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FORMATION OF 2,3,6,8-TETRAAZABICYCLO[3.2.1]OCT-3-ENE DERIVATIVES IN REACTION BETWEEN 2-ACYL-3-IMIDAZOLINE 3-OXIDES AND HYDRAZINE AND THEIR OXIDATION TO THE CORRESPONDING NITROXYL RADICALS AND 1,2,4-TRIAZINE 4-OXIDE

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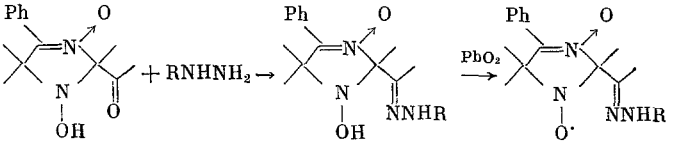
UDC 542.91 : 547.781.3 : 547.234

In the reaction between 2-acetyl-4-phenyl-3-imidazoline 3-oxide (I) [1] and methylhydrazine, semicarbazide, and thiosemicarbazide, carried out at 20°C, the corresponding monosubstituted hydrazones (II)-(IV) are formed, which are smoothly oxidized by the action of PbO_2 in acetone to the corresponding nitroxyl radicals (V)-(VII) (Tables 1 and 2).



(I) (II) — (IV) (V) — (VII)

R = Me (II), (V); $CONH_2$ (III), (VI); $CSNH_2$ (IV), (VII).

Different results are obtained in the reaction between (I) and hydrazine carried out under similar conditions. In the UV spectrum of the condensation product (VIII), the absorption of the phenylnitrone group is absent, and in the IR spectrum there are no bands of the stretching vibrations of the C=N → O group. In the PMR spectrum of (VIII), a signal of two OH groups, a signal of the NH group, and a broad signal of phenyl ring protons are observed in the weak field (Table 3). The signals of protons of the four methyl groups in the PMR spectrum of (VIII) appear over a broader range than in the case of compounds (II)-(IV). The strong-field signal at 0.48 ppm corresponds to the methyl group falling within the zone screened by the phenyl ring. In the ^{13}C NMR spectrum of (VIII), four signals of the methyl carbon atoms, three signals of quaternary C atoms, four signals of phenyl carbon atoms, and a signal of the C=N group are observed (Table 4). The products of

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TABLE 1. Spectral Characteristics of Monosubstituted Hydrazones of 2-Acetyl-3-imidazoline 3-Oxide

Compound	UV spectrum λ, nm (log ε)	IR spectrum		PMR spectrum δ, ppm in CD_3OD		
		ν C=N→O	other bands	RC*	2,5-CH_3	CH_3C=N
(II)	224(4,15), 286(4,02)	1570	3280(NH), 3220(OH)	7,3–7,7 (3H) 7,8–8,1 m (2H)	1,71 s (3H) 1,60 s (3H) 1,41 s (3H)	1,77 s (3H)
(III)	224(4,32), 288(4,06)	1570	1670(C=O), 3470(NH) 3300(NH), 3240(OH)	7,4–7,7 m (3H) 8,0–8,2 m (2H)	1,70 s (3H) 1,60 s (3H) 1,41 s (3H)	1,80 (3H)*
(IV)	224 (4,18), 278(4,53) 346 p (2,86)	1570	3420(NH), 3240(OH)	7,5–7,8 m (3H) 8,1–8,3 m (2H)	1,71 s (3H) 1,60 s (3H) 1,42 s (3H)	1,90 s (3H)*
(V)	226(4,17), 234(4,15) 286(4,09), 380 p(2,48)	1550	3300(NH), 3250(NH)			
(VI)	226(4,30), 288(4,08)	1535	1710(C=O), 3450(NH) 3200 br (NH)			
(VII)	230(4,18), 286(4,45)	1545	3420(NH), 3300(NH) 3180(NH)			

* In DMSO-d_6.

