Original Article

HALOGENATION OF AROMATIC ACETYLENE AMINO ALCOHOLS AND THE STUDY OF THEIR PROPERTIES

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Abstract

The article presents the results of the study of acetylenic amino alcohols synthesized by aminomethylation of 1-hexyn-3-ol, with secondary amines by the Mannich reaction, in the presence of a copper salt catalyst. The influence of various factors (temperature, pressure and time, as well as the nature of organic solvents) on the synthesis process has been studied. Hydrochlorides were obtained by hydrohalogenation. Dihalogenated hydroxyamines have been synthesized by halogenation. As a result of the experiments, dichloro- and dibromine-containing products were obtained that were not previously described in the literature. All of them are highly soluble in low molecular weight alcohols and chloroform. The structure of the synthesized substances was established by IR, MPR 'H and 13C NMR spectroscopy. The frequency was determined by GLC on an LKhM-72-MD chromatograph with a flame ionization detector. The reaction products were separated by column chromatography on silica gel eluting with hexane. The physicochemical, growth-regulating and herbicidal properties of the synthesized amino compounds and dihalogen-containing hydroxyamines have been determined. The results of studying the herbicidal properties of the synthesized preparations against widespread weeds, such as amaranth and barnyard grass in crops of such cultivated plants as beans and chickpeas, showed high efficiency. The results obtained in the test for growth-regulating activity showed that at relatively high concentrations (0.2% aqueous solution) they have an inhibitory effect, and at relatively low concentrations they exhibit stimulating properties. A study on the growth of the regulatory and herbicidal activity of the synthesized amino compounds was carried out at the Institute of Genetics and Experimental Plant Biology of the Academy of Sciences of the Republic of Uzbekistan.

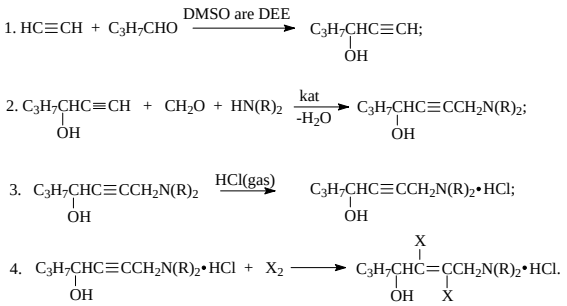
Keywords: Acetylene alcohols, aromatic amino alcohols, Favorsky reaction, Mannich reaction, halogenation, hydrohalogenation, rostregulating activity, herbicides, hydroxyamines.

Introduction

Many halogen-containing compounds synthesized on the basis of secondary acetylenic amino alcohols have physiological activity [1,5,15-19] and they are widely used in various sectors of the economy as herbicides, fungicides, defoliants, growth regulators and drugs, metal corrosion inhibitors. etc. However, studies on obtaining halogen-containing products based on acetylenic compounds are, for some reason, very little studied, and the available literature data are contradictory or have a patent character [4]. In this regard, in this work, we studied the possibility of synthesizing some previously unknown halogen-containing amino compounds from secondary acetylenic alcohol (1-hexyn-3-ol).

In this case, the condensation of n-butyric aldehyde [4–6] with acetylene yielded the corresponding acetylenic alcohols. The influence of various factors (temperature, pressure and time, the nature of organic solvents) on the synthesis process has been studied. Subsequently, the synthesized alcohols by the Mannich reaction were

converted into the corresponding amino alcohols by aminomethylation with a mixture of paraformaldehyde + piperidine and diphenylamine, according to the following scheme:



Where: (R)2 =-diphenylamino-dibenzylamino; X-chlorine or bromine.

Similar schemes were proposed in the work /6/ when carrying out the reactions of aminomethylation of a number of tertiary acetylenic alcohols (AC).

The reaction was carried out in a dioxane medium with the participation of catalysts - copper(I) chloride, copper(I) acetate, copper(I) bromide or iodide in the temperature range of 70-100°C and for a duration of 5-7 hours.

As a result of the experiments, 2 new acetylenic amino alcohols (AAS) were obtained, which were not previously described in the literature. They are highly soluble in low molecular weight alcohols and chloroform. Their yields, elemental composition and some physicochemical constants are given in Table 1.

