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aizhan.mamyrbekova@ayu.edu.kz, a-mamitova@mail.ru, chechinao@yandex.ruSYNTHESIS AND PHYSICOCHEMICAL PROPERTIES  
OF ACETYLENE AMINO ALCOHOLS

**Abstract.** The article is given an overview of publications devoted to the synthesis of acetylenic amino alcohols and the possibility of obtaining on their basis of microbiologically active compounds by interaction with phenyl isocyanate and phenyl isothiocyanate. Acetylene amino alcohols having not only biological activity, but also other valuable properties, are also the basis for obtaining their derivatives. The yield of derivatives of acetylene amino alcohols by Manich reaction was 66-73%. Implementation of the reaction at high temperature leads to the passing of side processes, in particular, the decomposition of acetylene alcohols, resin formation and others.

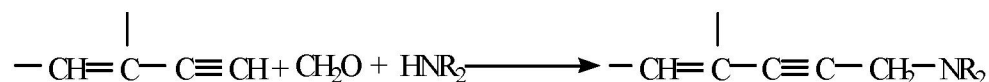
Absorption spectra corresponding to functional groups and bonds of acetylene amino alcohols are observed on IR spectra. Physical and chemical characteristics of acetylene amino alcohols were determined: boiling point, chromatographic characteristics of R<sub>f</sub> substance, elemental composition of carbon, hydrogen, nitrogen (mass.) and gross formulas.

**Key words:** acetylene amino alcohols, carbamic acids, carbamates, thiocarbamates, microbiological activity.

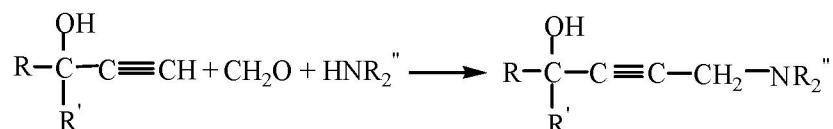
**Introduction.** From the point of view of various specific properties of compounds, compounds with an amino group in the composition of which there is an acetylene bond are of particular interest [1-6], because among them there are compounds that differ in chemical, physiological and biological properties.

One of the most important ways to produce amino acids in the acetylene range is the amino methylation reaction of the German chemist Karl Mannich. To continue this reaction, you need three components - the first substrate to be used for aminomethylation (in our case, acetylenic alcohol), the second is carbonyl (formaldehyde in our case), and the third is the amino component (in our case, dialkyl (diaryl) amines) [7-9]. As a result of the reaction, the product of aminomethylation is formed and water, the so-called Mannich base.

V. Nazarov and his colleagues approve that vinyl acetylene homologs do not react with amines and paraffin even with prolonged heating at atmospheric pressure, but when introduced into the reaction medium in a catalytic amount of iron salts (FeCl<sub>3</sub>), the reaction occurs easily and gets amino acid derivatives in good yields ( up to 90%) [10]:

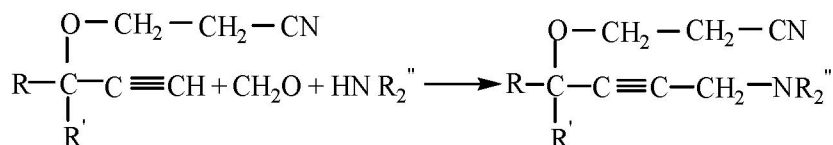


The interaction of amines of acetylene alcohols with paraformam has been the themes of many studies. E. Jones and his colleagues obtained the corresponding acetylenic amino acids with a small yield by the interaction of  $\alpha$ -ethynylcarbinol with trioxymethylene and secondary amines [11]:



These alcohol acetates under the reaction conditions of Mannich give acetylenic amino alcohols in high yield (50-90%). Based on these data, the authors concluded that it inhibits the reactions of the hydroxyl group in  $\alpha$ -conditions, close to the three bonds of acetylene alcohol.

