A STUDY OF FURAN COMPOUNDS

XXXVII. The Structure of Bromo Derivatives of 1, 6-Dioxaspiro[4.4]nonanes*

A. A. Ponomarev and A. D. Peshekhonova

Khimiya Geterotsiklicheskikh Soedinenii, Vol. 5, No. 3, pp. 403–405, 1969

UDC 547.727:542.944.1

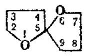
By means of dioxane dibromide the bromination of number of homologs of 1, 6-dioxaspiro[4.4]nonane was achieved, as a result of which nine mono and dibromo-derivatives of spiranes were obtained which have not been described in the literature. It was established that bromine enters into position 4 and 9 of the 1, 6-dioxaspiro[4.4]nonane ring.

Fittig [2] and other later authors [3, 4] studied the reaction in which bromine in ethereal solution undergoes a substitution reaction with 1, 6-dioxaspiro[4.4]nonane with the formation of crystalline dibromo-derivative, the structure of which has not been established.

Further, it was shown [5] that dioxane dibromide (DDB) in ether is a very effective brominating agent for spiranes of the 1, 6-dioxaspiro[4.4]nonane group. By using DDB it was possible to obtain for the first time a series of mono- and dibromo-derivatives of 1, 6-dioxaspiro[4.4]nonane and its homologs (depending on the molar ratios of the reagents) in high yield**.

The structure of the compounds obtained remained unelucidated. Evolution of hydrogen bromide during the reaction and the fact that the bromo-substitutes interact on heating with an excess of diethylamine, piperidine, and sodium methoxide and ethoxide and form the corresponding salts of the amines or sodium bromide indicate that the bromine in these compounds is not complexly bound [5].

From the concept of the spiranes of this series as cyclic acetals [6] by analogy with the behavior of the aliphatic acetals, one might suggest that bromine must firstly attack the carbon atoms 4 and 9 of the molecule of 1, 6-dioxaspiro[4.4]nonane situated in the α-position to the former carbonyl carbon.



Experimental verification of this suggestion was conducted by bromination of various polyalkyl substitutes of 1, 6-dioxaspiro[4.4]nonane under previously accepted standard conditions [5]. The results are presented in the table.

It was found that all spiranes which possess at least one atom of hydrogen in position 4 and 9, such as 2, 7-dimethyl-(I), 2, 7, 7-trimethyl-(II), 2, 7-dimethyl-9-ethyl-(III), and 2, 7-dimetheyl-7-ethyl-1, 6-dioxaspiro[4.4]nonane (IV), are able (depending on the ratio of the reagents) to form both di- and monobromo-derivatives with yields of 62–76%.

At the same time the spiranes which do not possess hydrogen atoms in position 9 (corresponding to position 4) such as 2, 7, 9, 9-tetramethyl-1, 6-dioxaspiro[4.4]nonane (V) and 2, 7, 9, 9-tetramethyl-7-ethyl-1, 6-dioxaspiro[4.4]nonane (VI), do not form dibromo-derivatives even in the presence of a large excess of brominating agent. In each case the only product of the reaction with a yield of 80–81% was the corresponding monobromo-derivative (IX, X).

The experiments indicate that bromination occurs in position 4 and 9 and that in the diamino-derivatives the bromine atoms are not found at single carbon atoms. Thus it follows that compounds **XII–XV** are 4, 9-diamino-derivatives of the corresponding spiranes **I–IV**. Compounds IX and X are 2, 7, 9, 9-tetramethyl-4-bromo- and 2, 7, 9, 9-tetramethyl-7-ethyl-4-bromo-1, 6-dioxaspiro[4.4]nonanes, respectively. At present the position of bromine in the monobromo-derivatives VIII and XI and the possibility that it may be situated at the carbon atoms 4 or 9 are not clear. On account of the presence of various substitutes in each of the cycles, these positions are heterodynamic. One should note that our conclusions are in agreement with data in the literature concerning the structure of bromo-derivatives of steroid sapogenines containing an acetal spirane group in the molecule [7–9].

EXPERIMENTAL*

Dioxane dibromide was obtained in accordance with a previously described method [10].

Spiranes **I**, **II**, and **IV** were synthesized as described earlier [1]. Compounds **III**, **V**, and **VI** were obtained by catalytic hydration of furan alcohols [11].

