

Processing and Physicochemical Calculations of the Results of the Synthesis Processes of Acetylene Amino Alcohol Esters

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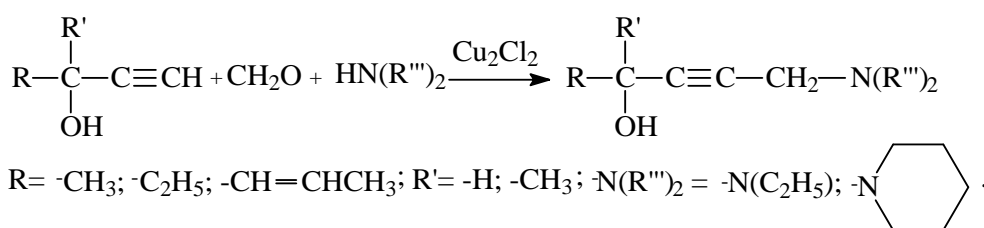
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Abstract: The article discusses the synthesis of acetylene and acetylene alcohol with the presence of ketones, the study of alternative conditions for obtaining halogenated derivatives of amino ethers based on them, the mathematical processing of the obtained results, and the implementation of physicochemical calculations.

Keywords: acetylene, acetylene alcohol, aminocyprate, aminoether, Mannix reaction, acrylonitrile, halogen, catalyst.

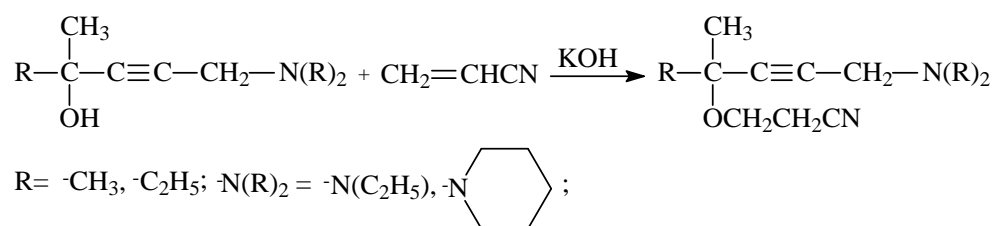
Today, scientific research is being conducted in the world to study the structure and reactivity of alkynes, to determine the processes of forming complex compounds with intermediate metals. In this regard, on the basis of the electronic structure and physical properties of alkynes, special attention is paid to determining the processes of their interaction with electrophilic and nucleophilic and metal complexes, synthesizing new organic compounds based on acetylene, and determining their physical and chemical properties.

Diethylamine, piperidine, paraform and acetylenic alcohol-3-methylbutyn-1-ol-3, 3-methylpentin-1-ol-3 and hexen-4-yn-1-ol-3 in dioxane solution based on Mannix reaction at 90-95 ° As a result of heating for 2-4 hours at a temperature of C in the presence of a Cu₂Cl₂ catalyst, the corresponding acetylenic amino alcohols (AAA) with a yield of 48-55% were synthesized according to the following scheme:



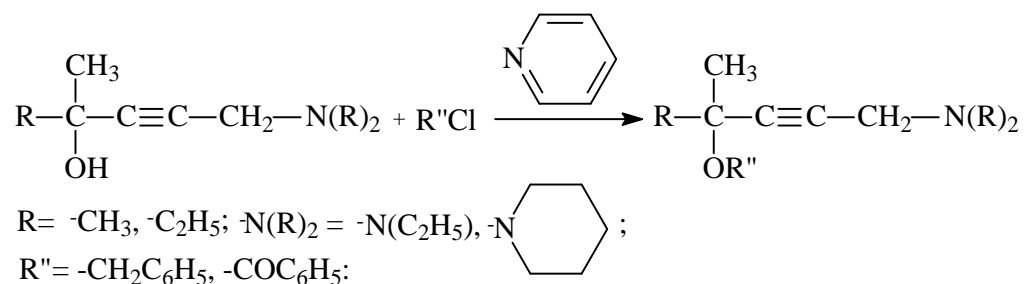
Some physicochemical constants of the synthesized AAA and their structure and composition were determined using physical research methods.

Synthesis of esters of acetylene amino surfaces. As a result of the reaction of AAA with acrylonitrile in the presence of the alkaline catalyst KON, their β-cyanoethyl ethers were obtained according to the following scheme:



The first of these two methods is easier to perform and the yield of the reaction is relatively high (65-78%) and the resulting product is easier to isolate. In the second method, the yield of the substance is 58-70%, but it is difficult to separate the reaction product and the initial product from each other. Next, as a result of reaction of AAA with benzyl and benzoyl chlorides in the presence of pyridine in benzene solution, their respective esters were synthesized.

