HETEROCYCLIC NITRO COMPOUNDS

VI.* REACTION OF 1-METHYL-3,5-DINITRO-1,2,4-TRIAZOLE WITH HYDRAZINES

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Depending on the conditions and nature of the hydrazine derivative, the reaction of 1-methyl-3,5-dinitro-1,2,4-triazole (I) with hydrazine leads either to the replacement of one of the nitro groups by a hydrazine residue or to its reduction to an amino (hydroxylamino) group. In both cases, the reaction takes place in position 5 of the triazole ring. The reaction of I with acetylhydrazine gives 5-azido-1-methyl-3-nitro-1,2,4-triazole.

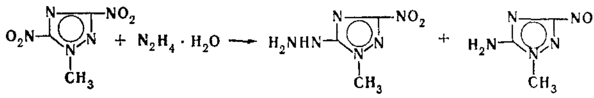
The synthesis of hydrazino derivatives of 1,2,4-triazole can be effected by the reduction of nitrosoaminotriazole [2] and diazonium salts [3,4] and by the cyclization of derivatives of diamino- and triaminoguanidines [5-9]. One of the routes to compounds of this type could be the replacement of a nitro group in nitro derivatives of 1,2,4-triazole by a hydrazine group.

Continuing a study of the reactions of nitro derivatives of 1,2,4-triazole with nucleophilic reagents [10, 11], in the present work we have studied the reaction of 1-methyl-3,5-dinitro-1,2,4-triazole (I) with hydrazine and its derivatives.

Depending on the conditions of performing the reaction and the nature of the hydrazino derivatives, they have a dual role with respect to nitro compounds: either as nucleophilic reagents or as reducing agents. Thus, the reaction of I with 95-100% hydrazine hydrate in dioxane at 10-15°C gives a mixture of 5-hydrazino-1-methyl-3-nitro-1,2,4-triazole (II) and 5-amino-1-methyl-3-nitro-1,2,4-triazole (III), and with a rise in the temperature the yield of the amine III rises. When the reaction is carried out with 25% aqueous hydrazine hydrate at a temperature of 40-50°C, the amine III is the sole reaction product. This method of obtaining 5-amino-1-methyl-3-nitro-1,2,4-triazole has proved to be more convenient than its synthesis from I by the action of ammonia [10].

The presence of a hydrazine group in II was shown by the preparation of the benzaldehyde hydrazone IV and the azido derivative V. Elimination of the hydrazino group from II by the action of silver acetate led to 1-methyl-3-nitro-1,2,4-triazole (VI) [12], which showed that it was located on the C_5 atom.

In contrast to unsubstituted hydrazine, the more nucleophilic methylhydrazine reacts with I to form only the substitution product 5-(α-methylhydrazino)-1-methyl-3-nitro-1,2,4-triazole (VII). The structure of VII as an α-methylhydrazino derivative was shown by the preparation from it of the benzaldehyde hydrazone VIII, and the position of the hydrazino group was shown by the reaction with nitrous acid, leading to 1-methyl-5-(methylnitrosoamino)-3-nitro-1,2,4-triazole (IX), obtained by independent synthesis from 1-methyl-5-methylamino-3-nitro-1,2,4-triazole (X) [9].



I II III

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*For Communication V, see [11].

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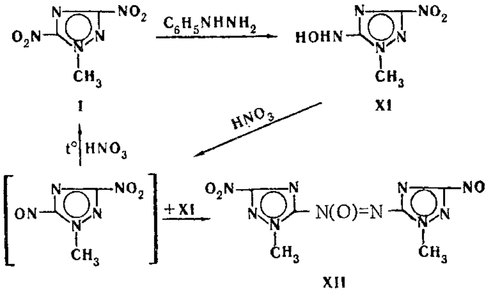
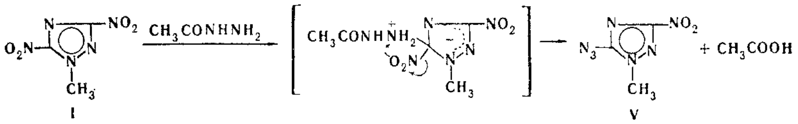
1,1-Dimethylhydrazine and phenylhydrazine react with I only as reducing agents with the formation of, respectively, the amine III and 5-hydroxyamino-1-methyl-3-nitro-1,2,4-triazole (XI). When XI was dissolved in nitric acid, a bright green coloration appeared through its oxidation to the nitroso derivative, which could not be isolated. Only the products of its further reactions were obtained: the azoxy compound XII when the reaction was performed in the cold and the methyldinitrotriazole I on heating:



The reaction of I with acetylhydrazine takes place in a peculiar fashion. The reaction product proved to be 5-azido-1-methyl-3-nitro-1,2,4-triazole (V). Apparently in this case a multicenter reaction takes place with a transition state including the dinitro derivative I and acetylhydrazine; the nitrous acid splits off from the dinitrotriazole molecule,nitrosating the hydrazine group with the simultaneous departure of an acetyl residue:



EXPERIMENTAL

Reaction of 1-Methyl-3,5-dinitro-1,2,4-triazole (I) with Hydrazine Hydrate. a. At 15°C (with cooling), 1.1 ml of 95-99% hydrazine hydrate was added dropwise to a solution of 2 g (0.0115 mole) of I [12] in 25 ml of dioxane. After 30 min, the mixture was filtered and the dioxane was evaporated off. The residue was dissolved in 10-15 ml of hot ethanol, the insoluble part being filtered off, and the solution was cooled after which the crystals of the hydrazino derivative II that had deposited were filtered off. The yield of the hydrazinotriazole II was from 30 to 70%, mp 162-163°C. Found %: C 22.30; H 3.97; N 52.92; mol. wt. (reverse ebullioscopy in dioxane) 160. $C_3H_6N_6O_2$. Calculated: C 22.80; H 3.80; N 53.20; mol. wt. 158. IR spectrum, cm^{-1}: 3470, 3380 (broad bands: N–H stretching vibrations); 1650 (N–H deformation vibrations), 1530, 1315 (nitro group).

The ethanol-insoluble residue was crystallized from a large volume of ethanol (50 ml to 1 g) and had mp 253-255°C (decomp.). Its properties (mp, IR spectrum, elementary analysis) are identical with those of the 5-amino-1-methyl-3-nitro-1,2,4-triazole described previously [10].

b. With stirring, 7 g (0.04 mole) of finely ground compound I was scattered in small portions into 70 ml of a 25% aqueous solution of hydrazine hydrate. A vigorous reaction took place with the evolution of gas, and the temperature rose to 45-50°C. After 15 min, the mixture was cooled, and the reaction product was filtered off and washed with water. The yield of the amine III was 5.0 g (86%), mp 254-256°C (decomp.).

5-Benzylidenehydrazino-1-methyl-3-nitro-1,2,4-triazole (IV). A mixture of 0.5 g (0.0031 mole) of II and 0.3 g of benzaldehyde in 30 ml of dioxane was heated in the boiling water bath for 30 min. The precipitate of the hydrazone IV that had deposited was filtered off. Yield 0.5 g (66%), mp 264-265°C (decomp.). Found %: C 48.90; H 5.08; N 34.26. $C_{10}H_{10}N_6O_2$. Calculated %: C 48.80; H 4.97; N 34.10.

5-Azido-1-methyl-3-nitro-1,2,4-triazole (V). a. A solution of 0.5 g (0.0031 mole) of compound II in 25 ml of 10% sulfuric acid was treated at 0°C with 0.23 g of sodium nitrite in 5 ml of water. After 15 min, the precipitate was filtered off, the filtrate was extracted with ethyl acetate, and the solvent was evaporated. The total yield of V was 0.25 g (47%), mp 126-127°C (from ethanol). Found %: N 58.43; mol. wt. 173. $C_3H_3N_7O_2$. Calculated %: N 58.00; mol. wt. 169. IR spectrum, cm^{-1}: 2167 (azide group), 1560-1530, 1315 (nitro group).

b. A solution of 4.5 g of acetylhydrazine in 15 ml of water was treated with 2 g (0.0115 mole) of the methyldinitrotriazole I in 25 ml of dioxane and the mixture was heated in the boiling water bath for 8 h. Then the solvent was evaporated off, and the residue was washed with water and crystallized from ethanol. Yield 0.65 g (33%), mp 126-127°C, giving no depression of the melting point with the substance obtained by method a. The IR spectrum and elementary analysis confirmed the structure of the compound as 5-azido-1-methyl-3-nitro-1,2,4-triazole.

Elimination of the Hydrazine Group from Compound II. A solution of 1 g (0.006 mole) of II in 20 ml of methanol was treated with 6.5 g of silver acetate and 30 ml of water and heated in the water bath for 45 min. The reaction mixture was filtered, diluted with water, and extracted with ethyl acetate. The solvent was evaporated off and the residue was crystallized from ethanol. This gave 0.15 g (19%) of a substance with mp 63-64°C identical with 1-methyl-3-nitro-1,2,4-triazol (VI) [12] (absence of a depression of the melting point of a mixture with authentic VI, R_f,* IR spectrum). Found %: C 27.60; H 4.79; N 49.16; mol. wt. 172. $C_4H_8N_6O_2$. Calculated %: C 27.91; H 4.65; N 48.84; mol. wt. 172. IR spectrum, cm^{-1} (broad band, N–H stretching vibrations), 1620 (N–H deformation vibrations), 1520, 1315 (nitro group).

5-(Benzylidene-α-methylhydrazino)-1-methyl-3-nitro-1,2,4-triazole (VIII). This was obtained in a similar manner to the hydrazone IV from compound VII. Yield 77%, mp 181°C (from ethanol). Found %: C 51.00; H 4.64; N 32.65. $C_{11}H_{12}N_6O_2$. Calculated %: C 50.76; H 4.61; N 32.32.

