVI) was formed from compound IX [6].

Assuming that the yields of the above products to a certain extent characterize the ease of ring formation, it can be seen that yields of compounds X, XI and XVI were 62–68%, i. e., approximately the same as those (63–76%) for the 7-alkyl- and 7, 7-dialkyl-substituted spirononenes obtained previously [2, 3]. However, even for the trialkyl-derivative XII the yields increase to 82% and reach 82–95% for the tetra- and pentaalkyl-derivatives XIII-XV which contain the 9, 9 gemdimethyl group. One should note that 2-methoxy-1, 6-dioxaspiro[4.4]non-3-ene is formed from 1-(α-furyl)-3-propanol, unsubstituted in the side chain with a yield of 53% [2, 3].

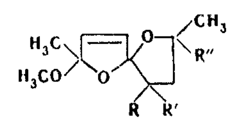
From the above fact one may conclude that ring formation under the conditions of electrolysis proceeds more readily in compounds with a branched chain, especially in the presence of the hema-dimethyl groups. This conclusion is in agreement with previous reports [12, 15, 23].

If the presence of the methyl group in position 5 of the furan ring in the alcohols has no marked effect on the formation of 2-methyl-2-methoxy-1, 6-dioxaspiro[4.4]non-3-enes, the properties of the latter are essentially dependent on this condition. For example, catalytic hydrogenation of similar systems over Raney nickel at room temperature leads to the formation of

*For part XXXV, see [1].

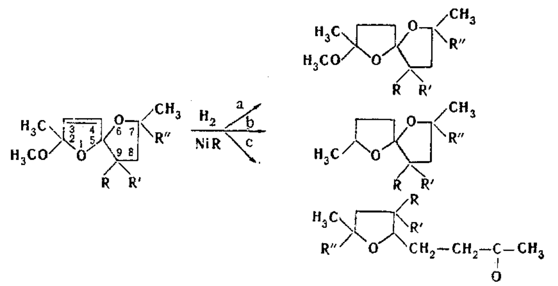
Table 1

Polyalkyl Substituted 2-Methoxy-1, 5-dioxaspiro[4.4]non-3-enes



Compound	R	R′	R″	Obtained from	Bp, ° C (pressure, mm)	n_D^{20}	d_4^{20}	MR_D found, %	MR_D calculated, %	Empirical formula	Found, % C	Found, % H	Calculated, % C	Calculated, % H	Yield, %
X	H	H	H	III	80—82 (8)	1.4510	1.037	47.85	48.44	$C_{10}H_{16}O_3$	65.38 65.53	8.53 8.62	65.19	8.75	62
XI	H	H	CH_3	VI	86—88 (8)	1.4472	1.007	52.64	53.06	$C_{11}H_{18}O_3$	66.65 66.40	9.49 9.18	66.64	9.15	66
XII	H	H	C_2H_5	VII	91.5—93 (8)	1.4521	1.001	57.23	57.68	$C_{12}H_{20}O_3$	68.02 68.33	9.93 9.50	67.89	9.50	82
XIII	CH_3	CH_3	H	IV	83—84 (7)	1.4540	1.000	57.46	57.68	$C_{12}H_{20}O_3$	67.45 67.25	9.46 9.46	67.89	9.50	93
XIV	CH_3	CH_3	CH_3	VIII	[mp. 41°]	—	—	—	—	$C_{13}H_{22}O_3$	68.08 68.09	9.45 9.77	68.99	9.80	82
XV	CH_3	CH_3	C_2H_5	V	106—107 (9)	1.4583	0.9879	66.41	66.91	$C_{14}H_{24}O_3$	69.67 69.56	10.21 10.07	69.96	10.07	95

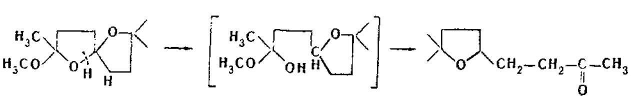
several products:



In all previously studied cases [2, 3, 5, 6] under these conditions the reaction proceeded only in direction **a**, (i. e., it was limited by the hydrogenation of the double bond). On hydration of **X–XII** and **XVI** where R = = R' = H), methoxyspirononane (direction a) either is not formed at all or is present in an insignificant amount (**X**). The corresponding spirononane and tetrahydrofuran ketone are formed in approximately equal quantities from compounds **XI** and **XVI**. Mainly spirononane and a small quantity of ketone are formed from compound **XII**. The total yield of the products was 62–88%.

