RESEARCH ON FURAN COMPOUNDS

XXXIII. Some New Homologs of 1,6-Dioxaspiro[4, 4]Nonane, Furan, and Tetrahydrofuran Alcohols*

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Pressure hydrogenation using Raney nickel or ruthenium on charcoal, of secondary and tertiary γ-furylalkanols is described. The products are the corresponding homologs of 1,6-dioxaspiro[4,4]nonane and tetrahydrofuran alcohols, the relative yields being determined by the structure of the initial furan alcohol and the type of catalyst.

As was previously shown [2–6], pressure catalytic hydrogenation of secondary and tertiary furan alcohols with a hydroxyl in the side chain at a tertiary carbon atom (γ-furylalkanols), gives the corresponding tetrahydrofuran alcohols and homologs of 1,6-dioxaspiro-[4, 4]nonane. It has also been shown that formation of the latter depends on the structure of the initial alcohol and the type of catalyst [5].

In order to obtain new homologs of 1,6 dioxaspiro [4, 6]nonane with a view to subsequently investigating substitution in the series, furyl alcohols with a methyl group at position 5 in the furan ring and various alkyl radicals at the first carbon atom in the side chain away from the ring were synthesized and catalytically hydrogenated. Table 1 shows the new furan alcohols.

The γ-furylalkanols were hydrogenated at 100–110 atm and 100–120° C in the presence of Raney nickel (NiR) or ruthenium on charcoal (5% Ru/C). This method gave a series of tetrahydrofuran alcohols (Table 2), and homologs of 1,6-dioxaspiro[4, 4]nonanes (Table 3). Such alkyl-substituted spirans were previously unknown.

The regularities previously noted were confirmed [1].

Use of the 5% Ru/C catalyst generally gave considerably higher yields than NiR.

The presence of alkyl substituents (especially isopropyl) in the side chain at the first carbon atom from the ring in the starting furan alcohol, facilitates cyclization, and formation of spirans. The yields of homologs of 1,6-dioxaspiro[4, 4]nonane from tertiary γ-furylalkanols were invariably higher (up to 48% with NiR) than from secondary ones (up to 33%). Obviously, a methyl group at position 5 in the furan ring also facilitates cyclization.

The UV spectra of furan alcohols IV–VIII were characterized by intense absorption at 220 nm lg ε ≃ ≃ 4.0–4.5, and a less intense one in the 275–280 nm region lg ε ≃ 1.5, appearing as inflections.

The IR spectra of the compounds synthesized confirm the characteristic peculiarities of their structure. Thus in the cases of furan alcohols IV–VIII, the vibrations frequencies of the furan ring (1620, 1570, 1468 cm^{-1}) and the bond =C—O—C= (1022, 1222 cm^{-1}) should be mentioned. The frequency of the —C—O—C— bond [8] (1080 cm^{-1}) indicates that a tetrahydrofuran ring is present in compounds IX–XIII.

The wide band at 3400–3450 cm^{-1} in the spectra of compounds IV–XIII corresponds to the valence vibration of an intermolecularly hydrogen bonded OH group. The 1125 cm^{-1} frequency, observed with alcohols IV–VI, IX–XI, corresponds to the valence vibration of the C—O bond of secondary alcohols, and in tertiary alcohols VII, VIII, XII, and XIII, that frequency is displaced to 1140 cm^{-1}.

The IR spectra of spirans XIV–XVIII contain a number of intense absorption bands in the 800–1300 cm^{-1} frequencies, characteristic of such bicyclic systems [9, 10].

The presence of a gem-dimethyl or isopropyl radical in the substances obtained found expression in the spectra in the form of a doublet band with frequencies 1370 and 1388 cm^{-1} (see figure).

EXPERIMENTAL*

3-(5'-Methyl-2'-furyl)hexan-5-one (I) was prepared from 5-methylfurfurylideneacetone and ethylmagnesium bromide, using the method of [11], yield 68%. Liquid, bp 111–113° (15 mm); d_4^{20} 1.0612; n_d^{20} 1.4715. Found: C 73.49, 73.54; H 8.80, 9.30%; MR_d 51.72, calculated for $C_{11}H_{16}O_2$: C 73.30; H 8.95%; MR_d 51.52.

UV spectrum (in MeOH): λ_{max}, mμ (lg ε): 217 (4.04); 278 (2.11). The IR spectrum has bands characteristic of the furan ring (1620, 1581, 1470 cm^{-1}).

