#### FURAN COMPOUNDS

### XLV.\* DEHYDROBROMINATION OF MONOBROMO DERIVATIVES

OF 1,6-DIOXASPIRO [4.4] NONANES

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A method for the synthesis of alkyl homologs of 1,6-dioxaspiro[4.4]-3-nonene (I) by dehydrobromination of bromo derivatives of 1,6-dioxaspiro[4.4]nonanes (II) was developed. Interesting isomeric transformations of spirononenes (I) into  $\gamma$ -furylalkanols (III) were discovered. The dehydrobromination reaction also makes it possible to determine the location of bromine for nonequivalent spiran rings.

The cleavage of hydrogen bromide from monospirans II was undertaken in order to obtain a new group of spirocyclic acetals (I). Precisely this type of unsaturated spirans and their derivatives are isolated from natural substances [2, 3]. Synthetic methods for obtaining such spirononenes are unknown (except for 2-methoxy-1,6-dioxaspiro[4,4]-3-nonenes [4, 5]).

The peculiarities of the chemical structure of the 1,6-dioxaspiro[4.4]nonanes (an inner, bicyclic acetal) have found their reflection in the peculiar transformations that occur during the dehydrobromination of their bromo derivatives (II). The obtaining of  $1-(\alpha-furyl)-3$ -propanol (IIIa),  $1-(\alpha-furyl)-3$ -butanol (IIIb), and 1-(5'-methyl-2'-furyl)-3-butanol (IIIc) (in yields up to 87%), respectively, in the case of monobromo-substituted 1,6-dioxaspiro[4.4]nonane (IIa) and its 2-methyl (IIb) and 2,7-dimethyl (IIc) homologs, instead of the expected spirononenes (I), was completely unexpected. The identity of alcohols IIIa-c and the previously known furylalkanols was established by comparison of their physical constants, IR spectra, and analytical data. An unsaturated spiran, 2,7-dimethyl-1,6-dioxaspiro[4.4]-3-nonene (Ic), which was spontaneously converted in several hours to IIIc (as confirmed by analytical data and IR spectroscopy), was isolated along with IIIc during the dehydrobromination of IIc. Instead of a band at 1630 cm<sup>-1</sup> (valence vibrations of an isolated C = C bond), two bands at 1570 and 1620 cm<sup>-1</sup>, characteristic for the 2,5-disubstituted furan ring [6], and a broad band at 3450 cm<sup>-1</sup> due to the valence vibrations of associated OH groups, and all the remaining frequencies in the spectrum of IIIa appeared in the spectrum.

In the dehydrobromination of monobromo-substituted 2,7-dimethyl-7-ethyl- (IId) and 2,7,9,9-tetramethyl-1,6-dioxaspiro[4.4]nonane (IIe) the only reaction products were the corresponding spirononenes: 2,7-dimethyl-7-ethyl- (Id) and 2,7,9,9-tetramethyl-1,6-dioxaspiro[4.4]-3-nonene (Ie). Their yields reached 83% (Table 1).

The IR spectra confirm the structures of spirononenes Ic-e. The bands at 1630-1635 cm<sup>-1</sup> ( $\nu_{C=C}$ ) and 3090 cm<sup>-1</sup> ( $\nu_{=CH}$ ) correspond to an isolated double bond. The very intense absorption from 1000 to 1150 cm<sup>-1</sup> is characteristic for the spiroacetal structure [7].

In accordance with the above facts, the formation of spirononenes I and their isomerization to furyl-3-alkanols can be represented as the result of the transformation (see page 1349).

Furylalkanols III can probably be formed from the initially formed unsaturated spirans I through unstable intermediates with an exocyclic bond (IV) [8]. The formation of the latter is possible as a result of

\*See [1] for Communication XLIV. † Deceased.

N. G. Chernyshevskii Saratov State University. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 11, pp. 1446-1449, November, 1970. Original article submitted September 29, 1969.

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Yield, %		99	60	83
n-1	vcc	983 1040 1075	985 1037 1080	983 1040 1050 1088
реста, сі	V=CH	3090	3090	3090
IR s	vc=c	1635	1630	1630
0/0	н	9,15	96'6	96'6
Calc,	υ	70,10	72,49	72,49
d, %	H	8,89, 8,53	9,72, 10,06	10,30, 10,19
Foun	U	69,44, 69,38	72,02, 71,70	72,23, 72,27
Fmnirical	formula	C9H14O2	C11H18O2	C <sub>11</sub> H <sub>18</sub> O <sub>2</sub>
<sup>ر</sup> ۵	calc.	42,18	51,42	51,42
IW	found	41,54	51,14	51,06
	nD <sup>20</sup>	1,4530	1,4555	1,4520
	d4 <sup>20</sup>	1,005	0,9679	0,9629
ړ ۳۳	(pressure, mm)	62—63 (10)	80-81 (10)	94—95 (10)
Storting	comp.	IIc	PII	II.e
	R <sup>2</sup>	Н	$C_2H_5$	H
	ĩX	Н	н	CH3
	ĸ	н	H	CH <sub>3</sub>
pun	odmoD	2	Id	le

TABLE 1. Alkyl-Substituted 1,6-Dioxaspiro[4,4]-3-nonenes\* сн.

