Original Article

SYNTHESIS AND PROPERTIES OF HALOGEN DERIVATIVES BASED ON β-CYANO ETHYL ESTERS OF ACETYLENIC AMINO ALCOHOLS

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Abstract

The current article is about the synthesis of acetylenic amino alcohols, their β-cyanoethyl ethers, and halogen-containing compounds that are based on halogen-containing compounds. The properties of these compounds have been studied by us. Halogenation of β-cyanoethyl ethers proceeds with the formation of them trans-dihalogen derivatives in high productivities. Has been found the rate of halogenation had been influenced by temperature. The average rate of the reaction is greatly significant in case the copper monochloride catalyst is present. Has been shown synthesized halogenated derivatives had an increased inhibitory activity against corrosion of steel and metal structures. The inhibitory properties were determined by the gravimetric method. The structure of the synthesized compounds was established by infrared (IR) and proton magnetic resonance (PMR) spectroscopy.

Keywords: acetylene, acetylene alcohol, acrylonitrile, cyano ethylation, acetylene ester, β-cyanoethyl ester, chlorine, bromine.

1. Introduction

The chemistry of acetylene and its derivatives is an important branch of organic chemistry. It was the industrial production of acetylene and the possibility of obtaining various compounds on its basis that increased the theoretical and practical significance of research in this area. Compounds containing a modeling atom N, Cl, Br, O have valuable performance properties: they can be used as biologically active compounds in medicine, agriculture; in the production of quality fragrances. At the same time, special attention is drawn to the synthesis of halogen derivatives on their basis, as well as to the study of their properties.

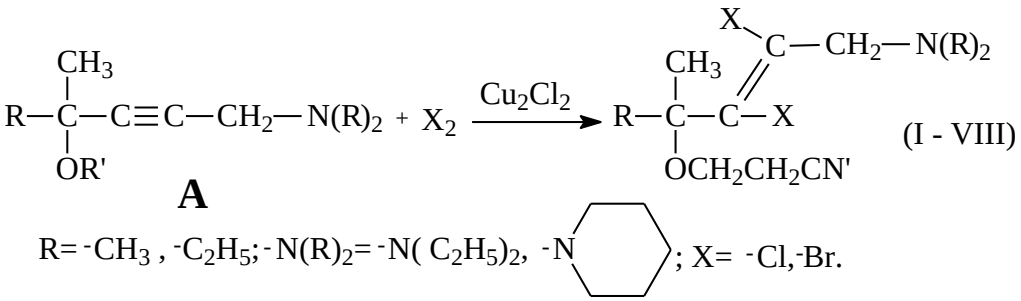
In this direction, work has been carried out on the synthesis of acetylenic alcohols and the study on this basis of the reactions of esterification, halogenation at the triple bond, as well as the study of various physicochemical or biological properties of the obtained compounds [1-3]. Conducted research, reflect the legitimacy of the tasks.

As is known [4,5], acetylenic amines in the form of their hydrochlorides easily interact with halogens, forming trans-dihalogenated allyl amines, and the resulting compounds are non-flammable. At the same time, the addition of halogens to the C≡C bond of acetylenic amines has not been sufficiently studied [6, 7]. We have previously investigated the chlorination and bromination of acetylenic aminoalcohols synthesized by the Mannich reaction [7,8]. It was found that when these reactions are carried out in a solvent such as diethyl ether, acetone, $CC1_4$, benzene, the corresponding ammonium halide salts are formed [9].

Catalysts are an important and essential component of chemical production. Non-precious catalysts available; they have attracted increased attention due to their activity in the reduction of oxygen-containing compounds [10]. The

reactions of halogenation of acetylenic aminoesters (Fig. 1A) in a $CHCl_3$ solution were carried out in the presence of Cu_2Cl_2 as a catalyst with the formation of trans-dihalogenated β-cyano ethyl esters compounds in high yields [11]. These reactions proceeded according to the following scheme:

Fig. 1. Halogenation reaction of acetylenic aminoesters.



