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ГЕТЕРОЦИКЛДІ БРОМАЦЕТИЛЕН СПИРТТЕРІ ЖӘНЕ ОЛАРДЫҢ АКРИЛ ЖӘНЕ МЕТАКРИЛ ЭФИРЛЕРІНІҢ СИНТЕЗІ

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Мақалада циклді және гетероциклді ацетилен спирттеріне натрий гипобромидінің әсерінен гетероциклді бромацетилен спирттерін, сондай-ақ литий алюминий кешендерін қолданып олардың акрил және метакрил эфирлерін алу әдісі келтірілген. Алынған өнімдердің

құрамы мен құрылымы элементтік анализ, ИҚ және ПМР спектрлерінің мәліметтерімен расталды. Зерттеу нәтижесінде литий алюминий гидридінің қатысуымен өнімнің шығуы барлық жағдайда 80 %-дан жоғары екендігі анықталды.

Негізгі сөздер: бромацетилен спирттері, ацетилен спирттері, литий алюминий кешені, тетрогидрофуран, пиперидин, пиридин, 4-метакрилокси-2,2-диметил-4-бромэтинитетрагидропиран, 4-Акрилокси-2,2-диметил-4-бромэтинитетрагидропиран, 1-Акрилокси-1-бромэтинилциклогексан.

СИНТЕЗ ГЕТЕРОЦИКЛИЧЕСКИХ БРОМАЦЕТИЛЕНОВЫХ СПИРТОВ И ИХ АКРИЛ -, МЕТАКРИЛОВЫХ ЭФИРОВ

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В статье представлен способ получения гетероциклических бромацетиленовых спиртов действием гипобромида натрия на циклические и гетероциклические ацетиленовые спирты, а также их акриловых и метакриловых эфиров с помощью литийалюминиевых комплексов. Состав и структура полученных продуктов подтверждены данными элементного анализа, ИК и ПМР спектров. В результате исследования, установлено, что в присутствии литийалюминийгидрида выход продукта во всех случаях выше 80 %.

Ключевые слова: бромацетиленовые спирты, ацетиленовые спирты, литийалюминиевый комплекс, тетрогидрофуран, пиперидин, пиридин, 4-Метакрилокси-2,2-диметил-4-бромэтинитетрагидропиран, 4-Акрилокси-2,2-диметил-4-бромэтинитетрагидропиран, 1-Акрилокси-1-бромэтинилциклогексан.

SYNTHESIS OF HETEROCYCLIC BROMACETYLENE ALCOHOLS AND THEIR ACRYL -, METHACRYL ETHERS

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The article presents a method for obtaining heterocyclic bromoacetylenic alcohols by the action of sodium hypobromide on cyclic and heterocyclic acetylene alcohols, as well as their acrylic and methacrylic esters using lithium aluminum complexes. The composition and structure of the obtained products were confirmed by the data of elemental analysis, IR and PMR spectra. As a result of the study, it was found that in the presence of lithium aluminum hydride, the product yield in all cases is higher than 80 %.

Keywords: bromoacetylenic alcohols, acetylenic alcohols, lithium-aluminum complex, tetrahydrofuran, piperidine, pyridine, 4-Methacryloxy-2,2-dimethyl-4-bromoethynyltetrahydropyran, 4-Acryloxy-2,2-dimethyl-4-bromoethynyl-bromoethynylcyclohexane.

Introduction

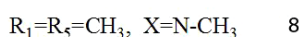
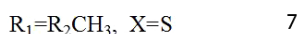
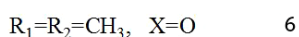
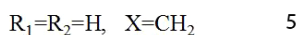
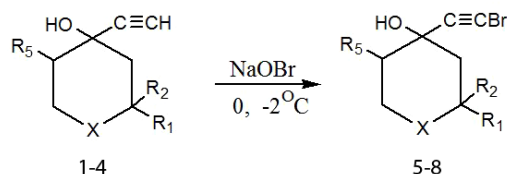
Fundamental research in the field of synthesis, the study of chemical transformations of new heterocyclic acetylene, polyacetylene compounds and their organoelement derivatives are one of the factors that ensure progress in the search for highly effective physiologically active

drugs and medicines. In addition, these compounds are a raw material base to produce new polymers, which largely determines the successful and intensive development of the chemistry and technology of macromolecular compounds. Particularly acute is the issue of providing monomers to obtain polymers with specific (surface-

active, complexing, ion-exchange, inhibiting, biologically active and other) properties, which have been significantly developed in recent years. In this regard, the development of methods to produce carbo- and heterocyclic bromoacetylenic alcohols and investigation of their properties is especially important. [1-4].

