borohydride was added, and the mixture was stirred at room temperature. The reaction was monitored by thin-layer chromatography on Silufol UV-254 plates in the 8:2 chloroform—methanol system. At the end of the reaction (4 h) the mixture was neutralized to pH 6 with acetic acid and evaporated to dryness. The residue was dissolved in 7 ml of water and extracted with ethyl acetate (6 × 5 ml). The ethyl acetate solution was dried over magnesium sulfate and evaporated. The residue was recrystallized from a 1:1 mixture of methanol and ethyl acetate. We obtained 0.32 g (72%) of compound Va.

Compounds Vb, c were obtained similarly (Table 3).

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HETEROCYCLIC NITRO COMPOUNDS.

24.* NITRATION OF 5-AMINO-1,2,4-TRIAZOLE AND 5-ACETAMIDO-1,2,4-TRIAZOLE WITH ACETYL NITRATE AND NITRONIUM SALTS

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UDC 547.792.3.7:542.958.1

The reaction of 5-amino-1,2,4-triazole and its derivatives with electrophilic reagents can occur at the hetero atoms of the ring (protonation [2-4], methylation [5, 6]), at the exocyclic nitrogen atom of the amino group (nitration with nitric acid and nitrating mixtures [7, 8]), or at both centers (acylation [9, 10]), depending on the conditions and on the nature of the reagent. The nitration of 1,2,4-triazole and its derivatives by nitronium salts leads to N-nitrotriazoles [11], and they undergo subsequent rearrangement to the C-nitro compounds. In order to investigate the direction of the reaction with an additional reaction center (amino group) in the molecule we undertook an investigation into the nitration of 5-amino-1,2,4-triazole (I) and 5-acetamido-1,2,4-triazole (II) by nonacidic nitrating agents (acetyl nitrate and nitronium salts).

*For Communication 23, see [1].

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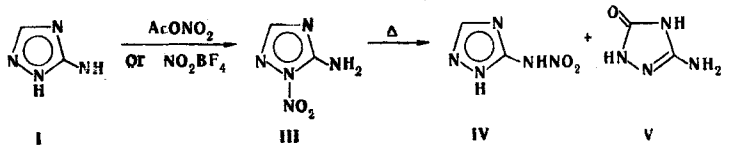
Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 8, pp. 1132-1135, August, 1979. Original article submitted October 30, 1978.

During nitration of the aminotriazole (I) by a mixture of equimolar amounts of acetic anhydride and nitric acid we obtained a product to which on the basis of elemental analysis and IR and PMR spectra we assigned the structure of N-nitro-5-amino-1,2,4-triazole (III).* In its IR spectrum there are strong bands at 1650 and 1260 cm^{-1}, which can be assigned to the vibrations of a nitro group attached to a nitrogen heteroatom in the ring [1]. In the PMR spectrum of the nitro derivative (III) the signal for the 3-H proton is observed in the downfield region (δ 10.15 ppm), and this is due to the strong withdrawing effect of the nitro group located at one of the heteroatoms. During thermal rearrangement of the nitro compound (III) in benzonitrile 3(5)-nitroamino-1,2,4-triazole (IV) and 3(5)-amino-1,2,4-triazole-5(3)-one (V) were identified in the reaction mixture by TLC and by means of the IR and PMR spectra.

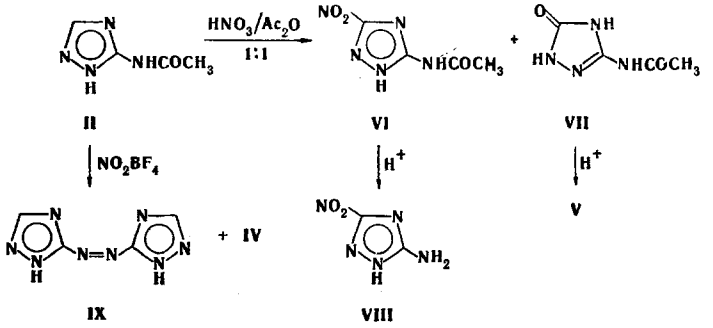
Nitration of the aminotriazole (I) with nitronium tetrafluoroborate in acetonitrile also occurs with the intermediate formation of the N-nitro derivative (III), which rearranges to the nitroaminotriazole (IV) as it accumulates:



The structure of the products obtained during nitration of the acetamidotriazole (II) with a mixture of nitric acid and acetic anhydride depends on the ratio of the latter. With an HNO_3:Ac_2O molar ratio of < 0.8 the nitrate of the initial (II) separates from the reaction mass. Increase in the HNO_3:Ac_2O ratio to 1-1.1 leads to the formation of 3-nitro-5-acetamido-1,2,4-triazole (VI) and 3(5)-acetamido-1,2,4-triazole-5(3)-one (VII). During acid hydrolysis of the acetyl group in compounds (VI) and (VII) 3-nitro-5-amino-1,2,4-triazole (VIII) and aminotriazolone (V) respectively are formed. The production of 3-nitro-5-acetamidotriazole (VI) is evidently the first example of the direct nitration of 1,2,4-triazole at a ring carbon atom. It was not possible to identify N-nitroacetamidotriazole in the reaction mixture, although its possible formation as an intermediate product, which then rearranges to the C-nitrotriazole (VI), cannot be ruled out.

