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WASTE-FREE SYNTHESIS OF DERIVATIVE ALCOHOL AND ITS PROPERTIES

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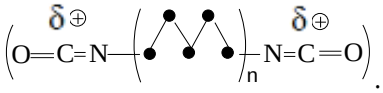
ABSTRACT
The chemical properties of the cinnamyl alcohol derivative have been synthesized and studied. Synthesis of new, previously unknown bis-cinnamoyl substituted-carbamate derivatives, N,N[1]--dichlorination, metallation, alkylation, nitrozozation reactions, growth-stimulating activity of N, N[1]-polymethylene bis [(cinnichoyl) -carbamates] has been studied.

KEYWORDS: derivatives, bis-cinnamyl, N_2, N_3-polymethylene-bis [(4-amino-azo-benzene) -urea], dichlorination, metallation, alkylation, nitrozozation, electrophilic substitution, biological growth-stimulating activity.

1. INTRODUCTION
One of the important sections of organic chemistry and synthesis is that diisocyanate groups have a complex electrophilic-nucleophilic structure with a predominance of electrophilic one, due to a large positive charge on the carbon



They are a reaction center in a nucleophilic attachment reaction for non-waste technologies for the production of new environmentally friendly compounds having a wide range of applications.
In the world, several dozen preparations are known - derivatives of substituted urea carbamates, widely used in various sectors of the national economy, which determines the relevance of researches [1-6].
From this point of view, the derivatives of cinnamon-substituted carbamates and bis-carbamates are of great interest as substances possessing various biological and pharmacological activities. In agriculture, they have found application as herbicides, pesticides, fungicides, insecticides, nematicides, bactericides, growth stimulators, etc. In medicine, they are used as antiviral, antitumor, anti-inflammatory, antidiabetic and other medicinal substances [7-12].

2. MATERIALS AND METHODS
The object of the study was the derivatives of cinnamon alcohol. Their physical and chemical properties, biostimulating activity were studied. IR spectra recorded on a VR-20 spectrometer in KBr tablets.

3. RESULTS AND DISCUSSION
We have developed research in the field of the synthesis of new substances. The reaction of cinnamic alcohol with diisocyanate was carried out and bis-cinnamoyl substituted carbamate derivatives were prepared according to the following scheme:

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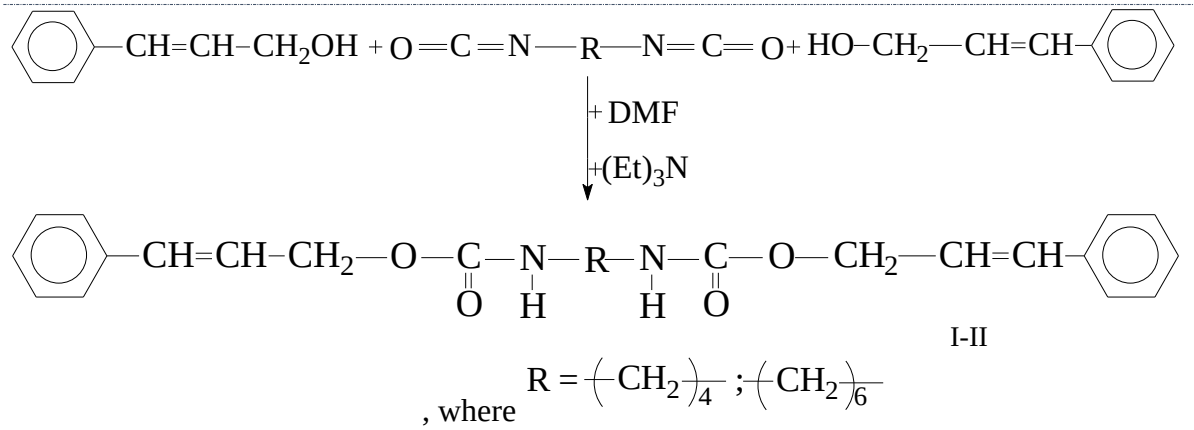