The reaction scheme is as follows:

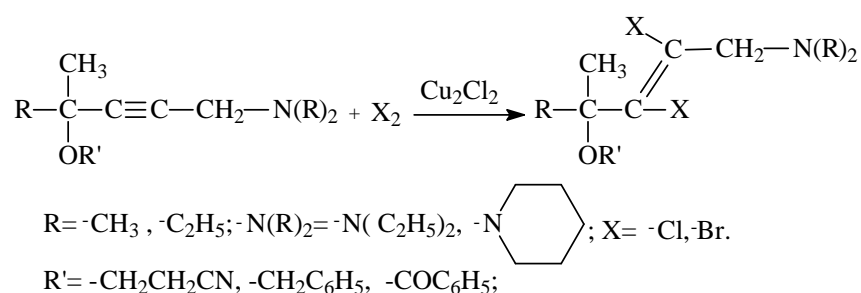


The yield of AAA β-cyanethyl, benzyl and benzoyl ethers obtained as a result of the above reactions is 70-75%.

In particular, in the IR spectrum of synthesized 5-diethylamino-(2-methylpent-3-yn-2-yloxy)propanenitrile, there is an average intense valence vibration characteristic of the tertiary amino group in the region of 2940-2810 cm⁻¹. A weak absorption peak in the region of 2240 cm⁻¹ is typical for the S≡S bond.

In order to further clarify the effect of the hydroxyl group on the halogen bonding of the three bonds in amino ethers (AAE), their β-cyanethyl, benzyl and benzoyl ethers were synthesized. Physico-chemical constants of obtained ethers were determined.

Halogenation reactions in the presence of Cu₂Cl₂ catalyst were studied in this AAE chloroform solution. As a result of the reaction, it was found that dihalogenated derivatives of the ethylene series AE are formed with high yield from the addition of halogens in the trans position to the triple bonds of AAE. The reaction takes place according to the following scheme:



Different substituents on the amino group have almost no effect on the reaction outcome. The yield of the product depends on such factors as the duration of the reaction, and it is noteworthy that the halogenation process is carried out in a chloroform solution at room temperature (20-40 oC) for 10 hours to 60-70%, and when carried out at a temperature of 50-60 oC, the reaction time is reduced by half, accordingly while the use of copper chloride catalyst increases the reaction yield to 68-70% for 4 hours at room temperature, increasing the temperature increases the reaction yield to 83% for only 2 hours. Therefore, the reaction yield is relatively high in the presence of a catalyst.

In this case, with an increase in the molar ratio of AAE and halogen: AAE = 2:1, the formation of the trans-dihalogen compound of the amino ether dominates in the reaction medium, and their yield reaches 68-70% in a time interval of 1.5 hours at a temperature of 40 oC.

The comparison of the obtained results shows that in the studied conditions, the formation of a p-complex between the C≡C bond and halogens and the breaking of the triangle in most cases require high temperature or the use of catalysts. Accordingly, the use of a copper monochloride catalyst significantly accelerates the exothermic addition of halogens to the S≡S bond and leads to trans-digaloid products in high yield.

The effect of temperature and duration on the reaction process is presented in Table 1, and based on the results, the reaction rate was determined (Figure 1).

Table 1 Synthesis of 5-(Diethylamino)-3-(3,4-dichloro-2-methylpent-3-en-2-yloxy)propanenitrile (solvent-chloroform)

Duration of reaction, hour	Product yield, %	The average speed of the reaction (W)	
		%/hour	Mol/l hour
Temperature 35 °C			
1	6,4	6,40	0,28
2	13,0	6,50	0,29
3	25,4	8,46	0,37
4	48,8	11,69	0,51
6	48,2	8,03	0,35
8	48,0	6,00	0,26
Temperature 45 °C			
1	10,8	10,80	0,48
2	21,0	10,50	0,47
3	40,2	10,05	0,44
4	64,2	14,41	0,63
6	78,3	13,05	0,58
8	75,5	9,43	0,42
Temperature 50 °C			
1	11,2	11,2	0,49
2	21,1	10,55	0,46
3	39,5	13,15	0,57
4	61,7	15,42	0,67
6	69,6	11,6	0,51
8	67,4	8,42	0,37

The results obtained as a result of the performed processes confirm that the halogens are in the trans state. In the initial conditions of the reaction, its rate is much higher and the halogen concentration changes rapidly, the maximum value of the reaction rate is reached at a temperature of 45 °C for 6 hours.

