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Chemical and Microbiological Hydrolysis of Epoxides of Acetylene Series

Mammad Veliyev[1*], Mammad Salmanov[2], Saida Aliyeva[2], Mahruza Shatirova[1], Gulnara Yagubova[2]
[1]*Institute of Polymer Materials of Azerbaijan National Academy of Sciences, Baku, Azerbaijan*
[2]*Institute of Microbiology of Azerbaijan National Academy of Sciences, Baku, Azerbaijan*
E-mail: [*]*mveliyev@mail.ru*
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Abstract

The chemical and microbiological hydrolyses of epoxide compounds of acetylene series have been comparatively carried out. It has been shown that as distinguished from chemical one in microbiological hydrolysis along with corresponding optically active glycols, ketoalcohols of acetylene series are also formed. It has been also defined that the synthesized glycols of acetylene series have bactericide properties related to sulfate-reducing bacteria at concentration of 100 - 200 mg/l. It has been established that an introduction of electron-acceptor chlorine atoms in molecules influence on decreasing of bactericide activity of acetylene glycols.

Keywords: Hydrolyze, Glycols, Epoxide, Ketoalcohols, Acetylene

1. Introduction

As it's known glycols find a wide application in many branches of a national economy and have one of the leading places among products of chemical industry. They are used as monomers for whole series of polymer materials, solvents, in production of plasticizers, for making of antifreezes, polyester resins, synthesis of esters of glycols, etc. The various methods of preparation of diols both by chemical [1-7], and by microbiological pathways [8-12] are known. Obtaining of the glycols of acetylene series is occupied the special place. Acetylene glycols possessing large chemical possibilities are successfully used for synthesis of new perspective unsaturated compounds, pharmaceutical preparations, monomers for preparation of high-molecular compounds, including biologically active substances and for solution of important theoretical problems.

Analysis and systematization of literature data evidence about availability of intensive process of expansion of sphere of microbiological chemistry—new reactions realized by microorganisms are revealed, circle of converted substances is more expanded, and new taxonomic groups of microorganisms are involved. Nowadays there are a lot of works reflecting rapid development of use of microorganisms in organic and petrochemical synthesis [13-15]. The preparation of active compounds by means of microorganisms is more economic and safe than application of chemical methods. For this reason this question is one of the most perspectives. In particular, an investigation of hydrolysis of epoxides by microorganisms has special interest for preparation of such compounds as glycols which have an important practical value.

The aim of this work is the synthesis of glycols of acetylene series both by chemical and microbiological hydrolysis of corresponding epoxide compounds of acetylene series. This work is also a continuation of investigations in the field of biodegradation of oil hydrocarbons by microorganisms conducted previously by authors [16-18].

2. Results and Discussion

The objects of investigation were monosubstituted acetylene compounds with epoxide ring prepared by previously described method [5]. The reaction on oxirane ring in presence of acidic catalysts has been carried out. It has been established that in the presence of 10% of aqueous solution of sulphuric acid the epoxides with terminal acetylene bonds (Ia-Xa) are subjected to hydrolysis on oxirane ring and in this case the corresponding glycols

(I-X) with high yields are formed (**Scheme 1**):

The structure of the synthesized glycols of acetylene series (I-X) has been established by analysis of their IR- and NMR-spectra. Proceeding of reaction on oxirane ring has been confirmed by disappearance of absorption band in the IR-spectra of compounds characteristic for methylene group (3065 cm^{-1}) and asymmetric valence vibration of oxirane ring (915 cm^{-1}). At the same time the absorption bands at 3400 cm^{-1} and in the field of 1000 - 1170 cm^{-1}, corresponding to hydroxyl group are saved. In this case the absorption bands at 2130 and 3300 cm^{-1}, confirming presence of terminal acetylene bond were identified.