2-(5'-Methyl-2'-furyl)-2-methylpentan-4-one (II) was prepared by a known method [13], yield 70%.

3-(5'-Methyl-2'-furyl)-2-methylhexan-5-one (III) was synthesized from 5-methylfurfurylideneacetone and isopropylmagnesium bromide [13], similarly to I, yield 76%.

3-(5'-Methyl-2'-furyl)-2-methylhexan-5-ol (IV), 2-(5'-methyl-2'-furyl)-2-methylpentan-4-ol (V), and 3-(5'-methyl-2'-furyl)-2-methylhexan-5-ol (VI) were prepared by hydrogenating the corresponding furan ketones I–III. Hydrogenation was effected in rotating steel autoclaves, using MeOH as the solvent, initial hydrogen pressure 100–110 atm and temperature 120°, in the presence of 10–12% Cu chromite catalyst based on the mass of the compound [14].

Under these conditions formation of the secondary furan alcohols was accompanied by insignificant amounts (3.5–5%) of the corresponding homologs of 1,6-dioxaspiro[4,4]nonane (XIV–XVI).

2-(5'-Methyl-2'-furyl)-2,4-dimethylhexan-4-ol (VII) and 3-(5'-methyl-2'-furyl)-2,5-dimethylheptan-5-ol (VIII) were synthesized

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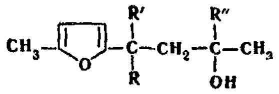
*For Part XXXII see [1].

*Assisted by L. M. Moskalenko

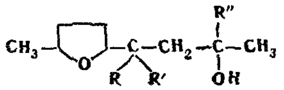
Table 1

Furan Alcohols 

Compound	R	R′	R″	Prepared from	Bp, °C (pressure, mm)	n_D^{20}	d_4^{20}	MR_D		Formula	Found, %		Calculated, %		Yield, %
								Found	Calculated		C	H	C	H	
IV	H	C_2H_5	H	I	99—101 (7)	1.4730	0.9693	52.75	53.03	$C_{11}H_{18}O_2$	72.23 71.94	9.66 10.13	72.49	9.96	83
V	CH_3	CH_3	H	II	90—92 (7)	1.4758	0.9760	52.63	53.03	$C_{11}H_{18}O_2$	72.62 72.80	9.65 9.63	72.49	9.96	84
VI	H	C_3H_7 iso	H	III	103—104 (6)	1.4728	0.9580	57.45	57.65	$C_{12}H_{20}O_2$	73.22 72.84	10.14 10.35	73.43	10.27	78
VII	CH_3	CH_3	C_2H_5	II	104—106 (7)	1.4740	0.9581	61.69	62.27	$C_{13}H_{22}O_2$	74.28 73.76	10.62 10.60	74.24	10.55	74
VIII	H	C_3H_7 iso	C_2H_5	III	112—114 (7)	1.4714	0.9466	66.29	66.89	$C_{14}H_{24}O_2$	74.88 74.90	10.96 10.54	74.95	10.78	75