Various substituents in the amino group did not affect the results of the reaction. The production of the process depended on such factors as the duration of the reactions, and it should be noted that halogenation in a solvent ($CHCl_3$) at a temperature of 20-40 ° C occurred with the accumulation of halogen derivatives in 10 hours; at 50-60°C, the reaction time was halved. The use of Cu_2Cl_2 as a catalyst made it possible to increase the product yield to 68-70% in 4 hours at a temperature of 18-20 ° C. An increase in temperature leads to an increase in the reaction products up to 83% in 2 hours.

2. Materials and Methods

This work was carried out in accordance with fundamental research and the scientific direction of the Department of General and Oil-Gas Chemistry of the National University of Uzbekistan during 2010 to 2020.

Structure of synthesized trans-dihalogen ethylenic amino esters was determined on the base of IR- and PMP-spectrums. Deformational of nitrile group in IR-spectrum of 5-(diethylamino-3,4-dichlorine-2-methylpent-3-en-2-iloxi)-propannitrile were observed in range 2895-2870 sm^{-1}; valent vibrations of middle intensively typical for ternary amino-group were observed in range 2965-2820 sm^{-1}, wheat absorption at 2160 sm^{-1} has been characteristical for bond –C≡C- and absorption corresponding to group CCl=CCl has been observed in range 560-635 sm^{-1}.

Peculiar absorption bands in the proton magnetic resonance (PMR) spectrum of 6-(diethylamino-4,5-dichlorine-3-methylhex-4-en-3-yloxy) propanenitrile: the protons of the δ (3H) methyl group appear at 1.33 ppm as singlet, the protons for the methyl group in the β position δ (2H) are shifted to 0.69 ppm in the form of a triplet, the protons of the methylene group at 1.5 ppm and the protons of the methyl group δ (6H) in the β state are 1.0 ppm. in the form of a triplet, a quartet relative to tertiary nitrogen. The protons of the methylene groups δ (6H) near the nitrogen atom and the cyanide group in the field are 2.58–2.64, and the protons of the methylene group δ (2H) near the halogen and double bond are 3.0 ppm. Individual protons of the methylene group δ (2H) next to the ester group - at 3.74 ppm.

The determination of the inhibitory properties of the synthesized substances was carried out by gravimetric method [12].

3. Results and Discussion

In the halogenation reaction, Cu_2Cl_2 was used as a catalyst in an amount of 0.005 mol based on the total mass of the reacting components.

3.1. Synthesis of 5-diethylamino-3-(3,4-dichlorine-2-methylpent-3-en-2-yloxy) propannitrile.

In flash will relax refrigerator gas-paining tube and mechanical mixer 22.2 g (0.1 mol) of 5-diethylamino-3-(2-methylpent-3-yn-2-yloxy) propane nitrile has been introduced which was dissolved in 50 ml of chloroform and then aright obtained reaction mixture at stirring during 2h at 35^0C 7.1 g (0.1 mol) purified gaseous chlorine has been added. Then reaction mixture has been kieped at room temperature during 10h. and after this it was treatment by solution of K_2CO_3 and washed by solution Na_2SO_4. The organic portion was separated, and the aqueous portion is extracted three times with chloroform. The organic portion and extract are combined and dried over $MgSO_4$ for 24 h. Then the solvent was distilled off and the residue was distilled under vacuum. The resulting dichlor derivative was isolated at 1900C at 10 mm Hg. with a result (23.15 g) 79.0%, its refractive index was 1.5301 and density detected in 1.2105 g/cm^3.

The rest of the dichlor derivatives of the other aminoesters were synthesized in a similar way and some of their physico-chemical constants (Table 1, I, III, V, VII compounds) of the obtained substances were determined.

3.2. Synthesis of 5-diethylamino-3-(3,4-dibromo-2-methylpent-3-en-2-yloxy) propannitrile.

In a three-necked flask with a reflux condenser, a dropping funnel and a mechanical stirrer, the catalyst monochloride (I) copper and 22.2 g (0.1 mol) of 5-diethylamino-3-(2-methylpent-3-yn-2-yloxy) propannitrile are introduced dissolved in 50 ml of chloroform, under cooling the reaction mixture with ice water, and 16.0 g (0.1 mol) of liquid bromine are added to the reaction mixture within 2 h. Then the reaction mixture was left for 10 h at the temperature 18-21˚C. Then, it was neutralized with saturated solution of K_2CO_3 and washed with a solution of Na_2SO_4. The organic (bottom) portion is separated through a separate funnel and the upper aqueous portion is extracted three times with chloroform.