In the NMR-spectra of glycols (I-X) there are signals as singlet with chemical shift at δ 2.65 ppm, corresponding to protons of hydroxyl groups. Protons of methylene group (2H, CH_2O) are appeared by signals as multiplet at δ 2.85-3.10 ppm., and proton of terminal acetylene bond – as triplet at δ 2.23 - 2.26 ppm.

The structure of the prepared glycols (I-X) has been also confirmed by counter synthesis—hydrolysis (10% aqueous solution of sulphuric acid) of epoxyethynyl- and propynylcarbinols (Ib-IIIb,VIb-XIIIb) and by further splitting (in the presence of potassium hydroxide) of the prepared products according to the known method [5] on the following scheme (**Scheme 2**):

The physical-chemical constants and spectral data of glycols of acetylene series (I-III, VI-VIII) prepared by both methods are identical.

The synthesized glycols of acetylene series (I-VI) were very reactive compounds and can be used in organic synthesis with the aim of preparation of new polyfunctional organic and silicoorganic compounds (derivatives) with practically useful properties.

The carried out microbiological experiments showed that strains from *Aspergillus*, *Fusarium*, *Mucor*, *Penicillium* genera realized biohydrolysis of epoxide compounds. As a result of screening of most active strain-degrader it was chosen the strain *Aspergillus niger* which had maximum degree of biohydrolysis. The obtained results are example of preparative method of hydrolysis of epoxides of acetylene series with use of microorganisms.

Analysis of products of biohydrolysis of epoxides by chromatographic and spectral methods evidenced that *Aspergillus niger,* as distinguished from chemical method realized biohydrolysis of epoxide compounds (Ia, IVa-VIIa,IXa,Xa) in two direction with formation of glycols (I, IV-VI, IX, X) (35% - 40%) and ketoalcohols (XI-XVI) (60% -65%) on the following scheme (**Scheme 3.**):

The physical-chemical and spectral data of glycols (I, IV-VI, IX, X) obtained as a result of microbiological hydrolysis and same data of chemical method were identical. In the IR-spectra of ketoalcohols (XI, XVI) along with absorption bands characteristic for terminal acetylene bond and hydroxyl group the absorption bands at 1740 cm^{-1}, inherent for carbonyl group have been also detected. In the NMR-spectra of compounds (XI-XVI) the following chemical shifts of protons are present (δ, ppm.): 2.22 - 2.25 t (HC≡C), 4.10 s (CH_2O), 1.90 - 2.00 t (CH_2-CO), 2.50 s (OH).

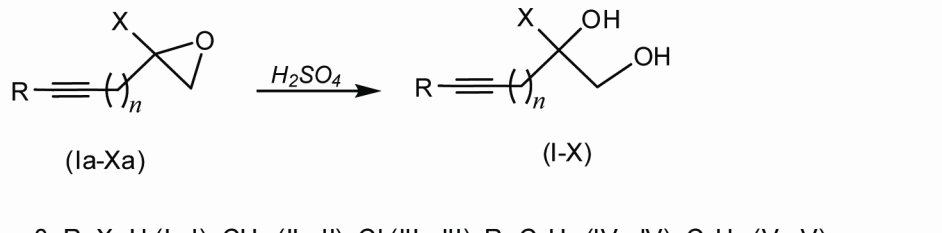
An advantage of microbiological method is simultaneous formation of glycols and ketoalcohols of acetylene series which are synthons in thin organic synthesis.

The synthesized glycols and ketoalcohols of acetylene series are very reactive compounds and can be used as synthons in thin organic synthesis for the purpose of preparation of new polyfunctional organic and organosilicon derivatives with practically useful properties. In particular, it has been shown that glycols (VI, VII) undergo the hydroxylation reactions on acetylene bond. Thiilation of glycols (VI, VII) with ethyl mercaptan proceeds in the presence of catalytic quantities of caustic potassium and leads to formation of the thioethylsubstituted unsaturated glycols from a cis-configuration (XVII, XVIII). Hydroxylation reaction of glycols (VI, VII) with trialkylsilanes proceeds in presence of rhodium acetylacetonedicarbonyl by Farmer's rule with formation of glycols on a trans-structure (XIX-XXII), as it's presented on the **Scheme 4**.