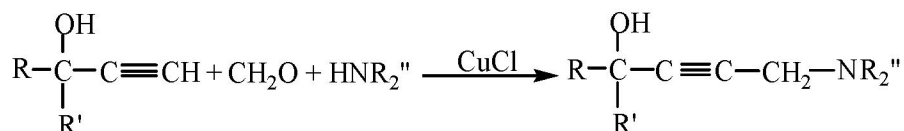
I.N. Nazarov and G.A. Schwechheimer [12] approve that in the presence of an excess amount of paraffin compared to equimol when heated amine with dioxane, are formed esters of acetylene and amine in good yields (56-96%).



The reactions of aminomethylation of acetylenic alcohols, benzoates and phenoxyacetates have also been investigated, and it has been proven that the Mannich reaction going hard with benzoate, especially phenoxyacetates, compared to acetates [13].

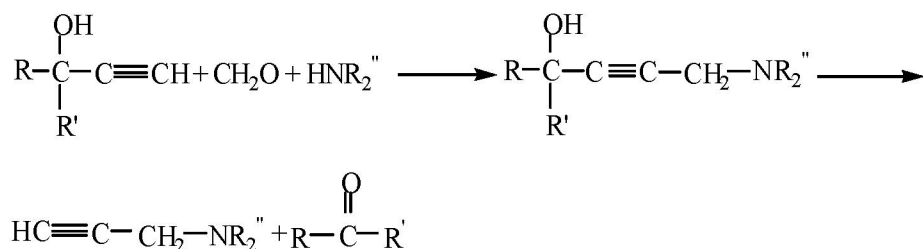
G.A. Schwechheimer [14] proposed a method for the aminomethylation of acetylenic alcohols with acetals. Given that acetals, acetylenic alcohols are easily formed, and saponified after the mannich reaction, this method is advantageous and can be widely used. However, all the methods described above, when performing the Mannich reaction, protection of the hydroxyl groups of acetylene alcohols is required, and after the saponification reaction for obtain an amino acetylenic alcohol with a free hydroxyl group, it prolongs the reaction by several stages for obtain the desired end product.

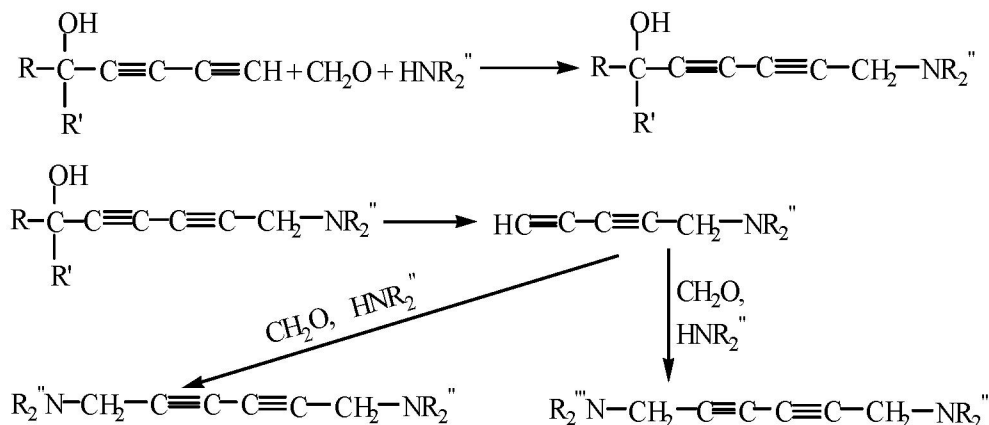
Therefore, in our opinion, recommended N.M. Lieberman and S.G. Kuznetsov method of amino-methylation of acetylene alcohols is convenient [15]:



These authors carefully studied the situation with the Mannich reaction and concluded that the reaction of aminomethylation easily occurs with the use of copper salt (I) as a catalyst for hydrogen atoms near the triple bond of acetylene alcohol. According to these scientists, in the case of the Mannich reaction, the process of aminomethylation is always accompanied by one valence copper (possibly with the formation of intermediate copper acetylide). If during the synthesis copper (II), with the help of formaldehyde, is reduced to copper (I) (in alkaline medium) then its catalytic capacity at the beginning of the reaction will probably be the same with copper (I). It has been established that in a neutral and weakly acidic medium (using the amine salt), the transition from copper (II) to copper (I) will be difficult and the yield of the reaction product decreases. The content of the catalyst has little effect on the reaction.

