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Synthesis and Structure of 8-Methyl-2-methylene-1,4,6,9-tetraoxaspiro[4.4]nonane*

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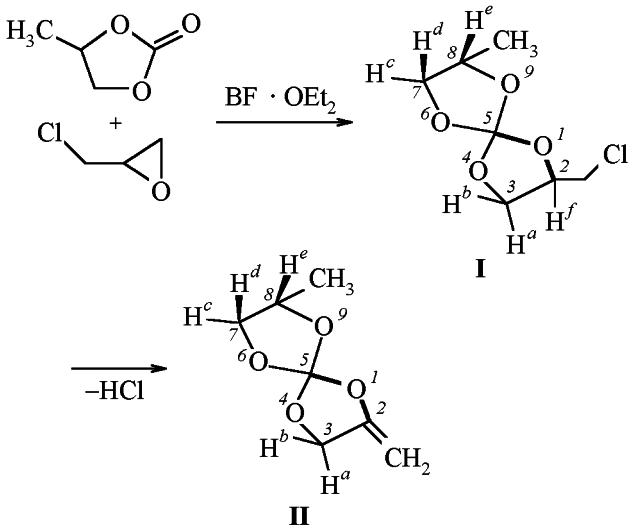
Abstract—By reacting propylene carbonate with epichlorohydrin 8-methyl-2-chloromethyl-1,4,6,9-tetraoxaspiro[4.4]nonane was obtained that afforded 8-methyl-2-methylene-1,4,6,9-tetraoxaspiro[4.4]nonane on dehydrochlorination. The spirocompounds synthesized are composed of stereoisomers mixtures containing: *cis,syn-*, *cis,anti-*, *trans,syn-*, *trans,anti*-isomers and *cis,syn-*, *cis,anti*-isomers, respectively. These isomers are distinguished by a different orientation of substituents in positions 2 and 8 with respect to two five-membered rings.

Unsaturated spiroorthoesters and spiroorthocarbonates are widely applied to preparation of polymer compositions that are capable of polymerization with no volume change or with its slight increase caused by ring opening [1, 2]. Although synthesis of this type compounds is described [2–4], no publications contain data on kinetics of their formation and consider their stereoisomeric composition. The synthetic procedures for preparation of each among these substances follow similar scheme but are quite different in details.

Here we report on the synthesis of 8-methyl-2-chloromethyl-1,4,6,9-tetraoxaspiro[4.4]nonane (**I**) that was obtained by reaction between propylene carbonate and epichlorohydrin, and of its dehydrochlorination product, 8-methyl-2-methylene-1,4,6,9-tetraoxaspiro[4.4]nonane (**II**).



I **II**

As showed the monitoring by GLC of the progress of compound **I** synthesis in the course of reaction alongside the target compound with retention time τ 35 min arose also relatively volatile side products (τ 20, 21, and 30.5 min). Considering the content of chlorine in these compounds, their ^{1}H NMR and IR spectra we deal here presumably with chloro derivatives of 1,4- and 1,3-dioxanes or 1,3-dioxolans with virtually equal molecular weight that arise by opening of the rings in compound **I**. The amount of reaction products with τ 20 and 21 min reaches maximum in 6 h (40 and 16 wt% respectively) whereas the content of impurity with τ 30.5 min weakly depends on time and is 7–9 wt%. The content of compound **I** in the reaction mixture attains 33–35 wt% within 10–12 h. Besides in the reaction mixture is present around 6% of side products (τ ~43 and 47 min) that apparently form by reaction between the volatile reaction products and epichlorohydrin.

The dehydrochlorination of compound **I** into compound **II** is not accompanied by side reactions as evidences GLC monitoring of the process. The maximal yield of the target product **II** was attained in 2 h.