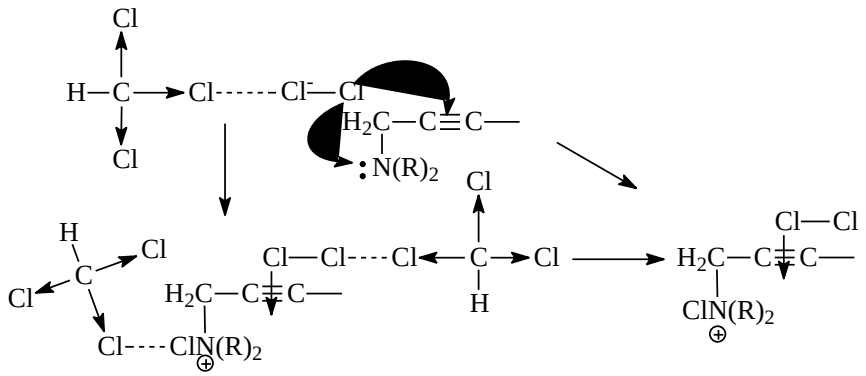
The combined chloroform extracts were dried over $CaCl_2$, then chloroform was distilled off and the rest was distilled under vacuum. The resulting dibrom derivative has boiled at 195-197^{0}C/10 mm Hg. And its result was fixed as (35.16 g) 81.0%, its n_D^{20} was 1.5285, and d_4^{20} was at the point 1.2295 g/cm^3.

The hydroxyl group of acetylenic amino alcohols has a different effect on the addition of the halogen to the triple bond, slowing down as the mass of the radical increases, that is, H> CH_3> C_2H_5. Moreover, the main effect arises from the action of the hydroxyl group on the triple bond in the state in which these substituents are retained, since the interaction of the intermolecular hydroxyl group with the triple bonds leads to an association. Based on these theoretical concepts, the interaction of acetylenic aminoesters with chlorine or bromine was studied in order to study the addition of a halogen at the triple bond [13-15]. Various substituents in the amino group practically do not affect the result of the reaction. Productivity depends on factors such as reaction time, and it should be noted that the halogenation process takes place in chloroform solution at room temperature (20-40^{0}C) by 60-70% for 10 h, and at 50-60^{0}C the reaction time is halved respectively. Thus, the use of a copper chloride catalyst increases the product yield to 68-70% within 4 hours at room temperature, while an increase in temperature leads to an increase in the product yield to 83% within 2 hours. It can be seen that the formation of trihalide ions by solvation of the halogen during the reaction without a catalyst increases the tendency to form a π-bond intermediate complex, while the solvation of the trihalide ions readily increases with increasing temperature. In turn, the use of a catalyst facilitates the decomposition of a halogen molecule into ions, and the formation of a carbocation due to a π-complex with a carbon atom at a triple bond allows ionized halogens to combine from opposite sides. Consequently, the product yield is relatively high in the presence of a catalyst. It is known that the halogenation of acetylene compounds with different structures depends largely on the nature of the solvents [16-18].

As noted in the literature, mainly in the halogenation of acetylene compounds in polar solvents, new compounds can be obtained, that is, the products of conjugated addition of halogens. In this regard, it should be mentioned that the reaction of acetylenic amino alcohol esters with halogens in the presence of a copper (I) chloride catalyst in an acetic acid solution resulted in the isolation of the corresponding acetoxy derivatives of monohalogenated amino esters in 18-30% yield. In this case, with an increase in the molar ratio of acetylenic amino ester (AAE) and halogen: AAE = 2: 1, a trans-dihalogenated ester compound of amino ketoalcohols is formed in the reaction

medium, and their yield increases to 68-70% at 40°C for 1.5 h. However, not all electrophiles possess such activity, and, as noted above, the electrophilic of halogens manifests itself only under certain conditions, and in this case, their interaction with the C≡C bond can take place. Thus, the halogen molecule must be polarized to the state Xδ + ─Xδ− for the formation of a carbocation. The formation of a nucleophile and an electrophile occurs when the solvent chloroform interacts with a halogen (Fig. 2).

