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**SYNTHESIS AND PROPERTIES OF CYCLOHEXYL AMINES
OF PROPARGYL SERIES****M.I.Shatirova, M.M.Movsum-zade*, U.Sh.Dzhafarova****Institute of Polymer Materials, NAS of Azerbaijan***A.Guliyev Institute of Chemistry of Additives, NAS of Azerbaijan**mshatirova@mail.ru*

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The possibility of synthesis of the secondary and tertiary cyclohexylamines of propargyl series by interaction of cyclohexylamine with propargyl bromide in the presence of sodium hydroxide has been studied. It has been established that the synthesized secondary amine undergoes the various chemical reactions – hydrosilylation, diene condensation and addition reactions on reactive centers with formation of new derivatives. In particular, it has been shown that N-prop-2-yn-1-ylcyclohexylamine due to N–H bond undergoes the reaction with acrylonitrile and epichlorohydrin (in the presence of boron trifluoride etherate) forming N-cyanoethyl-N-prop-2-yn-1-ylcyclohexylamine and N-epoxy-N-prop-2-yn-1-ylcyclohexylamine, respectively. Under action of 10% aqueous solution of hydrochloric acid N-cyanoethyl-N-prop-2-yn-1-ylcyclohexylamine is subjected to the hydrolysis forming unsaturated carboxylic acid. N-epoxy-N-prop-2-yn-1-ylcyclohexylamine due to oxirane ring in interaction with concentrated sulphuric acid leads to the formation of the corresponding glycol of acetylene series and in the reaction with propargyl alcohol – to the formation of the corresponding ether-alcohol with two terminal acetylene bonds. The prepared compounds have been identified by the methods of IR-spectroscopy and NMR. The control over the course of the reaction was carried out by a method TLC on plates with aluminum oxide in the various systems of solvents, developer – iodine.

Keywords: cyclohexylamine, propargyl bromide, norbornadiene, hydrosilylation, carboxylic acid.

doi:

Introduction

Amine-containing compounds as syntheses are widely used in the creation of new, diverse, highly effective physiologically and biologically active substances [1–3]. In this aspect, the preparation of amine-containing unsaturated compounds is of definite scientific and practical interest [4, 5]. In particular, research in the field of synthesis and study of the properties of derivatives of alicyclic amines of the cyclohexane series indicates the promise of searching compounds with physiological and biological activity [6, 7]. The introduction of a multiple bond, including acetylene, into the molecules of alicyclic amines contributes to an increase in biological activity, a decrease in toxicity and irritation of the compound [8].

Experimental part

The IR spectra of the synthesized compounds were recorded on a spectrophotometer ALPHA FT-IR ("BRUKER" Germany) on a

ZnSe crystal in the range of wave numbers 600–4000 cm⁻¹. The ¹H NMR spectra were recorded Fourier spectrometer FT-300 on a ("Bruker" Germany). Tetramethylsiloxane (TMS) was used as an internal standard, and CDCl₃ was the solvent.

N-Prop-2-yn-1-ylcyclohexylamine (I). 2.0 g (0.05 mol) of sodium hydroxide, 2 ml of water, 5.0 g (0.05 mol) of cyclohexylamine were placed in a reaction flask and 6 g (0.05 mol) of propargyl bromide were dropped in with vigorous stirring for 20 minutes. After 2 h, the organic layer was separated; by distillation, compound I was obtained with a boiling range of 82–83⁰C (9 mm), n_D^{20} – 1.4591, d_4^{20} – 0.8727, yield – 73.6%. Found, %: C 78.60, H 11.12, N 10.13. C₉H₁₅N. Calculated, %: C 78.77, H 11.02, N 10.21.

Similarly, **N,N-diprop-2-yn-1-ylcyclohexylamine (II)** was obtained from 5.0 g (0.05 mol)

of cyclohexylamine and 12 g (0.1 mol) of propargyl bromide with a boiling range of 129–130°C (10 mm), n_D^{20} – 1.4831, d_4^{20} – 0.9049. Found, %: C 82.21, H 9.60, N 8.10. $C_{12}H_{17}N$. Calculated, %: C 82.30, H 9.79, N 8.00.

