SYNTHESIS OF TRIAZOLONES AND C-AMINOTRIAZOLES BY THERMAL CONDENSATION OF CARBAMIDOAMIDRAZONES

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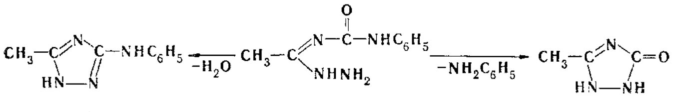
Either triazolones or C-aminotriazoles — or both — are formed in the thermal condensation of carbamidoamidrazones, depending on their structure.

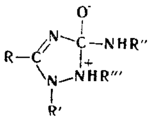
We have previously reported the synthesis of carbamidoimino esters and carbamidoamidrazones [1, 2]. The present paper is devoted to the study of some transformations of carbamidoamidrazones that lead to the formation of triazole and triazolone derivatives.

The starting carbamidoamidrazones (I-VI, Table 1) were synthesized by the reaction of carbamidoimino esters with hydrazine, methylhydrazine, and phenylhydrazine. Heat treatment of the carbamidoamidrazones leads to intramolecular condensation which only give, in a number of cases, triazole derivatives. Thus, when N''-phenylcarbamido-N'-methylacetamidrazone (III) is heated, it cyclizes with splitting out of water to give 1,5-dimethyl-3-anilino-1,2,4-triazole (VIII). Similar condensation on heat treatment of 1,6-bis(N'-methylacetamidrazono-N''-carbamido)hexane (V) gives N,N'-bis(1,5-dimethyl-1,2,4-triazol-3-yl)hexamethylenediamine (X), while N''-β-naphthylcarbamido-N-phenylacetamidrazone (IV) gives 1-phenyl-3-methyl-5-β-naphthylamino-1,2,4-triazole (IX).



VII I XI

The intramolecular cyclization of N''-phenylcarbamidoacetamidrazone (I) proceeds in two directions to give 3-methyl-1,2,4-triazol-5-one (XI) and 3-methyl-5-anilino-1,2,4-triazole (VII). In both cases, the reaction proceeds through a step involving the formation of an intermediate with the following structure:



Depending on the character of the substituents attached to the nitrogen atoms, either water or aniline splits out to give, respectively, a triazole or a triazolone.

The formation of only triazolone derivatives is observed in the thermal condensation of some carbamidoamidrazones. Thus, when we heated amidrazone II we were unable to isolate a triazole derivative but obtained 1-phenyl-3-methyl-1,2,4-triazol-3-one (XII) in 70% yield. The similar cyclization of 1,4-bis(N''-phenylcarbamido-N-phenylamidrazone)butane (VI) gives 1,4-bis(1-phenyl-5-hydroxy-1,2,4-triazol-3-yl)butane (XIII).

The structure and composition of the compounds obtained in this study are confirmed by the results of elementary analysis and the IR spectra. The spectra of C-aminotriazoles VII-X contain absorption bands of an NH bond at 3310 cm^{-1} and of a C=N bond at 1610-1660 cm^{-1}, but C=O vibrations are absent. The IR spectra of triazolones XI-XIII contain absorption bands of the stretching vibrations of NH groups (3050-3200 cm^{-1}), C=O (1708-1740 cm^{-1}), and C=N groups (1600-1610 cm^{-1}).

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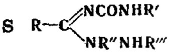
TABLE 1. Carbamidoamidrazones



$R-C\begin{matrix}{\nearrow}NCONHR' \\ {\searrow}NR''NHR'''\end{matrix}$

Compound	R	R′	R″	R‴	mp, ℃ (from alcohol)	Empirical formula	Found, %			Calc., %			Yield, %
							C	H	N	C	H	N	
I*	CH_3	C_6H_5	H	H	172	$C_9H_{12}N_4O$	56,3	6,6	28,8	56,1	6,3	29,2	88
II†	CH_3	C_6H_5	H	C_6H_5	148	$C_{15}H_{12}N_4O$	67,8	6,1	20,3	67,3	6,0	20,8	63
III	CH_3	C_6H_5	CH_3	H	96	$C_{10}H_{14}N_4O$	58,0	6,5	27,1	58,3	6,8	27,2	70
IV	CH_3	$C_{10}H_7$	H	C_6H_5	190	$C_{19}H_{18}N_4O$	71,7	5,5	17,8	71,8	5,7	17,6	75
V					130	$C_{14}H_{30}N_8O_2$	49,1	8,4	32,3	49,4	8,8	32,8	82
VI					140	$C_{32}H_{34}N_8O_2$	68,5	6,4	19,9	68,1	6,1	19,9	84

*With mp 172° [1].

†With mp 147-148° [1].

TABLE 2. C-Aminotriazoles and Triazolones

Compound	mp, ℃ (from alcohol)	Empirical formula	Found, %			Calc., %			Yield, %
			C	H	N	C	H	N	
VII	212	$C_9H_{10}N_4$	62,2	5,7	31,2	62,1	5,7	32,2	35
VIII	120	$C_{10}H_{12}N_4$	63,4	6,5	29,7	63,8	6,4	29,7	70
IX	280	$C_{19}H_{16}N_4$	76,2	5,3	18,3	76,2	5,3	18,7	60
X	164	$C_{14}H_{26}N_8$	54,9	8,3	36,2	54,5	8,5	36,6	60
XI*	223	$C_3H_5N_3O$	36,4	4,9	41,6	36,4	5,1	42,4	50
XII†	152	$C_9H_9N_3O$	61,8	5,1	24,0	61,8	5,2	24,0	70
XIII	270	$C_{20}H_{20}N_6O_2$	63,5	5,3	22,7	63,9	5,3	22,8	70

*With mp 243° [4].

†With mp 163-164° [5].

EXPERIMENTAL

The IR spectra of KBr pellets of the compounds were recorded with a UR-10 spectrometer.

Carbamidoamidrazones I-IV and dicarbamidoamidrazones IV-VI were synthesized by the method in [1] by reaction of the appropriate carbamidoimino ester and dicarbamidoimino ester with hydrazine or its derivatives in a solvent. Some of the properties and yields of the compounds are presented in Table 1.

Cyclization of Carbamidoamidrazones I-IV and Dicarbamidoamidrazones V and VI. A 5-10-g sample of the carbamidoamidrazone or dicarbamidoamidrazone was heated in a glass reactor with an outlet tube at 200-250° in vacuo (5-10 mm) for 2 h. The resulting C-aminotriazole or triazolone was recrystallized from hot ethanol. The synthesized compounds are colorless substances that are soluble on heating in alcohol, water, dioxane, dimethylformamide, less soluble in benzene, and insoluble in saturated hydrocarbons. The properties and yields of the synthesized C-aminotriazoles (VII-X) and triazolones (XI-XIII) are presented in Table 2.

In the cyclization of I, the resulting C-aminotriazole (VII) sublimes under the indicated conditions, while triazolone XI remains in the pot. The substances were recrystallized from ethanol.

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