PRODUCTS OF THE REACTION OF N, N'-DIFORMYLHYDRAZINE WITH 1-SUBSTITUTED 3, 5-DIAMINO-1, 2, 4-TRIAZOLES

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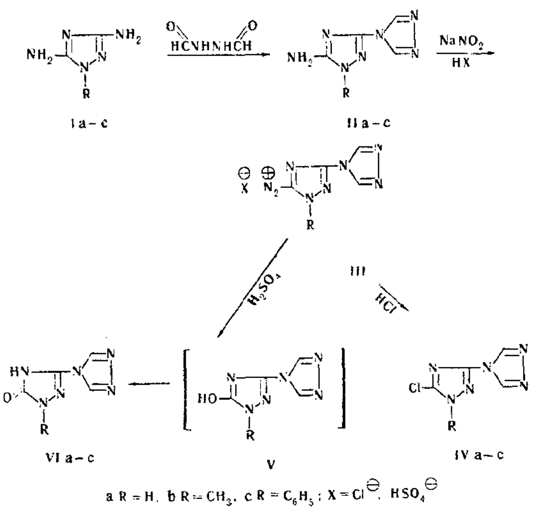
Products of the reaction of 3, 5-diamino-1-methyl- and 3, 5-diamino-1-phenyl-1, 2, 4-triazines with N, N'-diformylhydrazine have been obtained; they have the structure of 5-amino-1-methyl- and 5-amino-1-phenyl-3-(1, 2, 4-triazol-4-yl)-1, 2, 4-triazoles, respectively. The presence of a free amino group was shown by the diazotization of the reaction products with the subsequent replacement of the diazonium group by halogen and hydroxyl. It has been shown by IR spectroscopy that the hydroxyl compounds exist in the triazolone form in the crystalline state.

The reaction of 3, 5-diamino-1, 2, 4-triazole (guanazole) (Ia) with diformylhydrazine (DFH) has been described in the literature, but different opinions exist on the structure of the products obtained [1–3]. We have reproduced this synthesis and have carried out the condensation of DFH with 3, 5-diamino-1-methyl- and 3, 5-diamino-1-phenyl-1, 2, 4-triazoles (Ib and Ic) under similar conditions. It was found that at a molar ratio of triazole to DFH of 1 : 2, only one amino group takes part in the reaction and the products have the structure of 5-amino-1-methyl- and 5-amino-1-phenyl-3-(1, 2, 4-triazol-4-yl)-1, 2, 4-triazoles (IIb and IIc), respectively. The IR spectra of the products obtained have an absorption band characteristic for a free NH_2 group: ν_{NH_2} for IIa 1650 cm^{-1}, for IIb 1670 cm^{-1}, and for IIc 1660 cm^{-1}.

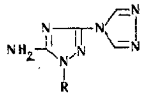
Compounds II are smoothly diazotized with the formation of the corresponding diazonium salts (III). On being heated in hydrochloric acid, the latter are converted into 5-chloro-3-(1, 2, 4-triazol-4-yl)-1, 2, 4-triazoles (IV). In the IR spectra of these compounds, the band at 1650–1675 cm^{-1} has disappeared.

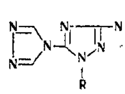


a R = H, b R = CH_3, c R = C_6H_5; X = $Cl^{\ominus}$, $HSO_4^{\ominus}$

Heating III in dilute sulfuric acid leads to the replacement of the diazonium group by hydroxyl. A band at 1650–1675 cm^{-1}, which is characteristic for the 1, 2, 4-triazolones, appears in the IR spectra of the compounds obtained. Thus, it has been shown that the compounds synthesized have the structure of 3-(1, 2, 4-triazol-4-yl)-1, 2, 4-triazol-5-ones (VIb) which is in harmony with modern ideas on the structure of hydroxy derivatives of α-nitrogen-containing aromatic heterocycles [5].

Since positions 3 and 5 are equivalent for the 1, 2, 4-triazoles unsubstituted on the nitrogen atoms [6], there can be no isomers for IIa but two isomeric forms A and B are possible for IIb and IIc:


A


B

We consider that structure A is more likely, since 5-amino-1-methyl-1, 2, 4-triazole does not react with DFH under similar conditions.

EXPERIMENTAL

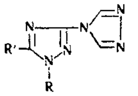
The initial compounds were obtained by methods described in the literature [7–10].

5-Amino-3-(1, 2, 4-triazol-4-yl)-1, 2, 4-triazoles (II). With careful mixing, 0.1 mole of a diaminotriazole and 0.2 mole of DFH were placed in an oil bath and heated to 180° C for 1 hr. The cooled mixture was recrystallized from boiling water, and the precipitate was dried under vacuum at 90° C (Table 1).

5-Chloro-3-(1, 2, 4-triazol-4-yl)-1, 2, 4-triazoles (IV). With stirring at a temperature of 3–5° C, 0.26 mole of sodium nitrite in the minimum amount of water was added over 30–40 min to a solution of 0.13 mole of II in HCl. The reaction mixture was kept at the same temperature for 30 min, and then the precipitate of inorganic salts was filtered off and the solution was boiled on a hotplate until the evolution of bubbles of gas ceased. Then it was cooled and brought to pH 6–7 whereupon a precipitate of III deposited. It was recrystallized from water and dried under vacuum at 90° C (Table 1).

3-(1, 2, 4-Triazol-4-yl)-1, 2, 4-triazol-5-ones (VI). A solution of 0.26 mole of sodium nitrite in the minimum amount of water was added to a stirred mixture of 0.13 mole of II in 50 ml of 1 N H_2SO_4 at 3–5° C. The mixture was kept at the same temperature for 30 min and was then heated in the water bath to 90–95° C over 1 hr and was kept at this temperature for 30 min. After cooling, the precipitate was filtered off and it was washed with water until SO_4^{2-} ions were absent from the wash-waters. The product was recrystallized from water and dried under vacuum at 90° C (Table 2).

Table 1



Compound	R	R′	Mp, °C	Empirical formula	Found, %				Calculated, %				Yield, %
					C	H	N	Cl	C	H	N	Cl	
Ia	H	NH_2	Above 350	$C_4H_5N_7 \cdot 1/4\ H_2O$	29.98	3.61	63.32	—	30.87	3.56	63.00	—	64
Ib	CH_3	NH_2	332—336	$C_5H_7N_7$	36.60	4.58	59.65	—	36.36	4.27	59.37	—	55
Ic	C_6H_5	NH_2	242	$C_{10}H_9N_7$	52.65	4.08	43.28	—	52.86	3.99	43.15	—	60
IVa	H	Cl	Above 350	$C_4H_3N_6Cl$	—	—	49.16	21.02	—	—	49.27	20.79	56
IVb	CH_3	Cl	215	$C_5H_5N_6Cl$	—	—	45.23	18.99	—	—	45.53	19.21	72
IVc	C_6H_5	Cl	160	$C_{10}H_7N_6Cl$	—	—	34.35	14.31	—	—	34.07	14.37	30

Table 2

3-(1, 2, 4-Triazol-4-yl)-1, 2, 4-triazol-5-ones

Compound	R	Mp, °C	Empirical formula	N, %		Yield, %
				found	calculated	
VIa	H	Above 350	$C_4H_4N_6O$	55.55	55.25	90
VIb	CH_3	271	$C_5H_6N_6O$	50.56	50.58	50
VIc	C_6H_5	235	$C_{10}H_8N_6O \cdot H_2O$	34.34	34.13	91

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