Scheme 4: Thiilation and hydrosilylation of glycols of acetylene series

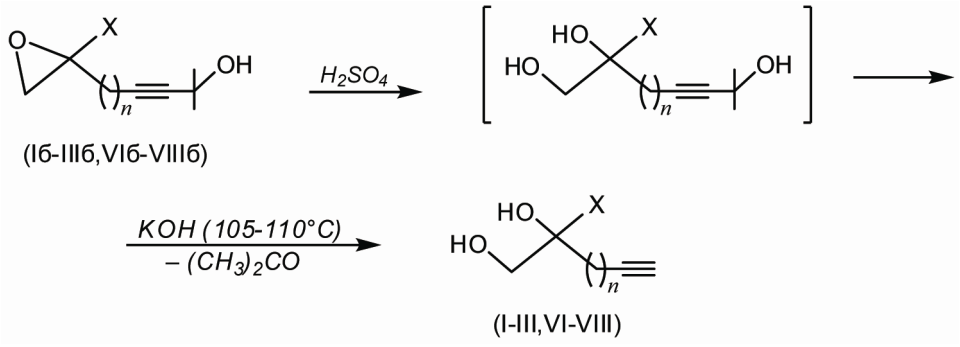
The structure of the synthesized compounds (XVII-XXII) has been established by the data of IR- and NMR-spectroscopy. The reaction proceeding on acetylene compounds has been confirmed by disappearance of absorption bands in the IR-spectra of compounds (XVII-XXII), characteristic for H-C≡C fragment (2135 and 3300 cm^{-1}). Thus in the spectra of compounds (XVII, XVIII) there are absorption bands at 625 cm^{-1} and in the field of 680 cm^{-1} - 725 cm^{-1}, characteristic for C-S bonds and cis- CH=CH groups. In the IR spectra of compounds (XIX-XXII) the absorption are identified at 1625 cm^{-1}, groups specifying presence of CH=CH and fluctuations at 986 cm^{-1} that testify formation of compounds (XIX-XXII) on a trans-structure.

In the NMR^{1}H spectra of compounds (XIX-XXII) signals of two protons were identified at double bonds (CH=CH) δ = 4.83 – 4.96 ppm and δ = 5.52 – 5.65 ppm. Spin-spin interaction constants (SSIC) of these protons are different 13.5 - 14 Hz that is connected on their trans-structure. In the NMR^{1}H spectra of compounds (XVII, XVIII) signals of protons CH=CH in the form of two doublets were identified δ = 6.45 and δ = 5.60 with the constant of spin-spin interaction J = 9 Hz that testify

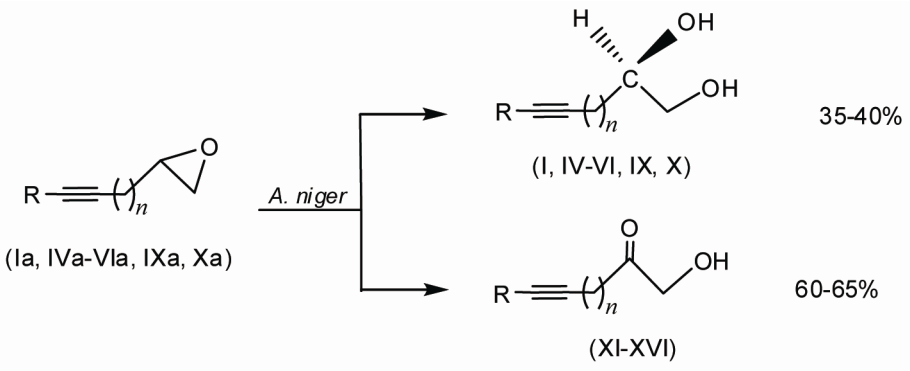


n=0, R=X=H (Ia,I), CH_3 (IIa,II), Cl (IIIa,III); R=C_2H_5 (IVa,IV), C_6H_5 (Va,V);
n=1, R=X=H (VIa,VI), CH_3 (VIIa,VII), Cl (VIIIa,VIII); R=C_2H_5 (IXa,IX), C_6H_5 (Xa,X);

Scheme 1. Chemical hydrolysis of oxiranes of acetylene series.

