

International Journal of Engineering Sciences & Research Technology

(A Peer Reviewed Online Journal)

Impact Factor: 5.164



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ABSTRACT

The article deals with the synthesis of derivatives of carbamates and bis-carbamates on the basis diacetone alcohol, development of optimal conditions of their obtaining and study of physico-chemical properties, and reactions of nitrozozirovaniye, halogenation. The results of the biological activity of N, N¹-tetramethylene bis [(diacetonoyl) carbamate] are presented. The relationship between structure and activity is established. A stimulating effect on the germination of seeds was noted depending on the concentration. The ways of their practical application are outlined.

KEYWORDS: carbamates, bis-carbamates, isocyanate, nitrozozirovaniye, halogenations, biological activity.

1. INTRODUCTION

In the chemistry of synthetic organic compounds, the direction of fine organic synthesis of matter has acquired special development, among which a significant role is played by the carbamate and bis-carbamate derivatives obtained on the basis of the isocyanate and diisocyanate.

Numerous studies in the field of derivatives of carbamates and bis-carbamates, conducted at the present time, are induced by not only theoretical, but also practical needs. From this point of view, derivatives of carbamates and bis-carbamates are of undoubted interest as substances possessing various technical, biological and pharmacological activities. They are successfully used in almost all branches of the national economy, in particular, in engineering as an additive to lubricating oils, vulcanization accelerators of rubbers, they are used both as initial products for the production of polymers and as inhibitors of corrosion [1-5].

In agriculture, they have found application as pesticides, herbicides, defoliant, growth stimulators, antiseptics and many others [6-9].

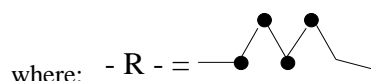
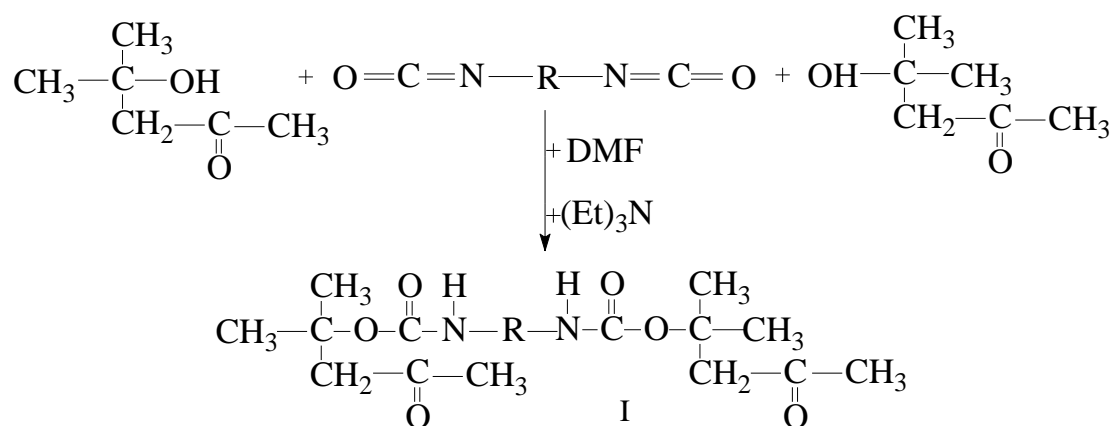
2. MATERIALS AND METHODS

The object of the study was the derivatives of N, N¹-tetramethylene bis [(diacetonoyl) carbamate]. The course of the reaction and the individuality of the compounds are monitored by TLC on aluminum oxide of the II degree of activity with the appearance of spots by iodine vapor. 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 presented earlier studies in the synthesis of new bis-carbamate derivatives and studied some of their chemical properties.

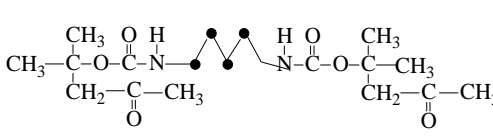
Thus, by the interaction of diacetone alcohol with diisocyanate, bis-carbamate derivatives were prepared according to the following reaction scheme:



The reaction of diisocyanate with diacetone alcohol was carried out at a molar ratio of reactants of 1: 2 at a temperature of 26-36 ° C for 3,5-4,0 hours. As a result of the reaction, N, N¹-tetramethylene bis [(diacetonyl) carbamate] (I) is formed, which is a colorless high melting powder that is hardly soluble in water and other hardly available organic solvents, which confirms the presence of two carbamate as well as poly-methylene. The physico-chemical parameters of the obtained product (I) are given in Table. 1.