Fig. 2. The scheme of the nucleophile formation and an electrophile



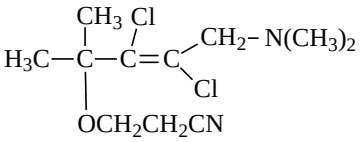
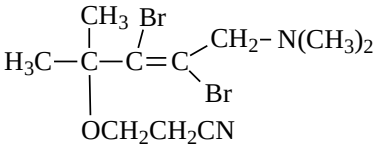
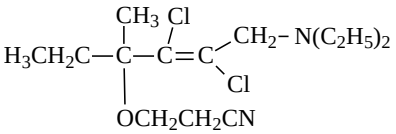
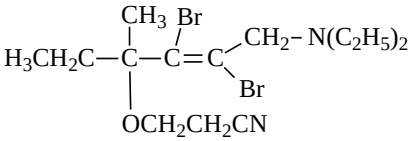
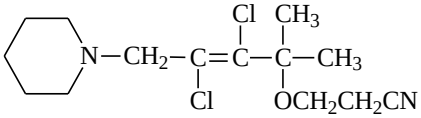
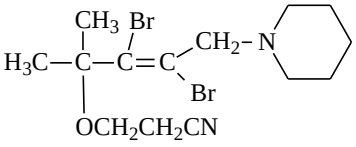
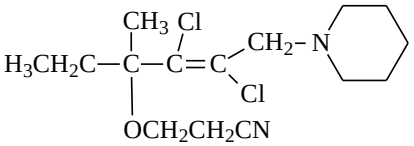
These cases can be expressed as follows: the addition of a halogen begins with the interaction of chloroform with it, in which a partially positively charged halogen binds to an unbound electron pair of the nitrogen atom, then a π-bonded halogen molecule is formed as a result. electrophilic halogen attack. A halogen atom, which is a sextet of electrons (i.e. positively charged), electrophilically attacks one of the carbon atoms bound to the π-bond and pulls out a pair of π-electrons, forming a bond with the carbon atom, and the second carbon loses the π-electron pair and becomes positive, turning into a charged carbocation.

The second carbon atom is nucleophilically attacked by the second halogen atom (electron-octet anion). In this case, a mainly trans compound is formed. This situation is explained by the fact that the attacking electrophilic particle first binds to two carbon atoms in the C≡C bond, forming a three-membered onium ring, and the second opens due to Waldenian reversion of the anion during the next nucleophilic attack. As a result, the attacking particles (X+ and X-) accumulate in a "trans state" with a double bond. It should be noted that dihalogenated compounds are formed at the initial stage of the reaction [16, 18, 19].

Boiling temperature, density and d_4^{20} of halogen derivatives of β-cianoethylenic esters (I-VIII) were determined and are presented in table 1. The halogenated derivatives of amino ethers synthesized by us are readily mobile, slightly yellow oil-like liquids with a peculiar amine odor.

The effect of the temperature and reaction time on the productivity of 5-(diethylamino-3,4-dichlor-2-methylpent-3-en-2-yloxy) propanenitrile (I) was studied (Fig. 3) and it was found that when chlorination in in the temperature range 30-50˚C, the best result is achieved at 45ºC. With increasing temperature, the productivity decreases with partial formation of unknown compounds. When the temperature rises to 50-55 ° C, the initial rate of the process is high and after 8 hours the product yield is about 30-35%.