TABLE 2. Yields, Melting Points, and Elementary Analysis Data of Compounds Synthesized

Compound	Yield, %	mp, °C	Found, %			Formula	Calculated, %		
			C	H	N		C	H	N
(II)	85	185–186	62,5	7,9	19,4	$C_{15}H_{22}N_4O_2$	62,1	7,6	19,3
(III)	43	211–212	56,3	6,7	22,3	$C_{15}H_{21}N_5O_3$	56,4	6,6	21,9
(IV)	98	199–201	53,3	6,2	21,2	$C_{15}H_{21}N_5O_2S$ [a]	53,7	6,3	20,9
(V)	96	104–105	62,3	7,2	19,4	$C_{15}H_{21}N_4O_2$	62,3	7,0	19,4
(VI)	90	186–188	56,9	6,3	21,8	$C_{15}H_{20}N_5O_3$	56,6	6,3	22,0
(VII) [c]	90	151–153	53,6	5,8	20,6	$C_{15}H_{20}N_5O_2S$ [b]	54,0	6,0	20,9
(VIII) [c]	93	175–177	60,4	7,3	20,6	$C_{14}H_{20}N_4O_2$	60,9	7,3	20,8
(IX)	90	173–174	64,9	7,2	9,9	$C_{15}H_{20}N_2O_3$	65,2	7,2	10,1
(X)	75	202–204	59,5	6,1	10,0	$C_{14}H_{17}FN_2O_3$ [d]	60,0	6,1	10,0
(XI)	95	189–191	66,5	7,0	9,5	$C_{16}H_{20}N_2O_3$	66,7	6,9	9,7
(XII) [c]	98	162–163	62,2	7,5	19,4	$C_{15}H_{22}N_4O_2$	62,1	7,6	19,3
(XIII) [c]	95	165–167	57,0	6,5	19,2	$C_{14}H_{19}FN_4O_2$ [e]	57,2	6,5	19,0
(XIV) [c]	98	167–168	63,2	7,1	18,4	$C_{16}H_{22}N_4O_2$	63,5	7,3	18,6
(XVI)	60	139–141	56,2	8,4	13,3	$C_{10}H_{18}N_2O_3$	56,1	8,4	13,1
(XVII)	20	143–145	58,8	8,9	15,2	$C_9H_{16}N_2O_2$	58,7	8,7	15,2
(XVIII) [c]	44	143–144	50,3	8,4	26,1	$C_9H_{18}N_4O_2$	50,5	8,4	26,2
(XIX) [c]	50	134–136	52,8	8,8	24,2	$C_{10}H_{20}N_4O_2$	52,7	8,8	24,6
(XX) [f]	70	127–129	54,9	9,2	28,4	$C_9H_{18}N_4O$	54,6	9,1	28,3
(XXIa)	45	152–154	63,1	6,4	11,3	$C_{13}H_{16}N_2O_3$	62,9	6,4	11,3
(XXIb)	55	156–158	62,3	6,3	11,6	$C_{13}H_{16}N_2O_3$	62,9	6,4	11,3
(XXIIa) [c]	96	168–170	59,6	6,9	21,1	$C_{13}H_{18}N_4O_2$	59,5	6,9	21,4
(XXIIb)	96	155–157	59,4	6,9	21,4	$C_{13}H_{18}N_4O_2$	59,5	6,9	21,4
(XXIV)	89	118–120	67,6	5,7	19,2	$C_{12}H_{13}N_3O$	67,7	6,0	19,4
(XXV)	80	187–189	68,6	5,6	18,6	$C_{13}H_{13}N_3O$	68,6	5,7	18,5
(XXVII)	62	35–36	55,0	6,9	27,7	$C_7H_{11}N_3O$	54,9	7,2	27,4

a) Found S 9.8%, calculated 9.9%.

b) Found S 9.4%, calculated 9.9%.