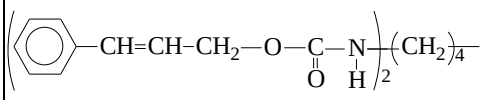
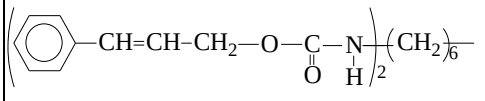
I-II

, where $R = -(CH_2)_4-$; $-(CH_2)_6-$

Reactions of diisocyanate with cinnamoyl-substituted alcohols were carried out at a molar ratio of reactants 1: 2, room temperature 25-36 ºC, for 3,5 hours. As a result of the reaction, N, N^1-polymethylene bis [(cinnamoyl-carbamates) are formed, which are colorless high-melting substances that are hardly soluble in water and other organic solvents, which confirms the presence of two rigid carbamate groups I-II.

The structure of the synthesized derivatives (cinnichoyl) carbamates was determined by IR spectroscopy and confirmed by elemental analysis (table 1).

Table 1. Physicochemical parameters of compounds I and II

	Structural formula	Output, %	Tm, ºC	R_f	Gross formula	Elemental analysis, %		M_M
						Calculated	Found	
						N	N	
1		97,6	178-179	0,71	$C_{24}H_{28}N_2O_4$	6,86	6,78	408
2		96,3	195-196	0,72	$C_{26}H_{32}N_2O_4$	6,42	6,29	436

As can be seen from table 1, the yield of N,N^1-polymethylene bis (cinnamoyl-carbamates) is rather high. The high yields of obtained bis-carbamates are apparently due to the high density and easy mobility of the electron charge on the carbon atom of the isocyanate group, that is susceptible to attack by a nucleophilic agent, as well as the absence of steric hindrances.

In the IR spectrum of N,N^1-polymethylene bis [(cinnichalo-carbamates), we can mention the distinguishing appearance of absorption bands of stretching vibrations -NHCOO (1590-1610 cm^{-1}), groups in carbamates (1680-1690 cm^{-1}), NH groups (3309 cm^{-1}), - (CH_2) -n groups (756-719 cm^{-1}), -CH = CH (cis) -690 and 1635 cm^{-1}, (trans) -3010 cm^{-1}.

We must emphasize that during the reaction of cinnamic alcohol with diisocyanates the reaction proceeded without the release of harmful by-products (HCN, CO, CO_2, NO, etc.)

To reveal the reactive capability of N-H groups of cinnamyl substituted bis-carbamates, the reactions of N, N^1-dichlorination, metallation, alkylation, nitrozozation were substituted.

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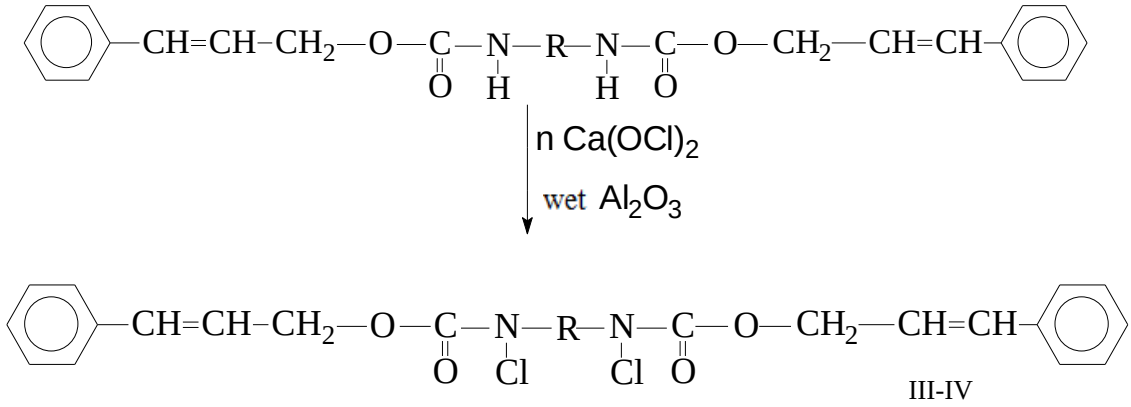
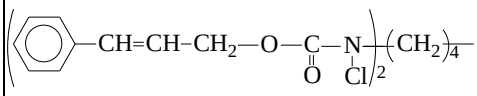
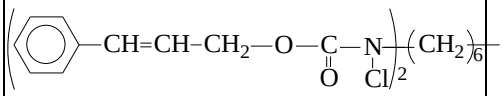
As a result of the reaction of N,N[1]-dichlorination of the derivatives of N,N[1]-polymethylene bis [(cinnichalo) - carbamates] with calcium hypochlorite on wet alumina for 27 hours in the presence of $CHCl_3$, compounds III and IV were obtained (see table 2).