It should be noted that the yields of synthesized AAS are almost independent of the nature of the catalysts used. Such their insignificant influence, despite the difference between the anions of these salts, indicates the polarization of the C≡C bond of the initial AS, mainly under the action of copper(I) ions. Based on this, in further experiments on the synthesis of AAS, Cu2Cl2, which is one of the most widely available copper(I) compounds, was used as a catalyst.

The nature of the starting amines also has a significant effect on the yield of AAS. Thus, when using diphenylamine under condensation conditions, the corresponding AAS is formed in the greatest amount (yield up to 40%)

At the same time, if its hydrochloride (HC) is used in the reaction, then the formation of AAS increases to 76.2 - 80.0%, the reason for which, obviously, is the increase in the solubility of the initial amine and, as a result, the creation of favorable conditions that increase the mobility of the atom hydrogen bonded to secondary nitrogen.

The kinetic features of aminomethylation of 1-hexyn-3-ol with aromatic amines were studied using the example of the synthesis of 1-dibenzylamino-2-heptin-4-ol, which was carried out in the temperature range of 70–100°C for 7 hours in the presence of copper(I) chloride.

The data obtained showed that with an increase in temperature and duration of the reaction, the yield of AAS increases. Under these conditions, the change in the rate of the process is also directly proportional to the temperature. However, the rate of the reaction at the same temperature decreases uniformly with increasing time, which, in all likelihood, is due to a decrease in the concentration of the initial reagents and dilution of the reaction medium formed by AAS.

In this case, the course of the reaction has a uniform character, and the dependence of its rate and AAS yield on the temperature and duration of the experiment is similar to the formation of other amino alcohols.

Based on the above kinetic data from the dependence on the rate of the process and on the reciprocal temperature in Arrhenius coordinates, the values of the energy of formation (E) of 1-dibenzylamino-2-heptin-4-ol were calculated, which are respectively equal to 2.44 kJ/mol (10.21 kcal /mol). This value of E of the studied reaction is characteristic of most nucleophilic interactions.

It should be noted that in all experiments on the synthesis of AAS, the amount of Cu2Cl2 used was in the range of 1.0–2.5% of the total mass of the initial components. It also turned out that the lack (or absence) of a catalyst in the system cannot be compensated for by increasing the temperature.

In addition, for all the reactions studied, the dependence of lgW on 1/T is linear, and the values of E found are relatively small, which probably indicates the high efficiency of the catalyst used and the nucleophilic nature of the process of formation of the obtained AAS. Quaternary salts of the synthesized acetylenic hydroxyamines were also obtained according to the procedure described in the literature [8]. Their yields, elemental composition, and physicochemical constants are shown in Table 1.

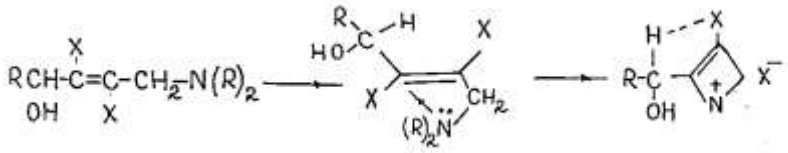
A study of the halogenation of the synthesized AAS in protic solvents (50% CH3COOH and 18% HCI) showed that this process proceeds much more difficult than that in the case of hexyn-1-ol-3. In this case, the temperature regime is 30-40°C for chlorination and bromination 35-50°C, respectively, and the reaction time in both cases was 8-9 hours. The outputs of the target products are in the range of 45-66%. Moreover, only trans-dihalogenvinylaminoalcohols were synthesized according to the scheme:

$$R-\underset{\underset{OH}{|}}{CH}-C\equiv C-CH_2-N(R)_2+X_2\longrightarrow -\underset{\underset{OH}{|}}{CH}-\overset{\overset{X}{|}}{C}=\underset{\underset{X}{|}}{C}-CH_2-N(R)_2$$

where R=-N(R)2 diphenylamino or dibenzylamino groups; X=Cl or Br

The products obtained, upon standing for 5-7 days, spontaneously completely crystallized and are poorly soluble in ether and benzene, but are readily soluble in methanol, ethanol, acetone, and chloroform.