1-Methyl-5-(methylnitrosoamino)-3-nitro-1,2,4-triazole (IX). a. A solution of 0.26 g (0.003 mole) of sodium nitrite in 7 ml of water was added to 0.5 g (0.0032 mole) of the methylamino derivative X [10] in 7 ml of 30% sulfuric acid at 0°C. After 2 h, the reaction product was filtered off and washed with water. Yield 0.35 g (59%), mp 128-129°C (from isopropanol). Found %: C 25.54; H 3.91; N 45.60; mol. wt. 181. $C_4H_6N_6O_3$. Calculated %: C 25.80; H 3.23; N 45.20; mol. wt. 186. IR spectrum, cm^{-1}: 1560-1520, 1315 (nitro group), 1480, 1090 (nitroso group).

b. The reaction was carried out with substance VII similarly, using a twofold excess of sodium nitrite. Yield 63%, mp 128-129°C. The substance was identical with the compound obtained by method a (absence of a depression of the melting point of a mixture, IR spectrum, elementary analysis).

Reaction of I with Dimethylhydrazine. To 30 ml of a 25% aqueous solution of 1,1-dimethylhydrazine was added 2 g (0.1 mole) of I and the mixture was kept for an hour and a half at room temperature. The precipitate that deposited was filtered off. Yield 0.45 g (27%), mp 255-257°C (decomp., from ethanol). The reaction product was identical with the amine III (absence of a depression of the melting point with authentic III, IR spectrum, elementary analysis).

Analogous results were obtained when the reaction was carried out in dioxane.

5-Hydroxylamino-1-methyl-3-nitro-1,2,4-triazole XI. A solution of phenylhydrazine in ether obtained from 3 g of phenylhydrazine hydrochloride (by treating it in 20 ml of water with 10 ml of 50% caustic soda solution and extracting three times with 20-ml portions of ether) was added to a solution of 2 g (0.0115 mole) of I in 25 ml of dioxane. The mixture was heated at 45°C for 3 h, the solvent was evaporated off, and the oil that separated was treated with 50 ml of ethyl acetate. The product that deposited was filtered off and recrystallized three times from ethanol. Yield 0.42 g (23%), mp 175°C. Found %: C 22.58; H 3.17; N 43.93. $C_3H_5N_5O_3$. Calculated %: C 22.60; H 3.15; N 44.00.

Oxidation of 5-Hydroxyamino-1-methyl-3-nitro-1,2,4-triazole (XI). a. 0.7 g (0.0044 mole) of XI was slowly scattered onto 15 ml of 92% nitric acid. The solution acquired an intense green coloration. After an hour, it was poured onto ice and extracted with ethyl acetate (3 × 10 ml). The ethyl acetate solution was evaporated and the residue was crystallized from ethanol. This gave 0.1 g (10%) of XII, mp 217-219°C. Found %: C 24.39; H 1.70; N 46.72. $C_6H_6N_{10}O_5$. Calculated %: C 24.20; H 2.01; N 47.00.

b. 0.7 g (0.0044 mole) of XI was slowly added to 15 ml of 92% nitric acid, and the mixture was then heated at 70-80°C for 2 h. The solution was poured onto ice and extracted with ethyl acetate, the solvent was evaporated, and the residue was crystallized from ethanol. Yield 0.4 g (52%), mp 95-96°C. The substance was identical with I (absence of a depression of the melting point with authentic I, IR spectrum).

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*Chromatography in a thin layer of alumina in the acetone–heptane (1 : 1) system [12].

LITERATURE CITED

1. L. I. Bagal and M. S. Pevzner, KhGS [Chemistry of Heterocyclic Compounds], 6, 558 (1970).
2. R. Stolle and W. Dietrich, J. Prakt. Chem., 139, 193 (1934).
3. J. Thiele and W. Manchot, Lieb. Ann., 303, 33 (1898).
4. W. Manchot and R. Noll, Lieb. Ann., 343, 1 (1905).
5. F. Kurzer and K. Douraghi-Zadeh, J. Chem. Soc., 1965, 3912.
6. H. H. Takimoto, C. C. Denault, and S. Hotta, J. Org. Chem., 30, 711 (1965).
7. H. Gehlen and N. Pollok, GFR Patent No. 36,433; C. A., 63, 13,275 (1965).
8. P. D. Oja, US Patent No. 3,183,241; C. A., 63, 4305 (1965).
9. C. F. Kröger, G. Etzold, and H. Beyer, Lieb. Ann., 664, 46 (1963).
10. L. I. Bagal, M. S. Pevzner, and V. Ya. Samarenko, KhGS [Chemistry of Heterocyclic Compounds], 6, 269 (1970).
11. L. I. Bagal, M. S. Pevzner, V. A. Samarenko, and A. P. Egorov, KhGS [Chemistry of Heterocyclic Compounds], 6, 702 (1970).
12. L. I. Bagal, M. S. Pevzner, N. I. Sheludyakova, and V. M. Kerusov, KhGS [Chemistry of Heterocyclic Compounds], 6, 265 (1970).