The chemical reaction scheme is the following, where $R = -(CH_2)_4- ; -(CH_2)_6-$



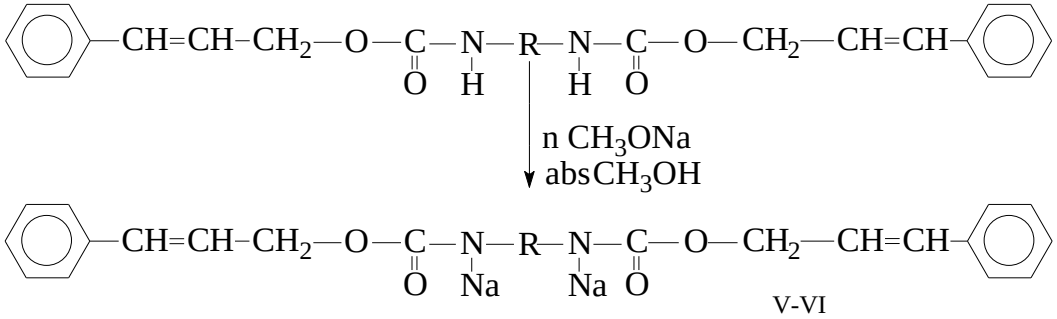
III-IV

Table 2. Physicochemical parameters of compounds III and IV

	Structural formula	Output, %	Tm, °C	R_f	Gross formula	Elemental analysis, %		M_M
						Calculated	Found	
						N	N	
1		88,8	178-174	0,68	$C_{24}H_{26}Cl_2N_2O_4$	6,86	6,78	408
2		90,4	192-193	0,63	$C_{26}H_{30}Cl_2N_2O_4$	5,54	5,36	505

Preparation of N, N[1]-disodium substituted N, N[1]-polymethylene bis [(cinnichoyl) carbamates] (V-VI).

Compounds I and II are subjected to directional N, N[1]-dimetallation on N-H reaction sites, by reaction with CH_3ONa in absolute methanol according to the following scheme:



V-VI

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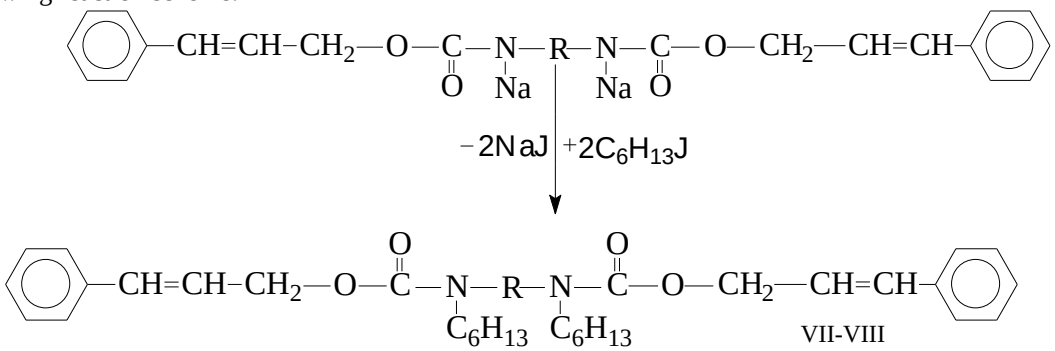
The outputs of V-VI were 91-93,4 %.