If they are dissolved in chloroform, then when standing for 48-50 hours, crystals of a new type stand out from the solution. Using potentiometric titration and TLC on Silufol nv-254 plates in the system chloroform: ethanol: acetone: toluene: acetic acid (20:4:4:5:I) it was proved that in this case halogen-containing alcohols are converted into ammonium salt-like substances of the type:



The formation of such products can be explained as follows: the synthesis of ammonium salts is possible by halogen cyclization of the initially formed intermediate (trans product) with the participation of a nitrogen atom and an active halogen located in the β-position with respect to the nitrogen atom. Probably, in these compounds, the hydroxyl group cannot be in the same plane with other reaction centers (α and β -carbon atoms):

$$R-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-\overset{\overset{X}{|}}{C}=\underset{\underset{X}{|}}{C}-CH_2-N(R)_2$$

Further, obviously, free tertiary nitrogen with an unpaired electron octet has a strong electron-acceptor effect, i.e. With its electron cloud, it attracts a relaxed halogen from the sphere of hydrogen bonding and thereby facilitates the rotation of the labile methylene group along the axis with the synthesis of a stable salt-like system. The free hydroxyl group under these conditions is not capable of forming a hydrogen bond, the stretching vibrations of which are quite clearly manifested in the IR spectrum. The observed intramolecular quaternization in heated chloroform is apparently due to structural features of the synthesized AAS.

It has been found that only trans isomers are formed upon halogenation of AAS. The constructed spatial model according to Stuart-Briegleb also indicates the impossibility of the formation of a cis-isomer, due to the fact that in this case the entry of bulky halogen atoms into the C≡C bond sphere is significantly hindered.

The yield of halogen-containing products and, accordingly, the rate of addition of halogens to AAS are significantly affected by both the temperature and the duration of the reaction. Moreover, AAS chlorination takes place under milder conditions than their bromination. So, in the case of carrying out the reaction in an environment of hydrochloric and acetic acids at 30-35°C, trans-isomers are formed with a yield of 45-48%. Bromination of AAS is relatively more difficult (at 35–50°C) and the yields of target products are 39–40%. This is obviously due to the fact that the more bulky bromine molecule is difficult to penetrate into the inner sphere of the AAS molecule, because. in this case, the formation of the π-complex due to the C≡C bond is more preferable, and the effect of the hydroxyl group, which has bending vibrations along the triple bond, becomes more pronounced in the medium of the solvents used.

As already noted, in the IR spectra of the initial AAS, the absorption of the amino group, the intramolecular hydrogen bond of the hydroxyl group with an unshared pair of electrons of the nitrogen atom, and the stretching vibrations of the methyl and methylene groups are pronounced. At the same time, the bands for the C≡C bond are almost absent in the spectra. This confirms the ease of introduction in acidic media of electrophilic agents from the opposite side of the eclipsed part of the molecule.

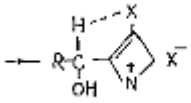
Thus, based on this, as well as on the basis of some of the above considerations, it can be assumed that during the halogenation of AAS, depending on the reaction conditions, the formation of the following compounds is possible:

1, $R-CH(OH)-C(X)=C(X)-CH_2-N(R)_2$

2, $R-C(=O)-CH=C(X)-CH_2-N(R)_2$

3, $\left[R-CH(OH)-C(X)=C=CH-HN^{+}(R)_2\right]X^{-}$

4, $R-CH(O)-C(X)=C(X)-CH_2-N(R)_2$

5. 

The kinetic features of AAS halogenation were studied using the example of bromination of 1-dibenzylamino-2-heptin-4-ol. In this case, the yield of trans-dibromide, depending on the reaction conditions, ranges from 6.0 to 53.4%. It is also seen from the data presented that the bromination of AAS proceeds under more severe conditions than their chlorination. In addition, at 60°C, after 7 hours, the rate of the process decreases sharply due to the formation of dark-colored oligomeric and polymeric products that are difficult to isolate and unidentifiable.

Similar patterns were also obtained during the chlorination of 1-diphenylamino-2-heptin-4-ol in 50% acetic acid at 30–45°C.