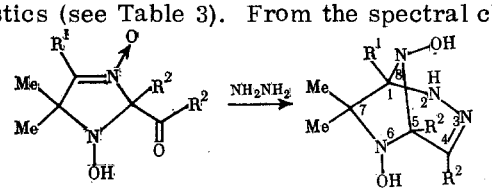
c) In the mass spectrum there is a peak of M^+ with intensity of 1-2%.

d) Found F 6.5%, calculated 6.8%.

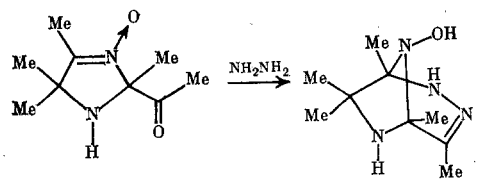
e) Found F 6.3%, calculated 6.5%.

f) Found mol. wt. 190 (ebulioscopically in acetone), calculated 198.

the reaction between other substituted 3-imidazoline 3-oxides (IX)-(XI) and hydrazine, (XII)-XIV) (Table 3), have similar spectral characteristics (see Table 3). From the spectral characteristics and the data of elemen-



(I), (IX)-(XI), (XV), (XVI) (VIII), (XII)-(XIV), (XVIII), (XIX)



(XVII) (XX)

$R^1 = Ph$, $R^2 = Me$ (I), (VIII); $R^1 = p\text{-}MeC_6H_4$, $R^2 = Me$ (IX), (XII); $R^1 = p\text{-}FC_6H_4$, $R^2 = Me$ (X), (XIII): $R^1 = Ph$, $R^2 + R^2 = (CH_2)_4$ (XI), (XIV); $R^1 = R^2 = Me$ (XV), (XVIII); $R^1 = Et$, $R^2 = Me$ (XVI), (XIX).

tary analysis, we assigned the structure of 2,3,6,8-tetraazabicyclo[3.2.1]oct-3-ene derivatives to compounds (VIII) and (XII)-(XIV).

In the reaction between the substituted 3-imidazoline 3-oxides (XV)-(XVII), with an alkylnitrone group in the heterocyclic ring, and hydrazine, products (XVIII)-(XX) with a similar structure are obtained.

In the reactions between substituted 2-acyl-3-imidazoline 3-oxides and hydrazine, the hydrazine reacts not only with the carbonyl, but also with the nitrone group [2].

TABLE 3. Spectral Characteristics of 2,3,6,8-Tetraazabicyclo[3,2,1]oct-3-ene Derivatives

Compound	UV spectrum	IR spectrum, cm^{-1}		PMR spectrum δ, ppm in DMSO-d_6; J, Hz						
	λ, nm (log ε)	ν NH	ν OH	RC^1	$CH_3—C^4$	$CH_3—C^5$	CH_3-C^7 exo	CH_3-C^7 endo	NH	OH
(VIII)	260 (3,48)	3335	3270	7,2–7,7 (5H)	1,81 (3H)	1,37 (3H)	0,48 (3H)	1,04 (3H)	6,12 (1H)	7,64 (2H)
(XII)	262 (3,47)	3350	3280	7,15 ($2H_A$) 7,40 ($2H_B$) J=8,0 2,25 (3H)	1,81 (3H)	1,34 (3H)	0,45 (3H)	1,02 (3H)	6,01 (1H)	7,64 (2H)
(XIII)	260 (3,49)	3340	3280	6,7–7,9 (4H)	1,93 (3H)	1,51 (3H)	0,53 (3H)	1,17 (3H)	–	– [a]
(XIV)	264 (3,47)	3300	3370 2800	7,2–7,7 (5H)	2,3 br (4H)	1,6 br (4H)	0,44 (3H)	1,04 (3H)	6,10 (1H)	7,64 (1H) 7,57 (1H)
(XVIII)	– [b]	3320	3200	1,01 (3H)	1,71 (3H)	1,25 (3H)	0,90 (3H)	1,01 (3H)	5,99 (1H)	7,44 (1H) 7,48 (1H)
(XIX)	– [b]	3320	3200	0,9 t (3H) 1,60 q (2H) J=6,0	1,71 (3H)	1,21 (3H)	0,94 (3H)	1,01 (3H)	6,06 (1H)	7,37 (1H) 7,44(1H)
(XX)	246 (3,45)	3320 3240	3100 2840	1,00 (3H)	1,70 (3H)	1,18 (3H)	0,87 (3H)	1,00 (3H)	5,90 (1H)	7,30 (1H)
(XXIIa)	262 (3,47)	3300	3360 2750	7,2–7,7 (5H)	1,88 (3H)	1,40 (3H)	0.46d (3H) J=7,0	3,15 q (1H)[c] J=7,0	6,17 (1H)	7,80 (1H) 8,10 (1H)
(XXIIb)	258 (3,49)	3310	2820	7,2–7,7 (5H)	1,83 (3H)	1,38 (3H)	3,20 q (1H) [c] J=7,0	0,97 d (3H) J=7,0	6,58 (1H)	7,63 (1H) 8,33 (1H)