Preparation of N, N^1-dihexyl substituted bis-carbamate derivatives

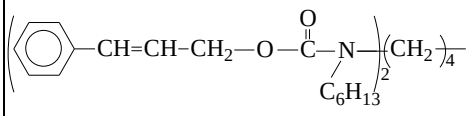
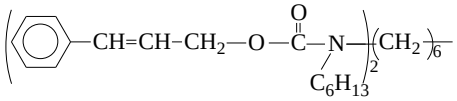
Hexylation on NH groups in bis-carbamates (I-II) with hexyl iodides is of undoubted interest for elucidating the reactive capability of the containing compounds. Hexylation reactions were carried out with the reaction of N, N^1-disodium derivatives of N, N^1-polymethylene bis [(cinnamoyl) carbamates] with hexyl iodide in dry benzene at a temperature of 25-30 °C and stirring, hexyl iodide was added dropwise during the 3,5- 4 hours according to the following reaction scheme:



The alkylation reaction proceeds exclusively through the nitrogen atoms N,N^1, which is explained by the relatively easy dissociation of sodium in this atom due to the presence of neighboring carbonyl groups. The yield is 94-95 %.

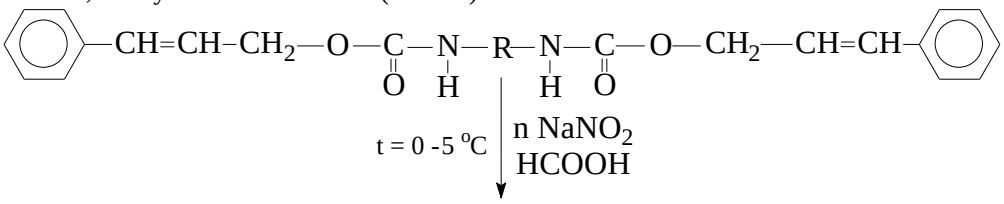
Physico-chemical parameters are given in table 3.

Table 3. Physico-chemical parameters of compounds VII-VIII

№	Structural formula	Output, %	Tm, °C	R_f	Gross formula	Elemental analysis, %		M_M
						Calculated	Found	
						N	N	
1		94,1	211-212	0,69	$C_{36}H_{52}N_2O_4$	4,86	4,73	576
2		95,6	219-220	0,66	$C_{38}H_{56}N_2O_4$	4,63	4,49	604

Preparation of N, N^1-dinitrozozirovanie N, N^1-polyalkylene bis - [(cinnichoyl) carbamates].

To determine the reactive capability of N-H groups of substituted bis-carbamates, we conducted nitrosation reactions. As a result of the reaction of N,N^1-dinitrozozation of the N,N^1-polyalkylene bis [(cinnichonyl) carbamate] derivatives with sodium nitrite (in excess) in formic acid, the corresponding N, N^1-dinitrozo substituted with IX-X, with yields from 86-93 % (Table 4).



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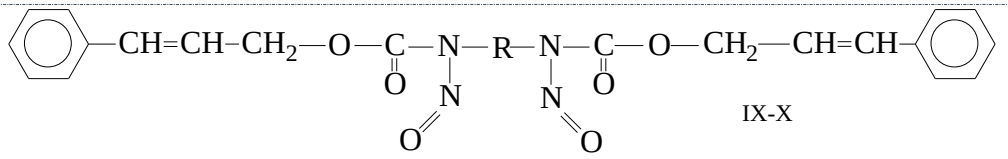
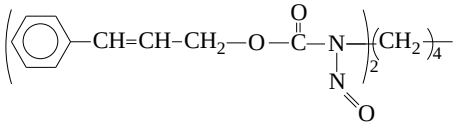
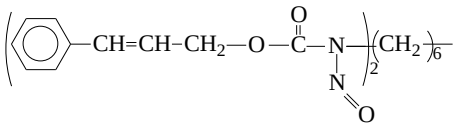