From the data obtained, it can be seen that the average rate of the process is quite high and it decreases with increasing reaction time in all cases due to a decrease in the concentration of the starting substances. In this case, the yield of trans-dichloride ranges from 40-49%. The kinetic curves of the dependence of the process rate have a uniform form, which indicates that the chlorination proceeds exactly according to the above scheme.

The dependence of the rate of the studied reactions of AAS bromination and chlorination on the reciprocal temperature for both cases is a straight line. According to the slope of the constructed straight lines, the values of E were found and they are respectively equal to 2.44 kJ / mol (10.21 kcal / mol)

Thus, the above results made it possible to establish the optimal conditions for AAS halogenation: during bromination, the temperature is 40-50°C and the reaction time is 7-9 hours, and in the case of chlorination, the temperature is 35-40°C and the process time is 6-8 hours.

On the basis of the obtained kinetic data, it can be assumed that the studied reactions with respect to both halogen and AAS are of the first order; the process corresponds to the laws of the electrophilic addition reaction.

All synthesized acetylenic alcohols, amino alcohols and their hydrochlorides are readily soluble in water, alcohol, chloroform, acetone, carbon tetrachloride, poorly soluble in hexane and benzene, and dichlorine and dibromo-containing hydroxyamines are soluble in dimethylformamide, acetone, chloroform and carbon tetrachloride, in water and alcohol dissolves poorly.

The halogenation of the synthesized acetylenic amino alcohols was carried out according to the known method [5,8,9]. At the same time, according to it, the original acetylenic amino alcohols were used in the form of hydrochlorides. Separation and identification of the resulting halogen-containing cis- and trans-isomers were carried out according to the procedure described in [5, 10]. From the results obtained, it follows that in all cases trans-isomers are mainly formed.

Growth-regulating and herbicidal properties of acetylenic amino alcohols and -dibromo-dichlor-containing products synthesized according to the method [4-7] were studied according to generally accepted methods.

Experimental part. The IR spectra of the synthesized compounds were taken on a UR-20 instrument in a thin layer in solution, and solid ones in the form of tablets with potassium bromide or sodium chloride. The 1H NMR spectra of the synthesized compounds were taken on a Varian XL-400 instrument. GLC was taken on an LKhM-72 MD chromatograph with a flame ionization detector. The reaction products were separated by column chromatography on silica gel eluting with hexane.

It should be noted that in the spectra of all obtained amino alcohols there are no absorption bands in the region of 3250–3230 cm–1, which are characteristic of stretching vibrations of ≡C–H bonds, which confirms the formation of target products.

The molecular structure of the synthesized halogenated amino alcohols was studied by IR, NMR, and 1H spectroscopy. So, in the IR spectra of halohydroxyamines, absorption bands characteristic of the OH group, the tertiary amino group were found; in the area of the so-called "fingerprints", also corresponding to the absorption of halogenated compounds. In particular, for I-diphenylamino 2,3-dibromo-2-hepten-4-ol in the region of 1120 cm-1, and at 800-600 cm-1, the bands characteristic of trans-dihalogen-containing compounds, which in the IR spectra of the initial products are usually not available. Further, in the region of 1650-1600 cm-1, stretching vibrations of halogen-substituted carbon appear at a multiple bond, absorptions in the region of 2980-2800 cm-1 correspond to the tertiary amino group, and at 3400-3270 cm-1, vibrations characteristic of the OH group appear.

In the PMR spectrum of 2,3-dichloro-I-dibenzylaminohepten-2-ol-4, the protons of the propyl group resonate in the field for CH3 groups and a triplet is formed at 0.90-1.0 ppm; protons of the -CH2 group appear as a multiplet at δ I.35-1.43 ppm. and at δ 1.80 ppm. The presence of a fragment of the Dibenzylamine part of the molecule was confirmed by resonance signals of >N-CH2 protons, found in a weaker field of 4.70-4.81 ppm, and methylene units at δ 1 .48-1.51 ppm.