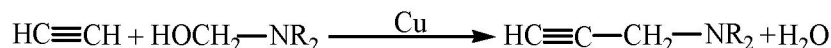
I.N. Azerbayev and his colleagues [16-18] proposed a convenient method for obtaining various acetylene amines by decomposing the amino alcohols of amino acetylene and diacetylene, followed by aminomethylation of the obtained products:





Although aminomethylation of acetylene compounds using the Mannich reaction is widely used at the laboratory level, its mechanism has not yet been confirmed by organic scientists.

The hypothesis that the aforementioned condensation reaction is accompanied by the formation of an intermediate product of amine and formaldehyde may be testified producing an acetylene base directly from methylolamines and acetylenes [19]:



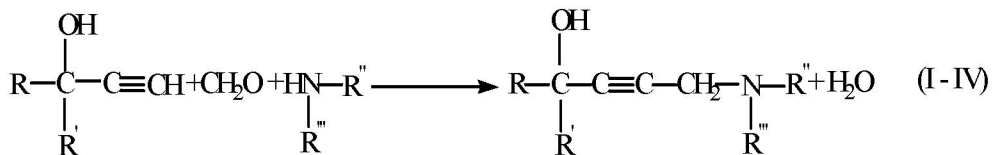
According to I.N. Azerbaev and his colleagues compared to hydrogen atoms near triple bonds in the composition of vinyl acetylene and vinyl acetylene, hydrogen atoms near triple bond in the composition of acetylene alcohols, are non-active under Mannich reaction conditions. In these cases, for reduce the activation energy of acetylenic compounds with using only the copper compound as a catalyst, they are involved in the condensation reaction with paraffin and secondary amines.

The synthesis of cycloalkyl and aryl derivatives of acetylenic amino alcohol and their holonolitic properties were studied in order to search for biologically active compounds. There is evidence that, when a carbon atom is replaced near the carboxyl groups with cycloalkyl, the biological activities of cycloalkyl derivatives of acetylene amino alcohols may be higher and more toxic compared to aryl derivatives [20].

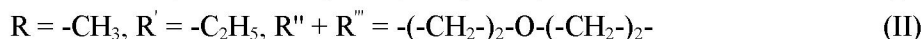
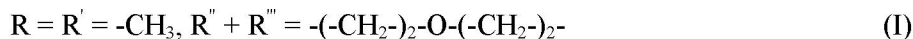
The authors of [21], continuing the search for biologically active compounds, were synthesized succinates, sulfonates, tartrates and adipates of pyrrolidine and rows of piperdiae, and were established that the cholinolytic properties of cyclopentyl and cyclohexyl derivatives are high.

Thus, acetylenic amino alcohols are not only biologically active, but are also the basis for obtaining derivatives with useful properties, and are capable of having such properties. In this regard, these compounds are of great interest.

**Methods.** Some amino alcohols have been obtained by aminomethylating acetylenic alcohols using Mannich reaction. For aminomethylation of acetylenic alcohols in the presence of formaldehyde, diphenylamine reacts with morpholine



where:



Carried out the reaction of aminomethylation in a dehydrated medium of dioxane while heating at the temperature of 80-90°C. As catalyst used is freshly prepared copper chloride.

**Results and discussions.** In tables 1 and 2 are presented the physics-chemical characteristics of the obtained acetylene aminoalcohols.

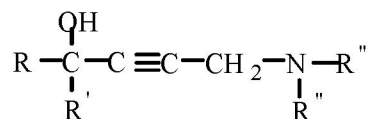


Table 1 – Physicochemical characteristics of the obtained acetylene aminoalcohols

Compound ordinal №	R	R'	R''	Output, %	t <sup>o</sup> <sub>heat</sub> , °C/ mm. mercury column	R <sub>f</sub>
I	-CH <sub>3</sub>	-CH <sub>3</sub>	(R'') <sub>2</sub> = -(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub>	72	128/4	0,31
II	-CH <sub>3</sub>	-C <sub>2</sub> H <sub>5</sub>	(R'') <sub>2</sub> = -(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub>	67	125/3	0,27
III	-CH <sub>3</sub>	-CH <sub>3</sub>	-C <sub>6</sub> H <sub>5</sub>	73	127/3	0,36
IV	-CH <sub>3</sub>	-C <sub>2</sub> H <sub>5</sub>	-C <sub>6</sub> H <sub>5</sub>	66	126/3	0,31