Increase in the HNO_3:Ac_2O molar ratio (1.2-1.4) reduces the yield of compound (VI), and further increase in the nitric acid content leads to the appearance of the nitroaminotriazole (IV). This is probably due to a change in the state of the nitric acid—acetic anhydride system and to the appearance of other nitrating agents in it [12, 13].

During the nitration of the acetamidotriazole (II) with nitronium tetrafluoroborate nitroaminotriazole (IV) and 5,5'-azo-1,2,4-triazole (IX) were isolated. The azo compound (IX) is possibly obtained as a result of nitrosation of the acetamidotriazole (II) by nitrogen oxides (or by the nitrosonium ion), which appear in the reaction mixture as a result of redox processes [14], with subsequent elimination of the acetyl group and further transformations of the diazotriazole.



EXPERIMENTAL

The IR spectra were recorded on a UR-20 instrument with the compounds in the form of films. The PMR spectra were recorded on a Perkin-Elmer R-12 instrument at 60 MHz with HMDS as internal standard. Thin-layer chromatography was performed on Silufol UV-254 plates.

*The exact position of the nitro group was not established.

Nitration of 5-Amino-1,2,4-triazole (I). To a mixture of 2.48 ml of nitric acid (d = 1.51) and 5.60 ml of acetic anhydride, while stirring at 0-5°C, we added 1 g of the aminotriazole (I) in small portions. The mixture was kept at this temperature for 1 h and then poured onto ice. The yellow precipitate was filtered off, washed with cold water to a neutral reaction, and dried over phosphorus pentoxide under vacuum. The yield of compound (III) was 0.84 g (54%). The product did not have a distinct melting point and slowly decomposed when heated in a capillary and during derivatographic analysis. IR spectrum: 3160, 1650 vs, 1510, 1340, 1320, 1305 w, 1260 vs, 1120 vs, 1020, 990, 870, 820 vs, 770, 740 cm^{-1}. PMR spectrum (DMSO), δ: 10.15 ppm (3-H). R_f = 0.87 (2:1 methylene chloride—ethanol). Found, %: C 19.1; H 1.9; N 53.8. $C_2H_3N_5O_2$. Calculated %: C 18.6; H 2.3; N 54.2.

B. To 2.4 g of nitronium tetrafluoroborate in 50 ml of dry acetonitrile at 10-12°C we carefully added 1 g of the aminotriazole (I). The mixture was kept at 10-15°C with periodic control of the presence of the initial, intermediate, and final reaction products (TLC, PMR spectrum). During the holding period a signal appeared in the PMR spectrum at 10 ppm. Its intensity at first increased and then began to decrease with the simultaneous appearance of a signal at 8.3 ppm. When the signal at 10 ppm had disappeared from the spectrum (after ∿ 1 h), the reaction mass was added to cold water, acidified to pH 1, and extracted with ethyl acetate. The extract was dried with magnesium sulfate. After distillation of the ethyl acetate we obtained 0.65 g (42%) of the nitroamine (IV): mp 210°C (with explosion, from water). Published data [15]: mp 212°C (with explosion). PMR spectrum (DMSO-d_6), δ: 8.50 (C—H), 7.70 ppm (N—H, disappearing on deuteration). R_f 0.52 (5:2 methylene chloride—ethanol + 2 drops of acetic acid). All the physicochemical characteristics correspond to the characteristics of an authentic sample of 3(5)-nitroamino-1,2,4-triazole.

Nitration of 5-Acetamido-1,2,4-triazole (II). A. To a mixture of 5.4 ml of concentrated nitric acid (d = 1.51) and 15 ml of acetic anhydride at 0-2°C we carefully added 4 g of acetamidotriazole (II). After 1 h the precipitate was filtered off, washed with ether, and dried. The yield of the colorless crystalline nitrate of the acetamidotriazole (II) was 4.4 g (75%); mp 178°C (decomp.). Its solutions in water have an acidic reaction. IR spectrum: 3180, 2920, 1720 (C=O), 1610, 1490, 1460, 1430, 1310, 1250, 1150, 1070, 1040, 1000, 970, 950, 880, 830, 815, 730 cm^{-1}. PMR spectrum (in DMSO), δ: 8.40 ppm (3-H). Found, %: C 25.7; H 3.9; N 36.9. Mol. wt (by potentiometric titration) 186. $C_4H_6N_4O \cdot HNO_3$. Calculated, %: C 25.4; H 3.7; N 37.0. Mol. wt. 189.