IX-X

Table 4. Physicochemical parameters of compounds IX and X

№ п/п	Structural formula	Output, %	Tm, °C	R_f	Gross formula	Elemental analysis, %		M_M
						Calculated	Found	
						N	N	
1		93,2	284(dec.)	0,74	$C_{24}H_{26}N_4O_6$	12,01	11,88	466
2		86,9	274(dec.)	0,71	$C_{26}H_{30}N_4O_6$	11,33	11,16	494

N, N^1-dinitrozozirovanie proceeds by the mechanism S_E. The attacking agent is $\overset{\oplus}{NO}$. As nitrous acid, which is the most common nitrosizing agent, does not exist in a free form, then sodium nitrite and hydrocyanic acid (conc. HCOOH) are used for the process.

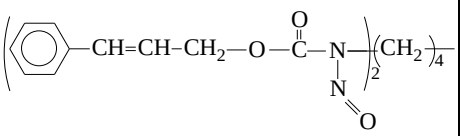
The resulting nitrous acid, when adding generates $\overset{\oplus}{NO}$, the reaction proceeds according to the scheme:

$$NaNO_2 + HCOOH \longleftrightarrow H_2\overset{\oplus}{N}O_2 \longleftrightarrow \overset{\oplus}{NO} + HCOONa + H_2O$$

N, N^1-dinitrozozirovanie is conducted while cooling the reaction mixture. Identification of N,N^1-dinitrozo compounds is carried out on the absorption bands of N-nitrozo groups. A strong band in the 1500-1420 cm^{-1} region is characteristic (table 5).

The structure of synthesized N,N^1-dinitrozo substituted ones is established by elementary analysis and IR spectra.

Table 5. IR spectra of the preparation IX-X

Structural formula	IR spectr, ν, cm^{-1}						
	—N—C—O— (O)	—C— (O)	N—N=O	$-(CH_2)_n-$	$-CH_2-$	N—CH_2	—CH=CH—
	1652	1710	1550-1424	754-718	2433-2860	1411	cis694

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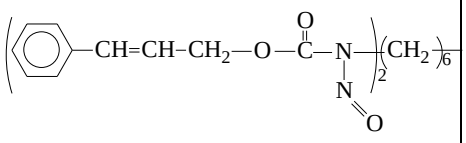
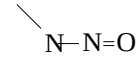
	1660	1712	1555-1430	762-721	2430-2856	1409	cis692

In the IR spectra, there are absorption bands for  1550-1430 cm^{-1}, a strong absorption band; and for the groups of 1710 cm^{-1}; for -762-721 cm^{-1}; - 690 cm^{-1}. Thus, a procedure for the preparation of N, N^1-polymethylene bis [(cinnichoyl) -carbamates] has been developed and their chemical properties in N-H reaction centers have been studied: N, N^1-dichlorination, dimetallation, dialkylation and dinitrozozation reactions with rather high yields.

Growth-stimulating activity of N, N^1-polymethylene bis [(cinnichoyl) -carbamates] (I).

Laboratory and field tests of this preparation (I) as growth stimulants of cotton, cucumber and tomato plants were conducted. For comparison, the well-known Rostlin stimulator was used. It has been established that N,N^1-polymethylene bis [(cinnichoyl) carbamate] possesses growth-stimulating activity at a concentration of 0,001% and is the most effective growth promoter for vegetable crops and cotton in the delineated conditions. Comparative tests have shown that our product exceeds the stimulator "Rostlin" in germination of cotton seeds and the development of its root system by almost 2,5 times.

Recommended further in-depth study in the field.

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