Forms and methods of research

In this work, bromoacetylenic alcohols (5-8) were synthesized from cyclic and heterocyclic acetylenic alcohols (1-4), obtained by us earlier [1] by interaction with sodium hypobromide, according to the following scheme:



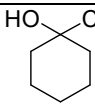
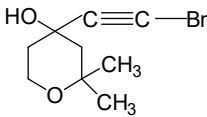
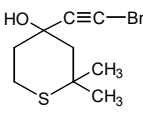
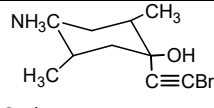
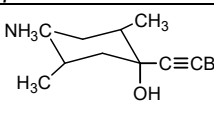
The resulting products (5–8) are colorless crystals (table 1). The composition and structure of bromoacetylenic alcohols are confirmed by

the data of elemental analysis, IR and PMR spectra (Table 2).

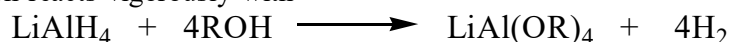
Table 1. Cyclic and heterocyclic bromoacetylenic alcohols (5-8)

Compound	Formula of compounds	Output, %	Bp (°C)	Found, %					Gross Formula	Calculated, %				
				C	H	Br	N	S		C	H	Br	N	S
5		75	50	47,0	5,1	39,0			C ₈ H ₁₁ OBr	47,30	5,41	39,40		
6		80	134 - 135	46,2	5,4	34,0			C ₉ H ₁₃ O ₂ Br	46,35	5,58	34,33		
7		73	96	43,2	5,1	32,0		12,5	C ₉ H ₁₃ SOBr	43,37	5,22	32,12		112,85
8		82	132	48,5	6,3	32,3	5,40		C ₁₀ H ₁₆ OBr	48,78	6,50	32,52	5,69	
8		25	210	48,6	6,4	32,0	5,20		C ₁₀ H ₁₆ OBr	47,78	6,50	32,52	5,59	

Table 2. Frequencies of stretching vibrations in IR spectra and values of chemical shifts in PMR spectra of cyclic and heterocyclic bromoacetylenic alcohols

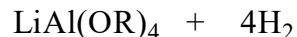
Compound	Formula of compounds	IR spectrum, ν cm ⁻¹			PMR spectrum, δ ppm		
		OH	C \equiv CBr	C \equiv C	N-CH ₃	CH ₃	3H
5		3370	564	2216	-	1,62	3,95
6		3320	565	2190	-	1.29	1.76
7		3378	572	2212	-	1.26	2.64
8	 β -isomer	3332	568	2210	2.78	1.20	2.03
8	 γ -isomer	3340	575	2215	3.00	1.32	2.24

To obtain alcoholates of bromoacetylenic alcohols, we used the properties of lithium aluminum hydride, which reacts vigorously with



Upon the interaction of (meth) acrylic acid chlorides with mixed lithium aluminum alcoholates of bromoacetylenic alcohols, we synthesized 1-methacryloxy-1-bromoethynylcyclohexane (9), 4-methacryloxy-2,2-dimethyl-4-bromoethynyltetrahydropyran (10), 1-acryloxy-bromo-ethynylcyclohexane (11) and 4-acryloxy-2,2-dimethyl-4-bromoethynyltetrahydropyran (12).

alcohols, producing hydrogen, and transforms into the corresponding alkoxy derivatives.

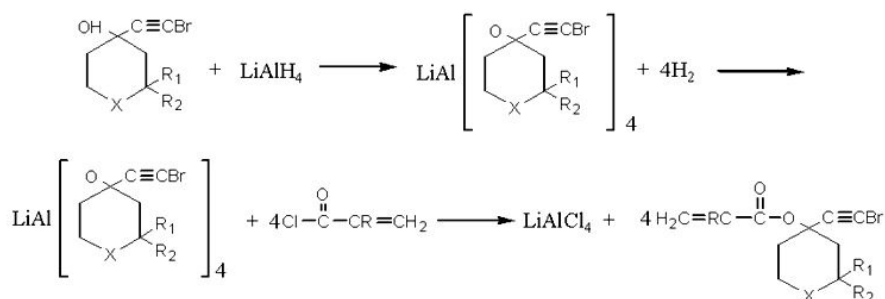


The reaction for producing esters includes two stages:

1. Formation of mixed alcoholate by interaction of bromine-containing tertiary acetylene alcohol with lithium aluminum hydride.