Table 2

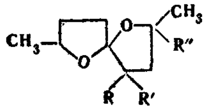
Tetrahydrofuran Alcohols



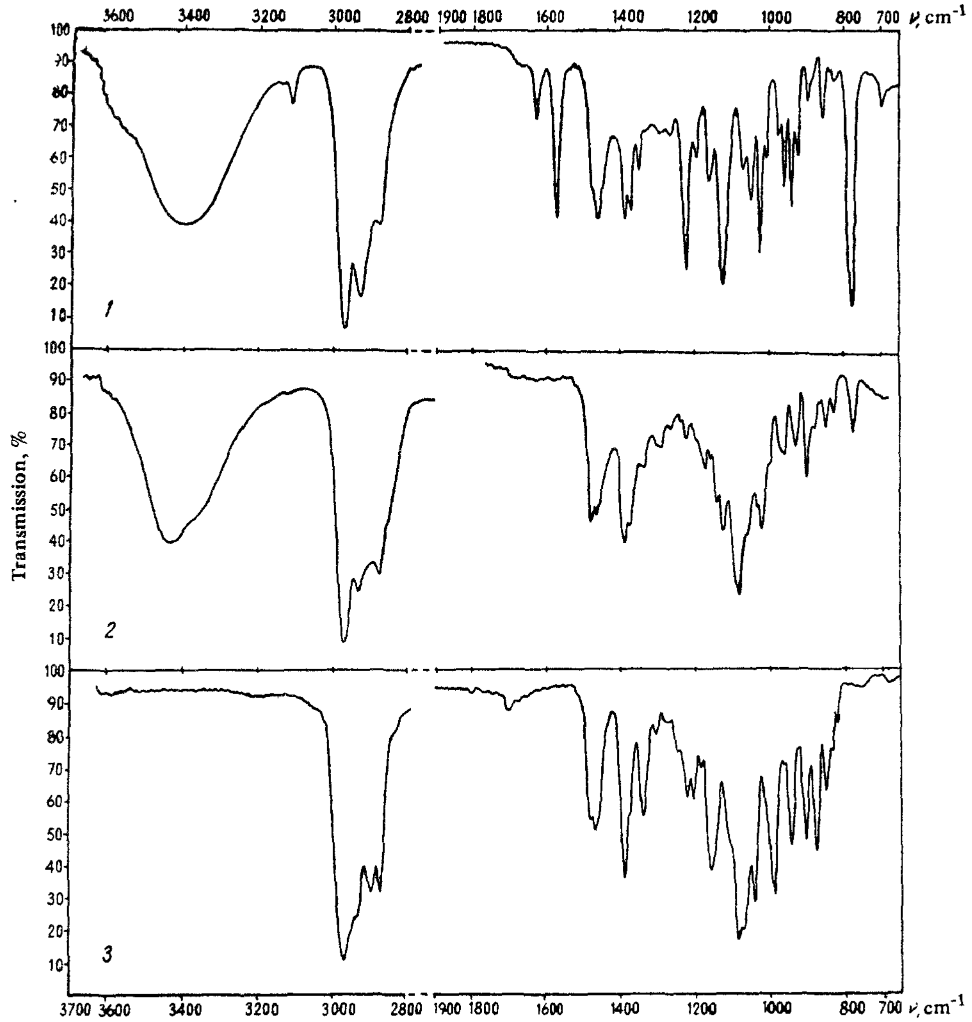
Compound	R	R′	R″	Prepared from	Bp, °C (pressure, mm)	n_D^{20}	d_4^{20}	MR_D		Formula	Found, %		Calculated %		% yield, based on the catalyst	
								Found	Calculated		C	H	C	H	NIR	5% Ru/C
IX	H	C_2H_5	H	IV	113—115 (10)	1.4578	0.9439	53.83	53.97	$C_{11}H_{22}O_2$	70.98 70.60	11.82 11.69	70.92	11.90	68	58
X	CH_3	CH_3	H	V	102—104 (10)	1.4538	0.9321	54.08	53.97	$C_{11}H_{22}O_2$	70.94 71.11	11.90 11.88	70.92	11.90	70	59,3
XI	H	C_3H_7 iso	H	VI	117—119 (10)	1.4575	0.9345	58.43	58.58	$C_{12}H_{24}O_2$	71.98 72.08	12.23 12.21	71.95	12.08	64	35
XII	CH_3	CH_3	C_2H_5	VII	112—114 (10)	1.4583	0.9311	62.85	63.20	$C_{13}H_{26}O_2$	72.85 72.61	12.32 12.04	72.84	12.23	35	—
XIII	H	C_3H_7 iso	C_2H_5	VIII	124—126 (10)	1.4668	0.9379	67.53	67.82	$C_{14}H_{28}O_2$	73.39 73.77	11.86 11.80	73.63	12.36	41.6	—

Table 3

Homologs of 1,6-Dioxaspiro[4,4]nonane



Compound	R	R'	R''	Prepared from	Bp, °C (pressure, mm)	n_D^{20}	d_4^{20}	MR_D		Formula	Found, %		Calculated, %		% yield, based on the catalyst	
								Found	Calculated		C	H	C	H	NiR	5% Ru/C
XIV	H	C_2H_5	H	IV	95—97 (25)	1.4418	0.9360	52.07	51.88	$C_{11}H_{20}O_2$	71.24 71.20	10.45 10.78	71.69	10.94	25.6	30.6
XV	CH_3	CH_3	H	V	87—89 (25)	1.4391	0.9393	51.61	51.88	$C_{11}H_{20}O_2$	71.59 71.80	11.06 10.68	71.69	10.94	25	31
XVI	H	C_3H_7 iso	H	VI	109—111 (25)	1.4465	0.9416	56.41	56.50	$C_{12}H_{22}O_2$	72.52	11.30	72.68	11.18	33	50
XVII	CH_3	CH_3	C_2H_5	VII	103—105 (20)	1.4442	0.9229	61.13	61.12	$C_{13}H_{24}O_2$	73.18 73.15	11.55 11.19	73.54	11.39	39	—
XVIII	H	C_3H_7 iso	C_2H_5	VIII	111—113 (20)	1.4477	0.9184	65.90	65.74	$C_{14}H_{26}O_2$	74.43 74.13	11.84 12.04	74.28	11.58	48	—



