CYCLIZATION AND DECOMPOSITION OF NITROGUANYLAZIDE IN ORGANIC SOLVENTS

A. G. Mayants, N. A. Klinova, and S. S. Gordeichuk

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When nitroguanylazide is heated in solution, it may cyclize to form a mixture of 5-nitroaminotetrazole and the diammonium salt of 5-nitroaminotetrazole or it may decompose, depending on the nature of the organic solvent.

It is known [1] that nitro guanylazide in aqueous solution cyclizes in the presence of basic agents to form salts of 5-nitroaminotetrazole (a). In the present work, we have investigated the possibility of cyclizing nitroguanylazide by heating it in organic solvents. In acetone or glacial acetic acid, only the decomposition of nitroguanylazide takes place with no cyclization. When solutions of nitroguanylazide in dioxane, ethanol, dichloroethane, or chloroform are heated, cyclization takes place with the formation of a mixture of 5-nitroaminotetrazole and the diammonium salt of 5-nitroaminotetrazole (b) as well as the decomposition of the nitroguanylazide (c), accompanied by the evolution of ammonia. The formation of the diammonium salt of 5-nitroaminotetrazole is obviously the result of the reaction of 5-nitroaminotetrazole with ammonia evolving during the decomposition of the nitroguanylazide.

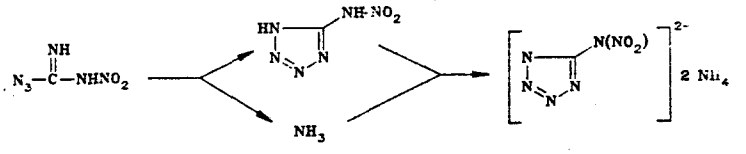

Table 1 shows the yield of cyclization products and the amount of nitroguanylazide having decomposed as functions of the nature of the organic solvent. Table 2 gives information on the amount having decomposed after heating alcoholic solutions of nitroguanylazide as a function of the nature of the alcohol.

EXPERIMENTAL

5-Nitroaminotetrazole and the Diammonium Salt of 5-Nitroaminotetrazole. A solution of 0.5-1.0 g (4-8 mmoles) of nitroguanylazide in dioxane, ethanol, dichloroethane, or chloroform is heated in a flask under reflux at a given temperature (see Table 1) for 20 h. The ammonia

TABLE 1. Decomposition of Nitroguanylazide in Organic Solvents

Solvent	Concn. of c, M	T, °C	Yield, %		Amt. of c having decomposed, %
			a	c	
Dioxane	0.512	70	84,0	6,3	9,7
Ethanol	0.512	70	25,0	21,4	53,6
Dichloroethane	0,076	70	—*	10.3	—
Chloroform	0,192	60	—*	8,7	—
Acetone	0,769	55	0,0	0,0	100
Acetic acid	0,512	70	0,0	0,0	100

*The low yield of 5-nitroaminotetraazole was not determined quantitatively.

TABLE 2. The Amount of Nitroguanylazide Having Decomposed

Alcohol	Concn. of c, M	T, °C	Atm. of c having decomposed, %
Methanol	1,098	64	46,9
Ethanol	0,769	78	35,0
1-Propanol	1,098	80	63,6
2-Propanol	1,098	80	70,7
tert-Butanol	0,769	80	66,7
iso-Butanol	0,769	80	64,4

V. V. Kuibyshev Polytechnic Institute, Kuibyshev, 443010. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 7, 945-946, July, 1987. Original article submitted February 25, 1986.

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evolved is trapped with Nessler's reagent. After the end of the period, the solvent is removed and the remaining product washed with ether and acetone. The ether is removed from the ether extract and the reaction product is recrystallized from a mixture of ethanol and benzene to give 5-nitroaminotetrazole. T_{mp} 139°C (with explosion). According to [1], T_{mp} is about 140°C. The UV spectrum of the compound isolated is identical with the UV spectrum of 5-nitroaminotetrazole [2]. After the washing with ether and acetone, the diammonium salt of 5-nitroaminotetrazole is left. T_{mp} 219-220°C. According to [1], T_{mp} is 220-221°C. Found: N 68.0%. Calculated for $CH_8N_8O_2$, N 68.3%.

Decomposition of Nitroguanylazide in Alcoholic Solutions. A solution of 0.5-1.0 g of (4-8 mmoles) nitroguanylazide in alcohol is heated in a flask under reflux at a given temperature (see Table 2) for 2 h. The solvent is then removed and the crystalline product remaining washed in 15 ml of 25% ammonia. After the removal of the water, the product is washed with acetone, dried and weighed. The product is the diammonium salt of 5-nitroaminotetrazole with T_{mp} 219-220°C. Found: N 68.3%. Calculated from $CH_8N_8O_2$: N 68.3%. The amount of nitroguanylazide having decomposed was calculated from the yield of the diammonium salt of 5-nitroaminotetrazole.

LITERATURE CITED

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2. A. G. Mayants, S. S. Gordeichuk, V. A. Shlyapochnikov, T. V. Gordeichuk and V. P. Gorelik, Khim. Geterotsikl. Soedin., No. 11, 1569 (1984).

NEW 2,2,6,6-TETRASUBSTITUTED 4-PIPERIDONES

V. Ya. Sosnovskikh and V. R. Katyanova

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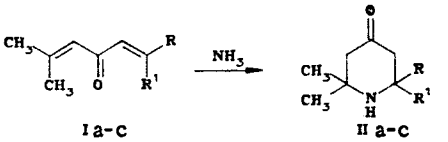
Heterocyclization of tetrasubstituted divinyl ketones formed during the condensation of mesityl oxide with aromatic ketones by the action of ammonia leads to new 2,2-disubstituted 6,6-dimentyl-4-piperidones.

A large number of papers [1] have been devoted to the synthesis of 2,2,6,6-tetramethyl-4-piperidone (triacetoneamine) and its different derivatives, but despite the increasing interest in the chemistry of sterically hindered piperidines, practically no information is available on the change in the nature of the substitution at the carbon atoms bound to nitrogen. There are data only on the preparation of 6,6-dimethyl-4-piperidone-2-spirocycloalkanes in the reaction of diacetoneamine with cyclopentanone and cyclohexanone [2].

We showed that the previously unreported 2,2,6,6-tetrasubstituted 4-piperidones (IIa-c) containing, in their structures, aromatic and heterocyclic radicals as well as methyl groups can be obtained by heterocyclization of divinyl ketones (Ia-c) by the action of ammonia: the divinyl ketones in their turn are formed by mixed condensation of mesityl oxide with aromatic ketones in the presence of N-ethylanilinomagnesium bromide [3].



Ia-c IIa-c

I, II a $R=CH_3$, $R^1=C_6H_5$; b $R=CH_3$, R^1=2-thienyl; c $R=R^1=C_6H_5$

The composition and the structure of piperidones IIa-c were confirmed by data of elemental analysis, and IR and PMR spectroscopy. In the IR spectra of these compounds in mineral

A. M. Gor'kii Ural State University, Sverdlovsk 620083.

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