

Dehydration of Hydrosilylation Products of α -Glycols Containing Terminal Acetylene Bond

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ABSTRACT. Dehydration reaction (pinacolone rearrangement) of hydrosilylation products of some α -glycols containing terminal acetylene bond, is studied. Dehydration products (products of pinacolone rearrangement) are isolated and identified. Comparison of these products with products formed in conditions of hydrosilylation (Speier's catalyst in isopropyl alcohol) of acetylene α -glycols allows to conclude that in the latter case pinacolones are not formed. © 2010 Bull. Georg. Natl. Acad. Sci.

Key words: dehydration, pinacolone rearrangement, hydrosilylation, α -glycols.

In the reaction conditions of hydrosilylation of acetylene α -glycols hydrosilylation occurs, basically, by Farmer's rule, however, in parallel, rather in small quantity, products of hydrosilylation by Markovnikov's rule are also formed. The basic process can be accompanied also by dehydration of formed hydrosilylation products. It was necessary to find out, whether there occurs a dehydration reaction (pinacolone rearrangement) of hydrosilylation products of α -glycols in these conditions. We synthesized hydrosilylation products of acetylene α -glycols containing terminal acetylene bond, and have carried out their dehydration, the formed pinacolones are isolated and investigated.

The following have been selected as initial glycols: 3,4-dimethyl-1-triethylsilylpentene-1-diol-3,4; 3,4-dimethyl-1-triethylsilylhexene-1-diol-3,4; and 3,5-dimethyl-1-triethylsilylhexene-1-diol-3,4; triethylhydridesilane as hydrosilylation agent and Speier's catalyst are used [1-3]. Dehydration of prepared hydrosilylation products of α -glycols is carried out in the presence of sulfuric acid as catalyst [4]. Dehydration products (products of pinacolone rearrangement) are isolated and identified.

The study of spectra of the obtained pinacolones

shows the presence in their molecules of carbonyl group (frequency 1700 cm^{-1}); the frequencies of hydroxyl groups are not found out, the frequency, characteristic of ethylene bond – 1600 cm^{-1} is observed. As is known, ethylene bond conjugated with carbonyl group, causes a strong absorption band in the region of 1600 cm^{-1} .

Experiment. Hydrosilylation of acetylene α -glycols containing terminal acetylene bond is carried out as follows: to a mix of 0.1 mole of initial acetylene α -glycol and 0.1 mole trialkylsilane the catalyst - 1 ml of 0.1 molar solution of H_2PtCl_6 in isopropyl alcohol is added. The mix is heated up 4 hours at $100\text{ }^\circ\text{C}$ by blending. The prepared material is exposed to fractional distillation under vacuum. Individual compounds are isolated by chromatography on Al_2O_3 column.

Dehydration of hydrosilylation products of α -glycols containing terminal acetylene bond is carried out as follows: silicon containing ethylene glycol (0.016 M) is placed in the distillation flask, 6N sulfuric acid (5.5 g) is added and the mix heated and distilled under vacuum. In these conditions, at first water is distilled, and at the further increase of temperature - mix of water and oily mass. The prepared material is exposed to fractional dis-

tillation under vacuum. Individual compounds are isolated by chromatography on Al_2O_3 column.

UR spectra are registered by spectrometer UR-10 in a thin layer of compound, in liquid paraffin. The purity of individual compounds is checked by means of gas-chromatography on the chromatograph CHROM 5 (Flame-ionization detector; column 1200 cm; carrier - fire brick; stationary phase - dodecyl phthalate; carrier gas - nitrogen, 30-32 ml/min; temperature of column 150 °C; temperature of dosimeter 190 °C).

3,3-dimethyl-1-triethylsilylpentene-1-one-4 (**I**) from 3,4-dimethyl-1-triethylsilyl-pentene-1-diol-3,4:

$\text{CH}_3\text{-CO-C(CH}_3)_2\text{-CH=CH-Si(C}_2\text{H}_5)_3$ (**I**): Yellow mobile liquid, b.p. 97-100° at 2 mm, yield 30%, n_D^{20} 1.4510, d_4^{20} 0.8452, $R_f = 0.93$ (Al_2O_3 , benzene-diethyl ether 3:2).

Anal. Calcd. for $\text{C}_{13}\text{H}_{26}\text{OSi}$: C, 69.02; H, 11.50; Si, 12.39. MR_D 71.48. M 226.

Found: C, 69.28; H, 11.84; Si, 12.15. MR_D 71.54. M 230.

3,4-dimethyl-1-triethylsilylhexene-1-one-4 (**II**) from 3,4-dimethyl-1-triethylsilylhexene-1-diol-3,4;

$\text{CH}_3\text{-CH}_2\text{-CO-C(CH}_3)_2\text{-CH=CH-Si(C}_2\text{H}_5)_3$ (**II**): yellow mobile liquid, b.p. 120-124° at 3.5 mm, yield 31%, n_D^{20} 1.4679, d_4^{20} 0.8821, $R_f = 0.87$ (Al_2O_3 , benzene-diethyl ether 3:2).

Anal. Calcd. for $\text{C}_{14}\text{H}_{28}\text{OSi}$: C, 70.00; H, 11.66; Si, 11.66. MR_D 76.11. M 240.

Found: C, 70.11; H, 11.91; Si, 11.43. MR_D 75.61. M 245.

3,5-dimethyl-1-triethylsilylhexene-1-one-4 (**III**) from 3,5-dimethyl-1-triethylsilyl-hexene-1-diol-3,4;

$(\text{CH}_3)_2\text{-CH-CO-CH(CH}_3\text{)-CH=CH-Si(C}_2\text{H}_5)_3$ (**III**): yellow mobile liquid, b.p. 95-100° at 1 mm, yield 42%, n_D^{20} 1.4499, d_4^{20} 0.8491, $R_f = 0.85$ (Al_2O_3 , benzene-diethyl ether 3:2).

Anal. Calcd. for $\text{C}_{14}\text{H}_{28}\text{OSi}$: C, 70.00; H, 11.66; Si, 11.66. MR_D 76.11. M 240.

Found: C, 70.27; H, 11.80; Si, 11.64. MR_D 75.79. M 246.

The presence of carbonyl group in compounds **I-III** was also confirmed by reaction with 2,4-dinitrophenyl hydrazine.

ორგანული ქიმია

ტერმინალური აცეტილენური ბმის შემცველი α -გლიკოლების ჰიდროსილილირების პროდუქტების დეჰიდრატაცია

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შესწავლილია ტერმინალური აცეტილენური ბმის შემცველი α -გლიკოლების ჰიდროსილილირების პროდუქტების დეჰიდრატაცია (პინაკოლინური გადაჯგუფება). გამოყოფილი და იდენტიფიცირებულია დეჰიდრატაციის (პინაკოლინური გადაჯგუფების) პროდუქტები. ამ პროდუქტების შედარება აცეტილენური α -გლიკოლების ჰიდროსილილირების პირობებში წარმოქმნილ პროდუქტებთან (სპეიერის კატალიზატორი იზოპროპილის სპირტში) უჩვენებს, რომ უკანასკნელ შემთხვევაში პინაკოლინები არ წარმოიქმნება.

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