It should be noted that the position of the substituent in the pyridine ring of the 2-azatriptycene molecule has an appreciable effect on the probability of the primary fragmentation of the molecular ion. Thus the $I_{[M-H]}/I_{M^+}$ ratio in the mass spectrum of 3-phenyl-2-azatriptycene (V) is less than one, whereas it is more than one in the mass spectrum of 1-phenyl-2-azatriptycene (VI); this is probably explained by steric factors [11].

Thus, the positive charge in the molecular ions of 2-azatriptycenes is localized primarily in the heterocyclic ring, and this is also responsible for all of the fragmentation pathways discussed above.

EXPERIMENTAL

The investigated compounds were obtained by the methods in [8, 9]. The mass spectra were recorded with an MKh-1303 spectrometer with direct introduction of the substances into the ion source at an ionization energy of 50 eV, an electron emission current of 1.5 mA, and temperatures close to the melting points of the substances.

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FORMATION OF DERIVATIVES OF 5,6-DIHYDROOXAZINO- AND 5,6-DIHYDROOXAZOLO[3,2-b]-1,2,4-TRIAZOLE IN THE REACTION OF 1-OXOALKYL-3,5-DINITRO-1,2,4-TRIAZOLES WITH POTASSIUM CYANIDE

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1,3-Dihydrooxazino- and 1,3-dihydrooxazolol[3,2-b]-1,2,4-triazoles were obtained instead of the expected 3-nitro-5-cyano-1,2,4-triazole derivatives in the reaction of 1-oxoalkyl-3,5-dinitro-1,2,4-triazoles with potassium cyanide. Their formation is due to the fact that primary attack by the cyanide anion is not directed at the ring C_5 atom but rather at the carbonyl group with subsequent intramolecular replacement of the nitro group.

The introduction of a cyano group in the ring of 1,2,4-triazoles can be realized by the Sandmeyer reaction [1]. A second possible method, viz., nucleophilic substitution at the ring carbon atom, has not been investigated, although the reaction of 1-substituted 3,5-dinitro- or 3-nitro-5-halo-1,2,4-triazoles with nucleophilic reagents is an effective method for the modification of the structure of compounds of this class [2, 3]. We attempted to obtain derivatives of 3-nitro-5-cyano-1,2,4-triazoles by the reaction of 1-oxoalkyl-3,5-dinitro-1,2,4-triazoles I and II with potassium cyanide. However, this attempt was unsuccessful.

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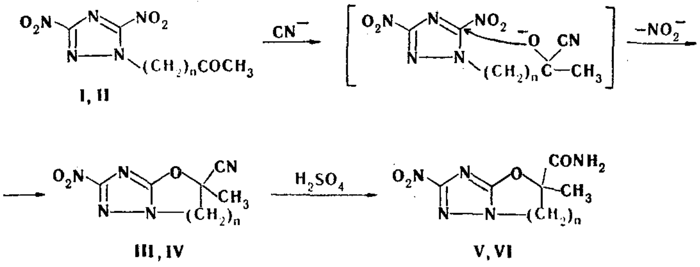
According to the analytical data, the reaction products obtained in this case corresponded to the empirical formulas of 1-oxoalkyl-3-nitro-5-cyano-1,2,4-triazoles, but their spectral characteristics did not confirm the structures of the expected ketones.

The IR spectra of III and IV did not contain the absorption band of a keto group at 1720-1750 cm^{-1}, but absorption at 1500-1600-cm^{-1}, which is not characteristic for monocyclic derivatives of 3-nitro-5-substituted 1,2,4-triazoles, including the ketones of this series [4], did appear in the spectra. Two absorption bands related to the vibrations of the nitro group (1550-1590 cm^{-1}) and a triazole ring at 1500-1530 cm^{-1} are usually noted in this region of the spectrum. We have previously noted the appearance of a third absorption band in the IR spectra of hydrogenated 1,3-oxazolotriazoles obtained by intramolecular replacement of the nitro group or bromine atom in the 5 position of the triazole ring [5, 6]. It is characteristic that an absorption band of a cyano group at 2200-2300 cm^{-1} was not recorded distinctly in the IR spectra, and the presence of this fragment in III and IV was proved by their hydrolysis in sulfuric acid to the corresponding amido derivatives V and VI, for which, as in the case of their precursors III and IV, the character of the IR spectra at 1500-1600 cm^{-1} is retained. The PMR spectra of III-VI (of the ABCD type for III and V, and of the AB type for IV and V) constitute evidence for the steric nonequivalence of the protons of their methylene groups, which could have developed in the case of the formation of a rigid ring system. Simple first-order PMR spectra are characteristic for starting ketones I and II [4]. The set of analytical and spectral data makes it possible to assign hydrogenated 1,3-oxazino- and 1,3-oxazolo[3,2-b]-1,2,4-triazole structures III and V and IV and VI, respectively, to the compound obtained. A heterocyclic system of the IV (VI) type was obtained in [5, 6], but dihydrooxazinotriazoles III and V were unknown. This reaction pathway is possible if the cyanide ion initially attacks the carbon atom of the carbonyl group rather than the ring C_5 atom to give a cyanohydrin anion with subsequent intramolecular nucleophilic replacement of the nitro group and cyclization to an annelated system.



I, III, V n=2; II, IV, VI n=1

EXPERIMENTAL

The PMR spectra of solutions of the compounds in d_6-acetone were recorded with a Perkin-Elmer R-12 spectrometer with hexamethyldisiloxane as the internal standard. The IR spectra of thin films of the compounds were recorded with a UR-20 spectrometer. The molecular masses were determined by inverse ebullioscopy in acetone.