B. To a mixture of 6.6 ml of concentrated nitric acid and 15 ml of acetic anhydride at 0-2°C we carefully added 4 g of the acetamidotriazole (II). The mixture was kept at 3-7°C for 1 h and then added to iced water. The precipitated acetamidotriazolone (VII) was filtered off and dried. The yield was 1.25 g (28%); mp 358°C (from water). IR spectrum: 3240, 1710 (C=O), 1680, 1640 (C=N), 1530, 1400, 1380, 1290, 1260, 1240, 1110, 1030, 1000, 970, 830, 725 cm^{-1}. PMR spectrum (in trifluoroacetic acid), δ: 2.08 ppm (CH_3). Found, %: C 33.7; H 3.9; N 40.0. $C_4H_6N_4O_2$. Calculated, %: C 33.8; H 4.2; N 39.5. The filtrate obtained after isolation of the triazolone (VII) was extracted with ethyl acetate. The extract was dried with magnesium sulfate. The residue after the removal of the solvent was crystallized from ethanol. The yield of the nitrotriazole (VI) was 2.4 g (44%); mp 233°C (decomp.), R_f 0.69 (1:20 ethanol—methylene chloride + 2 drops of acetic acid). IR spectrum: 3315, 3230, 1715 (C=O), 1600, 1560 (NO_2), 1530, 1500, 1420, 1380, 1310 (NO_2), 1280, 1260, 1245, 1225, 1140, 1120, 1085, 1065, 1050, 1020, 1010, 890, 870, 840, 800, 785, 710 cm^{-1}. PMR spectrum (acetone-d_6): 2.30 (CH_3), 11.30 ppm (NH, disappearing with the addition of D_2O). Found, %: 28.2; H 2.7; N 40.7. Mol. wt. 170. $C_4H_5N_5O_3$. Calculated, %: C 28.1; H 2.9; N 41.0. Mol. wt. 171.

C. To a mixture of 3.5 ml of concentrated nitric acid and 3.8 ml of acetic anhydride at a temperature between 0 and −2°C we added 1 g of acetamidotriazole. After 2 h the reaction mixture was added to iced water and extracted with ethyl acetate. The residue after the removal of the solvent (0.2 g) contained, according to TLC (with markers) and the PMR spectrum, nitroaminotriazole (IV) and nitrotriazole (VI).

D. To 3.2 g of nitronium tetrafluoroborate in 70 ml of dry acetonitrile at 10-12°C we added 2 g of acetamidotriazole (II) in small portions. The mixture was kept at 10-15°C for 1 h, the reaction mass was added to water, and the dark-yellow precipitate was filtered off. The yield of the azotriazole (IX) was 0.15 g; mp higher than 400°C. The product was insoluble in organic solvents. It was purified by dissolution in alkali and precipitation

with hydrochloric acid. Its IR spectrum (3120, 3080, 3030, 1580, 1480, 1450, 1400, 1340, 1300, 1280, 1180, 1130, 1030, 1010, 970, 940, 905, 770, 740 cm^{-1}) was identical with the spectrum of an authentic sample of the azotriazole, obtained by the method in [16]. Found, %: C 28.5; H 2.8; N 67.5. $C_4H_4N_8$. Calculated, %: C 29.2; H 2.44; N 68.3.

From the filtrate after removal of the azotriazole by repeated extraction with ethyl acetate we isolated 0.1 g (12%) of the nitroaminotriazole (IV), which was identified by its melting point, IR and PMR spectra, and TLC data.

3-Amino-1,2,4-triazole-5-one (V). A. A 0.2-g sample of compound (III) was heated in 5 ml of benzonitrile at 100°C for 36 h. The mixture was cooled, and the precipitated aminotriazolone (V) was filtered off. The yield was 0.1 g; mp 287°C (decomp.). IR spectrum: 3400, 3180, 1700, 1650, 1530, 1350, 1300, 1150, 1040, 1020, 870, 850, 805, 760, 710 cm^{-1}. Found, %: C 23.7; H 3.9; N 55.7. $C_2H_4N_4O$. Calculated, %: C 24.0; H 4.0; N 56.0. In the filtrate after isolation of the aminotriazolone (V) and evaporation we identified the nitroaminotriazole (IV) (TLC, PMR spectrum).

B. A mixture of 1 g of the acetamidotriazolone (VII) and 28 ml of 20% hydrochloric acid was heated at 100°C for 7 h. The mixture was evaporated to dryness on a water bath, and the residue was recrystallized from ethanol. The yield was 0.5 g (71%); mp 287°C (decomp.). The IR spectrum and melting point correspond to published data [16].

3-Nitro-5-amino-1,2,4-triazole (VIII). A mixture of 1.6 g of the acetamidotriazole (VI) and 34 ml of 10% hydrochloric acid was boiled for 5 h. The precipitate was filtered off, washed to a neutral reaction with water, and recrystallized from alcohol. The yield was 0.6 g (49%); mp 240°C (decomp.). IR spectrum: 3460, 3340, 3245, 3180, 1660, 1590, 1520, 1445, 1400, 1330, 1310, 1125, 1040, 1010, 845, 760, 670 cm^{-1}. PMR spectrum (DMSO), δ: 13.35 and 6.90 ppm (NH, disappearing with the addition of D_2O). R_f 0.35 (5:1 methylene chloride–ethanol + 2 drops of acetic acid). Found, %: C 16.5; H 3.0; N 48.4. Mol. wt. 147. $C_2H_3N_5O_2 \cdot H_2O$. Calculated, %: C 16.3; H 3.4; N 47.8. Mol. wt. 147.

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