TETRAZOLE DERIVATIVES.

27.* STRUCTURES OF THE PRODUCTS OF AUTOTRANSFORMATION OF THE 1-(1-METHYL-5-TETRAZOLYL)-3,5-DIPHENYLVERDAZYL RADICAL

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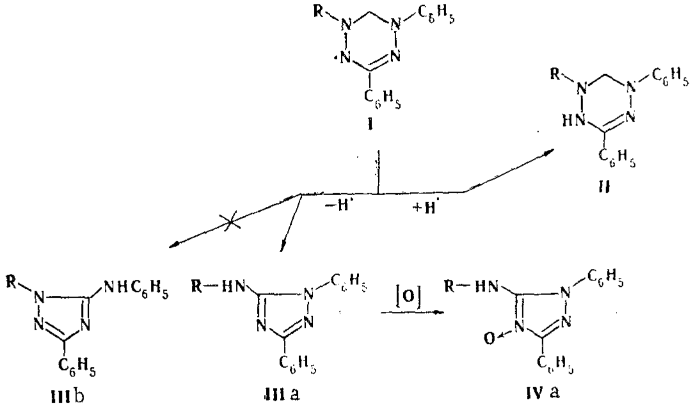
It was established by mass spectrometry that one of the products of the spontaneous transformation of the 1-(1-methyl-5-tetrazolyl)-3,5-diphenylverdazyl radical has the 1,3-diphenyl-5-(1-methyl-5-tetrazolylamino)-1,2,4-triazole structure. The latter undergoes oxidation to give an N-oxide derivative involving the N_4 atom of the triazole.

It has been shown [2] that the 1-(1-methyl-5-tetrazolyl)-3,5-diphenylverdazyl radical (I) is converted spontaneously (especially when it is heated) to leucoverdazyl (II) and a triazole derivative (III), which is formed as a result of recyclization of I and subsequent disproportionation. According to data from the UV, IR, and PMR spectra, the structure of triazole III can be represented by alternative structures IIIa and IIIb [2]:



R= 1-methyl-5-tetrazolyl

We attempted to carry out the oxidative cleavage of III at the exocyclic $N-C_5$ bond of the triazole in order to establish its structure from the decomposition products. Similar cleavage occurs in the oxidation of 1,3-diphenyl-5-anilino-1,2,4-triazole to 1,3-diphenyl-1,2,4-triazol-5-one [3]. However, under the oxidation conditions in [3] from III we obtained an N-oxide derivative (IV). When the reaction is carried out for a longer time, an unidentifiable resinous product is formed in place of IV.

The structures of III and IV were established by means of mass spectrometry, while the structures of I and II were confirmed by the same method (see Table 1).

A molecular-ion peak [M^+] with m/z 319, which is in agreement with the calculated value (the isotope correction was 23.9%, as compared with the theoretical value of 20.9% calculated for $C_{16}H_{15}N_8$), was recorded in the mass spectrum of I. The fragment ions with m/z 77 and 83 confirm the presence of C_6H_5 and R fragments in starting I. The elimination of N_2, N_3, and CH_3N_3 particles from M^+ and of a CH_3N_2 particle from the $[M-N_2]^+$ ion (ions with m/z 291, 277, 262, and 248, respectively) proves not only the presence of an R substituent but also the position of the methyl group in the tetrazole ring [4]. The presence of $[C_6H_5CN]^+$ (m/z 103), $[C_6H_5CNH]^+$ (104), $[C_6H_5N_2]^+$ (105), $[C_6H_5—\overbrace{C=N—NH}]^+$ (118) and $[C_6H_5—\overbrace{N—N=C}—C_6H_5]^+$

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*See [1] for Communication 26.

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TABLE 1. Mass Spectra of I-IV

Compound	m/z values (relative intensities of the peaks in percent of the maximum peak)*
I	39 (11,4); 41 (9,8); 42 (8,3); 44 (25,8); 51 (28,7); 52 (6,6); 63 (8,6); 64 (36,8); 65 (23,7); 76 (7,9); 77 (97,2); 78 (11,0); 83 (7,3); 90 (6,3); 91 (100,0); 92 (25,1); 103 (22,9); 104 (83,9); 105 (70,3); 106 (11,5); 118 (13,6); 129 (30,3); 144 (16,7); 159 (8,3); 193 (6,5); 194 (40,1); 195 (6,5); 212 (12,8); 222 (33,2); 223 (16,2); 248 (35,7); 262 (16,8); 263 (8,8); 276 (6,3); 277 (5,1); 291 (11,6); 319 (90,4); 320 (21,0)
II	39 (7,9); 43 (22,1); 44 (5,6); 50 (5,8); 51 (28,0); 52 (7,7); 55 (5,0); 64 (10,7); 65 (10,3); 76 (7,5); 77 (97,6); 78 (17,3); 83 (14,2); 91 (71,3); 92 (14,2); 93 (7,2); 103 (11,8); 104 (100,0); 105 (99,7); 106 (29,0); 111 (8,1); 131 (7,2); 194 (26,3); 211 (15,8); 221 (14,9); 222 (37,1); 223 (6,0); 262 (5,3); 320 (33,3); 321 (6,9)
III	39 (16,4); 41 (25,0); 43 (27,1); 50 (6,2); 51 (32,3); 52 (6,7); 53 (5,3); 55 (17,5); 56 (6,9); 57 (21,6); 63 (9,8); 64 (29,0); 65 (23,1); 67 (9,3); 69 (10,7); 71 (10,3); 76 (11,6); 77 (91,4); 78 (6,9); 81 (6,1); 82 (8,5); 83 (9,0); 90 (7,5); 91 (100,0); 92 (19,5); 97 (5,3); 103 (28,7); 104 (27,7); 105 (9,6); 116 (6,6); 117 (5,1); 118 (17,3); 129 (36,5); 144 (24,7); 149 (5,4); 158 (7,0); 159 (13,4); 167 (7,0); 193 (6,5); 194 (19,1); 219 (5,0); 247 (51,1); 248 (9,2); 261 (18,5); 262 (6,5); 275 (6,4); 290 (16,8); 318 (80,2); 319 (16,9)
IV	41 (14,5); 43 (34,2); 44 (7,5); 45 (15,0); 46 (5,6); 50 (7,6); 51 (38,0); 52 (7,0); 53 (5,2); 55 (6,2); 63 (11,3); 64 (35,6); 65 (23,1); 67 (6,6); 76 (11,9); 77 (93,5); 78 (7,8); 82 (5,3); 83 (15,5); 90 (7,2); 91 (100,0); 92 (20,5); 103 (26,5); 104 (25,6); 105 (34,0); 116 (5,5); 117 (5,6); 118 (35,4); 129 (80,6); 130 (8,7); 144 (19,5); 158 (6,7); 159 (10,9); 193 (6,9); 194 (22,5); 237 (5,6); 247 (30,2); 248 (5,9); 261 (14,2); 262 (5,6); 275 (5,2); 290 (12,1); 318 (60,0); 319 (12,2); 334 (7,8)