Table 2 – Elemental composition of acetylenic amino alcohols

Compound ordinal №	found, %			Brutto formula	calculated, %		
	C	H	N		C	H	N
I	65,62	9,33	7,72	C <sub>10</sub> H <sub>17</sub> NO <sub>2</sub>	65,57	9,29	7,65
II	67,30	9,71	7,20	C <sub>11</sub> H <sub>19</sub> NO <sub>2</sub>	67,00	9,64	7,11
III	81,54	7,21	5,32	C <sub>18</sub> H <sub>19</sub> NO	81,51	7,17	5,28
IV	81,83	7,65	5,13	C <sub>19</sub> H <sub>21</sub> NO	81,72	7,53	5,02

From table 1 it can be seen that the yield of acetylenic amino alcohols at the Mannich reaction is in the range of 66-73%. Compared to acetylene alcohols, these values are slightly low. Because, in our opinion, this is due to the high temperature of the process, as well as the production of side reactions such as decomposition of acetylene alcohols, coating with resin, and other additional reactions.

Table 3 – The main absorption zone of the IR spectra of acetylenic amino alcohols

Compound ordinal №	Connections or groups					
	C≡C	C-N	C-O-C	-CH <sub>2</sub> -	C <sub>6</sub> H <sub>5</sub>	O-H
	Vibration of Valence Frequency, ν, cm <sup>-1</sup>					
I	2207	1219	1195	1921	—	3625
II	2195	1220	1185	1924	—	3614
III	2200	1220	1190	1923	1580	3623
IV	2213	1220	1195	1924	1585	3621

From table 3 it can be seen that, depending on the bond and the main groups, the oscillation frequency of the IR spectra of acetylene amino alcohols is shown in the characteristic vibration zones, so proves their structure.

**Conclusion.** Thus, the synthesis of acetylenic alcohols, glycols and aminoalcohols is realizable processes without obstacles. With a high yield, acetylene amino alcohols under Favorsky reaction conditions in a medium of dried diethyl ether in the presence of thoroughly crushed technical potassium hydroxide at low temperature are obtained with a process of condensation of ketones with acetylene (to obtain acetylene alcohols) acetylene alcohols with ketone (to obtain symmetric and asymmetric acetylene glycols), at the conditions of Chodkiewicz-Kadio reaction of diacetylenic glycols, acetylene alcohols with bromoacetylene alcohols.

Also, with the interaction of acetylenic alcohols with formaldehyde and dialkylamines (or cyclic amines) under the conditions of the Mannich reaction in the presence of copper (I) chloride in the catalytic

content and in the medium of the dried diethyl ether can be obtained synthesis of glokolev and amino alcohols.

With this, by synthesis several acetylenic amino alcohols were obtained. Our upcoming goal is to investigate the biological properties of salt-like esters - carbamates and thiocarbamates, after synthesis obtained through interaction their with phenyl isocyanate and phenyl isothiocyanate.

Such interest is not only based on the above information, but is also related to the data obtained in recent times. For example, with French scientists were found among compounds of a substance with medicinal properties, similar the above substance [22, 23] and Chinese scientists have found carbamate compounds with high action against microorganisms [24]. Russian scientists claim that some of the carbamites have fungicidal properties significantly [25].