2. Esterification of the intermediate with (meth) acrylic acid chloride.

The reaction scheme can be depicted as follows:



где, при $\text{X}=\text{CH}_2$, $\text{R}_1=\text{R}_2=\text{H}$, $\text{R}=\text{CH}_3$, H (9, 10)
 $\text{X}=\text{O}$, $\text{R}_1=\text{R}_2=\text{CH}_3$, $\text{R}=\text{CH}_3$, H (11, 12)

The reaction was carried out in a stream of an inert gas, in a tetrahydrofuran or pyridine medium in the presence of a radical polymerize-

tion inhibitor (Irganox 1010) without isolation of an intermediate product. The yield in all cases

was above 80%, the structure of the synthesized compounds is confirmed by counter synthesis.

The constants and data of elemental analysis of the obtained products are presented in

Table 3. The data of IR and PMR spectroscopy confirm the structure of the synthesized compounds (Table 4).

Table 3. Physicochemical constants of methacrylic and acrylic esters of bromine-containing cyclic and heterocyclic acetylenic alcohols

Compound	Bp (°C), mp (°C)	n _d ²⁰ %	Output, % (%)	Found, %, % Calculated, %, %		
				C	H	Br
9	<u>124-125</u> 236	1,5115	84	<u>53,29</u> 53,13	<u>5,50</u> 5,53	<u>29,30</u> 29,52
10	85	-	87	<u>51,60</u> 51,82	<u>5,42</u> 5,65	<u>26,20</u> 26,58
11	<u>113-120</u> 665	1,5355	83	<u>51,30</u> 51,36	<u>5,15</u> 5,06	<u>21,10</u> 31,13
12	55		82	<u>51,20</u> 51,17	<u>5,0</u> 5,23	<u>27,50</u> 27,87

* - using LiAlH₄

Table 4. Frequencies of stretching vibrations in IR spectra and values of chemical shifts in PMR spectra of acrylic and methacrylic esters of cyclic and heterocyclic bromoacetylene alcohols

Compound	IR spectrum, ν cm ⁻¹			PMR spectrum, δ ppm		
	C=C	C=O	C≡C	CH ₃	-CH ₂	CH ₂ =CH ₂ -
9	1632	1735	2208	1.96	1.62	5.72-5.56
10	1636	1730	2206	1.2-1.4	1.5-2.3	6.19-5.55
11	1638	1730	2210	-	1.58	5.9-5.7
12	1638	1720	2210	1.24	1.8	6.2-6.0

Experimental part

1-Bromoethynylcyclohexan-1-ol (5). In a three-necked flask with a capacity of 25 ml was loaded 50 ml of 10N sodium hydroxide solution and 100 ml of distilled water. The mixture was cooled to -5 °C. With vigorous stirring, 11 ml of bromine was slowly added dropwise. After the end of the dropping, a solution of 24.8 g of 1-ethynylcyclohexan-1-ol in 10 ml of diethyl ether was added dropwise after 30 minutes. The reaction was continued for 4-5 hours until the solution became discolored, after which the mixture was saturated with ammonium chloride, extracted with ether. The ether solution was washed with water, dried with calcium chloride. After distilling off the ether and recrystallization of the residue from hexane gave 30,44g (75% of theory) bromoethynylcyclohexan-1-ol with Mp = 53-55 °C.

Found, %: C 47.00; H 5.10, Br 39.00;

Calculated, %: C 47.30; H 5.41, Br 39.40

C₈H₁₁OBr.

IR spectrum, cm⁻¹: 3370 (OH), 2216

(C≡C), 564 (C≡CBr),

PMR spectrum, ppm: 1.62 (CH₃), 3.95 (OH).

2,2-Dimethyl-4-

bromoethynyltetrahydropyran-4-ol (6).

Under the above conditions, 2,2-dimethyl-4-bromoethynyltetrahydropyran-4-ol with Tm = 139-140 °C was obtained from 30.8 g of 2,2-dimethyl-4-ethynyltetrahydropyran-4-ol with Mp = 139-140 °C. The yield was 80% of theoretical.

Found, %: C 46.2; H 5.4, Br 34.00;

Calculated, %: C 47.30; H 5.41, Br 39.40 C₈H₁₁OBr.

IR spectrum, cm⁻¹: 3320 (OH), 2190 (C≡C), 565 (C≡CBr),

PMR spectrum, ppm: 1.29 (CH₃), 1.76 (3H).