IR spectra: 1) 2-(5'-methyl-2'-furyl)-2-methylpentan-4-ol (V); 2) 2-(5'-methyl-2'-tetrahydrofuryl)-2-methylpentan-4-ol (X); 3) 2, 7, 9, 9-tetramethyl-1, 6-dioxaspiro[4, 4]nonane (XV).

as described in [4] from ethylmagnesium bromide and II and III respectively.

3-(5'-Methyl-2'-tetrahydrofuryl)hexan-5-ol (IX), 2-(5'-methyl-2'-tetrahydrofuryl)-2-methylpentan-4-ol (X), 3-(5'-methyl-2'-tetrahydrofuryl)-2-methylhexan-5-ol (XI), 2-(5'-methyl-2'-tetrahydrofuryl)-2,4-dimethylhexan-4-ol (XII), 3-(5'-methyl-2'-tetrahydrofuryl)-2,5-dimethylheptan-5-ol (XIII), and also 2,7-dimethyl-9-ethyl-1,6-dioxaspiro[4,4]nonane (XIV), 2,7,9,9-tetramethyl-1,6-dioxaspiro-[4,4]nonane (XV), 2,7-dimethyl-9-isopropyl-1,6-dioxaspiro[4,4]-nonane (XVI), 2,7,9,9-tetramethyl-7-ethyl-1,6-dioxaspiro[4,4]-nonane (XVII), and 2,7-dimethyl-9-isopropyl-1,6-dioxaspiro[4,4]-nonane (XVIII), were obtained by hydrogenating alcohols IV–VIII in absolute MeOH in an autoclave, under hydrogen pressure 100-110 atm, and temperature 120°. The catalysts used were NiR and 5% Ru/C, 10% of the mass of the material.

Compounds I, IV–XVIII were obtained for the first time.

The UV spectra were observed in MeOH solution, using a SF-4 spectrophotometer, the IR spectra were observed over the range 700–3700 cm^{-1}, using a twin-beam IR/UR-10 spectrophotometer (Zeiss), with NaCl and LiF prisms. All the compounds were observed as capillary films between KBr plates.

REFERENCES

1. A. A. Ponomarev, I. A. Markushina, and L. V. Popova, KhGS [Chemistry of Heterocyclic Compounds], 411, 1967.

2. A. A. Ponomarev, V. A. Afanas'ev, and N. I. Kurochkin, ZhOKh, **23**, 1426, 1953; DAN, **87**, 983, 1952.

3. A. A. Ponomarev, Z. V. Til, I. A. Markushina, and K. M. Sapunar, ZhOKh, **27**, 110, 1957; DAN, **93**, 297, 1953.

4. A. A. Ponomarev, Z. V. Til, A. D. Peshekhonova, and V. P. Reshetov, ZhOKh, **27**, 1369, 1957.

5. A. A. Ponomarev, V. A. Sedavkina, and Z. V. Til, ZhOKh, **33**, 1303, 1963.

6. A. A. Ponomarev, A. S. Chegolya, N. S. Smirnova, and V. N. Dyukareva, KhGS [Chemistry of Heterocyclic Compounds], 163, 1966.

7. A. R. Katritzky and J. M. Lagowsky, J. Chem. Soc., 657, 1959.

8. H. Tschamler and R. Leutner, Mon., **83**, 1502, 1952.

9. C. R. Eddy, M. E. Wall, and M. K. Scott, Anal. Chem., **25**, 266, 1953.

10. A. A. Ponomarev and I. A. Markushina, ZhOKh, **31**, 554, 1961.

11. A. A. Ponomarev and V. A. Sedavkina, Uch. zap. SGU, **71**, 143, 1959.

12. N. I. Shuikin, A. D. Petrov, V. G. Glukovtsev, I. F. Bel'skii, and G. V. Skvortsova, Izv. AN SSSR, OKhN, 1682, 1964.

13. A. A. Ponomarev, M. V. Noritsina, and A. P. Kriven'ko, KhGS [Chemistry of Heterocyclic Compounds], 923, 1966.

14. A. A. Ponomarev, Synthesis and Reactions of Furan Compounds [in Russian], Izd. SGU, Saratov, 97, 1960.

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