Bromination of spiranes **I–VI** was conducted by means of DDB in ethereal solution by a previously described method [5]. Data concerning the first obtained bromoproducts of **VII–XV** are presented in the table.

REFERENCES

1. A. A. Ponomarev, A. D. Peshekhonova, and I. A. Markushina, KhGS [Chemistry of Heterocyclic Compounds] 397, 1969.

2. R. Fittig, Ann., **256**, 50, 1890.

3. E. Granichstedten and F. Werner, Mon., **22**, 315, 1901.

4. A. Hinz, G. Meyer and G. Schucking, Ber., **76B**, 676, 1943.

---

* For part XXXVII, see [1].

**In this regard one should note that saponification of the compound occurs during the action of bromine on the homologs of the above spirane.

*With the participation of T. I. Gubina and L. M. Moskalenko

Table 1

Mono and Diamino Derivatives of Homologs of 1, 6-Dioxaspiro[4.4]nonane

Compound	Obtained from	Molar ratio of spirane in DDB	Bp, ° C (pressure, mm)	n_D^{20}	d_4^{20}	MR_D		Empirical formula	Found, %			Calculated, %			Yield, %
						found	calculated		C	H	Br	C	H	Br	
VII	I	1 : 1	69,5—71 (3)	1.4820	1.3420	49.95	50.41	$C_9H_{15}BrO_2$	45.38 45.06	6.39 6.66	33.81 33.11	45.97	6.86	33.99	76
VIII	II	1 : 1	72,5—74 (2,5)	1.4750	1.2800	54.78	55.03	$C_{10}H_{17}BrO_2$	48.05 47.88	6.81 6.91	31.94 32.09	48.20	6.88	32.08	66.5
IX	V	1 : 1	88—89,5 (4)	1.4785	1.2580	59.29			50.41 50.37	7.51 7.34	30.16 30.88				64
							59.65	$C_{11}H_{19}BrO_2$				50.20	7.28	30.37	
IX	V	1 : 2	72—74 (1,5)	1.4783	1.2580	59.28			50.37 49.87	7.53 7.61	30.84 30.85				81
X	VI	1 : 2	94—96 (2)	1.4808	1.2100	68.48	68.89	$C_{13}H_{23}BrO_2$	52.74 53.30	7.89 8.01	27.26 27.80	53.61	7.96	27.44	80
XI	IV	1 : 1	87—88 (3)	1.4770	1.2583	59.10	59.65	$C_{11}H_{19}BrO_2$	50.44 50.31	7.42 7.26	30.65 30.86	50.20	7.28	30.37	76.5
XII	I	1 : 2	86—87 (1,5)	1.5150	1.6878	57.42	58.18	$C_9H_{14}Br_2O_2$	34.46 34.58	4.44 4.41	50.80 50.69	34.42	4.49	50.90	62
XIII	II	1 : 2	98—100 (2)	1.5020	1.5440	62.78	62.80	$C_{10}H_{16}Br_2O_2$	36.12 35.77	5.07 4.98	48.88 48.47	36.61	4.91	48.72	68
XIV	III	1 : 2	108—110 (2)	1.5066	1.4970	67.98	67.41	$C_{11}H_{18}Br_2O_2$	—	—	46.64 46.34	38.62	5.30	46.72	75
XV	IV	1 : 1	106—107 (2,5)	1.5045	1.5000	67.58	67.41	$C_{11}H_{18}Br_2O_2$	39.24 39.32	5.39 5.69	46.27 46.34	38.62	5.30	46.72	27*

---

* In addition to XV, compound XI was obtained with a yield of 51%.

5. A. A. Ponomarev and A. D. Peshekhonova, ZhOKh, **30**, 147, 1960.
6. A. A. Ponomarev, Uch. zap. SGU, v. khim., **71**, 111, 1959.
7. R. Marker, D. Turner, A. Shabica and P. Ulshafer, J. Am. Chem. Soc., **63**, 1032, 1941.
8. C. Djerassi, A. Mastinez, and G. Rosenkranz, J. Org. Chem., **16**, 303, 1951.
9. G. Mueller and L. Norton, J. Am. Chem. Soc., **76**, 303, 1951.
10. A. P. Terent'ev and L. A. Yanovskaya, ZhOKh, **22**, 1594, 1952.
11. A. A. Ponomarev and A. D. Peshekhonova, KhGS, 771, 1967

21 January 1967

Chernyshevskii Saratov State University