```
A. D. Sinegibskaya, E. G. Kovalev,
and I. Ya. Postovskii
```

Cleavage of one alkyl group occurs in the reaction of 4-amino-3,5-di (alkylthio)-1,2,4-triazoles with hydrazine hydrate.

As a rule, nitrogen-containing heterocyclic alkylthic compounds exchange an alkylthic group for a hydrazine group on reaction with hydrazine hydrate [1].

In an attempt to accomplish this reaction in the case of 3,5-di (methylthio)-4-amino-1,2,4-triazole (I), we observed cleavage of one methyl group to give 3-methylthio-4-amino-1,2,4-triazoline-5-thione (II) instead of the expected hydrazinolysis. It was shown by means of gas-liquid chromatography (GLC) that the methyl group is split out as methane, and, consequently, the C_{aliph} -S bond is cleaved in the reaction with hydrazine hydrate, while the C_{het} -S bond is cleaved during ordinary hydrazinolysis. The reaction of I with hydrazine hydrate probably has redox character and proceeds via the following scheme:



To ascertain the generality of the reaction we obtained a series of S-alkyl derivatives (III-VII) with identical and different alkyl groups attached to the sulfur atom.



In the reaction of hydrazine hydrate with diethyl derivative III, one ethyl group is split out to give thione VIII. When S-methyl-S'-ethyl derivative VII is heated with hydrazine hydrate, a methyl group is split out to give S-ethyl compound VIII, and 4-amino-3-hydrazino-1,2,4-triazole-5-thione (X) is simultaneously formed in low yield. It must be supposed that initially formed thione VIII undergoes partial hydrazinolysis, since the latter gives hydrazine X on reaction with hydrazine hydrate. The di-n-propyl, di-n-butyl, and dibenzyl compounds (IV-VI) do not undergo this sort of cleavage or hydrazinolysis.



S. M. Kirov Ural Polytechnic Institute, Sverdlovsk. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 12, pp. 1708-1710, December, 1973. Original article submitted February 6, 1973.

© 1975 Plenum Publishing Corporation, 227 West 17th Street, New York, N.Y. 10011. No part of this publication may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, microfilming, recording or otherwise, without written permission of the publisher. A copy of this article is available from the publisher for \$15.00.



Com- pound	R	R'	mp , ° C	Empirical formula	Found, %			Calc., %			a%
					с	н	s	с	н	s	Yield
III IV V VII VIII	$\begin{array}{c} C_2H_5\\ n-C_3H_7\\ n-C_4H_9\\ CH_3\\ H\end{array}$	$\begin{array}{c} C_{2}H_{5} \\ n-C_{3}H_{7} \\ n-C_{4}H_{9} \\ C_{2}H_{5} \\ C_{2}H_{5} \end{array}$	$\begin{array}{c} 125-126^{a}\\ 90-91b\\ 75-76^{b}\\ 123-124^{d}\\ 165-166^{a} \end{array}$	$\begin{array}{c} C_6 H_{12} N_4 S_2 \\ C_8 H_{16} N_4 S_2 c \\ C_{10} H_{20} N_4 S_2 \\ C_5 H_{10} N_4 S_2 \\ C_4 H_8 N_4 S_2 \end{array}$	35,5 41,5 46,1 31,6 27,0	5,9 6,9 7,4 5,4 4,5	31,6 24,6 33,7 36,2	35,7 41,4 46,1 31,6 27,3	5,9 6,9 7,7 5,3 4,6	31,4 24,7 33,7 36,4	67 60 30 70 77

^a From water. ^b From aqueous alcohol. ^c Found: N 24.1%. Calculated: N 24.1%. ^d From butyl alcohol.

An amino group in the 4 position has a substantial effect on the trend of the reaction. This follows from the fact that 3,5-dimethylthio-1,2,4-triazole (IX), which is obtained in the deamination of I, does not undergo reaction with hydrazine hydrate. Quantum-mechanical calculations of model compounds Ia and Xa by the Hückel MO method showed that the amino group, owing to its electron-donor properties, sharply increases the negative charge on C_{het} ; this is apparently the reason why attack on the cyclic carbon atom by hydrazine hydrate does not occur. Thus transfer of electrons by hydrazine hydrate to the electron-acceptor triazole ring primarily causes localization of them in the C_{het} -S bond; this leads to strengthening of the latter and cleavage of the S- C_{aliph} bond, which is unusual for such systems. This cleavage becomes more likely, the stronger the donor attached to the sulfur atom, which hinders this sort of localization. It must be supposed that it is because of this that the greater electron-donating residue (the methyl group) in VII is split out, while in triazole IX, which has a labile proton, this proton is transferred to hydrazine hy-drate in basic media, and the compound, becoming negatively charged, is not capable of reduction (addition of electrons) and can participate only in substitution reactions.

EXPERIMENTAL

3,5-Di (alkylthio)-4-amino-1,2,4-triazoles (III-V, VII) and 3-Ethylthio-4-amino-1,2,4-triazoline-5thione (VIII) (Table 1). These compounds were obtained by methods similar to those described for I, II, and VI [2].

 $\frac{3-\text{Methylthio-4-amino-1,2,4-triazoline-5-thione (II).}{4-amino-1,2,4-triazole (I)} \text{ A } 0.5-\text{g } (2.8 \text{ mmole}) \text{ sample of } 3,5-\text{di}(\text{methyl-thio})-4-\text{amino-1,2,4-triazole (I)} \text{ was refluxed in 5 ml of hydrazine hydrate for } 12 \text{ h, after which the solvent was removed by distillation to give } 0.25 \text{ g } (74\%) \text{ of II with mp } 186-187^\circ \text{ (needles from water).}}$

<u>3-Ethylthio-4-amino-1,2,4-triazoline-5-thione (VIII)</u>. A. A 0.75-g (3.7 mmole) sample of 3,5-di (ethyl-thio)-4-amino-1,2,4-triazole (III) was refluxed in 10 ml of hydrazine hydrate for 12 h, after which the mix-ture was cooled and filtered to give 0.2 g of III. The hydrazine was removed from the filtrate by distillation, and the residue was crystallized from water to give 0.47 g ($72^{\%}$) of VIII with mp 165-166°.

<u>B.</u> A 1.3-g (6.8 mmole) sample of 3-methylthio-5-ethylthio-4-amino-1,2,4-triazole (VII) was refluxed in 10 ml of hydrazine hydrate, after which the hydrazine was removed by distillation, and the colorless 3hydrazino-4-amino-1,2,4-triazoline-5-thione (X) was removed by filtration and crystallized from water to give 0.15 g (15%) of a product with mp 224-225°, which was identical to the compound obtained by the method in [3]. The filtrate was evaporated to precipitate 1 g (83%) of VIII with mp 165-166° (from water).

<u>3-Hydrazino-4-amino-1,2,4-triazoline-5-thione (X)</u>. A 0.5-g (2.8 mmole) sample of VIII was refluxed for 12 h in 5 ml of hydrazine hydrate, after which the hydrazine was removed by distillation, and the residue was crystallized from water to give 0.1 g (41%) of product. A total of 0.2 g of starting VIII was isolated from the mother liquor.

LITERATURE CITED

- 1. A. Dornow, H. Menzel, and P. Marx, Ber., 97, 2173, 2185 (1964).
- 2. J. Sandström, Acta Chem. Scand., 15, 1209 (1961).
- 3. R. J. Dickinson and N. W. Jocobsen, Anal. Chem., <u>41</u>, 1324 (1969).