The structure of purified compounds **I** and **II** (content of the main substance 97.8 wt%) was determined from NMR and IR spectra. The analysis of IR spectra showed that compounds **I** and **II** are spiroorthocarbonates with substituents in positions *2* and *8* (chloromethyl and methyl in compound **I**, methylene

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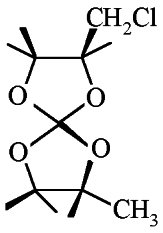
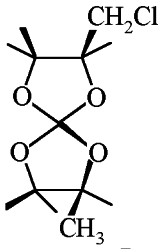
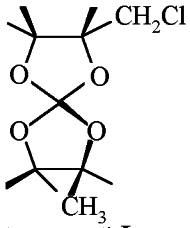


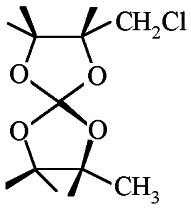
cis, sin-**I**



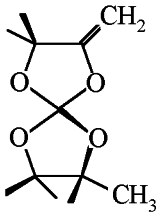
cis, anti-**I**



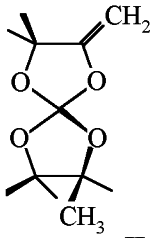
trans, anti-**I**



trans, sin-**I**



cis, sin-**II**



cis, anti-**II**

and methyl in **II**), and the substances consist of a mixture of *cis,syn-*, *cis,anti-*, *trans,syn-*, *trans,anti*-isomers (compound **I**) and *cis,syn-*, *cis,anti*-isomers (compound **II**) according to nomenclature suggested for orientation of substituents with respect to the planes of two hydrocarbon spirorings [5]. From the integral intensity of absorption bands at 923 and 855 cm^{-1} in the spectrum of compound **I**, and at 970 and 871 cm^{-1} in that of compound **II** the ratio of *cis, anti-* to *cis,syn*-stereoisomers was estimated as 1 : 1.

The structure of compounds synthesized and the presence of stereoisomers is confirmed by ^1H and ^{13}C NMR spectra. The spectrum of compound **I** is fairly complicated and consists of superimposed spectra of isomers close in structure. In the region 3.95–4.15 ppm appears a group of multiplets (four doublets of doublets. i.e., 16 peaks, HOM2DJ) that may belong to protons of CH_2 group if they are non-equivalent. On decoupling the complex multiplet simplified into a system of four superimposed doublets. In keeping with the structure the isomers with different orientation of the substituents are observed in the spectrum . The methyl group is seen as two doublets with slightly different chemical shifts (δ 1.35 and 1.34 ppm, ^3J 6.1 Hz) evidencing the existence of stereoisomers in compound **I**. In the ^1H NMR spectrum of compound **II** the multiplet at 1.3–1.40 ppm originates from two overlapped doublets (δ 1.39 and 1.38 ppm, ^3J 6.1 Hz). For the multiplets at 3.6–3.8 and 4.2–4.3 ppm (proton signals from CH_2 group in the ring with methyl substituent) the decoupled spectrum contains well resolved two groups of superimposed four peaks; however due to equal values of ^2J and ^3J the observed groups consist of three lines. In the ^{13}C NMR spectrum appears a double set of peaks from carbon atoms. We presume that this fact evidences the presence in compound **II** of two *cis,syn-* and *cis, anti*-isomers in 1 : 1 ratio. The isomers have the same structure but are distinguished by the spatial arrangement of the methyl group.

EXPERIMENTAL

IR spectra were recorded on spectrometer Specord 75IR from thin film. ^1H and ^{13}C NMR spectra were registered on Gemini 200 instrument at operating frequencies 200 and 50 MHz respectively from solutions in $CDCl_3$, reference TMS. GLC analysis was performed on chromatograph 3700 equipped with column 2.5 m long, stationary phase OV-225 on Chromaton N-AW, oven temperature programmed in the range 35–225°C, carrier gas helium, flow rate 30 ml min^{-1}.