\*Only one representative of this group of unsaturated spirans (2,2,7,7-tetramethyl-1,6-dioxaspiro[4,4]-3-nonene, isolated from

Japanese hop oil) was previously known [2]







breaking of the  $C_5-O_6$  acetal bond when the bromine is located at  $C_4$  in monobromospirans II, and breaking of the  $O_1-C_5$  bond if the bromine is located at  $C_9$  (direction "1"). For cleavage at the other acetal bonds (direction "2"), 4,5-dihydrofuranyl unsaturated alcohols (V) would have formed, whose physical properties and, especially, IR spectra should differ substantially from the properties of furylalkanols. Meanwhile, the presence of precisely the furan ring was demonstrated in the isolated hydroxylcontaining compounds (IIIa-c).

We previously [9] determined the structure of monobromospirans IIa and c as that of the 4- or 9-monobromo derivatives. However, the position of bromine in the molecules of such spirans, where, as a result of the presence of different substituents in each of the rings, the 4 and 9 positions are nonequivalent (e.g., IIb, d, and e), remained unclear.

The solution of this problem was possible on the basis of a determination of the structure of furan alcohols III, formed during the dehydrobromination of II. Thus, for example, furylalkanol IIIb was formed from bromospiran IIb; this is possible only if the bromine atom is located at  $C_4$  and the spiran ring is cleaved at the  $C_5-O_6$  bond.

The conversion of spirononenes I to compounds with an exocyclic bond (IV) with subsequent rearrangement of IV to the energetically more favorable furan system is probably related to that rare exception where an electrophilic hydrogen attached to carbon  $(C_9)$  has a certain lability owing to the presence of a neighboring activating group [10]. In this case, the role of the latter apparently belongs to the potential carbonyl carbon  $(C_5)$ .

The well-known position that the stability of a cyclic isomer increases with the number of substituents has found confirmation also in the case of the isomeric transformations of spirononenes I. Only spirononenes with several alkyl substituents (Id and e) were stable.

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#### EXPERIMENTAL

Monobromospirans IIa-e were obtained by bromination of 1,6-dioxaspiro [4.4]nonanes with dioxane dibromide in ether [9, 11].

Alcohol solutions of alkalis, alkoxides, and secondary amines were used as dehydrobrominating agents. A typical method for the dehydrobromination of monobromospirans II with KOH in methanol is presented below.

A solution of 0.05 mole of bromospiran II in methanol was added dropwise to a refluxing solution of 5.6 g (0.1 mole) of KOH in 20 ml of methanol. The formation of a white crystalline precipitate of potassium bromide was observed immediately. The reaction mixture was refluxed with vigorous stirring for 25-30 h. The methanol was then removed at reduced pressure, and the residue was treated twice with ether. The precipitate of potassium bromide was filtered and washed with ether. The yield of potassium bromide was quantitative. The combined ether extracts were washed with water and dried with calcined magnesium sulfate. The residue after removal of the ether was distilled in vacuo. The products obtained by dehydrobromination under these conditions are given below.

 $\frac{1-(\alpha-\text{Furyl})-3-\text{butanol (IIIb).}}{1.022, \text{ and } n_D^{20} 1.4750.}$  Found %: C 68.60; H 8.16; MR<sub>D</sub> 38.64. C<sub>8</sub>H<sub>12</sub>O<sub>2</sub>. Calculated %: C 68.54; H 8.63; MR<sub>D</sub> 39.18. Literature data [12]: bp 124-127° (54 mm),  $n_D^{20} 1.4743$ .

Spirononene Ic and 1-(5'-Methyl-2'-furyl)-3-butanol (IIIc). These were obtained [in 66% (see Table 1) and 27% yields, respectively] from IIc. Compound IIIc had bp 95-96° (10 mm),  $d_4^{20}$  1.002, and  $n_D^{20}$  1.4762. Found %: OH 11.22, 11.32; MR<sub>D</sub> 43.47. C<sub>9</sub>H<sub>14</sub>O<sub>2</sub>. Calculated %: OH 11.03; MR<sub>D</sub> 43.79. Literature data [13]: bp 136-138° (55 mm),  $n_D^{20}$  1.4760.

Compound Ic was converted to IIIc in several hours, as indicated by the change in the physical constants, analytical data, and IR spectroscopy.

Compounds Id and e were obtained from IId and e, respectively (Table 1).

The IR spectra were obtained with a double-beam UR-10 spectrophotometer (Zeiss) using sodium chloride, lithium fluoride, and potassium bromide prisms. The compounds were studied in a capillary-thin layer between potassium bromide plates.

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