STRUCTURE OF BROMO DERIVATIVES OF 1,6-DIOXASPIRO[4,4]NONANES

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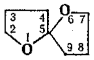
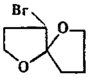
The PMR spectra of 1,6-dioxaspiro[4.4]nonane and its monobromo and dibromo derivatives indicate that bromination of 1,6-dioxaspiro[4.4]nonanes proceeds at the 4 and 9 positions of the spiran ring.

Under the previously adopted standard conditions [1], bromination of polyalkyl-substituted 1,6-dioxaspiro[4.4]nonanes proceeds at the 4 and 9 positions, i.e., at the α position with respect to the potential carbonyl carbon (C_5). The bromine atoms in the dibromo derivatives are not on the same carbon atom [2].

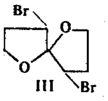
We have definitively confirmed the structure of the bromospirans by a study of the PMR spectra of 1,6-dioxaspiro[4.4]nonane (I) and its monobromo (II) and dibromo (III) derivatives.



I



II



III

In the spectrum of I the signals with chemical shifts of 1.87 and 3.47 ppm (intensity ratio 2 : 1) correspond to the eight protons of the four $C-CH_2$ groups and the four protons of the two OCH_2 groups (see Fig. 1). These chemical shifts are characteristic for such spiroacetal structures [3].

Compound II has a more complex spectrum consisting of several groups of lines. The integral intensity of the signals at 1.95-2.90 ppm is six, which corresponds to the six protons of the three $C-CH_2$ groups. Almost all of the chemical shifts of these protons differ from those for I as a result of the effect of the bromine atom. The four protons of the OCH_2 groups (3.85 and 3.98 ppm) and the proton of the $C-CH$ group (4.18 and 4.25 ppm), with a total intensity of five, contribute to the group of lines in the weaker field region.

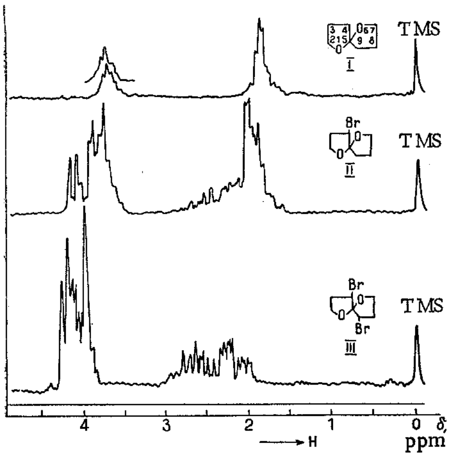


Fig. 1. PMR spectra of 1,6-dioxaspiro[4.4]-nonane (I) and its monobromo (II) and dibromo (III) derivatives.

The same intensity of the signals from the OCH_2 protons in the spectra of I and II is direct proof that hydrogen is replaced by bromine in only one of the $C-CH_2$ groups. The choice between the possible structures of bromospiran II (C_4-Br or C_3-Br) was made in favor of C_4-Br on the basis of the results of bromination of polyalkylspirans [2] and from the general concepts of the reactivities of acetals.

In the spectrum of III the group of lines from 2.0 to 2.90 ppm can be assigned to the four protons of the $C-CH_2$ groups, the signals of which, as in the case of II, are shifted downfield under the influence of the bromine atom. The OCH_2 protons are characterized by a signal at 4.0 ppm. The signals with chemical shifts of 4.10-4.30 ppm belong to the proton of the $C-CH$ group. The ratio of the

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intensity of the signal of the C−CH_2 protons to the intensity of the C−CH and OCH_2 multiplet is 2 : 3. Consequently, the bromine atoms in III are situated on different carbon atoms (C_4 and C_9).

Thus it can be considered to be completely proved that II has the 4-bromo-1,6-dioxaspiro[4.4]-nonane structure and that III has the 4,9-dibromo-1,6-dioxaspiro[4.4]nonane structure.

The purity of I-III was monitored by thin-layer chromatography. One spot was obtained for each of these compounds during two-stage chromatography on a thin layer of aluminum oxide [R_f 0.484 for I, 0.458 for II, and 0.523 for III with hexane−ethyl acetate (9 : 1)]. Consequently, in all cases (except I) we were dealing with only one of the isomers, the problem of the configuration of which still remains unexplained.

EXPERIMENTAL

Compound I was synthesized by electrolytic methoxylation of α-furyl-3-propanol with subsequent hydrogenation of 2-methoxy-1,6-dioxaspiro[4.4]-3-nonene [4].

Compounds II and III were obtained by bromination of I with dioxane dibromide in ether [1].

The PMR spectra in carbon tetrachloride were obtained with a JNM-C-60 spectrometer (60 MHz). The chemical shifts are presented in parts per million relative to tetramethylsilane (TMS), which was taken as zero.*

LITERATURE CITED

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