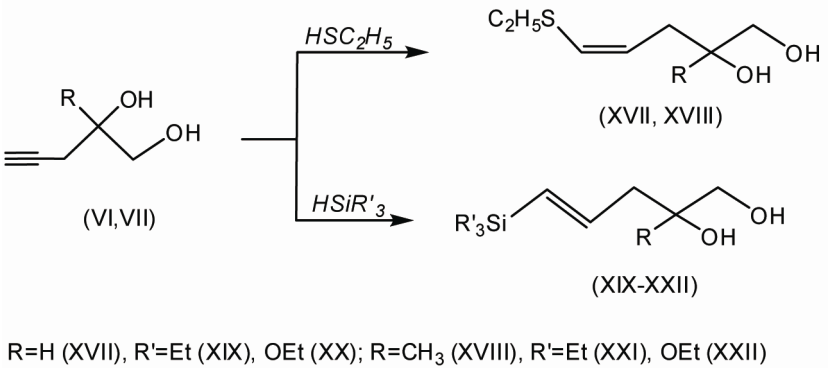


Scheme 2. Counter synthesis of glycols of acetylene series.



n=0, R=H (XI), C_2H_5 (XII), C_6H_5 (XIII); n=1, R=H (XIV), C_2H_5 (XV), C_6H_5 (XVI)

Scheme 3. Microbiological hydrolysis of epoxides of acetylene series.



R=H (XVII), R'=Et (XIX), OEt (XX); R=CH_3 (XVIII), R'=Et (XXI), OEt (XXII)

Scheme 4. Thiilation and hydrosilylation of glycols of acetylene series.

to compounds formation on cis-structure.

The synthesized glycols of acetylene series (I-X) have been tested for bactericidal activity on sulfate-reducing bacteria (SRB) by standard techniques [19-22]. It has been established that they possess bactericidal properties against SRB at concentration of 100 - 200 mg/l. The results of laboratory tests give the grounds to conclude that the high bactericidal effect of the investigated glycols of acetylene series, apparently, is the result of complex influence of acetylene bond and hydroxyl groups of molecules. It was revealed that an introduction of electron-acceptor groups in molecule of acetylene glycols (III, VIII) in comparison with glycols (I, II, IV-VII, IX, X) bactericidal activity reduces to –70% at concentration of 100 mg/l which at such concentration glycols (I, II, IV-VII, IX, X) has a bactericidal activity of 95% - 98%.

Thus, at carrying out of this work the chemical and microbiological methods of preparation of glycol and ketoalcohols on the basis of hydrolyses of epoxides of acetylene series have been developed. However it's necessary to emphasize that as a result of implemented chemical hydrolysis only glycols were formed but at microbiological hydrolysis the formation both of glycols and ketoalcohols was observed. The carried out experiments showed the advantages of new direction—microbiological synthesis.

3. Experiment Materials

The IR-spectra of the synthesized compounds were taken on spectrometer UR-20 within the range of 400 - 4000 cm^{-1} in thin layer. The spectra NMR ^1H were recorded on apparatus "Tesla BS –487 B" (80 MHz). Hexamethyldisiloxane, solvent-CCl_4 was used as an internal standard. The optical rotation was measured on polarimeter Perkin-Elmer-141. The purity of compounds was controlled by the method of TLC on plates Silufol UV-254, in various systems of solvents (benzene: diethyl ether, 5:1, developer-iodine) and by the method of reversed-phase liquid chromatography on highly effective liquid chromatography of firm "Kovo" (Czech) with UV-spectrophotometric detector (λ = 254 nm). The column with sizes 3.3 × 150 mm with reversed phase "Separon SGX C18" was used. Temperature 25˚C, mobile phase: methanol:water (75:25 rev.%), feed rate 0.3 ml/min.