N-(3-Methyldiethylsilyl)prop-2-en-1-yl-cyclohexylamine (III). In a 250 ml flask, 6.6 g (0.05 mol) of compound (I) were placed and 0.1 g of a rhodium acetylacetonate dicarbonyl catalyst was added. While stirring, 5.1 g (0.05 mol) of methyldiethylsilane was added and boiled at 55–60°C for 8 hours. After distillation, unreacted compounds were subjected to vacuum. 72.6% of the compound (III) was isolated: Boiling range 114–115°C (9 mm), n_D^{20} – 1.4580, d_4^{20} – 0.8270. Found, %: C 70.37, H 12.10, Si 11.88, N 5.71. $C_{14}H_{29}NSi$. Calculated, %: C 70.29, H 12.22, Si 11.74, N 5.86.

N-(Methylenebicyclo[2.2.1]heptadiene-2,5-yl)-N-prop-2-yn-1-ylcyclohexylamine (IV). A mixture of 3.4 g (0.025 mol) of the compound (I) and 1.6 g (0.025 mol) of the CPD was heated in the presence of 0.05 g of hydroquinone in a sealed ampoule for 8–10 hours at 175–180°C. At the end of the reaction, the reaction mixture was subjected to vacuum distillation. At the same time, unreacted starting components were distilled off, and the target product was subjected to repeated distillation and the adduct (IV) was separated from Boiling range 101–102°C (9 mm), n_D^{20} – 1.4971, d_4^{20} – 0.9294. 68.6%. Found, %: C 82.60, H 10.56, N 6.82. $C_{14}H_{21}N$. Calculated, %: C 82.72, H 10.42, N 6.90.

N-Cyanoethyl-N-prop-2-yn-1-ylcyclohexylamine (V). With stirring, 5.7 g (0.1 mol) of freshly distilled acrylic acid nitrile was added to 11.65 g (0.085 mol) of compound (I). While there is an increase in the temperature of the reaction mixture. After the calculated amount of nitrile was added, the contents of the flask were heated for 7 hours at a temperature of 80–90°C, and then fractionated. The resulting product (V) has a batch of 121–122°C (9 mm), n_D^{20} – 1.4711, d_4^{20} – 0.9126. 78.2%. Found, %: C 75.98, H

9.42, N 14.86. $C_{12}H_{18}N_2$. Calculated, %: C 75.80, H 9.54, N 14.74.

N-Epoxy-N-prop-2-yn-1-ylcyclohexylamine (VI). 9.3 g (0.1 mol) of epichlorohydrin was poured into the flask under reflux with stirring. 5.4 g (0.04 mol) of compound (I) was added during 20 minutes at a temperature of 30°C. The mixture was cooled to 5–7°C and treated with 9.6 g of KOH in 8 ml of water. The organic layer was extracted with ether and dried over anhydrous $MgSO_4$. Then the ether was distilled off, the "Edgeright" inhibitor (aldol- α -naphthalene) was added and dispersed under vacuum. Compounds obtained (VI) with a batch of 147–148°C (9 mm), n_D^{20} – 1.4871, d_4^{20} – 0.9553. Found, %: C 74.43, H 9.86, N 7.17. $C_{12}H_{19}NO$. Calculated, %: C 74.57; H, 9.91; N 7.25.

Hydrolysis of N-cyanoethyl-N-prop-2-yn-1-ylcyclohexylamine (VII). 9.5 g (0.05 mol) of freshly distilled compound (V) were placed in a reaction flask equipped with a mechanical stirrer and reflux condenser. Then to the contents of the flask with vigorous stirring, 60 ml of conc. sulfuric acid. When this was observed heating the reaction mixture and the formation of salt. The next day, the reaction mixture was stirred at a temperature of 50–60°C for 6–8 hours, and then treated with water and 25 ml of sulfuric ether was added. The aqueous layer was separated from the organic layer and the latter was dried over calcined $MgSO_4$. After distilling off the solvent, (VII) was isolated from the residue by vacuum distillation with a batch of 100–101°C (2 mm), n_D^{20} – 1.5531, d_4^{20} – 1.1190, 74.4%. Found, %: C 68.73, H 9.28, N 6.54. $C_{12}H_{18}N_2$. Calculated, %: C 68.86, H 9.15, N 6.69.

