QUESTION OF THE MECHANISM OF THE FORMATION OF 5-HYDRAZINO-TETRAZOLE FROM 5-DIAZOMETHYLAZOTETRAZOLE IN ACIDIC MEDIA

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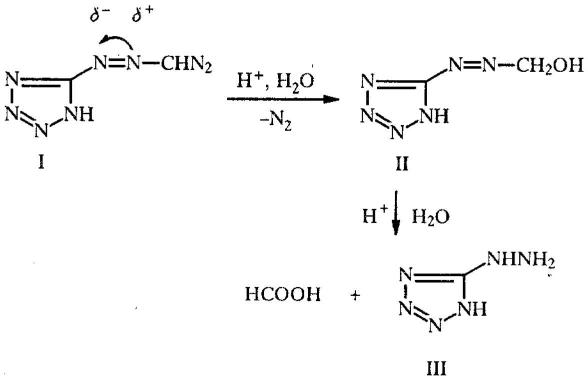
The heating of the hydrate of 5-diazomethylazotetrazole in an aqueous medium led to the isolation, for the first time, of 5-hydroxymethylazotetrazole — the proposed intermediate product in the isolation of 5-hydrazinotetrazole from 5-diazomethylazotetrazole in acidic media. It was established that 5-hydrazinotetrazole is not formed when 5-hydroxymethylazotetrazole is treated with hydrochloric acid under different conditions. In this connection, an improved reaction mechanism, not including 5-hydroxymethylazotetrazole as an intermediate compound, was proposed. It was shown that not all of the 5-diazomethylazotetrazole enters into the reaction with water. The proposition was expressed that the product which did not enter into the reaction is the Z-isomer.

According to the hypothetical mechanism in [1], the treatment of 5-diazomethylazotetrazole (I) with aqueous solutions of acids leads to the formation of the intermediate 5-hydroxymethylazotetrazole (II), which is further converted to 5-hydrazinotetrazole (III).



With the object of synthesizing the compound (II), we studied the reaction of the compound (I)·H_2O with water. The aqueous suspension of the diazo compound (I)·H_2O was heated for 1 h and 2.5 h. Part of the substance thereby reacted with water and went over into the solution, and the other part remained unreacted. The results of the experiments showed that the amount of the unreacted diazo compound (I) is virtually independent of the reaction time and comprises 9-14%. The compound (II) was successfully isolated from the aqueous solution and identified, whereby its yield was also virtually independent of the reaction time and comprised 82-86%. The comparison of the temperatures of decomposition and the IR spectra of the samples of the diazo compound (I)·H_2O, which did not enter into the reaction, and of the initial material showed their regular change, namely the significant decrease in the decomposition temperature from 164-168°C [the initial (I)·H_2O] to 152-156°C (the unreacted substance) and the marked increase in the difference of the intensity of the bands of the stretching vibrations of the

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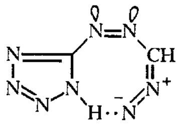
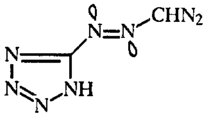
azo group (1584 cm^{-1}) and the diazo group (2160 cm^{-1}) for the unreacted sample, As was indicated in the work [1], changes in the temperatures of decomposition and the comparative intensity of the absorption bands of the azo and diazo groups in different samples of (I)·H_2O are evidently associated with the change in the quantitative proportion of the isomers (differences in the frequencies of the absorption bands could not be found; this is probably associated with their large width). Proposing an analogy with the data on the Z-,E-isomerism of derivatives of five-membered heterocycles containing unsaturated substituents [2, 3], as well as taking into account the possibility of the intramolecular H...N interaction with the formation of rings more than six-membered [4], the occurrence of the diazo compound (I) in the following Z- and E-isomeric forms should be considered probable (the Z- and E-conformations characteristic of conjugated, sterically hindered diazo compounds [5] can be ignored due to the absence of steric hindrance in the given case).



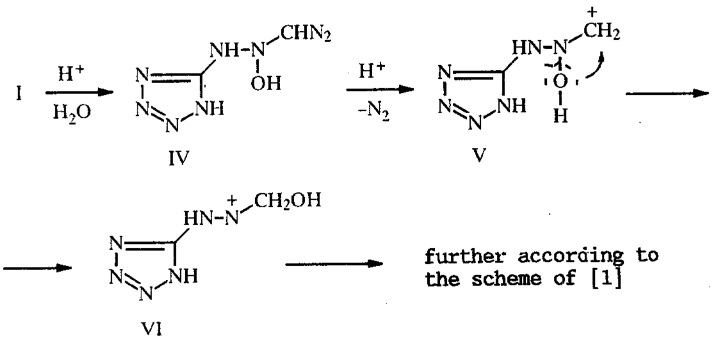
Z-isomer



E-isomer

The possible formation of the N-H...N^- hydrogen bond is determined by the acidic character of the hydrogen of the NH group of the tetrazole ring [6]. For the structures presented, the Z-isomer should have lower reactivity since it is known that the intramolecular hydrogen bond prevents the interaction of the compound with both the reagent molecules and with the solvent molecules [7]. The same isomer should also probably have a lower decomposition temperature since it is known that the Z-isomers of azo compounds are usually less stable [8]. An indirect argument in favor of the identity of the unreacted sample of (I)·H_2O as the Z-isomer is also its low quantity (~12%), since it is known that the synthesis of azo compounds leads preferentially to the isolation of the more stable E-isomer [9]. Therefore, it can be assumed that the E-isomer reacts more rapidly in the treatment of the mixture of isomers of the diazo compound (I)·H_2O with water, and the Z-isomer remains unreacted.