The physical-chemical data of compounds I, IV coincide with literature data [23,24]. The microbiological investigations were implemented by the microscopic fungi isolated from water and ground of oil-polluted coastal sites of Caspian Sea along the Absheron peninsula [15,17]. In this case 4 more active strains of fungi conducted biohydrolysis of epoxides from genera: *Aspergillus, Fusarium, Mucor, Penicillium* were selected. The microbiological hydrolysis was studied by using of the most active strain *Aspergillus niger* 44.

4. Experiment Methods

4.1. Chemical Method

Chemical hydrolysis of epoxide compounds (Ia-XIa). To 20 ml 10% aqueous solution of sulphuric acid was gradually added 3.4 g (0.05 mol) 1.2-epoxy-3-butin (Ia). In view of significant isolation of heat a reaction flask was cooled in the process of reaction by ice water. After half-hour mixing the reaction was finished. The aqueous solution was saturated by common salt and multiply was extracted by ester and then by chloroform. After distillation of solvent glycol (I) with T_m 39˚C - 40˚C, yield 85.4% was isolated. Found, %: C 55.90, H 7.16. $C_4H_6O_2$. Calculated, %: C 55.80, H 7.03.

The compounds (II-X), chararacterizing by following constans was analogously prepared:(II) M.p. 55˚C - 56˚C, yield 82.5%. Found, %: C 60.31, H 8.12. $C_5H_8O_2$. Calculated, %: C 60.2, H 8.05. (III), M.p. 64˚C - 65˚C, yield 80.1%. Found, %: C 39.70, H 4.24. Cl 29.30. $C_4H_5ClO_2$. Calculated, %: C 39.86, H 4.18, Cl 29.41; (IV), M.p 47˚C - 48˚C, yield 82.3%. Found, %: C 63.24, H 8.62. $C_6H_{10}O_2$. Calculated, %: C 63.13, H 8.83; (V), M.p.76˚C - 77˚C, yield 85.2%. Found, %: C 74.16, H 6.01. $C_{10}H_{10}O_2$. Calculated, %: C 74.05, H 6.22; (VI), M.p. 44˚C - 45˚C, yield 90%. Found, %: C 59.82, H 8.20. $C_5H_8O_2$. Calculated, %: C 59.98, H 8.05. (VII), M.p. 59˚C - 60˚C, yield 85.8%. Found, %: C 63.02, H 8.74. $C_6H_{10}O_2$. Calculated, %: C 63.13, H 8.83. (VIII), M.p.67˚C - 68˚C, yield 83.4%. Found, %: C 44.56, H 5.18, Cl 26.48. $C_5H_7ClO_2$. Calculated, %: C 44.63, H 5.25, Cl 26.35; (IX), M.p.52˚C - 53˚C, yield 83.1%. Found, %: C 65.42, H 9.38. $C_7H_{12}O_2$. Calculated, %: C 65.59, H 9.43; (IX), M.p.52˚C - 53˚C, yield 83.1%. Found, %: C 65.42, H 9.38. $C_7H_{12}O_2$. Calculated, %: C 65.59, H 9.43; (X), M.p.81˚C - 82˚C, yield 86.8%. Found, %: C 74.81, H 6.73. $C_{11}H_{12}O_2$. Calculated, %: C 74.97, H 6.86.