Table 1 Bromine and chlorine derivatives on the base of β-cianoethyl esters of acetylene aminoalcohols

№	Structure of molecule	Name and brutto-formula	Yield, %	T.b./^{0}C mm.m.st.	n_D^{20}	d_4^{20}
I		5-(dimethylamino-3,4-dichlorine-2-methylpent-3-en-2-iloxy)-propannitril $C_{13}H_{22}N_2OCl_2$	79.0	190/10	1.5301	1.2105
II		5-(dimethylamino-3,4-dibromine-2-methylpenten-3-en-2-iloxy)-propannitril $C_{13}H_{22}N_2OBr_2$	81.0	195-197/10	1.5285	1.2295
III		6-(diethylamino-4,5-dichlorine-3-methylhex-4-en-3-iloxy)-propannitril $C_{14}H_{24}N_2OCl_2$	80.0	193/10	1.5525	1.2210
IV		6-(diethylamino-4,5-dibromine-3-methylhex-4-en-3-iloxy)-propannitril $C_{14}H_{24}N_2OBr_2$	83.0	198-199/10	1.5895	1.2945
V		5-(pyperidino-3,4-dichlorine -2-methylpent-3-en-2-iloxy) propannitril $C_{14}H_{22}N_2OCl_2$	77.0	196/10	1.5685	1.4215
VI		5-(pyperidino-3,4-dibromine-2-methylpent-3-en-2-iloxy)-propannitril $C_{14}H_{22}N_2OBr_2$	82.0	201-202/10	1.5975	1.3125
VII		6-(pyperidino -4,5-dichlorine-3-methylhex-4-en-3-iloxy)-propannitril $C_{15}H_{24}N_2OCl_2$	78.0	197-198/10	1.5785	1.3045

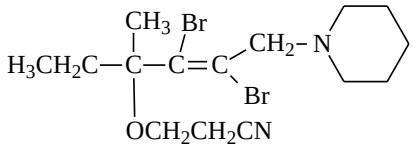
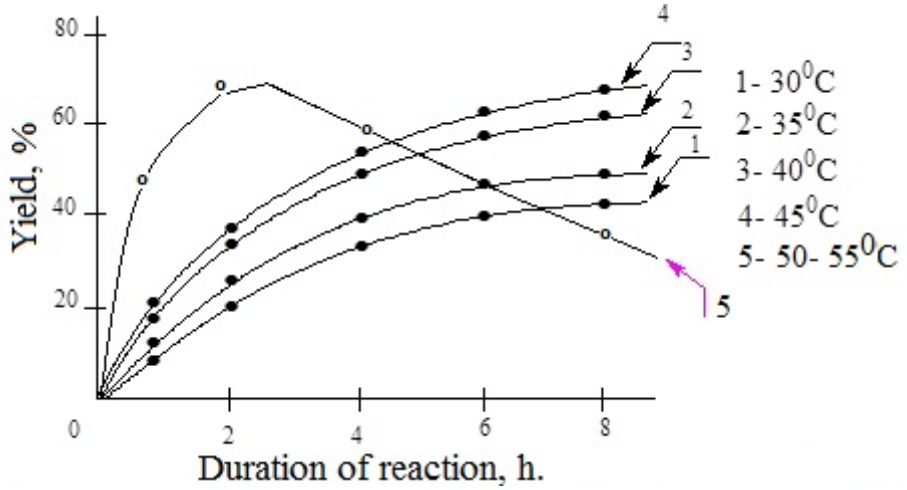
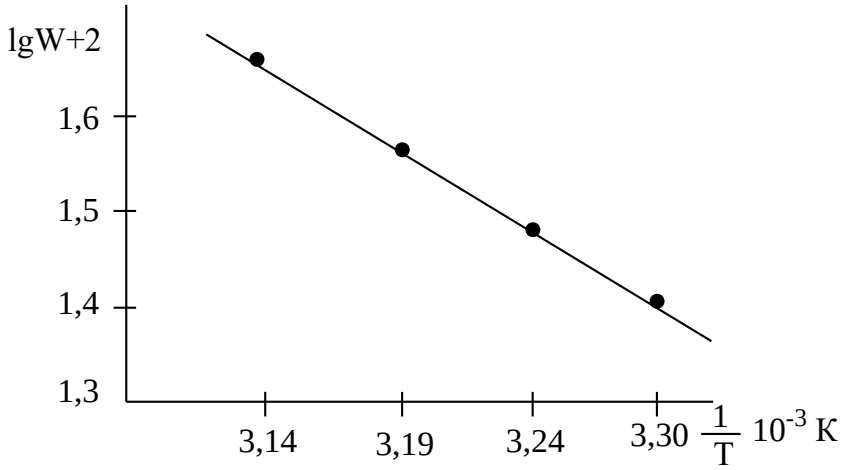
VIII		6-(pyperidino-4,5-dibromine-3-methylhex-4-en-3-iloxy)-propannitril $C_{15}H_{24}N_2OBr_2$	77.0	203-204/10	1.7985	1.3550

Fig. 3. Influence of temperature and duration of reaction on productivity of 5-(diethylamine-3,4-dichlorine-2-methylpent-3-en-2-iloxi)-propannitril.