Synthesis of acetylenic amino alcohols

AAS was synthesized by the well-known Mannich reaction. Powdered paraformaldehyde, as well as widely available amines such as diphenyl-, dibenzylamine-, were used as aminomethylating agents. To carry out the reactions in a three-necked flask equipped with a stirrer, a reflux condenser, and a thermometer, mixtures of 1-hexyn-3-ol, paraformaldehyde, the corresponding amine, dry dioxane, and an anhydrous catalyst, copper (I) acetate, chloride, or bromide, were prepared in certain ratios. . Next, the resulting reaction mixture was intensively stirred while heating in an oil bath (at a temperature of 95-100°C) for 4-6 hours. Then the mixture was diluted with 10% potassium carbonate solution, the organic layer was separated, and the aqueous layer was extracted with chloroform. The organic part and chloroform extracts were combined, dried over potassium carbonate, and the solvents were distilled off. The residue (thick dark liquid) was subjected to vacuum distillation.

Synthesis of 1-diphenylaminoheptin-2-ol-4. A mixture of 9.8 g (0.1 mol) of hexin-1-ol-3, 16.9 g (0.1 mol) of diphenylamine and 3.8 g (0.13 mol) of paraformaldehyde was heated for 6 hours in the presence of 0. 25 g copper(I) acetate in 250 ml dioxane. This yielded 12.4 g (44.3%) of the reaction product with a melting point of 90-91°C.

Bromination of AAS. In this case, these alcohols were also used in the form of GC. An appropriate amount of GC AAS in chloroform was placed into a round bottom flask equipped with a stirrer and an addition funnel, and a stoichiometric amount of bromine was added dropwise to it. The content of the flask was heated to 35-40°C and maintained under vigorous stirring for 6 hours. After cooling the mixture, it was neutralized with a potassium carbonate solution. The aqueous part was separated and extracted with chloroform. Then, the organic part, combined with the extracts, was dried over magnesium sulfate. After distillation of chloroform, the solid residue was recrystallized from ethanol.

Synthesis of 2,3-dibromo-1-diphenylaminohepten-2-ol 4 ml of chloroform obtained 3.76 g (48.25) of the target product with Tm. 151-152°C.

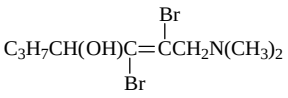
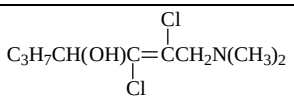
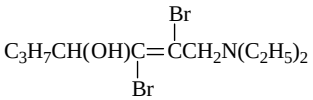
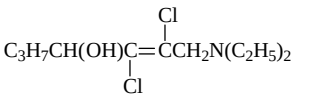
Table 1.

Data on yields and some physicochemical constants of the synthesized aromatic amino alcohols

№	Aromatic amino alcohols	outputt (%)	Melting temperature (°C)	Elemental composition (%)								
				Calculated				Gross - formula	Found			
				C	H	N	Halogen		C	H	N	Halogen
1	2	3	4	5	6	7	8	9	10	11	12	13
I	$C_3H_7CHC\equiv CCH_2N(C_6H_5)_2$ OH	40,0	90	81.07	7.52	5.01		$C_{19}H_{21}ON$	81.10	7.40	5.10	
II	$C_3H_7CHC\equiv CCH_2N(CH_2C_6H_5)_2$ OH	54,0	61	82.08	8.14	4.56		$C_{21}H_{25}ON$	82.20	8.10	4.45	
III	$C_3H_7CHC\equiv CCH_2N(CH_2C_6H_5)_2 \bullet HCl$ OH	76.2	207-208	72,26	6,97	4,43	11,25	$C_{19}H_{22}ONCl$	72,30	6,90	4,50	11,30
VI	$C_3H_7CHC\equiv CCH_2N(CH_2C_6H_5)_2 \bullet HCl$ OH	80.0	216-218	73,36	7,57	4,07	10,33	$C_{21}H_{25}ONCl$	73,40	7,60	4,00	10,30