The study of the reaction of the isolated compound (II) with aqueous solutions of hydrochloric acid was conducted under different conditions with the variation in the concentration of the acid, the ratio of the reagents, and the temperature. The results of the experiments thereby showed that the hydrazino derivative (III), expected according to the scheme of [1], is not formed; an unidentified resin-forming substance was isolated in all cases. Starting from that, we considered it expedient to propose an improved scheme for the formation of the hydrazino derivative (III) from compound (I) not including the intermediate compound (II).



The Michael reaction – the acid-catalyzed addition of water at the –N═N– activated bond of the compound (I) with the formation of the diazo derivative (IV) – probably proceeds in the initial stage; the Michael reaction is described in the literature for compounds containing the activated azo bond [10]. The direction of the hydration is determined by the presented distribution of the charges (δ– and δ+) at the nitrogen atoms of the azo group of the compound (I), on account of the electron-acceptor character of the tetrazole ring [11] and the electron-donor character of the diazo group [12]. Further, it is evident that the intermediate diazo compound (IV) decomposes in an acidic medium with the release of nitrogen and the formation of the carbocation (V) according to the generally accepted mechanism for the decomposition of diazo compounds in an acidic medium

[13]. The subsequent rearrangement of the cation (V) may lead to the intermediate (VI) figuring in the known scheme [1]. In this connection, the proposed mechanism of the reaction corresponds with the literature data [1].

EXPERIMENTAL

The IR spectra were taken on the UR-20 spectrophotometer using KBr tablets. The initial compound (I)·H_2O was obtained according to the method of [1] with the utilization of sulfuric acid.

The data of the elemental analysis of the compound (II) for C, H, and N correspond with the calculated data.

5-Hydroxymethylazotetrazole (II) ($C_2H_4N_6O$). The suspension of 1.0 g (7.81 mmole) of the compound (I)·H_2O in 70 ml of water is heated at ~95°C. The hot reaction mass is then filtered from the unreacted compound (I)·H_2O, and the water is removed from the filtrate. The compound (II) remaining has the decomposition temperature of 170°C; after crystallization from water, the decomposition temperature is 173°C. The IR spectrum is as follows: 995 cm^{-1}, 1060 cm^{-1}, 1205 cm^{-1} (the tetrazole ring), 1585 cm^{-1} (the azo group), and 3230 cm^{-1} broad (OH).

REFERENCES

1. A. G. Mayants, V. N. Vladimirov, N. M. Razumov, and V. A. Shlyapochnikov, Zh. Org. Khim., **27**, 2450 (1991).
2. A. V. Khramchikhin, V. A. Ostrovskii, and M. D. Stadnichuk, Zh. Obshch. Khim., **61**, 1617 (1991).
3. V. S. Bogdanov, B. I. Ugrak, M. A. Kalik, V. K. Zav'yalova, and M. M. Krayushkin, Izv. Akad. Nauk, Ser. Khim., No. 3, 735 (1991).
4. A. V. Afonin, B. V. Trzhtsinskaya, N. D. Abramova, and L. V. Baikalova, Izv. Akad. Nauk, Ser. Khim., No. 10, 2285 (1991).
5. V. A. Nikolaev, V. V. Popik, and I. K. Korobitsyna, Zh. Org. Khim., **27**, 505 (1991).
6. R. Elderfield (ed.), Heterocyclic Compounds [Russian translation], Vol. 8, Mir, Moscow (1969), p. 11.
7. S. P. Kobzev, M. A. Simonov, A. M. Romantsevich, K. Yu. Chotii, N. M. Mironenko, and I. A. Opeida, Zh. Prikl. Khim., **64**, 1528 (1991).
8. N. V. Vasil'eva, Theoretical Introduction to Organic Synthesis [in Russian], Prosveshchenie, Moscow (1976), p. 127.
9. D. Barton and U. D. Ollis (ed.), General Organic Chemistry [Russian translation], Vol. 3, Khimiya, Moscow (1982), p. 289.
10. V. I. Markovskii, G. A. Marchenko, S. S. Novikov, and V. I. Slovetskii, Izv. Akad. Nauk, Ser. Khim., No. 11, 2838 (1975).
11. A. G. Mayants, V. S. Klimenko, V. V. Erina, K. G. Pyreseva, S. S. Gordeichuk, V. N. Leibzon, V. S. Kuz'min, and Yu. N. Burtsev, Khim. Geterotsikl. Soedin., No. 8, 1067 (1991).
12. V. A. Pal'm, Introduction to Theoretical Organic Chemistry [in Russian], Vysshaya Shkola, Moscow (1974), p. 57.
13. S. D. Isaev, G. G. Zhalnina, Z. N. Murzinova, S. I. Lastovenko, and A. G. Yurchenko, Zh. Org. Khim., **24**, 142 (1988).