The structure of the synthesized compound (I) is determined by the IR spectrum method and elemental analysis data. In the IR spectrum of N, N¹-tetramethylene bis [(diacetonyl) carbamate] there is a broad absorption band in the region of 1430 cm⁻¹, characteristic for -NH-CH₂-, and the absorption band in the region of 1684 cm⁻¹ that corresponds to the absorption of -NHCOO - bond, the absorption band at 3313 cm⁻¹ indicates the presence of N-H groups, the absorption band in the region of 757-728 cm⁻¹ is characteristic for (NHCOO) groups.

Table 1. Physicochemical parameters of compounds (I)

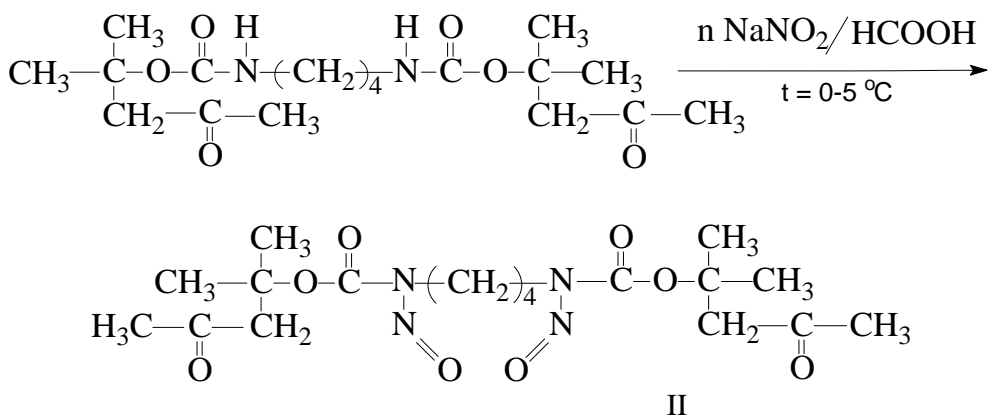
Structural formula	Output, %	Tm, °C	R _f	Gross formula	Elemental analysis, %		M _M
					Calculated	Found	
					N	N	
	88,6	244-245	0,64	C ₁₈ H ₃₀ N ₂ O ₆	7,56	7,51	370

To reveal the reactivity of N-H reaction centers of bis-carbamate, we carried out N, N¹-dinitrosation and chlorination reactions.

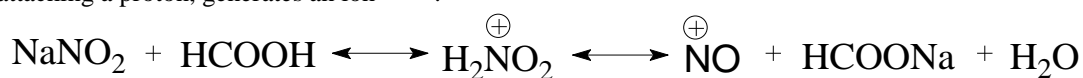
Preparation of N, N¹-dinitroso-substituted N, N¹-tetramethylene bis [(diacetonyl) carbamate] (II).

As a result of the N, N¹-dinitrosozoic reaction of the bis [(diacetonyl) -carbamate] by sodium nitrite (in excess) in formic acid, the corresponding N, N¹-dinitroso substituted bis [(diacetonyl) carbamate] was obtained in 84,4% yield (Table 2)

N, N¹-dinitrosation proceeds by the mechanism of electrophilic substitution:



The attacking NO^{\oplus} agent is nitrosonium. Since nitrous acid, which is the most common nitrosating agent, does not exist in a free form, sodium nitrite and a strong acid (HCOOH) are used for the process. The resulting nitrous acid, attaching a proton, generates an ion NO^{\oplus} :



N, N¹-dinitrosation is carried out with cooling (0-5 ° C) of the reaction mixture. The increase in temperature is undesirable, since this reduces the yield of the desired product, and sometimes affects the direction of the reaction.

Table 2. Physicochemical parameters of N, N¹-dinitroso substituted compounds (II)

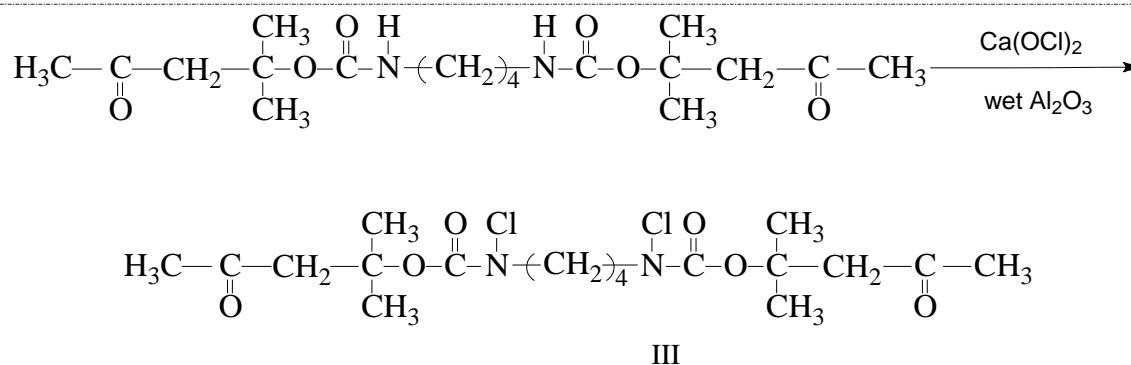
Structural formula	Output, %	Tm, °C	R _f	Gross formula	Elemental analysis, %		M _M
					Calculated	Found	
					N	N	
	84,4	295-297(dec.)	0,68	C ₁₈ H ₂₈ N ₄ O ₈	13,08	12,94	428

Identification of N, N¹-dinitroso compounds is carried out along the absorption bands of N-nitroso groups. A very strong absorption band in the region of 1530-1440 cm⁻¹ for groups is characteristic.