Таблица 2

Характеристики галогенпроизводных ароматических аминоспиртов

№	Chlorine or bromine-containing amino alcohols	output (%)	Melting temperature (°C)	Elemental composition (%)								
				Elemental composition (%)				Gross - formula	Found			
				C	H	N	Halogen		C	H	N	Halogen
1	2	3	4	6	7	8	9	10	11	12	13	14
V		45,3	205	34,28	5,40	4,44	50,8	$C_9H_{17}ONBr_2$	34,00	5,55	4,25	51,00
VI		49,5	176	47,78	7,57	6,19	31,38	$C_9H_{17}ONCl_2$	47,55	7,70	6,35	31,25
VII		45,6	110	38,48	6,12	4,08	46,64	$C_{11}H_{21}ONBr_2$	38,65	6,25	4,00	46,35
VIII		52,0	102	51,96	8,32	5,50	27,92	$C_{11}H_{21}ONCl_2$	52,16	8,20	5,65	27,80

Studies of growth-regulating and herbicidal properties of synthesized dichlorine and dibromine-containing amino compounds. Currently, one of the urgent tasks of chemical science is the creation of highly effective herbicides, growth-regulating and defoliating drugs necessary for agriculture [5-2,8-10]. It should be noted that most of the currently used such substances are difficult to obtain and expensive, poisonous and insoluble in water, which greatly limits their scope. Based on this, the herbicidal and growth-regulating properties of the above described compounds were studied in detail [15–19].

The results of the test for growth-regulating activity (I-XII) of the selected drugs showed that they have an inhibitory effect at relatively high concentrations (0.2% aqueous solution), and at relatively low concentrations they exhibit stimulating properties. Especially in the case of using a 0.0002% solution of preparations III, IV, VI-VIII, the average growth of bean and chickpea roots increases and amounts to 125 and above 150%, respectively, compared to the control (Table 1). It should be noted that at the same time, with an increase in the growth of the roots of beans and chickpeas, their aerial parts also develop symbatically.

The results of studying the herbicidal properties of the synthesized preparations against widespread weeds such as amaranth and barnyard grass in crops of such cultivated plants as beans and chickpeas are shown in Table 3. At the same time, compounds VI, VII, VIII showed a strong (from 85 to 100 %)), and substances IV, V - average (50-60%) herbicidal activity.

Table 3

Growth-stimulating and herbicidal actions of the obtained amino compounds and their halogen derivatives in relation to beans and chickpeas and weeds (temperature 25-260)

Connections	Growth of the main stem of beans and chickpeas, % to control					The death of weeds,% of control				
	Drug concentration, % (wt)					Drug concentration, % to control (kg/ha)				
	0,2	0,02	0,002	0,0002	0,00002	0,2	0,5	1,0	2,0	3,0
I.	-	-	+	+++	++	-	-	-	+	+
II.	-	+	+	+++	++	-	-	-	+	+
III.	-	-	++	++++	+++	-	-	-	+	+
IV.	-	-	++	++++	+++	-	-	+	++	++
V.	-	-	+	+++	-	-	-	+	++	++
VI.	-	-	+	++++	-	-	-	+	+++	+++
VII.	-	+	++	++	+++	-	+	+	+++	+++
VIII.	-	-	++	++++	++	-	+	+	+++	+++

* (-) - under the specified conditions does not show stimulating activity (+) - minimal stimulation - 100%, (++) - stem growth up to 125%, (+++) - growth up to 150% (++++) growth over 150%

** (-) - Under the indicated conditions, does not show inhibitory activity (+) Minimal inhibition - up to 30%, (++) inhibition up to 60%, (+++) - inhibition of 90% or more (weeds - amaranth spiky and chicken millet)

Conclusion. Four aromatic amino alcohols and their quaternary salts were synthesized by the Mannich reaction. And also on their basis, 8 dihalogen-containing hydroxyamines were obtained. Their structures and some physicochemical constants have been established. The optimal conditions for the formation of these substances in each individual case are determined. The growth-regulating and herbicidal properties of the compounds obtained have been studied in detail.