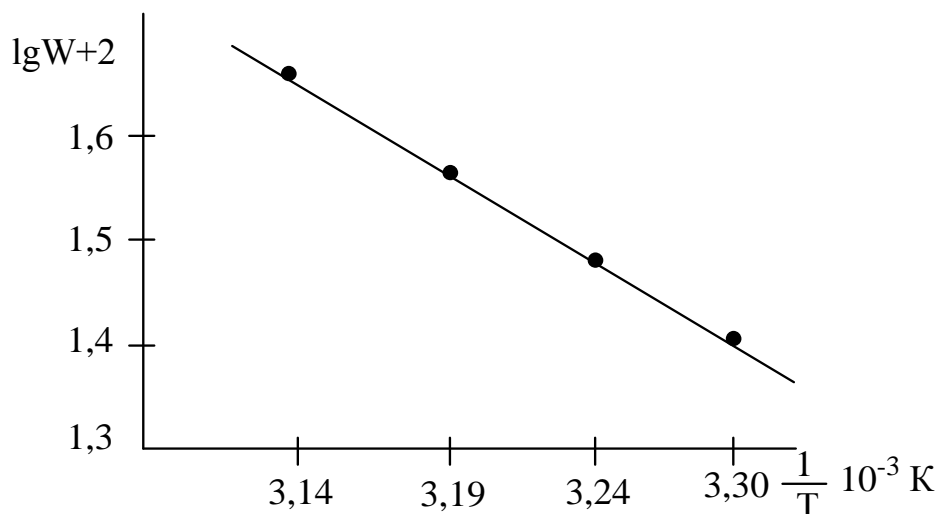


Figure 2. Dependence of the reaction rate of the formation of 5-diethylamino-(3,4-dichloro-2-methylpent-3-en-2-yloxy)propanenitrile on the inverse value of temperature.

The structure of synthesized trans-dihalogenated ethylene amino ethers (Table 2) was studied based on IR and ^{15}N NMR spectra. Here, in the IR spectrum of 5 diethylamino-3-(3,4-dichloro-2-methylpent-3-en-2-yloxy)propanenitrile, deformation vibrations of the nitrile group in the region $2895\text{--}2870 \text{ cm}^{-1}$, valence vibrations characteristic of the tertiary amino group at an average intensity of 2960 cm^{-1} . In the 2820 cm^{-1} region, a weak absorption line in the 2160 cm^{-1} region is characteristic of the S=S bond, and absorption lines belonging to the SCl=CCl group appear in the $560\text{--}635 \text{ cm}^{-1}$ region.

Also, characteristic absorption lines in the ^{15}N NMR spectrum of 6-diethylamino-(4,5-dichloro-3-methylhex-4-en-3-yloxy) propanenitrile: d (3N) protons of the methyl group at 1.33 m.u. in the field in the form of a singlet, the protons of the methyl group d (3N) in the β state are 0.69 m.u. triplet, d (2N) protons of the methylene group are 1.5 m.u. protons of the methyl group d (6N) in the b position relative to the quartet and tertiary nitrogen in the field are 1.0 m.u. methylene group d (6N) protons near the triplet, nitrogen atom and cyanide group in the field 2.58-2.64 methylene group d (2N) protons near the multiplet, halogen and double bond in the field 3.0 m.u. singlet in the field, the protons of the methylene group d (2N) next to the ether group are 3.74 m.u. triplet absorption lines were observed in the field.

Currently, special quantum chemistry programs ASDFREE12, RHF, SCF-MO, MINDO/3, MNDO, AM1 have been created, of which Chem 3D Ultra 8.0 is a program developed for substances that exhibit acidic properties or react with hydrogen atoms in their molecules. 3d structure of the molecule, quantum-chemical calculations, spatial structure of the molecule, charge and electron density distribution in the atoms of the molecule were studied in order to determine the molecular derivatives, reactivity and reaction centers of the synthesized acetylene amino alcohol esters. Studies were performed using Hyper Chem software (Figure 3).