Preparation of N, N¹-dichloro-substituted N, N¹-tetramethylene bis [(diacetonoyl) carbamate] (III)

We have developed an efficient, affordable, cheap, environmentally friendly method for the N, N¹-dichlorination of bis-carbamate with calcium hypochlorite on wet Al₂O₃. The scheme of the chemical reaction is as follows:





The yield of the product is 91,5 %, Tm = 179-180 ° C.

Thus, methods for the preparation of N, N¹-tetramethylene bis [(diacetonoyl) carbamate] have been developed and its chemical properties in N-H reaction centers have been studied: nitrosation and chlorination reactions.

4. EXPERIMENTAL PART

The course of the reaction and the individuality of the compounds are monitored by TLC on aluminum oxide of the II degree of activity with the appearance of spots by iodine vapor. The IR spectra are recorded on a spectrometer VR-20 spectrometer in KBr tablets.

Synthesis of N, N¹-tetramethylene bis [(diacetonoyl) carbamate] (I)

5 ml of triethylamine, 30 ml of DMF, 14,0 g (0,1 mole) of tetramethylenediisocyanate dissolved in 25 ml of DMF were added dropwise with stirring at room temperature to 23,2 g (0,2 mole) of diacetone alcohol. The reaction mixture was stirred for 3,5 hours at room temperature 36-39 ° C. At the end of the time, the contents of the flask are transferred to a glass, water is added. The precipitation is washed with TLC. After drying, a colorless powder is obtained, the yield is 88,6 %; Tm = 244-245 ° C.

Synthesis of N, N¹-dinitroso-substituted I (II)

0,5 grams of sodium nitrite are added in portions over a period of 3,5-4,0 hours to 3,7 g (0,01 mole) I dissolved in 100 ml of formic acid, constantly stirring at a temperature of 0-5 ° C. After the end, the mixture is poured into a glass, water is added, the precipitate formed is filtered off, washed with benzene and dried, TLC is on "Silifol" plates, yield – 84,4%; Tm = 295-297 ° C (dec.).

Synthesis of N, N¹-dichloro-substituted I (III)

3,7 g (0,01 mol) I, 50 ml CCl₄, 20 g wet alumina are placed together and 4,4 g calcium hypochlorite is added there dropwise at a temperature of 40 ° C for 24 hours. It is filtered off, washed with ether and alcohol, dried and (III) is obtained in a yield of 91,5 %; Tm = 179-180 ° C.

Found, %: C 49,01; H 6,22; N 6,28; Cl 16,11.

Calculated for C₁₈H₂₈Cl₂N₂O₆; %: C 49,20; H 6,37; N 6,37; Cl 16,17.

To prove the structure of N, N¹-dichloro-substituted (III) element analysis of silver salts (AgNO₃ solution) was carried out.

Field tests on the growth-promoting activity of the drug (I)

After the initial tests for the growth-stimulating activity of the preparation (I), field tests were conducted on the farm of S.Azamov in the Kasbinsky's district of the Kashkadarya region in the period from April to October 2017.

For the first time, the obtained Rostermulator (I), in particular N, N¹-tetramethylene bis [(diacetonoyl) carbamate] (I) was tested at a concentration of 0,001% (i.e., diluted 750 times). Cucumbers of the variety "Uzbekistan-740", tomatoes of "Temp" variety, medium-fiber cotton of the variety "6524", corn and sunflower on the area of 24669 hectares were used in the farm.

There were received extra 10361 tons. cotton, which amounts to an anticipated economic effect of about 4 billion sums only for cotton growing. Similarly, good results were obtained on tomatoes, cucumbers, sunflower and corn.

Thus, the drug (I), recommended by us in a solution of 0,001% concentration, exceeds many of the known drugs in stimulating activity and is less toxic ($LD_{50} = 4380 \text{ md / kd}$).

The results and discussion may be combined into a common section or obtainable separately. They may also be broken into subsets with short, revealing captions.

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CITE AN ARTICLE

Makhsumov, A. G., Valeeva, N. G., Nabiev, U. A., & Iskandarov, O. (2018). SYNTHESIS OF THE DERIVATIVE DIACETONE ALCOHOL AND ITS PROPERTIES. *INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY*, 7(12), 205-209.