Thus in all cases examined the main directions are **b** and **c**, i. e., not only hydrogenation of the double bond but also hydrogenolysis.

Reaction **b**, which comprises the hydrogenolysis of bond CH_3O—C and the formation of the ketone is apparently the result of hydrogenolysis at the $-O_1-C_5$ bond and subsequent cleavage of a molecule of methyl alcohol from the arising semiacetal:



The above account indicates that there is a marked weakening of the CH_3O—C and $-O_1-C_5$ bonds in the spirononenes of the above mentioned structure in comparison with analogous compounds not containing a methyl radical in position 2 [2, 3]. In addition, it is of interest to note that, under the same conditions, hydrogenation of compound **XIII**, which differs from **XI** and **XII** only by the presence of the gem-dimethyl group in position 9, leads to the formation of the corresponding methoxyspirononane (**XIII**) with a yield of 83% and a small quantity of spirononane (**XXIV**).

This is of interest in relation to the question concerning the laws in subsequent catalytic transformations of furan derivatives during hydrogenation of the compounds on nickel, which, in accordance with the principle of energetic conformation, proceed with more difficulty the higher their energetic barrier, calculated from the mean bond energies [16, 17]. However, structural characteristics of the molecule cause the value of the latter to fluctuate within large limits as it does in the case examined.

The UV and IR spectra provide frequent confirmation of the structure of the tetrahydrofuran ketones. An intensive band in the spectrum at 1725–1728 cm^{-1} corresponds to the frequency of the valency oscillation of the C=O bond of the ketones. The presence of the tetrahydrofuran ring is confirmed by the 1088 cm^{-1} frequency, characterizing the valency oscillation of the C—O—C bond of tetrahydrofuran [18]. The position and intensity of the maximum absorption in the UV spectra (λ_{max} 285 nm, $\log_\varepsilon$ 1.84 in methanol; λ_{max} 289 nm, $\log_\varepsilon$ 1.7 in isoctane) and the bathochromic effect on transfer from methanol to isooctane also provide evidence for the presence of the ketone group in the compounds **XIX**, **XXI**, and **XXVII**. Compounds **VI**, **VII**, **X–XV**, **XVII**, **XIX–XXIII**, **XXV–XXVII** were obtained for the first time.

EXPERIMENTAL*

Ketone I was obtained on hydrogenation of 5-methylfurfurylidene acetone in the presence of Raney nickel. Hydrogenation was conducted in a rotating steel autoclave at room temperature in a medium of methyl alcohol and at an initial hydrogen pressure of 120 atm, and was terminated by the absorption of a calculated quantity of hydrogen. Yield was 76%, which exceeds the yield of this ketone by the well-known methods [19]. bp 96–97° C (11 mm); d_4^{20} 1.009; n_D^{20}, 1.4720. Found: C 70.88, 71.07; H 8.00, 7.73; MR_D 46.26. Calculated for $C_9H_{12}O_2$, %: C 71.03; H 7.95; MR_D 42.28. According to data in the literature [19], bf 97–98° C (12 mm).

The ketone II and furanic alcohols III, IV, V and IX were synthesized according to methods described in the literature [6, 9, 13, 20].

The furanic alcohols VI and VII were obtained from compound I and methyl- and ethylmagnesium bromide respectively with yields of 83 and 77%.

Compound **VI**: Bp 98–100° C (7 mm); d_4^{20} 0.9925; n_D^{20} 1.4749. Found, %: C 71.01, 70.92; H 9.79, 9.35. MR_D 47.71. Calculated for $C_{10}H_{16}O_2$, %: C 71.39; H 9.59; MR 48.41.