a) in CD_3OD.
b) Changes with time.
c) $H—C^7$ signal.

TABLE 4. Data of $^{13}C-\{^1H\}$ Spectra of Compounds (VIII), (XXIIa), and (XXIIb)

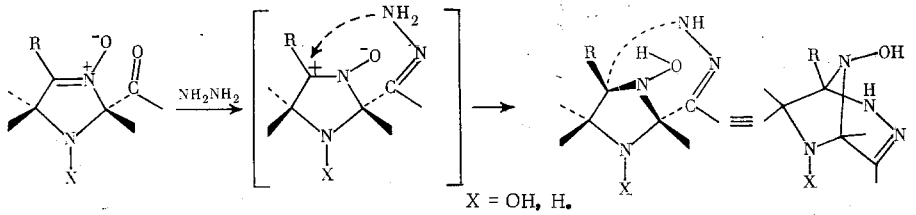
Compound	CH_3[a]	C	C_6H_5	C=N
(VIII)	18,4 (C^4) 20,8 (C^5) 22,5 (C^7) endo 27,7 (C^7) exo	72,2 (C^7)[b] 79,9 (C^5) 82,5 (C^4)	126,4 127,5 127,9 138,7	146,4
(XXIIa)	18,5 (C^4) 18,9 (C^5) 22,3 (C^7) exo	72,8 (C^7)[c] 80,0 (C^5) 80,3 (C^4)	126,8 127,6 127,9 138,0	149,2
(XXIIб)	16,3 (C^4) 19,6 (C^5) 14,2 (C^7) endo	79,0 (C^7)[c] 79,8 (C^5) 80,7 (C^4)	125,7 126,1 126,2 139,4	144,9

a) In the assignment of signals of exo- and endo-methyl groups at C^7, 2-exo-methyl-, 2-endo-methyl-, and 2,2-dimethylbicyclo[2.2.1]heptanes (norbornanes) [3] served as model compounds.

b) In analogy with the corresponding signals of compound (XXIIa).

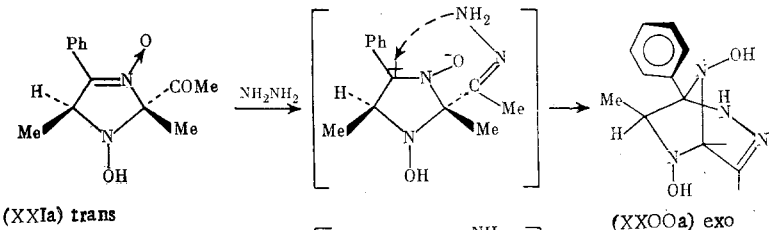
c) The C^7 signal in the form of a doublet in the $^{13}C-\{^1H\}$ NMR spectrum with external resonance irradiation of protons.