*The peaks with intensities $\geqslant$ 5% are presented.

(194) ions confirms the structure of the 3,5-diphenylverdazyl residue.

It is interesting to note that during recording of the mass spectra with vaporization of a sample of verdazyl radical I, it does not have time to undergo appreciable conversion to triazole derivative IIIa, as evidenced by the absence of the ions with m/z 318 and 247 that are charcteristic for the latter (Table 1).

An M^+ peak with m/z is recorded in the mass spectrum of II (with a 20.7% isotope correction). Most of the fragment ions are similar to the fragments in the mass spectrum of verdazyl radical I, and this indicates their structural similarity.

The ions with m/z 83 — R^+ (β cleavage relative to the triazole ring), 97 — $[RN]^+$ (β cleavage relative to the tetrazole ring), 105 — $[C_6H_5N_2]^+$, and 194 —$[C_6H_5\overline{C{=}N{-}N}{-}C_6H_5]^+$ [5]. constitute evidence in favor of the IIIa structure [5]. Their formation is impossible for IIIb.

The fragmentation of the M^+ ion of IV, which is associated with the loss of 16 amu, i.e., an oxygen atom, is a characteristic feature of N-oxide compound [6]. This immediately excludes from consideration for IV the structure of a hydroxylamine derivative, the fragmentation of which is different in character [7]. The presence of an ion with m/z 237, which arises as a result of the elimination of an RN particle from M^+, corresponds to an N-oxide of the 1,3-diphenyl-1,2,4-triazole ring. Considering the fact that higher electron density is localized on the N_4 atom than on the N_2 atom in 1,2,4-triazoles [8] and that the N oxidation of heterocycles that contain many nitrogen atoms usually takes place at the nitrogen atom with the maximum electron density [9], the structure of IV in the IVa form should be considered preferable.

The significant shift to weak field of the signals of the protons of the CH_3 (4.02 ppm) and NH (11.64 ppm) groups in the PMR spectrum of IVa as compared with the position of the signals of these protons in the spectrum of IIIa (3.80 and 10.62 ppm, respectively) is also in agreement with structure IVa.

Thus the recyclization of verdazyl radical I with the subsequent formation of asymmetrical triazole derivative IIIa takes place with cleavage of the N_1-N_2 bond of the tetrazine ring. Since 1-(5-tetrazolyl)- and 1-(2-methyl-5-tetrazolyl)-3,5-diphenylverdazyl radicals are completely stable [10, 11], it may be assumed that the reason for the instability of verdazyl radical I is the steric effect of the methyl group, which distorts the tetrazine ring [12].

EXPERIMENTAL

The PMR spectra of solutions of the compounds in d_6-DMSO were recorded with a Perkin-Elmer R-12B spectrometer with hexamethyldisiloxane as the internal standard. The IR spectra of KBr pellets of the compounds were recorded with a UR-20 spectrometer. The UV spectra of solutions of the compounds in ethanol were measured with an SF-4A spectrophotometer. The mass spectra were obtained with a Varian MAT-311A spectrometer at an accelerating voltage of 3 kV, a cathode emission current of 300 μA, an ionizing voltage of 70 eV, and sample-vaporization temperatures of 100-140°C.

The synthesis of I-IIIa was accomplished by the methods in [2, 10].

1,3-Diphenyl-5-(1-methyl-5-tetrazolylamino)-1,2,4-triazole 4-Oxide (IVa). A 12-ml sample of a 30% solution of H_2O_2 was added to a hot solution of 0.29 g (0.91 mmole) of 1,3-diphenyl-5-(1-methyl-5-tetrazolylamino)-1,2,4-triazole (IIIa) in 29 ml of acetic acid, and the mixture was refluxed for 1 h. It was then filtered, and the filtrate was concentrated to a volume of 5 ml. The concentrate was cooled, and the resulting precipitate was separated to give 0.21 g (70%) of IVa with mp 184.5°C (long colorless needles from ethanol). UV spectrum: $\lambda_{\max}$ 250 nm (log ε 4.25). IR spectrum: 3060, 2810, 1600, 1556, 1508, 1451, 1359, 1129, 888, 769, 736, 718, and 688 cm^{-1}. PMR spectrum: 4.02 (3H, s, CH_3), 7.44-8.12 (10H, m, C_6H_5), and 11.64 ppm (1H, s, NH). Found: C 57.9; H 4.0; N 33.9%. $C_{16}H_{14}N_2O$. Calculated: C 57.5; H 4.2; N 33.5%.

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