References:

1. Rakitin Yu.V., Plant growth regulators and herbicides. – M.: Nauka, 1978.360.s. (in Russian)

2. Azerbaev I.N., Sarbaev T.T. Chemistry regulates plant growth. -Alma-Ata: Science, 1968. -p.8 (in Russian)

3. Atavin A.T., Dmitrieva Z.T., Trofimov B.A. biologically active compounds. –L.: Nauka, 1968. -p.113 (in Russian)

4. Chemistry of acetylene. Rep. Ed. M.F. Shostakovsky. Moscow: Nauka Publishing House, 1968. -528 p. (in Russian)

5. Zokirov S. S. Juraboev F. M. Turgunov E. Research Of Synthesis Of Acetylene Amino Alcohols And Study Of Their Properties. International Journal of Disaster Recovery and Business Continuity SSN: 2005-4289 IJDRBC Copyright@2020 SERSC Vol.11, No. 3, (2020), pp. 2850-2857

6. Libman N.M., Kuznetsov S.G. Amino alcohols of the acetylenic series. 1. Obtaining 1,1-disubstituted-4-dialkylaminobutyn-2-tin-1. // Journal. Org. Chemistry. -1960. -T.30. –p.1197 (in Russian)

7. Zokirov S., Mamazhanov M. M., Kadirova G. A., Robilddinova M. S. Research Of 3-Methyl-1-Butyne-3-0l Halogenation Processes And Study Of Their Antimicrobial Properties. International Journal of Disaster Recovery and Business Continuity SSN: 2005-4289 IJDRBC Copyright@2020 SERSC Vol.11, No. 3, (2020), pp. 2677-2685

8. Kurbanov A.I., Sirlibaev T.S., Kultaev K.K. Halogenation and hydrohalogenation of some acetylenic amino alcohols // Zh. appl. chemistry. -1985. -No. 11 -p. 2583-2586 (in Russian)

9. Turgunov E., Yuldashev A., Sadikov M.K. Quaternary ammonium salts of acetylenic amines // Reports of the Academy of Sciences of the Republic of Uzbekistan. -2010. -#2. -p.64-67. (in Russian)

10. E. Turgunov et al. Synthesis of hologen-containing compounds based on propargylamines. // Journal. org. chemistry. -1999. -vol.35. -Issue. 8. -p.1161-1164. (in Russian)

11. Kotlyarevsky I.L., Shvartsberg M.S., Fisher L.B. Reactions of acetylenic compounds. -Novosibirsk: Nauka, 1967. -354s. (in Russian)

12. Babayan A.T., Grigoryan A.A. Research in the field of quaternary ammonium compounds // Zhurn. org. chemistry. -1956. -vol.26. -#7. -since 1945 (in Russian)

13. Rose J.D., Gale R.A. Acetylene reactions. Part V. Reactions of phenylacetylene with secondary amines. J. Chem. Soc., Perhin L. 1949. No. 1. R.792 (in Russian)

14. Turgunov E., Kholmuradova L.E., Dzhumagulov Sh.Kh. Catalytic hologenation of acetylenic mono- and diamines, Zh. UNIVERSUM. No. 4. s.- 2018 (in Russian)

15. A.S. No. 1624941 2-chloro-3-hydroxy-1-hexenyl acetate as a herbicide against amaranth and chicken millet. A.I. Kurbanov, S. Zokirov, T.S. Sirlibaev, R.K. Koblov, S.Tarikov, V.G. Kolyadin. from 1.10.1990 (in Russian)

16. A.S. No. 1617689. 1-Dimethylaminoheptin-2-ol-4 as a herbicide against amaranth and gray mice. S. Zokirov, A.I. Kurbonov, T.S. Sirlibaev, R.K. Koblov, S.Tarikov, F.S. Fatkhuddinov. dated 1.09.1990 (in Russian)

17. A.S. No. 1609094. 1-Morpholino-2-heptin-4-ol as a herbicide against breadth and a cotton growth stimulant. S. Zokirov and others 07/22/1990 (in Russian)

18. A.S. No. 1640837. Propylethynyl carbinol diethylaminoethyl ether exhibiting herbicidal activity against amaranth and growth-stimulating activity against cotton. S. Zokirov and others. from 1.12.1990 (in Russian)

19. Zokirov S.S., Zokirov S., Zhuraboev F., Akhmedov B., Okundadaev A., Khaydarov O. Synthesis of acetylene alcohols and study of their influence on the growth, development and productivity of cotton. // Development of science and technology. STJ. -2018-№5 –p.25-31. (in Russian)

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