4.2. Microbiological Method

Microbiological hydrolysis of epoxide compounds (Ia, IVa-VIa, IXa, Xa). a) **Preparation of fungi biomass.** For preparation of biomass of selected fungi 3l fermenter filled by 1l liquid nutrient medium (wort) was used. In this case to a medium was added 10 ml of liquid paraffin and 0.005 ml antifoam silicon for prevention of pouring. The incubation was carried out under temperature 25˚C - 27˚C. Then the suspension of mycelium and collection of

1-week culture of the investigated microorganisms was added. After two-day incubation mycelium was filtered, washed by sterile water and placed back in fermenter, which already filled by 1l pH 7 phosphate buffer (0.1 M) solution, and also a medium was enriched by nitrogen and air. A yield of product was provided by phased treatment of probes: for each probe mycelium was filtered and the prepared fungi biomass used in further experiments for implementing the biohydrolysis. After decantation a liquid phase was treated by NaCl and then was extracted twice by ether. The organic layer was dried ($MgSO_4$), and then was evaporated in vacuum.

b) **Biohydrolysis.** Biohydrolysis was carried out in Erlenmeyer flasks (0.5l), containing buffer phosphate (0.1l, 0.1M, pH 8) and 10% fungi biomass prepared from previous experiment. The solution of epoxides of acetylene series (Ia, IVa) (0.1 - 1 g) in EtOH (1 ml) was poured into medium, and a flask was incubated under temperature 27˚C for 1 - 4 days. After decantation a liquid phase was treated by NaCl, and then twice extracted by ester. The organic layer was dried by ($MgSO_4$), and then was evaporated in vacuum. After removal of ester by re-crystallization the products (I, IV-VI, IX, X) and (XI, XVI) were separated.

(I): M.p. 39˚C - 40˚C (from benzene), $[\alpha]_D^{25}$ = –29.6 (c 2.42, EtOH); (IV): M.p. 47˚C - 48˚C (from benzene), $[\alpha]_D^{25}$ = –20.3 (c 2.21, EtOH); (V): M.p. 76˚C - 77˚C (from benzene), $[\alpha]_D^{25}$ = -22.2 (c 2.39, EtOH); (VI): M.p. 44˚C - 45˚C (from benzene), $[\alpha]_D^{25}$ = –38.1 (c, 2.51, EtOH); (IX): M.p. 52˚C - 53˚C (from benzene), $[\alpha]_D^{25}$ = –23.7 (c 2.44, EtOH); (X): M.p. 81˚C - 82˚C (from benzene), $[\alpha]_D^{25}$ = -26.4 (c 2.82, EtOH); (XI): B.p. 67˚C - 68˚C (100 mm.merc.c.), n_D^{20} = 1.4490, d_4^{20} 1.0636; Found, %: C 57.28, H 4.60. $C_4H_4O_2$. Calculated %: C 57.14, H 4.79; (XII): B.p. 76˚C - 77˚C (100 mm.merc.c.), n_D^{20} = 1.4695, d_4^{20} 1.0272; Found, %: C 64.39, H 7.06. $C_6H_8O_2$. Calculated, %: C 64.27, H 7.18; (XIII): B.p. 92˚C - 93˚C (100 mm.merc.c.), n_D^{20} = 1.5605, d_4^{20} 1.1694; Found, %: C 74.78, H 5.16. $C_{10}H_8O_2$. Calculated, %: C 74.99, H 5.02; (XIV): B.p. 73˚C - 74˚C (100 mm.merc.c.), n_D^{20} = 1.4535, d_4^{20} 1.0277; Found, %: C 61.09, H 6.27. $C_5H_6O_2$. Calculated, %: C 61.21, H 6.16; (XV): B.p. 79˚C - 80˚C (100 mm.merc.c.), n_D^{20} = 1.4729, d_4^{20} 1.0098; Found, %: C 66.50, H 7.82. $C_7H_{10}O_2$. Calculated, %: C 66.64, H 7.99; (XVI): B.p. 97˚C - 98˚C (100 mm.merc.c.), n_D^{20} = 1.5640, d_4^{20} 1.1561. Found, %: C 75.71, H 5.62. $C_{11}H_{10}O_2$. Calculated, %: C 75.84, H 5.78.