N-Prop-2-yn-1-yl-N-(2-hydroxy-4-oxahept-6-ynyl)cyclohexylamine (VIII). 8.4g (0.15 mol) of propargyl alcohol containing 0.2 ml of boron trifluoride etherate with stirring and cooling (0–5°C) added 12.6 g (0.065 mol) of compound (VI). The reaction mixture was stirred for 5 hours at 22–25°C. Then low-boiling substances were removed from the reaction mixture, and the residue was introduced dropwise into a flask containing a solution of diethyl ether and 15 g of finely divided caustic potassium. After

that, the reaction mixture was stirred for another 5 hours at 13–15°C. Then the solvent was removed and the substance (VIII) was isolated by distillation in vacuum with a bath of 120–121°C (2 mm), n_D^{20} – 1.5001, d_4^{20} – 1.8926. Found, %: C 76.59, H 9.73, N 5.84. $C_{15}H_{23}NO_2$. Calculated, %: C 76.55, H 9.85, N 5.95.

N-Prop-2-yn-1-yl-N-(2,3-dihydroxypropyl)cyclohexylamine (IX). 9.7 g (0.05 mol) of epoxide (VI) was gradually added to 20 ml of a 10% aqueous solution of sulfuric acid. Due to significant heat release, the reaction flask was cooled in the reaction processes with ice water. After a half hour of stirring, the reaction was complete. The aqueous solution was saturated with sodium chloride and extracted several times with ether and then with chloroform. After distilling off the solvent, diol (IX) was isolated by recrystallization with a T_{melt} 88–89°C (19 mm). Yield 68.7%. Found, %: C 68.03, H 10.14, N 6.51. $C_{12}H_{21}NO_2$. Calculated, %: C 68.21, H 10.02, N 6.63.

Results and discussion

In this regard, and the continuation of the study [9–14] in this work was of some interest to study the possibility of synthesizing new functionally N-substituted derivatives of the propargyl cyclohexylamines, as well as studying their certain chemical properties.

It was shown that the interaction of propargyl bromide with cyclohexylamine in the presence of sodium hydroxide, depending on the molar ratio of the reacting components, produces corresponding secondary and tertiary cyclohexylamines of the propargyl series (I, II) with a yield of 73.6 and 75.4%, respectively:

The obtained compounds (I, II) were characterized by the methods of IR spectroscopy, NMR and the of elemental analysis. In the IR spectrum of the synthesized compounds,

there are characteristic absorption bands in the 2115–2135, 2235, 3300, and 3350–3320 cm^{-1} regions, characteristic for $C\equiv C-H$, $C-N$, and $N-H$ bonds, respectively. In the NMR spectrum, a singlet signal with a chemical shift $\delta=4.41$ ppm, characteristic of the proton of the secondary amino group (1H, NH), is identified. Terminal acetylene protons of the propargyl fragment (1H, $HC\equiv C$, J 2.3 Hz) appear in the range $\delta=2.25$ –2.50 ppm in the form of a triplet. Methylene proton of the fragment (2H, NCH_2 , J 2.4 Hz) are observed at $\delta=3.52$ ppm in the form of a doublet. The protons of the cyclohexane ring are identified in the region $\delta=1.40$ –1.80 ppm.

Synthesized cyclohexylamines of the acetylene series (I, II), due to the active terminal acetylene and $N-H$ bonds, enter into the reactions of hydrosilylation, diene condensation, additions, etc. forming new derivatives. In particular, it is shown that secondary amines enter into hydrosilylation reactions with methyldiethylsilane (at 55–60°C) in the presence of rhodium acetylacetonate dicarbonyl by a triple bond according to the Farmer rule with the formation of silicon-containing cyclic unsaturated amine in the trans structure (III). The diene condensation of the cyclohexylamine acetylene series with the cyclopentadiene proceeds (at 180–185°C) also along a triple bond with the formation of the cyclohexylamine norbornadiene series (IV) with a yield of 68.6% according to the scheme:

