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STUDIES IN THE FIELD OF CHEMISTRY OF NITRO COMPOUNDS (TO 100TH BIRTHDAY ANNIVERSARY OF S. S. NOVIKOV)

Reactions of 1,1-Diamino-2,2-dinitroethylene with Diamines

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Abstract—Reactions of 1,1-diamino-2,2-dinitroethylene with diamines were studied.

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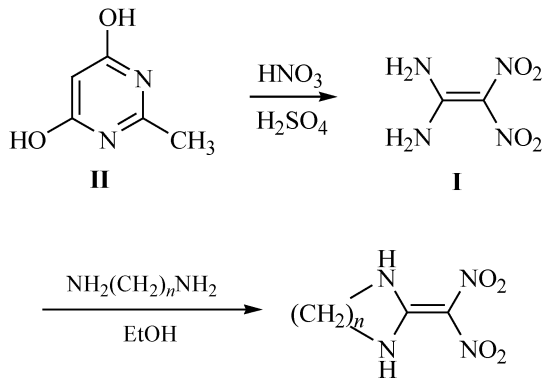
1,1-Diamino-2,2-dinitroethylene (**I**, FOX-7) is a promising high-density thermally stable power-consuming compound [1, 2], which can be also of interest as a mother substance for the synthesis of various derivatives of 1,1-diaminoethylene. There are some publications devoted to the chemical transformations of **I** [2–7]. In particular, it was shown that compound **I** reacts with oxalyl chloride by the both amino groups to form a corresponding imidazolidinedion [2], can play a role of the amine component of Mannich's reaction [3], is halogenated and nitrated by the nitromethylene group [4], is denitrated under the action of peroxoacids [5], and reacts with amines and hydrazine with the replacement of one or two amino groups [6, 7].

Although there are published data on the fact that compound **I** reacts with various diamines and hydrazine [6, 7], no experimental details (reaction conditions such as solvent, duration, catalytic agent, yield, and product characteristics) are given in these publications.

To find out how easily these reactions occur, we have studied the reaction of 1,1-diamino-2,2-dinitroethylene with 1,2-diaminoethane, 1,3-diaminopropane, and 1,4-diaminobutane. Initial diaminonitromethylene (**I**) was synthesized by the nitration of 4,6-dihydroxy-2-methylpyrimidine (**II**) (see the scheme).

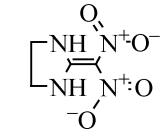
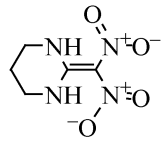
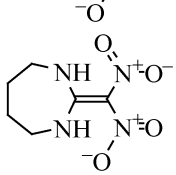
The results obtained are given in the table where the yields of the corresponding diamino-derivatives prepared from 1,1-diiododinitroethylene are shown for comparison [8].

Scheme.



II **I**

Comparative results of the synthesis of cyclic dinitroethylenediamines from compound **I** and 1,1-diiododinitroethylene

Substence	Yield, %	mp, °C	Published data [8]
	80	261–262	Yield 74%, mp 261–262°C
	87	260 (decomposition point)	Yield 60%, mp 243–244°C
	50	213–214	Yield 91%, mp 211–212°C

As follows from the table, the yields of the corresponding cyclic diamines obtained from **I** and from 1,1-nitromethylene are close to each other, however the reactivity of **I** is essentially lower (a long-term heating of compound **I** at the presence of a diamine excess is necessary). The attempts to introduce 1,5-diaminopentane into the reaction were unsuccessful, apparently because of a low probability of the octatomic cycle closure under the reaction conditions. We cannot realize reaction of **I** with *ortho*-phenylenediamine either.

The resulting substances can be of interest as potential nitrogen oxide donors, power-consuming compounds, and reagents for the organic synthesis, in particular for obtaining 1,1-diaminoehtylene derivatives.

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM300 instrument with TMS as the interior standard. The IR spectra were recorded on a Specord M82 spectrometer, melting points were determined on a Boetius table at a heating rate of 4 deg min^{-1}. Spectral characteristics of the synthesized compounds coincide with corresponding published data.

1,1-Diamino-2,2-dinitroethylene (IX) was obtained by the procedure described in [9] from 2-methyl-4,6-dihydroxypyrimidine, yield 75%, decomposition point >220°C.

2-(Dinitroethylene)imidazolidine (III). Diaminodinitroethylene (1.5 g, 10.1 mmol) and 2.5 ml (38 mmol) of ethylenediamine were boiled with stirring in 20 ml of ethanol up to the disappearance of the initial compound according to TLC (20–24 h). The solvent was distilled off, the residue was mixed with water, and the precipitate was filtered off and dried on the filter. Yield 1.4 g (80%). Mp 261–262°C.

2-(Dinitromethylene)hexahydropyrimidine (IV). Diaminodinitroethylene (1.5 g, 10.1 mmol) was boiled with stirring in 20 ml of ethanol with 2 ml (24 mmol) of 1,3-diaminopropane up to the disappearance of the initial compound according to TLC (20–24 h). The reaction mixture was mixed with water, the precipitate was filtered off and dried on the filter. Yield 1.64 g (87%), 1.4 g (80%), decomposition point 260°C.

2-(Dinitromethylene)-1,3-diazepan (V). Diaminodinitroethylene (1.5 g, 10.1 mmol) was boiled with stirring in 12 ml of ethanol with 2 ml (20 mmol) of 1,3-diaminobutane up to the disappearance of the initial compound according to TLC (13–15 h). The precipitate was filtered off, washed first with ethanol and then with water, and dried on the filter. Yield 1.0 g (50%), mp 213–214°C (decomposition).

CONCLUSION

It was shown that 1,1-diamino-2,2-dinitroethylene is a promising mother compound for the synthesis of various saturated 1,3-diazaheterocycles containing a dinitromethylene group in the second position.

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