Addition of ethyl mercaptan to glycol (VI, VII). General methodology. To the boiling solution 0.08 mole of glycol (VI or VII) and 0.4 g of KOH in 10 ml of methyl alcohol and within 1 hour it was added 11.7 g of ethyl mercaptan. After heating within 2 hours to reaction mass was added 50 ml of ether, then washed by water and dried up over $MgSO_4$. The solvent was removed and with distillation in vacuum the compounds (XVII, XVIII) were isolated by the following constants: (XVII), B.p. 97˚C - 98˚C (1 мм), n_D^{20} 1.4805, d_4^{20} 1.0133, yield 63.6%. Found, %: C 51.70, H 8.54, S 19.87. $C_7H_{14}O_2S$. Calculated, %: C 51.82, H 8.69, S 19.76; (XVIII), B.p. 105˚C - 106˚C (1mm), n_D^{20} 1.4840, d_4^{20} 1.0056, yield 64.8%. Found, %: C 54.38, H 9.03, S 18.28. $C_8H_{16}O_2S$. Calculated, %: C 54.50, H 9.15, S 18.19.

Hydrosilyation of glycols (VI, VII) with triethyl-(or trietoxy)silane. 0.32 mol of compounds (VI or VII) and 0.32 mole of triethyl (or trietoxy) silane in the presence of 0.01 g of rhodium acetylacetonatdicarbonyl was mixed during 7 hours under the temperature 55°C - 60°C and subjected to the vacuum distillation the compounds (XIX-XXII) were isolated with the following constants: (XIX), B.p. 121˚C - 122˚C (1 mm), n_D^{20} 1.4730, d_4^{20} 0.9335, yield 72.4%. Found, %: C 61.20, H 11.09, Si 12.82. $C_{11}H_{24}O_2Si$. Calculated, %: C 61.05, H 11.18, Si 12.97; (XX), B.p. 126˚C - 127˚C (1 mm), n_D^{20} = 1.4785, d_4^{20} 1.1011, yield 78.3%. Found, %: C 49.82, H 9.28, Si 10.51. $C_{11}H_{24}O_5Si$. Calculated, %: C 49.91, H 9.15, Si 10.62; (XXI), B.p. 125˚C - 126˚C (1 mm), n_D^{20} = 1.4765, d_4^{20} 0.9338, yield 73.8%. Found, %: C 62.41, H 11.22, Si 12.03. $C_{12}H_{26}O_2Si$. Calculated, %: C 62.54, H 11.37, Si 12.19; (XXII), B.p. 129°C - 130˚C (1 mm), n_D^{20} = 1.4820, d_4^{20} 1.1647, yield 78.6%. Found, %: C 51.62, H 9.30, Si 10.19. $C_{12}H_{26}O_5Si$. Calculated, %: C 51.76, H 9.41, Si 10.08.

5. Conclusions

The methods of preparation of glycols of acetylene series by the chemical (in the presence of 10% aqueous solution of sulphuric acid) and microbiological (in the presence of *Aspergillus niger*, *Fusarium*, *Mucor*, *Penicillium*) hydrolysis of the corresponding epoxide compounds of acetylene series have been developed. In using of microbiological method the epoxide compounds unlike chemical method are hydrolyzed in two directions with formation of the corresponding optically active glycols and ketoalcohols. It has been established that the synthesized glycols of acetylene series undergo the thiilation reaction with ethylmercaptane with formation of thioethyl substituted unsaturated glycols with *cis*-configura- tion. Unlike this the analogous hydrosilylation reaction of glycols with trialkylsilanes proceeds with formation of trialkylsilyl substituted unsaturated glycols with *trans*-structure.

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