1-Methacryloxy-1-

bromoethynylcyclohexane. (9)

While stirring in a stream of inert gas, a solution of 16.24 g (0.08 mol) of 1-bromoethynylcyclohexane-1-ol in 50 ml of THF was added dropwise to a solution of 0.76 g (0.02 mol) of lithium aluminum hydride in 100 ml of tetrahydrofuran (THF) and was heated until the complete evolution of hydrogen. Then 8.36 g (0.08 mol) of methacrylic acid chloride was added to the reaction mixture at 10 °C. Heated at 60 °C for 3 h, after which it was decomposed on

cooling with 5% hydrochloric acid solution. acid and extracted with ether. The ether extract was dried with calcium chloride. After distilling off the solvent, the residue was distilled to obtain 18.21 g (84% of theoretical) 1-methacryloxy-1-bromoethynyl-cyclohexane with Bp = 124-125 °

C at 266 Pa, $n_D^{20}=1,5115$, $d_4^{20}=1,2843$

MRd found 63.30, calculated 62.36.

Found, %: C 53.29; H 5.50; Br 29.30.

Calculated, %: C 53.13; H 5.53; Br 29.52

$C_{12}H_{15}O_2Br$. (-C≡C-),

1632 (-CH₂) and 1725 (C = O).

PMR spectrum, ppm 1.96 (-CH₃), 1.62 (-CH₂-), 5.72-5.56 (CH₂ = C-).

1-Acryloxy-1-bromoethynylcyclohexane (11)

Under similar conditions, from 0.76 g (0.02 mol) of lithium aluminum hydride, 16.2 g (0.08 mol) of 1-bromoethynylcyclohexan-1-ol and 7.24 g (0.08 mol) of acrylic acid chloride by heating at 60 °C for 3 h received 17.06 g (83% of theoretical) 1-acryloxy-1-bromoethynylcyclohexane with Bp = 118-120 °C at 665 Pa, $n_D^{20}=1,3766$, MRd calc. 57.74, found. 58.23.

Found, %: C 51.30; H 5.15; Vg 31.10

Calculated, %: C 51, 36; H 5.06; Br 3 1.13

$C_{13}H_{13}O_2Br$

IR spectrum, cm⁻¹: 2210 (-C≡C) 1638 (-C = CH₂) and 1730 (C = O).

PMR spectrum, ppm 1.58 (-CH₂-), 5.9-5.7 (CH₂-C-).

4-Acryloxy-2,2-dimethyl-4-bromoethynyltetrahydropyran (12).

A solution of 18.64 g (0.08 mol) of 2,2-dimethyl-4-bromoethynyltetrahydropyran-4-ol in 50 ml of pyridine was added dropwise to a solution of 0.76 g (0.02 mol) of lithium aluminum hydride in 100 ml of pyridine with stirring in a stream of inert gas. Heated until complete evolution of hydrogen. Then 7.24 g (0.08 mol) of acrylic acid chloride was added to the reaction mixture at 10 °C. It was heated at 80 °C for 3 h, after which it was decomposed on cooling with a 5% hydrochloric acid solution and extracted with benzene. The benzene extract was dried with calcium chloride. After distilling off the solvent, the residue was crystallized from a solution of benzene: ethanol (1: 2) to give 18.82 g (82%) of 4-acryloxy-2,2-dimethyl-4-bromoethynyltetrahydropyran with Mp-55 °C.

Found, %: C 50.20; H 5.0; Br 27 50.

Calculated, %: C 50.17; H 5.23; Br 27.87

$C_{12}H_{15}O_3Br$.

IR spectrum, cm⁻¹: 2210 (-C≡C-), 1638 (-C = CH₂) and 1720 (C = O).

PMR spectrum, ppm 1.24 (-CH₃), 1.80 (-CH₂-), 6.20 (CH₂ = CH₂).

4-Methacryloxy-2,2-dimethyl-4-bromoethynyltetrahydropyran (10).

Under similar conditions from 0.76 g (0.02 mol) of lithium aluminum hydride, 18.6 (0.08 mol) of methacrylic acid chloride for 3 hours at 85-86 °C, after recrystallization from a benzene: ethanol solution (1:2) received 20.94 g. (87% of theoretical) 4-methacryloxy-2,2-dimethylbromoethynyltetrahydropyran with Mp = 85 °C.

Found, %: C 51; 60; H 5.42; Br 26.20.

Calculated, %: C 51.82; H 5.65; Br 26.58
 $C_{13}H_{17}O_3Br$.

IR spectrum, cm⁻¹: 2206 (-C≡C-), 1635 (H₂C = CH₂) and 1730 (C = O).

PMR spectrum, ppm 1.2-1.4 (-CH₃), 1.5-2.3 (-CH₂-), 6.19-5.55 (CH₂ = CH₂).

Conclusion

Based on the research results, the following conclusions can be drawn:

1. A procedure has been developed for the synthesis of heterocyclic bromoacetylene alcohols by the action of sodium hypobromide on cyclic and heterocyclic acetylene alcohols, as well as their acrylic and methacrylic esters;

2. It was found that in the presence of lithium aluminum hydride, the product yield was higher than 80 %.

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