Compound **VII**: bp 106–107° C (7 mm); d_4^{20} 0.9830; n_D^{20} 1.4788. Found, %: 72.30, 72.05; H 9.96, 9.71. MR_D 52.57. Calculated for $C_{11}H_{18}O_2$, %: C 72.49; H 9.96; MR_D 53.03.

Compound **VIII** was prepared from compound II and methyl magnesium bromide [24]. Yield was 75.5%; bp 91–93° C (7 mm); d_4^{20} 0.9618; n_D^{20} 1.4730. Found, %: C 73.46, 73.43; H 9.87, 9.65. MR_D 57.25. Calculated for $C_{12}H_{20}O_2$, %: C 73.43; H 10.27; MR_D 57.65.

Electrolytic alkylation of the γ-furylalkanols was conducted in an electrolyzer with a nickel cathode and carbon anode, the arrangement of which has been described previously [21, 22].

2-Methoxy-2,7-dimethyl-1,6-dioxaspiro[4.4]non-3-ene (X). A 73 g quantity of freshly prepared furanic alcohol III and 5 g of ammonium bromide were dissolved in 220 ml of methyl alcohol and transferred to the electrolyzer. Electrolysis was conducted at a temperature of −15° C with a current of 4–2 A and a voltage of 10–12 V. When electrolysis was complete, the solution was treated with sodium methoxide (1.2 g metallic sodium in 20 ml methyl alcohol). The methyl alcohol and ammonia were removed by distillation in a water bath at reduced pressured, and the precipitate of sodium bromide was removed by filtration and washed with ether. After removing the ether, the residue was distilled under vacuum.

The electrolytic methoxylation of the furanic alcohols (**IV–IX**) was conducted by a similar method, as a result of which 1,6-dioxaspiro[4.4]-non-3-enes (**XI–XV**) (Table 1) and also spiro[3H-cyclopentafuran-2,2-(5-methoxy-5-methylfuran] (**XVI**) [6] were obtained; bp was 99–100° C (5 mm); n_D^{20}, 1.4761; yield, 68%.

Data concerning the conditions of electrolysis of the solutions of furanic alcohols are presented in Table 2.

In the IR spectra of the methoxyalkylspirononenes there is a frequency of valence oscillation of the C=C bond of 1640 cm^{-1}. The presence of the methoxyl group is confirmed by the frequency of 2832 cm^{-1}. The gem-dimethyl group is characterized by the double bond 1372–1385 cm^{-1}.

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*With the participation of T. I. Gubina.

Table 2

Conditions of Electrolysis of the γ-Furylalkanols

γ-Furylalkanols	Quantity of original substance	Current, A	Voltage, V	Temperature in the electrolyzer, °C
III	0.47	4—3	9—21	−15
IV	0.29	4—3	8—18	−23
V	0.25	4—3	11—18	−23
VI	0.34	4—3,5	8—20	−13
VII	0.23	4—2,5	9—18	−20
VIII	0.20	4—3	10—15	−20

Hydrogenation of compounds **X–XVI** was conducted in rotating steel autoclaves at room temperature in a medium of absolute methyl alcohol at an initial hydrogen pressure of 100–120 atm. Raney nickel at a concentration of 10% in relation to the weight of the substance was used as the catalyst. Hydrogenation was completed when hydrogen ceased to be absorbed. Usually the quantity of absorbed hydrogen was equivalent to 1.5–2 mole/mole substance.

The following compounds were obtained from **X** during hydrogenation under these conditions. **2-Methoxy-2, 7-dimethyl-1, 6-dioxaspiro[4.4]nonane (XVII)** with a yield of 15.5%; bp 89–91° C (17 mm); d_4^{20} 1.0160; n_D^{20} **1.4436**. Found, %: C 64.70; 64.79; H 10.02, 9.79; MR_D 48.65. Calculated for $C_{10}H_{18}O_3$, %: C 64.49; H 9.74; MR_D 48.91. **2, 7-Dimethyl-1, 6-dioxaspiro[4.4]nonane (XVIII)**, yield 7.5%; mp 94–96° C (67 mm); n_D^{20} 1.4386. Data in the literature [9]: bp 167–169° C (760 mm); n_D^{20} 1.4389. **1-(5'-Methyl-2'-tetrahydrofuryl)butan-3-one) (XIX).** Yield was 54%; bp 102–104° C (17 mm); d_4^{20} 0.9899; n_D^{20} 1.4605. Found, %: C 68.90, 68.72; H 9.71, 9.64; MR_D 43.39. Calculated for $C_9H_{16}O_2$, %: C 69.19; H 10.32; MR_D 43.21.

