azide was performed in the presence of crown ethers. The yield of 5-phenyltetrazole was determined with the accuracy of ± 3%. In all cases, 5-phenyltetrazole had the characteristics corresponding to the data of [3].

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REACTION OF SALTS OF NITROAMINOTETRAZOLES WITH ALKYL IODIDES

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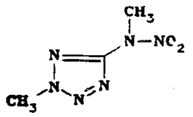
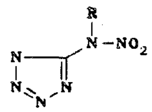
UDC 547.795.1

The reaction of salts of 5-nitroaminotetrazole, 1- and 2-methyl-5-nitroaminotetrazole, and 2-ethyl-5-nitroaminotetrazole with alkyl iodides is studied. It is established that salts of 2-methyl- and 2-ethyl-5-nitroaminotetrazole are alkylated at the nitroamine group while salts of 1-methyl-5-nitroaminotetrazole are alkylated at the second nitrogen atom of the tetrazole fragment with the subsequent splitting off of the methyl group at the 1-position of the tetrazole ring and further alkylation of the nitroamine group. It is shown that salts of 5-nitroaminotetrazole are initally alkylated at the second nitrogen atom of the tetrazole fragment and then at the nitroamine group. It is hypothesized that the initial alkylation of salts of 1-methyl-5-nitroaminotetrazole and 5-nitroaminotetrazole at the second nitrogen atom of the tetrazole fragment results from their nitroimino tautomeric form.

The preparation of dialkyl derivatives of 5-nitroaminotetrazole, I-III, by the reaction of salts of 5-nitroaminotetrazole with methyl iodide (I), the alkylation of 5-nitroaminotetrazole with diazomethane (I), and the nitration of the corresponding dialkyl derivatives of 5-aminotetrazole (I-III), was described earlier [1].


I


II,III

II $R=CH_3$; III $R=C_2H_5$

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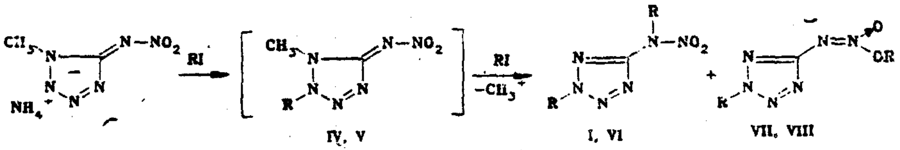
In the present work, we have investigated the possibility of obtaining dialkyl derivatives of the tautomeric form of 5-nitroaminotetrazole, 5-nitroaminotetrazoline (IV, V), by the reaction of salts of nitroaminotetrazoles with alkyl iodides in aqueous media. It is known [2] that some nitroaminotetrazoles are present in aqueous solutions in the tautomeric, nitroiminotetrazoline form.

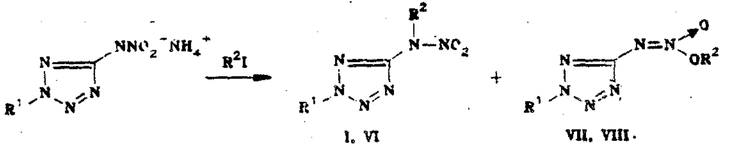
Alkylation products I and VI-VIII containing the alkyl group at the 2-position of the tetrazole fragment were unexpectedly obtained as the products of the reaction of the ammonium salt of 1-methyl-5-nitroaminotetrazole with ethyl and methyl iodides in aqueous acetone solution. This can be explained by the formation in the reaction of the expected dialkyl derivatives of nitroiminotetrazoline (IV and V) which are apparently unstable compounds and decompose with the splitting off of the methyl group at the 1-position of the tetrazole ring and the addition of an alkyl group to the nitroimine fragment according to the scheme:



I, IV, VII R=CH_3; V, VI, VIII R=C_2H_5

If alkylation of the salt of 1-methyl-5-nitroaminotetrazole took place at the nitroamino group, then compound II would have to have been formed, but this is not found among the reaction products.

In order to identify compounds I and VI-VIII obtained from the salt of 1-methyl-5-nitroaminotetrazole, we synthesized them by alkylating salts of 2-alkyl-5-nitroaminotetrazole in aqueous acetone solution with ethyl and methyl iodide according to the scheme:

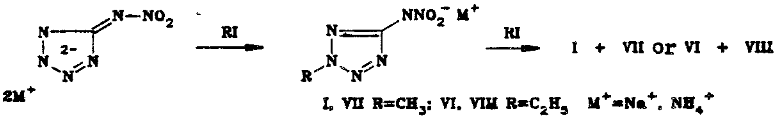


I, VII $R^1=R^2=CH_3$; VI, VIII $R^1=R^2=C_2H_5$

The mixture of isomers VI and VIII was separated by means of preparative chromatography. To isolate individual compounds I and VI, we treated the corresponding mixture of N- and O-isomers, I, VII and VI, VIII, with 40% H_2SO_4 until the O-isomers were decomposed [3].