2-Nitro-7-cyano-7-methyl-6,7-dihydrooxazino[3,2-b]-1,2,4-triazole (III). A solution of 1.17 g (18 mmole) of potassium cyanide in 10 ml of water was added to a solution of 3 g (13 mmole) of ketone I [4] in 25 ml of ethyl acetate, and the mixture was stirred at room temperature for 8 h. The organic layer was separated and washed with water, the solvent was removed by distillation, and the residue was crystallized from ethanol to give 2.28 g (84%) of a product with mp 167-168°C. IR spectrum (cm^{-1}): 730 m, 780 w, 840 s, 905 w, 950 s, 1090 s, 1160 m, 1185 m, 1255 m, 1270 m, 1310 vs, 1340 w, 1360 w, 1380 w, 1440 w, 1450 m, 1470 m, 1530 vs, 1570 vs, and 1580 vs. PMR spectrum: 2.95 (m, 2H, CH_2), 4.50 (m, 2H, CH), and 2.0 ppm (s, 3H, CH_3). Found: C 40.6; H 3.5; N 33.9%; M 202. $C_7H_7N_5O_3$. Calculated: C 40.2; H 3.3; N 33.5%; M 209.

2-Nitro-6-cyano-6-methyl-5,7-dihydrooxazolo[3,2-b]-1,2,4-triazole (IV). This compound, with mp 176-177°C (from ethanol), was similarly obtained in 66% yield from ketone II [4]. IR spectrum (cm^{-1}): 730 w, 750 w, 780 m, 820 w, 860 m, 940 w, 1095 m, 1150 m, 1210 m, 1250m, 1270m, 1310 m, 1330 m, 1390 w, 1415 m, 1440 s, 1470 m, 1530 vs, 1565 vs, and 1590 s. PMR spectrum: 4.90 (d, 1H, H_A), 5.39 (d, 1H, H_B; $J_{H_AH_B}$ = 19 Hz), and 2.30 ppm (s, 3H, CH_3). Found: C 37.0; H 2.6; N 35.8%; M 200. $C_6H_5N_5O_3$. Calculated: C 36.9; H 2.6; N 35.9% M 195.

2-Nitro-7-carbamido-7-methyl-6,7-dihydrooxazino[3,2-b]-1,2,4-triazole (V). A 0.5-g (2.4 mmole) sample of III was added in parts with stirring and cooling to 5 ml of concentrated H_2SO_4, after which the mixture was stirred for 3 h. It was then poured into 20 ml of ice water, and the aqueous mixture was allowed to stand for 10 h. The desired product was extracted with ethyl acetate (four 20-ml portions), the extract was washed with water, and the solvent was evaporated. The residue was crystallized from ethanol to give 0.43 g (80%) of a product with mp 162-163°C. IR spectrum (cm^{-1}): 705 m, 750 m, 790 m, 830 w, 860 m, 940 m, 1040 w, 1095 m, 1115 m, 1160 m, 1190 m, 1250 m, 1270 m, 1320 s, 1340 m, 1410 m, 1440 m, 1480 m, 1520 vs, 1570 vs, 1590 vs, 1680 vs, and 1705 vs. PMR spectrum: 2.55 (m, 2H), 4.15 (m, 2H, CH_2), 1.75 (s, 3H, CH_3), and 7.4 ppm (NH_2). Found: C 37.3; H 4.3; N 30.7%; M 222. $C_7H_9N_5O_2$. Calculated: C 37.0; H 4.3; N 30.8%; M 227.

2-Nitro-6-carbamido-6-methyl-5,7-dihydrooxazolo[3,2-b]-1,2,4-triazole (VI). This compound, with mp 156-157°C (from ethanol), was similarly obtained in 70% yield by hydrolysis of VI. IR spectrum (cm^{-1}): 730 s, 750 w, 790 w, 820 w, 865 m, 920 w, 1040 w, 1095 m, 1150 m, 1200 s, 1230 w, 1270 m, 1300 w, 1320 s, 1400 m, 1450 m, 1470 w, 1540 vs, 1570 vs, 1660 s, and 1700 vs. PMR spectrum: 4.60 (d, 1H, H_A), 5.03 (d, 1H, H_B, $J_{H_AH_B}$ = 11 Hz), 2.0 (3H), and 7.83 ppm (2H, NH_2). Found: C 33.7; H 3.4; N 33.1%; M 210. $C_6H_7N_5O_4$. Calculated: C 33.8; H 3.3; N 32.9%. M 213.

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SYNTHESIS OF SOME ESTERS AND AMIDES OF 2-SUBSTITUTED 4,6-BIS(p-CARBOXYPHENOXY)-sym-TRIAZINE

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A number of corresponding esters and amides were obtained by the reaction of the chlorides of 2-substituted 4,6-bis(p-carboxyphenoxy)-sym-triazines (CPT) with ethanol and some primary amines in the presence of a hydrogen chloride acceptor. It was observed that hydrazine and hydrazine hydrate have a cleavage effect on the C—O bond of chloride of CPT in the 4 and 6 positions even at 0°C. Dihydrazides of CPT were synthesized at -40°C.

We have previously synthesized 2-substituted 4,6-bis(p-carboxyphenoxy)-symtriazines (CPT) and their chlorides. These substances may find application as monomers for polycondensation [2, 3].

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