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### **АЦЕТИЛЕН АМИНОСПИРТТЕРІНІҢ СИНТЕЗІ ЖӘНЕ ФИЗИКА-ХИМИЯЛЫҚ ҚАСИЕТТЕРІ**

**Аннотация.** Мақалада ацетилен аминспирттерін синтездеуге бағышталған жарияланымдарға шолу жасалып, оларды фенилизоцианат және фенилизотиоцианатпен әрекеттестіру арқылы микробиологиялық белсенді заттарды алу мүмкіншілігі қарастырылған. Ацетилен аминспирттері биологиялық белсенді ғана емес басқа да пайдалы қасиеттерге ие туындыларды алуға негіз болуымен қатар өздері де сондай қасиеттерге ие болуы ықтимал. Ацетилен аминспирттерінің шығымы Манних реакциясы жағдайында 66-73% аралығында болды. Реакцияның жоғары температурада жүруіне байланысты кейбір қосымша реакциялардың – ацетилен спиртінің ыдырауы, шайырлану және т.б. байқалды. ИҚ-спектрлерінде ацетилен спирттерінің функционалдық топтары мен байланыстарына тән жұтылу жолақтарының барлығы дерлік анықталды. Ацетилен аминспирттерінің физика-химиялық сипаттамалары: қайнау температурасы, заттың хроматографиялық сипаттамасы  $R_f$ , көміртек, сутек, азоттың элементтік құрамы (масс.) және брутто-формулары анықталды.

**Түйін сөздер:** ацетилен аминспирттері, карбамин қышқылдары, карбаматтар, тиокарбаматтар, микробиологиялық белсенділік.

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### **СИНТЕЗ И ФИЗИКО-ХИМИЧЕСКИЕ СВОЙСТВА АЦЕТИЛЕНОВЫХ АМИНОСПИРТОВ**

**Аннотация.** В статье дается обзор публикаций, посвященных синтезу ацетиленовых аминспиртов и возможности получения на их основе микробиологически активных соединений взаимодействием с фенилизоцианатом и фенилизотиоцианатом. Ацетиленовые аминспирты, обладающие не только биологической активностью, но и другими ценными свойствами, являются также основой для получения их производных. Выход производных ацетиленовых аминспиртов по реакции Манниха составил 66-73%. Осуществление реакции при высокой температуре приводит к протеканию побочных процессов, в частности, разложение ацетиленовых спиртов, смолообразование и другие. На ИК-спектрах наблюдаются спектры поглощения, соответствующие функциональным группам и связям ацетиленовых аминспиртов. Определены физико-химические характеристики ацетиленовых аминспиртов: температуры кипения, хроматографическая характеристика вещества  $R_f$ , элементный состав углерода, водорода, азота (масс.) и брутто-формулы.

**Ключевые слова:** ацетиленовые аминспирты, карбаминовые кислоты, карбаматы, тиокарбаматы, микробиологическая активность.