We identified the isomeric compositions through a comparison of the IR spectra, the refractive indices n_D and the R_f constants, and the retention times in GLC. It turned out that the reactions of the salts of 1- and 2-methyl-5-nitroaminotetrazole with methyl iodide gave the same compound (the R_f values and retention times for the corresponding N- and O-isomers were the same and the indices of refraction and the IR spectra of the isolated N-isomers were the same). At the same time, the refractive indices of the N-isomers were the same as the refractive index of I, obtained by the authors of [1]. Consequently, the structure of the N-isomers being formed corresponds to I, so that the structure of the O-isomers must obviously correspond to VII. In a similar way, using TLC, the refractive indices, the IR spectra, and elementary analyses, it was shown that the reaction of salts of 1-methyl- and 2-ethyl-5-nitroaminotetrazole with ethyl iodide formed, correspondingly, the same diethyl derivatives of 5-nitroaminotetrazole (N- and O-isomers). This shows unambiguously that the methyl group is split off during the alkylation of salts of 1-methyl-5-nitroaminotetrazole. Consequently, the structure of the N-isomer corresponds to the product alkylated at the second nitrogen atom of the terazole fragment, i.e., to VI, and the structure of the O-isomer corresponds to VIII.

Mixtures of N- and O-isomers I, VII and VI, VIII, respectively, were also obtained in the reaction of diammonium and disodium salts of 5-nitroaminotetrazole with ethyl and methyl iodide. On the basis of the data concerning the nitroimine tautomeric form of 5-nitroaminotetrazole in aqueous solutions [2], we hypothesized that the alkylation of salts of 5-nitroaminotetrazole, as well as of salts of 1-methyl-5-nitroaminotetrazole, may take place initially at the second nitrogen atom of the tetrazole ring. To test this hypothesis, the alkylation of the disodium salt of 5-nitroaminotetrazole was carried out with ethyl iodide, as a result of which it was possible to isolate the monoalkylation product, the sodium salt of ethyl-5-nitroaminotetrazole. To answer the question of the location of the ethyl group (the primary nitroamine, 2-ethyl-5-nitroamino-tetrazole or the secondary nitroamine, 5-(N-ethyl-N-nitroamino)-tetrazole), the polarographic reduction of the salt in alkaline medium was studied. It is known [4] that primary aromatic nitroamines, 2-ethyl-5-nitroaminotetrazole among them [5], are polarographically inactive in alkaline medium; secondary aromatic nitroamines, however, are reduced in alkaline medium [6]. The ethyl-5-nitroaminotetrazole salt isolated proved to be polarographically inactive in alkaline medium, indicating the structure to be 2-ethyl-5-nitroaminotetrazole. The same was indicated by a comparison of the UV spectra of the isolated compound and authentic 2-ethyl-5-nitroaminotetrazole [2]. Consequently, the reaction of salts of 5-nitroaminotetrazole with alkyl iodides proceeds according to the scheme:



EXPERIMENTAL

Reaction of salts of alkyl-5-nitroaminotetrazole with Alkyl Iodides. A 0.2 mole portion of methyl or ethyl iodide is added to a solution of 0.1 mole of the appropriate nitroaminotetrazole salt in 50% aqueous acetone (modulus 10). The reaction mass is held under reflux with stirring at 40°C (for methyl iodide) or 60°C (for ethyl iodide) for 20 h. Then 0.1 mole of the alkyl iodide is added to the flask and the mixture held for another 10 h under the same conditions. The acetone and excess alkyl iodide are then removed from the reaction mixture, the reaction product is extracted with ether (4 × 40), and the extract passed through a column of Al_2O_3 and dried over $MgSO_4$. After the ether has been distilled off and the product pumped down at 40°C to a residual pressure of 5-10 mm Hg, a mixture of isomers I and VII (40%) or VI and VIII (25%) is obtained. I, VII, Found: C 22.9%; H 3.7%; N 53.2%. Calculated for $C_3H_6N_6O_2$: C 22.8%; H 3.8%; N 53.1%. VI and VIII, Found: C 32.4%; H 5.5%; N 44.8%. Calculated for $C_5H_{10}N_6O_2$: C 32.2%; H 5.4%; N 45.1%.

Isolation of 2-methyl-5-(N-methyl-N-nitroamino)tetrazole (I) from a Mixture of Isomers I and VII; Isolation of 2-ethyl-5-(N-ethyl-N-nitroamino)tetrazole (VI) from a Mixture of Isomers VI and VIII. A small quantity of the mixture of isomers (or ethanolic solution of the mixture) is added to 40% H_2SO_4 and held at 20-40°C until the O-isomers, VII or VIII, are decomposed (the purity of the I or VI remaining in solution is monitored by TLC). The I or VI is then extracted with ether, and the extract passed through a column of Al_2O_3 and dried over $MgSO_4$. After the ether is removed and the product pumped down at 40°C to a residual pressure of 5-10 mm Hg, separate I or VI is obtained. I. IR spectrum: 1295, 1580 cm^{-1} ($N\text{-}NO_2$). Found: C 22.9%; H 3.9%; N 53.1%. Calculated for $C_3H_6N_6O_2$: C 22.8%; H 3.8%; N 53.1%. VI. IR spectrum: 1288, 1580 cm^{-1} ($N\text{-}NO_2$). Found: C 32.3%; H 5.3%; N 45.0%. Calculated for $C_5H_{10}N_6O_2$: C 32.2%; H 5.4%; N 45.1%.