From compound XI: 2, 7, 7-Trimethyl-1, 6-dioxaspiro[4.4]nonane (XX) with a yield of 31%. bp was 72–74° C (25 mm); d_4^{20} 0.9462; n_D^{20} 1.4351. Found, %: C 70.37, 70.77; H 10.76, 10.86; MR_D, 47.24. Calculated for $C_{10}H_{18}O_2$, %; C 70.55; H 10 66; MR_D 47.27. **1-(5', 5'-Dimethyl-2'-tetrahydrofuryl)butan-3-one (XXI)**, yield 31.5%; bp 112–114° C (18 mm); d_4^{20} 0. 9710; n_D^{20} 1. 4559. Found, %: C 69.98, 69.92; H 10.70, 10.42; MR_D 47.65. Calculated for $C_{10}H_{18}O_2$, %: C 70.55; H 10.66%; MR_D 47.83.

From compound XII, 2, 7-Dimethyl-7-ethyl-1, 6-dioxaspiro[4.4]-nonane (XXII), with a yield of 67.3%; bp 92–93°C (25 mm); d_4^{20} 0.9387; n_D^{20}, 1.4408; Found, %: C 71.88, 72.05; H 11.08, 11.12; MR_D 51.82. Calculated for $C_{11}H_{20}O_2$, %; C 71.69; H 10.94; MR_D 51.88. **1-(5'-Methyl-5'-ethyl-2'-tetrahydrofuryl)butan-3-one (XXVII)** with a yield of 10.6%; bp 103–105° C (5 mm); d_4^{20} 0.9724; n_D^{20} 1.4630. Found, %: C 71.44, 70.88; H 11.01, 10.80 ; MR_D 52.26. Calculated for $C_{11}H_{20}O_2$, %: C 71.69; H 10.94; MR_D 52.45.

From Compound XIII. 2-Methoxy-2, 7, 9, 9-tetramethyl-1, 6-dioxaspiro[4.4]nonane (XXIII) with a yield of 83.3%; bp 101–103° C (15 mm); d_4^{20} 0.9907; n_D^{20} 1.4501. Found, %: C 66.96, 66.92; H 10.21, 9.83; MR_D 58.14. Calculated for $C_{12}H_{22}O_3$, %: C 67.25; H 10.35 ; MR_D 58.15. **2, 7, 9, 9-Tetramethyl-1, 6-dioxaspiro[4.4]nonane (XXIV)**; yield was 4.5%; bp 87–89° C (25 mm); n_D^{20} 1.4390; data in the literature [13]: bp 87–89° C (25 mm); n_D^{20} 1.4391.

On hydrogenation of compound **XVI** the following compounds were obtained. **Spiro[3H-cyclopentafuran-2, 2'-(5'-methyl)tetrahydrofuran] (XXV)**, yield 41.5%; bp 103–104° C (20 mm); d_4^{20} 1.019; n_D^{20} 1.4680. Found, %: C 71.89, 71.96; H 9.72, 9.68 MR_D 49.72. Calculated for: $C_{11}H_{18}O_2$, %: C 72.51; H 9.93; MR_D 49.68. **1-(α-Cyclopentatetrahydrofuryl)butan-3-one (XXVI)**, yield 46%; bp 98–99° C (5.5 mm); d_4^{20} 1.045; n_D^{20} 1.045; n_D^{20} 1.4815. Found, %: C 72.08, 71.91; H 9.73 9.37; MR_D 49.68. Calculated for $C_{11}H_{18}O_2$, %: C 72.51; H 9.93; MR_D 50.25.

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Chernyshevskii Saratov State University