

Partial Catalytic Hydrogenation of Acetylenic α -Glycols Containing Silicium and Terminal Triple Bond

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ABSTRACT. Partial catalytic hydrogenation of acetylenic α -glycols containing silicium and terminal triple bond: 3,4-dimethyl-1-triethylsilyl-pentin-1-diol-3,4; 3,4-dimethyl-1-triethylsilyl-hexin-1-diol-3,4; 3-(1-hydroxycyclohexyl)-1-triethylsilylbutin-1-ol-3; and 3-(1-hydroxycyclopentyl)-1-triethylsilylbutin-1-ol-3, at presence of Lindlar's catalyst is investigated. The appropriate products of hydrogenation, ethylene- α -glycols containing silicium and terminal double bond are isolated and identified. By studying the ^1H NMR spectra of the hydrogenation products it is found that they are trans isomers. © 2010 Bull. Georg. Natl. Acad. Sci.

Key words: α -glycols, terminal acetylene bond, partial hydrogenation.

In the reaction conditions of hydrosilylation of acetylenic 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. Investigating the said products of hydrosilylation by a method of ^1H NMR, it was established that these products are trans isomers [1]. For identification of minor products of hydrosilylation, we have tried to synthesize appropriate cis isomers by another way, via magnesium organic synthesis.

By means of magnesium organic synthesis initial acetylenic α -glycols were synthesized: 3,4-dimethyl-1-triethylsilyl-pentin-1-diol-3,4 (I); 3,4-dimethyl-1-triethylsilyl-hexin-1-diol-3,4 (II); 3-(1-hydroxycyclohexyl)-1-triethylsilylbutin-1-ol-3 (III); and 3-(1-hydroxycyclopentyl)-1-triethylsilylbutin-1-ol-3 (IV) (Table). For selective hydrogenation of these acetylenic α -glycols up to appropriate ethylene derivatives Lindlar's catalyst was used. It is known that Lindlar's catalyst, prepared by deactivating (or poisoning) a conventional palladium catalyst by treating it with lead acetate and quinoline, permits alkynes to be converted to alkenes

without further reduction to an alkane. The addition of hydrogen is stereoselectively syn, and as a result cis alkenes are formed [2, 3].

However, as our experiments have shown, as a result of partial catalytic hydrogenation of acetylenic α -glycols containing silicium and terminal triple bond by hydrogen, in the presence of Lindlar's catalyst, contrary to expected cis isomers of ethylene α -glycols containing silicium and terminal double bond, trans isomers of these glycols are formed exclusively (Table). Products of hydrogenation were isolated, purified by distillation in vacuum and by thin layer chromatography with aluminum oxide.

Investigation of IR-spectra of the obtained hydrogenated glycols has shown that, as opposed to IR-spectra of initial acetylenic glycols, there is no absorption band at 2150 cm^{-1} , characteristic of acetylenic compounds, and there is an absorption band, characteristic of ethylene compounds (1625 cm^{-1}). Besides, in the IR-spectra of these compounds there is always a strong band of absorption at 800 cm^{-1} , which is characteristic of IR-spectra of hydrosilylation products by Farmer's rule.

Table.

 Acetylenic α -glycols containing silicon and terminal triple bond (I-IV), and products of their catalytic hydrogenation (V-VIII)

I	$\begin{array}{c} \text{OH} \quad \text{OH} \\ \quad \\ \text{CH}_3 - \text{C} - \text{C} - \text{C} \equiv \text{C} - \text{Si}(\text{C}_2\text{H}_5)_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	V	$\begin{array}{c} \text{OH} \quad \text{OH} \\ \quad \\ \text{CH}_3 - \text{C} - \text{C} - \text{CH} = \text{CH} - \text{Si}(\text{C}_2\text{H}_5)_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$
II	$\begin{array}{c} \text{OH} \quad \text{OH} \\ \quad \\ \text{C}_2\text{H}_5 - \text{C} - \text{C} - \text{C} \equiv \text{C} - \text{Si}(\text{C}_2\text{H}_5)_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	VI	$\begin{array}{c} \text{OH} \quad \text{OH} \\ \quad \\ \text{C}_2\text{H}_5 - \text{C} - \text{C} - \text{CH} = \text{CH} - \text{Si}(\text{C}_2\text{H}_5)_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$
III	$\begin{array}{c} \text{OH} \quad \text{OH} \\ \quad \\ \text{C}_6\text{H}_{11} - \text{C} - \text{C} \equiv \text{C} - \text{Si}(\text{C}_2\text{H}_5)_3 \\ \\ \text{CH}_3 \end{array}$	VII	$\begin{array}{c} \text{OH} \quad \text{OH} \\ \quad \\ \text{C}_6\text{H}_{11} - \text{C} - \text{CH} = \text{CH} - \text{Si}(\text{C}_2\text{H}_5)_3 \\ \\ \text{CH}_3 \end{array}$
IV	$\begin{array}{c} \text{OH} \quad \text{OH} \\ \quad \\ \text{C}_5\text{H}_9 - \text{C} - \text{C} \equiv \text{C} - \text{Si}(\text{C}_2\text{H}_5)_3 \\ \\ \text{CH}_3 \end{array}$	VIII	$\begin{array}{c} \text{OH} \quad \text{OH} \\ \quad \\ \text{C}_5\text{H}_9 - \text{C} - \text{CH} = \text{CH} - \text{Si}(\text{C}_2\text{H}_5)_3 \\ \\ \text{CH}_3 \end{array}$