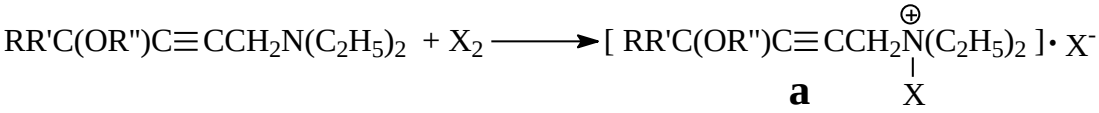


Therefore, all kinetic measurements of the rate were carried out at a given temperature, and the dependence of the income of 5-(diethylamino-3,4-dichloro-2-methylpent-3-en-2-yloxy) propanenitrile on the reverse temperature has a straight line (Fig. 4). According to this graph, the values of the activation energy for chlorination of acetylenic aminoesters were found.

Fig. 4. Dependence of ratio of 5-(diethylamine-3,4-dichlorine-2-methylpent-3-en-2-iloxi)-propannitril formation on reverse temperature.

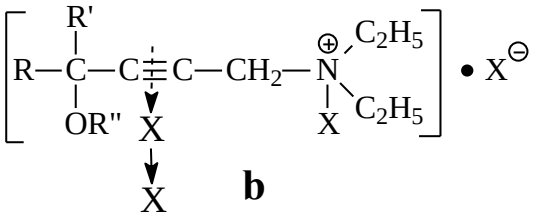


An additional π-bond is formed in the halogen molecule due to the unbound electron pair of one atom and the free 3- and 4d-orbitals of the other, and they are isolated as crystalline products (a) [11, 16]:



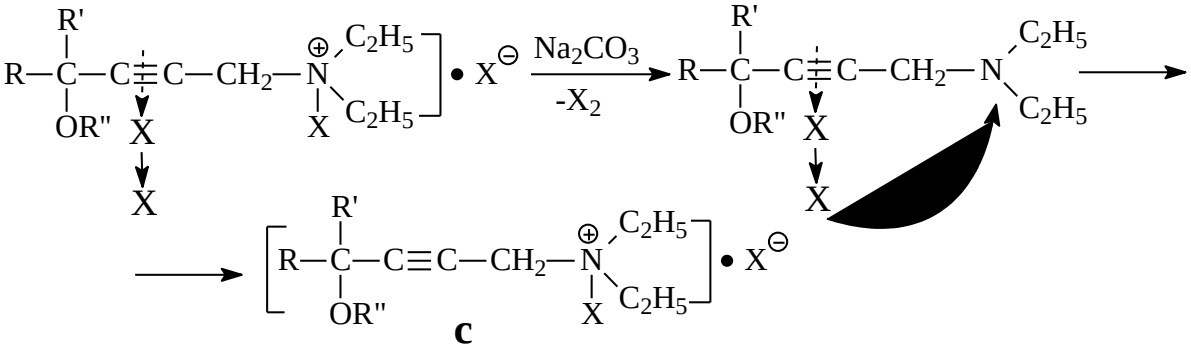
a

During the halogenation of esters of acetylenic amino alcohols in carbon tetrachloride, diethyl ether or acetone, it was found that the C≡C bond forms with halogens π-connected complex (b) of the type [16]:



b

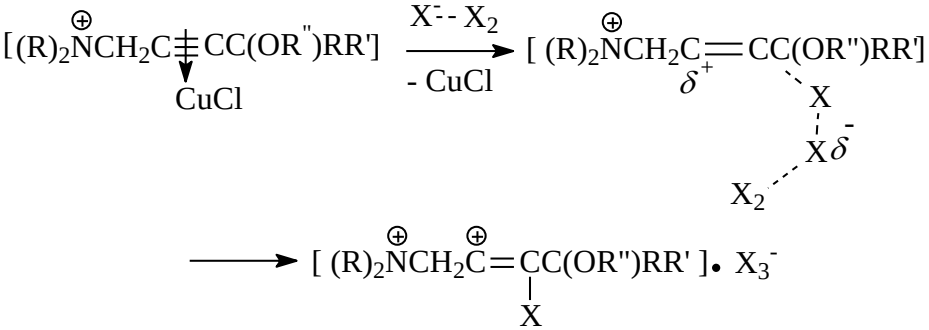
After neutralization of the aqueous solution of the obtained products with sodium carbonate, the first aminoesters containing the π-halogen complex at the C≡C bond were isolated (c) [9, 11]:



c

In these substances, after a day, halogen molecules migrate to the nitrogen atom, that is, with the formation of halogen compounds Comparison of the results obtained shows that, under the studied conditions, the formation of a π-complex between the C≡C bond and halogens and the breaking of these bonds often requires high temperatures or the use of catalysts.

Accordingly, the use of a catalyst based on copper monochloride significantly accelerates the exothermic addition of halogens with a C≡C bond and leads to the formation of trans-dihalogenated products in high yield. At the same time, isolated π-complexes were identified for the first time, which indicates an electrophilic reaction (d) [8-9]:



d

Additional chlorination and bromination to obtain tetra halogenated derivatives does not give the desired result due to the steric barrier. This is confirmed by the data of IR spectroscopy, elemental analysis and dipole moments.

Halogenated derivatives of all synthesized aminoesters are readily soluble in water, alcohol, acetone, and carbon tetrachloride [17-26].

Action of different factors including reaction time and temperature in synthesize of acetylenic amino esthers and their halogen derivatives (Table 2). At comparatively higher temperatures (50-55^{0}C), product yields turned out to be relatively low (Fig. 3).

Table 2 Results of synthesis of 5-(dimethylamino-3,4-dichlorine-2-methylpent-3-en-2- iloxy)-propannitril (solvent–chlorophorm)

Duration of reaction. h.	Yield of product, %	Average rate of reaction (W)	
		%/h	mol/l h.
Temperature 30^{0}C			
1	4.5	4.50	0.20
2	10.8	5.40	0.24
3	22.3	7.43	0.33
4	43.5	10.87	0.48
Temperature 35^{0}C			
1	6.4	6.40	0.28
2	13.0	6.50	0.29
3	25.4	8.46	0.37
4	47.9	10.97	0.52
Temperature 40^{0}C			
1	8.6	8.60	0.38
2	18.9	9.45	0.42
4	36.8	9.20	0.41
6	50.0	8.33	0.37
8	58.1	7.25	0.32
Temperature 45^{0}C			
1	10.8	10.80	0.48
2	21.0	10.50	0.47
3	40.2	10.05	0.44
4	54.2	13.05	0.58

Elemental analysis of the synthesized compounds showed that the composition corresponded to its gross formula, and the obtained values are presented in table 3.

Table 3 Indexes of trans-dihalogen derivatives of oxyaminonitriles (I-VIII)

№ compounds	Found,%			Brutto-formulas	Calculated, %		
	C	N	X		C	N	X
I	52.90	9.11	24.13	$C_{13}H_{22}N_2OCl_2$	53.25	9.55	24.18
II	40.10	7.61	42.14	$C_{13}H_{22}N_2OBr_2$	40.86	7.33	41.82
III	54.18	9.30	23.13	$C_{14}H_{24}N_2OCl_2$	54.73	9.12	23.08
IV	42.68	7.10	39.86	$C_{14}H_{24}N_2OBr_2$	42.45	7.07	40.34
V	54.66	8.80	22.58	$C_{14}H_{22}N_2OCl_2$	55.09	9.18	23.23
VI	42.66	7.11	40.07	$C_{14}H_{22}N_2OBr_2$	42.66	7.11	40.55
VII	55.88	8.68	21.77	$C_{15}H_{24}N_2OCl_2$	56.43	8.77	22.21
VIII	43.61	6.86	38.88	$C_{15}H_{24}N_2OBr_2$	44.14	6.86	39.15

At the initial stage, the rate of halogenation was high and there is a rapid change in the concentration of halogen over time (table 4). The maximum speed was observed at 35 ° C after 2 hours. The data obtained once again confirm the electrophilic mechanism of the addition of halogens to the triple bond of the studied aminoesters as a whole.