Separation of a Mixture of Isomers VI and VIII. The mixture of VI and VIII is dissolved in 6 volumes of eluent (benzene/hexane/diethyl ether, 11:3:1) and poured into a column previously filled with eluent and L 100/400 grade silica gel. Eluent is gradually added dropwise to the column and samples are withdrawn which are analyzed by TLC for the product content. After pure eluent, VI is washed from the column and then with pure eluent again. To recover VIII, the column is plushed with ether. Pure VI and VIII are obtained after the solutions are dried over $MgSO_4$; then the solvent removed and the products pumped down. Found: C 32.1%; H 5.3%; N 45.2%. Calculated for $C_5H_{10}N_6O_2$: C 32.2%; H 5.4%; N 45.1%. IR spectrum VI: 1288, 1580 cm^{-1} ($N\text{-}NO_2$).

We investigated the products of the reaction of salts of 1- and 2-methyl-5-nitroaminotetrazole and salts of 5-nitroaminotetrazole with methyl iodide by means of TLC (Silufol plates, 11:3:1 benzene/hexane/ether eluent, developed in iodine vapor), GLC (on a Tsvet-1 instrument, katharometer detector, OV-17 phase on shimolite, carrier gas helium). We determined the refractive indices of the individual N-isomers of I and measured the IR spectra. The characteristics were the same for all of the samples: $R_{f\ I}$ 0.44; $R_{f\ VII}$

0.17; retention time for I, 105 sec at 50°C, for VII, 180 sec at 105°C; IR spectra of I, identical; refractive index of I, n_D^{20}, 1.5052 (from data in [1], n_D^{20} is 1.5052).

We investigated the products of the reaction of salts of 1-methyl- and 2-ethyl-5-nitroaminotetrazole and salts of 5-nitroaminotetrazole with ethyl iodide by means of TLC (Silufol plates, 11:3:1 benzene/hexane/ether eluent, developed in iodine vapor). We measured the IR spectra and determined the refractive indices of the individual N-isomers of VI. The characteristics of all of the samples were the same: $R_{f\ VI}$ 0.64; IR spectrum of VI identical, refractive index of VI, n_D^{20}, 1.4890.

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TWOFOLD REACTIVITY OF 1,2-DISUBSTITUTED DIHYDRO-N-HETEROAROMATIC SYSTEMS.

10.* SYNTHESIS AND AROMATIZATION OF FERROCENE-CONTAINING HANTZSCH ESTERS

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1-Ferrocenylphenyl-4-aryl(furyl)-2,6-dimethyl-3,5-diethoxycarbonyl-1,4-dihydropyridines and 4-ferrocenyl-2,6-dimethyl-3,5-diethoxycarbonyl-1,4-dihydropyridines (Hantzsch esters) have been prepared, and their reactions with triphenylcarbenium and 1-oxo-2,2,6,6-tetramethyl-piperidinium perchlorate salts have been studied. Treatment with triphenylmethyl perchlorate results in oxidation of the ferrocenyl substituent to the ferrocenium cation, whereas treatment with the oxoammonium cation results in aromatization and the formation of salts containing a pyridinium cation and a neutral ferrocene ring. A 4-ferrocenyl-containing Hantzsch ester which was unsubstituted at the nitrogen atom constituted a single exception to this trend; it could be aromatized only upon treatment with sulfur.

The twofold reactivity of 1,2(4)-disubstituted 1,2(4)-dihydrohetero-aromatic compounds with respect to aromatization reagents has been described previously [2], and was found to depend on the relationship between the electrophilicity and oxidizing ability of the aromatizing agent. Strong oxidizing agents with weak electrophilic characteristics, such as 1-oxo-2,2,6,6-tetramethylpiperidinium perchlorate [2], direct the reaction along the oxidative pathway, leading to loss of hydrogen and preservation of the α-substituent [3-5], whereas strong electrophiles which are not strong oxidizing agents, such as triphenylcarbenium perchlorate, direct the reaction along an electrophilic pathway, resulting in cleavage of anion-stabilizing substituent groups, such as indole or CH-acids [2].

It was therefore of interest to us to examine the reactivity of these two cations on ferrocenyl-containing Hantzsch esters, since it is well known that aromatization of ferrocenyl-containing Yanov σ-complexes [6] or 1,4-dihydropyridines [7] involves preliminary oxidation

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*For Communication 9, see [1].

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