Investigation of ^1H NMR spectra of hydrogenation products has shown that these spectra belong to such spectra as AB, as well as NMR-spectra of the appropriate hydrosilylation products. Values of spin-spin coupling constants of vinyl protons, $J_{\text{AB}} = 19.2$ Hz (for 3,4-dimethyl-1-triethylsilyl-pentyn-1-diol-3,4) and 19.5 Hz (for 3,4-dimethyl-1-triethylsilyl-pentyn-1-diol-3,4), testifies that these compounds are trans isomers. Investigation of NMR-spectra of other ethylenic α -glycols containing silicon and terminal double bond, obtained by hydrogenation in the presence of Lindlar's catalyst, has shown that these compounds are trans isomers.

In addition, to establish the spatial configuration of liquid products of hydrogenation van Arkel rule was used; when two isomers differ appreciably in dipole moment, Van Arkel rule is applied, which states that the isomer with the higher dipole moment (μ) possesses the higher boiling point, density and refractive index [4]. Hence, according to the Van Arkel rule, refraction of geometrical cis isomer is less than refraction of appro-

priate trans isomer. However, values of refraction and IR_D of 3,4-dimethyl-1-triethylsilyl-hexyn-1-diol-3,4 obtained from acetylenic α -glycol by hydrosilylation and by hydrogenation, practically coincide, confirming their trans configuration.

In these conditions it is possible to give the following explanation of the abnormal formation of trans isomers: as a rule, the process of heterogeneous catalysis proceeds on the surface of the catalyst. As is known, during heterogeneous catalysis, molecules with multiple bonds bind the surface of the catalyst by means of p-electrons [5]. Thus, in the case of acetylenic α -glycol containing silicon and terminal triple bond, its molecule will be fixed on the surface of the catalyst by means of p-electrons and complex formation; the other part of α glycol molecule (in particular, a triethylsilyl radical) will be removed from the surface of the catalyst. Though it is possible to explain the formation of trans isomers by the ability of acetylenic glycol to complex formation, however, in this case steric factors of the glycol molecule play a certain role.

ორგანული ქიმია

სილიციუმისა და ტერმინალური აცეტილენური ბმის შემცველი α -გლიკოლების არასრული კატალიზური ჰიდრირება

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(წარმოდგენილია აკადემიის წევრის დ. უგრეხელიძის მიერ)

შესწავლილია სილიციუმის და ტერმინალური აცეტილენური ბმის შემცველი α -გლიკოლების: 3,4-დიმეთილ-1-ტრიეთილსილილპენტინ-1-დიოლ-3,4-ის, 3,4-დიმეთილ-1-ტრიეთილსილილჰექსინ-1-დიოლ-3,4-ის, 3-(1-ჰიდროქსიცეკლოჰექსილ)-1-ტრიეთილსილილბუტინ-1-ოლ-3-ის და 3-(1-ჰიდროქსიცეკლოპენტილ)-1-ტრიეთილსილილბუტინ-1-ოლ-3-ის არასრული კატალიზური ჰიდრირება ლინდლარის კატალიზატორის თანაობისას. გამოყოფილი და იდენტიფიცირებულია შესაბამისი ჰიდრირების პროდუქტები - სილიციუმის და ტერმინალური ეთილენური ბმის შემცველი α -გლიკოლები. ჰიდრირების პროდუქტების ^1H ბმრ სპექტრების შესწავლის შედეგად დადგენილია, რომ ეს ნაერთები მიეკუთვნება ტრანსნიზომერებს.

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