The IR spectrum of compound (III) absorption bands is absent at 2135 and 3300 cm^{-1} , characteristic of the terminal acetylene bond. In this case, the absorption bands at 1625 and 770 cm^{-1} are characteristic for the $HC=CH$ and $Si-C$ bonds, respectively. The presence of bands at 1290 and 965 cm^{-1} in the IR spectrum confirms the formation of the *trans*-isomer. In the 1H -NMR spectrum of compound (III), the signals of two protons at

the double bond ($\text{HC}=\text{CH}$) with chemical shifts $\delta=4.82\text{--}4.94$ ppm are identified. and $\delta=5.50\text{--}5.64$ ppm. Spin-Spin Coupling Constants (SSCC) of these protons, which are equal to $13.5\text{--}14.5$ Hz, which is associated with their trans-structure. In the IR spectrum of compounds (IV) there are no bands belonging to the acetylene bond, and at the same time bands at 1645 cm^{-1} , characteristic of $\text{C}=\text{C}$ bonds, were found.

The resulting N-propargylcyclohexylamine, thanks to the N–H bond, also reacts with acrylonitrile and epichlorohydrin forming new derivatives of propargylcyclohexylamine. It was revealed that the reaction with acrylonitrile proceeds (at $80\text{--}90^\circ\text{C}$) with the formation of N-cyanoethyl-N-propargylcyclohexylamine (V) with a yield of 78.2%. The synthesis of N-epoxy-N-propargylcyclohexylamine (VI) is carried out by the interaction of epichlorohydrin with N-propargylcyclohexylamine followed by dehydrochlorination of the resulting chlorohydrins by the reaction:

The reaction with epichlorohydrin proceeds at an equimolecular ratio of the reacting components at 20°C with a yield of 71.6%.

In the IR spectrum of compounds (V), absorption bands at 3345 and 2245 cm^{-1} , which are characteristic for N–H and $\text{C}\equiv\text{N}$ bonds are identified. In the spectrum of compound (VI), along with the absorption bands characteristic for N–H, bands at 3065 , 1245 , and 950 cm^{-1} , characteristic of the oxirane ring, were also found.

The synthesized cyanogen-containing propargylcyclohexylamine (V) under the action of a 10% aqueous solution of hydrochloric acid undergoes hydrolysis and the corresponding unsaturated carboxylic acid (VII) is formed with a yield of 74.4% according to the scheme:

In the IR spectrum of compound (VII) there is no band at 2245 cm^{-1} , characteristic of the $\text{C}\equiv\text{N}$ bond. At the same time, absorption bands (1720 and 3460 cm^{-1}) belonging to the carboxyl group were found.

It is established that epoxypropargylcyclohexylamine (VI), due to the oxirane ring, reacts with propargyl alcohol to form an ether alcohol with two terminal acetylene bonds (VIII). The epoxide (VI) obtained in the presence of a 10% aqueous solution of sulfuric acid undergoes hydrolysis on an oxirane cycle, with product formation of the corresponding glycol of the acetylene series (IX) in high yields:

In the IR spectra of compounds (VIII, IX), the absorption bands characteristic for the oxirane ring ($3065, 915\text{ cm}^{-1}$) are absent. In this case, the bands in the region of $1100\text{--}1160$ and $3450\text{--}3560\text{ cm}^{-1}$, which are characteristic of C–O–C and O–H bonds, respectively, are identified.

Thus, as a result of the research, it was revealed that the synthesized amine-containing acetylenic compounds are highly reactive and can be used as modifiers of epoxy and polyester resins and as synthons for the production of various classes of organic compounds, including their biologically and physiologically active substances and their analogues.

Conclusion

1. A method has been developed for the synthesis of cyclohexylamines of the propargyl series based on the reaction of the interaction of propargyl bromide with cyclohexylamine in the presence of caustic potassium. It was shown that, depending on the molar ratio of the reacting components, the corresponding secondary and tertiary cyclohexylamines of the propargyl series with high yields are formed.
2. The reaction of hydrosilylation of the synthesized cyclohexylamine propargyl series with methyldiethylsilane was studied and it was shown that the reaction proceeds at $55\text{--}60^\circ\text{C}$ in the presence of rhodium acetylacetonate dicarbonyl along the terminal acetylene bond according to Farmer's rule with the formation of silycon-containing unsaturated cyclohexylamine *trans*-structure.