Table 4 Rate of halogenation of 5-(diethylamino)-3-(2-methylpent-3-in-2-iloxy)-propannitril in dependence of chlorine concentration (35°C).

Duration of reaction, h.	Concentration of chlorine, mol	k; M^{-1}, s^{-1}
0	0.0241	0
18	0.0238	0.0290
22	0.0221	0.1706
24	0.0213	0.2272
51	0.0178	0.2879
68	0.0153	0.3405
116	0.0119	0.3665
131	0.0081	0.6256
172	0.0062	0.6954
184	0.0043	1.0380
226	0.0036	1.0455

Obtained results have proved the fact that halogen atoms are in trans-position at double correction in molecules of synthesized compounds.

Along with the above, the effect of some of the obtained halogenated derivatives of enyloxyamines on the corrosion of metals was also studied and the results obtained are presented in tables 5-7.

Table 5 Action of some inhibitors on the base of halogen derivatives of amino oxynitriles on steel-20 corrosion

Inhibitor	Concentration of inhibitor, g/l	C_0	$C_к$	Z%	*Y*
I. 5-(diethylamino-3,4-dichlorine-2-methylpent-3-en-2-iloxi)-propannitril	0.5	37.6231	0.2310	99.3	128.5
III. 5-(diethylamino-3,4-dichlorine-2-methylpent-3-en-2-iloxi)-propannitril	1.0	37.6231	0.2460	99.4	131.8
I-1-A (known inhibitor)	1.0	37.6231	0.3271	99.1	115.0

Table 6 Indexes 5-(diethylamino-3,4-dichlorine-2-methylpent-3-en-2-iloxy)-propannitrile against corrosion of steel in two-phase water-hydrocarbon medium

Compo-unds	Time, h.	Concentration, g/l		Middle lost of mass, %	Middle rate of corrosion, g/m^2,h	Degree rate of protection, %	Note
		Water H_2S	amount of inhibitor				
I	24	0.8	0.5	0.0058	0.13	75.9	On water
		1.0	1.0	0.0026	0.06	88.9	30 g/l NaCl was added
	24	0.8	2.6	0.0027	0.06	88.9	
			-	0.0239	0.54	-	
		1.1	1.0	0.0041	0.09	83.2	
	72	1.1	-2.0	0.0053	0.04	84.6	
			-	0.0340	0.26	-	
III	24	0.9	0.5	0.0175	0.39	27.8	
			1.0	0.0155	0.35	35.2	
		1.1	-	0.0239	0.54	-	
			1.0	0.0230	0.52	33.0	
				0.0344	0.78	-	

Table 7 Protection action of 5-(diethylamino-3,4-dichlorine-2-methylpent-3-en-2-iloxy)-propannitrile on steel in water-oil medium

Reaction time, h	The amount of urotropine injected, g / l	Average loss, g	Corrosion rate, g / m^2 hour	Degree of protection, %
30	0.1	0.0016	0.036	61.3
	0.4	0.0013	0.030	67.8
	0.6	0.0012	0.027	71.0

	1.6	0.0010	0.022	76.3
	_	0.0041	0.093	_
78	0.1	0.0018	0.013	65.8
	0.4	0.0018	0.013	65.8
	0.8	0.0021	0.010	73.7
	1.6	0.0019	0.014	72.6
	-	0.0050	0.008	-

Conclusions

Have been found, acetylenic aminoesters containing oxypropanenitrile fragments easily enter into reactions of electrophilic addition of halogens with the formation of trans-structure products.

At the same time, if the ratio of the reacting components halogen: ether is equal to 2:1 it is possible to achieve encouraging results.

Along this, high inhibitory properties of halogenated aminoesters have been established, that, in synergy with urotropin, give positive results.

Conflicts of interest

There are no conflicts to declare.

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