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## REFERENCES

- [1] Azerbaev I.N., Gusev B.P., Tatarchuk V.V. // News of Kazakh SSR Academy of Sciences, chemical series, **1974**, N 3, 87-91 (in Rus.).
- [2] Azerbaev I.N., Kasymkhanova R.F., Erzhanov K.B. Synthesis of some nicotines of asymmetrically substituted acetylene glycols. Alma-Ata: Science, **1972**. 200 p. (in Rus.).
- [3] Pershin G.N., Milovanova S.N., Menkaure A.L., Simakova T.G., Baramova M.A., Kotlyarevsky I.L. // News of Kazakh SSR Academy of Sciences, chemical series, **1970**, N 8, 1904-1908 (in Rus.).
- [4] Kotliarevskii I.L., Andrievskaia E.K., Fisher L.B. // News of Kazakh SSR Academy of Sciences, chemical series, **1985**, N 2, 397-405 (in Rus.).
- [5] Nurkenov O.A., Seilkhanov T.M., Fazylov S.D., Issayeva A.Zh., Seilkhanov O.T., Zhaksybayeva G.Sh. Obtaining and research of the supramolecular complexes of alkaloid salsoline with cyclodextrins by NMR spectroscopy // News of the National academy of sciences of the Republic of Kazakhstan. Series chemistry and technology. 2019. Vol. 1, N 433. P. 64-69. ISSN 2518-1491 (Online), ISSN 2224-5286 (Print). <https://doi.org/10.32014/2019.2518-1491.9>
- [6] Nurkenov O.A., Fazylov S.D., Issayeva A.Zh., Seilkhanov T.M., Zhivotova T.S., Shulgau Z.T., Kozhina Zh.M. Complexes of inclusion of functionally-substituted hydrasone of isonicotic acid with cyclodextrins and their antiradical activity // News of the National academy of sciences of the Republic of Kazakhstan. Series chemistry and technology. 2018. Vol. 6, N 432. P. 57-66. ISSN 2518-1491 (Online), ISSN 2224-5286 (Print). <https://doi.org/10.32014/2018.2518-1491.27>
- [7] Azerbaev I.N., Bosiakov Iu.G., Erzhanov K.B. The book the Chemistry of acetylene and calcium carbide. Alma-Ata: Science, **1972**. 245 p. (in Rus.).
- [8] Azerbaev I.N., Mukanov U., Sarbaev T.G. // The Publication of Kazakh State University. Chemistry and chemical technology, **1997**, VIII, 79-84 (in Rus.).
- [9] Patent № WO2007071428-A2. Smith S., Read D. New organic compounds useful for induction of resistance in plants, and for curative/preventive control of phytopathogenic fungi and bacteria in agricultural crops e.g. Academic Press: London, UK. 1997 (in Eng.).
- [10] Nazarov I.N., Krasnaia Zh.A., Vinogradov V.P. // Russ. J. Gen. Chem., **1958**, 28, 2, 395-399 (in Rus.).
- [11] Jones E.R., Morezak J., Beder H. J. // Chem. Soc., **1947**, № 8, 1523-1527 (in Rus.).
- [12] Nazarov I.N., Shvekhgeimer G.A. // Russ. J. Gen. Chem., **1956**, 26, 3, 813-819 (in Rus.).
- [13] Nazarov I.N., Kruglikova R.I., Nikolaev G.M. // Russ. J. Gen. Chem., **1959**, 29, 3, 1859-1867 (in Rus.).
- [14] Shvekhgeimer G.A. // News of Kazakh SSR Academy of Sciences, chemical series, **1957**, № 10, 1265-1267 (in Rus.).
- [15] Libman N.M., Kuznetsov S.G. // Russ. J. Gen. Chem., **1992**, 30, 4, 1197-1201 (in Rus.).
- [16] Azerbaev I.N., Gusev B.P., Tatarchuk V.V., Shovkan' A.Ia. // Bulletin of the Academy of Sciences of the Kazakh SSR, **1964**, 4, 60-63 (in Rus.).
- [17] Azerbaev I.N., Gusev B.P., Tatarchuk V.V. // News of Kazakh SSR Academy of Sciences, chemical series, **1964**, 3, 87-91 (in Rus.).
- [18] Gusev B.P., Tatarchuk V.V., Azerbaev I.N., Kucherov V.F. // News of Kazakh SSR Academy of Sciences, chemical series, **1965**, 3, 846-851 (in Rus.).
- [19] Gusev B.P., Tatarchuk V.V., Azerbaev I.N., Kucherov V.F. // News of Kazakh SSR Academy of Sciences, chemical series, **1986**, 7, 1209-1213 (in Rus.).
- [20] Golikov S.N., Kuznetsov S.G., Libman N.M., Loktionov S.I., Zatsepin E.P. // Chemical and pharmaceutical journal, **1998**, 12, 21-25 (in Rus.).
- [21] Semenova N.N., Safonova A.A., Klochkova I.N., Noritsina M.V. // Chemical and pharmaceutical journal, **1999**, 12, 12-14 (in Rus.).
- [22] France № 2866886. 02.09.2005. Derivatives of aryl- and heteroaryl-alkylcarbamates, their preparation and use as medicines // Abouabdellan A., Bartsch Li R., Hoor-Naert Ch., Ravet A. (in Eng.).
- [23] France № 2865205. 22.07.2005. Ariloxipicolinamide derivatives, their preparation and use in therapy // Abouabdellan A., Almario G.A., Froissant J., Hoor-Naert Ch. (in Eng.).
- [24] Yao Bin, Shen Xiao-lan, Yang Qian-hua, Xu Bing-xiang. // Acad. J. Second Mil. Med. Univ., **2005**, № 5, 558-560 (in Eng.).
- [25] Alekseeva E.O., Popkov S.V., Talismanov V.S. // Advances in chemistry and chemical technology, **2008**, 22 (6), 95-98 (in Rus.).