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PROPARGİL SIRA TSİKLOHEKSİLAMİNLƏRİN SİNTEZİ VƏ XASSƏLƏRİ**M.İ.Şatirova, M.M.Mövsumzadə, U.Ş.Cəfərova**

Tsikloheksilamininin propargil bromidlə kalium qələvisinin iştirakında qarşılıqlı təsiri zamanı propargil sıra ikili və üçlü tsikloheksilaminlərin sintezinin mümkünlüyü öyrənilmişdir. Müəyyən olunmuşdur ki, sintez olunmuş ikili aminlər reaksiyaqabilili mərkəzlər hesabına hidrosililləşmə, dien kondensasiyası və birləşmə reaksiyaları kimi müxtəlif kimyəvi reaksiyalara daxil olaraq yeni törəmələr əmələ gətirirlər. O cümlədən, N-prop-2-in-1-itsikloheksilaminin N-H rabitənin hesabına akrilonitrillə və epixlorhidrinlə üçfəzlərli bor efiratinin iştirakında reaksiyaya daxil olaraq müvafiq N-sianetil-N-prop-2-in-1-itsikloheksilamin və N-epoksi-N-prop-2-in-1-itsikloheksilamin əmələ gətirdiyi göstərilmişdir. N-sianetil-N-prop-2-in-1-itsikloheksilaminin duz turşusunun 10%-li sulu məhlulunun təsirindən hidrolizə uğrayaraq doymamış karbon turşusunun, N-epoksi-N-prop-2-in-1-itsikloheksilamin isə oksiran halqasının hesabına qatı sulfat turşusu ilə qarılıqlı təsirdən asetilen sıra qlikolların əmələ gəlməsinə gətirib çıxarır. Həmçinin, müəyyən olunmuşdur ki, N-epoksi-N-prop-2-in-1-itsikloheksilaminin propargil spirti ilə reaksiyası zamanı iki terminal asetilen rabitəli müvafiq efirospirtlər əmələ gəlir. Alınmış birləşmələrin quruluşları İQ və NMR spektroskopiya üsullarının köməyi ilə eyniləşdirilmişdir. Reaksiyanın gedişatına nəzarət müxtəlif həlledici sistemlərdə alüminium oksid örtüklü plastinkalardan ibarət NTX üsulu ilə həyata keçirilmiş və aydınlaşdırıcı kimi yoddan istifadə olunmuşdur.

Açar sözlər: tsikloheksilamin, propargil bromid, norbornadien, hidrosililləşmə, karbon turşusu.

СИНТЕЗ И СВОЙСТВА ЦИКЛОГЕКСИЛАМИНОВ ПРОПАРГИЛОВОГО РЯДА**М.И.Шатирова, М.М.Мовсумзаде, У.Ш.Джафарова**

Изучена возможность синтеза вторичного и третичного циклогексиламинов пропаргилового ряда взаимодействием циклогексиламина с пропаргилбромидом в присутствии едкого калия. Установлено, что синтезированный вторичный амин вступает в различные химические реакции — реакции гидросилилирования, диеновой конденсации и присоединений по реакционноспособным центром с образованием новых производных. В частности показано, что N-проп-2-ин-1-илциклогексиламин, благодаря N-H связи, вступает в реакцию с акрилонитрилом и эпихлоргидрином в присутствии эфира трифтористого бора, образуя N-цианэтил-N-проп-2-ин-1-илциклогексиламин и N-эпокси-N-проп-2-ин-1-илциклогексиламин, соответственно. Под действием 10%-ного водного раствора соляной кислоты N-цианэтил-N-проп-2-ин-1-илциклогексиламин подвергается гидролизу, образуя непредельную карбоновую кислоту. N-эпокси-N-проп-2-ин-1-илциклогексиламин благодаря оксирановому кольцу, при взаимодействии с концентрированной серной кислотой приводит к образованию соответствующего гликоля ацетиленового ряда, а в реакции с пропаргильным спиртом — к образованию соответствующего эфироспирта с двумя терминальными ацетиленовыми связями. Полученные соединения идентифицированы методами ИК- и ЯМР-спектроскопии. Контроль за ходом реакции осуществляли методом ТСХ на пластинках с окисью алюминия в различных системах растворителей, проявитель — йод.

Ключевые слова: циклогексиламин, пропаргилбромид, норборнадиен, гидросилилирование, карбоновая кислота.