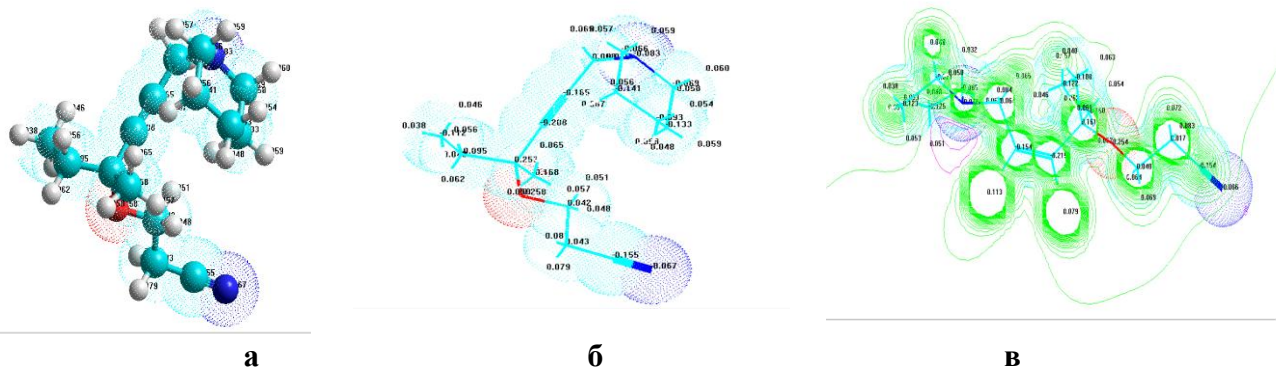


Figure 3. 3d structure of 5-piperidino-(2-methylpent-3-en-2-yloxy)propanenitrile (a), distribution of charges (b) and electrons (v) in the molecule

The 3d structure of the molecule shows that the heterocyclic ring structure is located in a plane. According to the analysis of the charge and electron density distribution values in the molecule, although the hydroxyl group and nitrogen atoms occupy the same position in the molecule, the electron distribution is partially different from each other.

Mathematical modeling of the process of halogenation of acetylene amino alcohol β -cyanethylether. Mathematical modeling of the experimental results obtained during the synthesis of 5-diethylamino-(3,4-dichloro-2-methylpent-3-en-2-yloxy) propanenitrile was carried out using the least squares method, and an analytical dependence graph was created to explain the experimental results. The following $f(x, a_1, a_2, \dots, a_k)$ least squares method was used in this process. In this case, the function $f(x, a_1, a_2, \dots, a_k)$ should be set in such a way that the squares of the obtained result are $f(x, a_1, a_2, \dots, a_k)$ and their displacements in the unit of size are $Y_i = f(x, a_1, a_2, \dots, a_k)$ should be less than the displacement dimensions.

$$S(a_1, a_2, \dots, a_k) = \sum_{i=1}^n [y_i - Y_i]^2 = \sum_{i=1}^n [y_i - f(x, a_1, a_2, \dots, a_k)]^2 \rightarrow \min(1)$$

The process was modeled as follows:

1. According to the results of the experiment, the appearance of the selected connection was determined.
2. The dependence coefficient in the function $Y = f(x, a_1, a_2, \dots, a_k)$ was selected and this dependence was extracted through a_i in the first function. 5 Diethylamino-(2-methylpent-3-yn-2-yloxy)-propanenitrile was mathematically modeled based on the results obtained in the presence of solvent chloroform based on the factors affecting the process, i.e. temperature, the average rate of the reaction in the halogenation reaction.

In the process of mathematical modeling of the obtained results, the reaction temperature and product yield were used.

$$t[1] := 30; t[2] := 35; t[3] := 40; t[4] := 45,$$

$$y[1] := 45.5; y[2] := 48.8; y[3] := 60.4; y[4] := 64.2.$$

Based on the mathematical results, the halogenation reaction was analyzed in general through a small number of experiments. The effect of reaction temperature and duration on product yield and reaction speed was studied on the basis of mathematical laws.

Mathematical processing of the results of halogenation processes of esters of acetylenic amino alcohols. Mathematical calculations 5-diethylamino-(3,4-dichloro-2-methylpent-3-en-2-yloxy) when the reaction duration of the halogenation process of 5-diethylamino-(2-methylpent-3-yn-2-yloxy)-

propanenitrile is carried out in 4 hours)- taking into account the high yield synthesis of propanenitrile, the following values were calculated using the MARLE-2018 program. Based on the obtained results, the dependence of the formation of dihalogen products as a result of the chemical reaction on temperature and reaction speed, mathematical processing and experimental results are expressed by the following function.

$$f_1 := a_1 * 30^3 + a_2 * 30^2 + 30 * a_3 + a_4; f_1 := 45.4737$$

$$f_2 := a * 35^3 + b * 35^2 + 35 * c + d; f_2 := 48.76666$$

$$f_3 := a * 40^3 + b * 40^2 + 40 * c + d; f_3 := 60.3584$$

$$f_4 := a * 45^3 + b * 45^2 + 45 * c + d; f_4 := 64.148738$$

Function $f = a * t^3 + b * t^2 + c * t + d$ bat = 30 ... 45, $f = 42 ... 65$;

The calculations showed that the mathematical modeling of the experimental results showed that the experiments were 94% accurate.

Quantum-chemical, molecular-dynamic calculations of the synthesized compounds were performed, the halogenation process was mathematically modeled, and the mechanism of formation of the obtained halogenated compounds was proposed.

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