8-Methyl-2-chloromethyl-1,4,6,9-tetraoxaspiro-[4.4]nonane (I). To a solution of 102 g (1 mol) of propylene carbonate and 1 ml of boron trifluoride etherate in 250 ml of anhydrous dichloromethane was added dropwise at stirring within 1 h a solution of 111 g (1.2 mol) of epichlorohydrin maintaining the temperature at 24–26°C. The stirring was continued for 6 h, and the mixture was left overnight. The catalyst was deactivated by addition of 2 ml of trimethylamine. Then at stirring was added by portions 500 ml of 8% water solution of NaOH. The organic layer was separated, the water layer was extracted

with dichloromethane. The combined organic solutions were washed with water, dried with $MgSO_4$, the solvent was evaporated, and the residue was subjected to fractional distillation in a vacuum. Yield 34%, bp 110–115°C (3 mm Hg) {publ.: bp 93–95°C (1.5 mm Hg) [4]}, n_D^{20} 1.465. IR spectrum, cm^{-1}: 2922 (CH_2), 2971 (CH_3), 2889 (CH); 1479 (CH_2), 1445 and 1376 (CH_3), 1325 (> CH), 1239; 1206, 1150, 1053, 1017 (C–O–C–O–C); 945, 923, 882, 855, 780 (skeleton); 762 (C–Cl). ^{1}H NMR spectrum, δ, ppm: 1.34–1.37 d (3H, CH_3), 3.55–3.70 m (3H, CH_2Cl, C^3H), 3.95–4.10 m (1H, C^7H), 4.15–4.30 (2H, C^3H and C^7H), 4.35–4.55 (2H, C^2H and C^8H). ^{13} NMR spectrum, δ_C, ppm: 17.64–17.80 q (CH_3), 43.03–43.09 d (CH_2Cl), 67.05–67.46 q (C^7, 70.75–70.91 d (C^3), 72.98–73.22 q (C^8), 74.80–75.05 q (C^2), 134.63–134.68 d (C^5). Found, %: C 43.64; H 6.93; Cl 18.52. $C_7H_{12}ClO_4$. Calculated, %: C 43.20; H 6.65; Cl 18.22.

8-Methyl-2-methylene-1,4,6,9-tetraoxaspiro-[4.4]nonane (II). To a solution of 10.21 g (0.15 mol) of sodium ethylate in 40 ml of anhydrous DMF at 35°C while stirring was added within 30 min 19.45 g (0.1 mol) of compound **I** in 40 ml of DMF. The mixture was stirred for 4 h at 60°C, Then the reaction mixture was poured into water, and the products were several times extracted into ether. The combined extracts were dried with $MgSO_4$, the solvent was evaporated, and the residue was subjected to fractional distillation in a vacuum. Yield 65°C, bp 84–87°C (4 mm Hg) {publ.: bp 79°C (4.8 mm Hg) [4]}, n_D^{20} 1.453. IR spectrum, cm^{-1}: 3113 ($=CH_2$), 2970 (CH_3), 2924 (CH_2), 2883 (CH); 1692 and 1642 (C=C), 1480 (CH_2), 1469 and 1380 (CH_3), 1345 (CH); 1237, 1213, 1143, 1057, 1020 (C–O–C–O–C); 970, 923, 871, 818, 789 (skeleton). ^{1}H NMR spectrum, δ, ppm: 1.36–1.40 d (3H, CH_3), 3.67–3.77 and 4.21–4.27 m (2H, C^7H_2), 3.96–3.99 and 4.41–4.46 m (2H, C^3H_2), 4.49–4.56 m (1H, C^8H), 4.62–4.66 m (2H, $=CH_2$). ^{13} NMR spectrum, δ_C, ppm: 17.81–17.88 d (CH_3), 66.61–66.83 d (C^7), 71.26–71.27 d (C^3), 78.70–78.77 d (C^8), 80.07–80.19 d ($=CH_2$), 135.05–136.25 d (C^2), 152.59–152.70 d (C^5).

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