In accordance with the bridged structure of the bicyclic products of the condensation of 2-acyl-3-imidazoline 3-oxides with hydrazine, we can expect the formation of two corresponding exo- and endo-isomers for the isomeric 2-acetyl-3-imidazoline 3-oxides, containing unequal substituents in the 5 position of the heterocyclic ring. In fact, in the reaction between (XXIa) and (XXIb) and hydrazine, exo- (XXIIa)



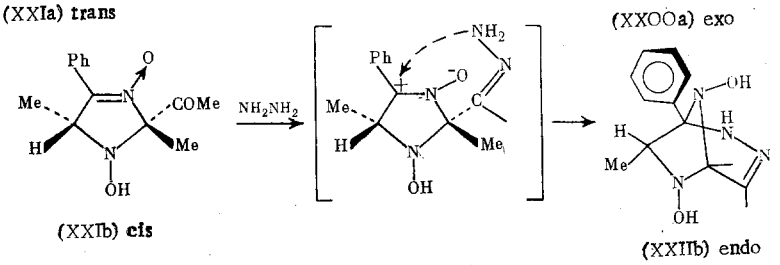
X = OH, H.

and endo-6,8-dihydroxy-4,5,7-trimethyl-1-phenyl-2,3,6,8-tetraazabicyclo[3.2.1]oct-3-enes (XXIIb) are formed:



(XXIa) trans

(XXOOa) exo



(XXIb) cis

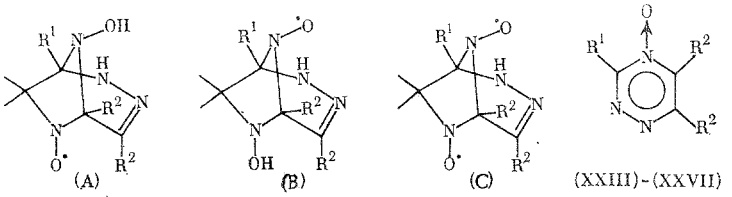
(XXIIb) endo

Isomers (XXIIa) and (XXIIb) have IR and UV spectra similar to those of compounds (VIII) and (XII)-(XIV), but have different melting points and ^1H and ^{13}C NMR spectra (see Tables 3 and 4). The PMR spectra of (XXIIa) and (XXIIb) differ mostly in the position of the methyl group doublets at C^7. The 0.51 ppm shift of this signal to the stronger field in the spectrum of the exo isomer is due, as in the case of (VIII), to the anisotropic effect of the phenyl ring present in the cis position to the CH_3 group. In the spectrum of the endo- isomer (XXIIb), this

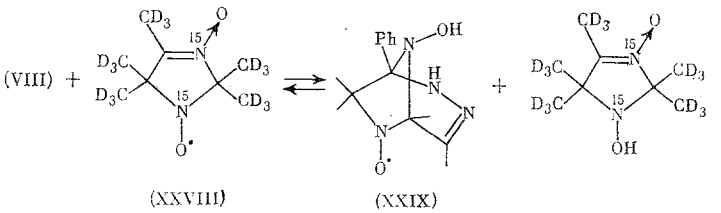
signal is observed at the same ppm value as the signals of the methyl groups at C^7 in 1-alkyl-substituted, 7,7,-dimethyl-2,3,6,8-tetraazabicyclo[3.2.1]oct-3-enes (XVIII), (XIX). In the ^{13}C NMR spectrum, the signal of the exo-CH_3 group of isomer (XXIIa) is shifted 8.1 ppm more to the weaker field than the signal of the endo-CH_3 group of (XXIIb). A larger difference in chemical shifts of the CH_3 groups than in exo- and endo-methylnorbornanes (5.3 ppm) [3] is apparently due to the deactivating action of the bridged hydroxylamino group in the (XXIIa) isomer.

From the structure of isomers (XXIIa) and (XXIIb), the structure of trans-(XXIa) and cis-isomers (XXIb) was unequivocally established; these are formed as a 45 : 55 mixture (according to PMR during the condensation of anti-N-(1-oximino-1-phenyl-2-propyl)hydroxylamine [4] with diacetyl. Isomers (XXIa) and (XXIb) were isolated in a pure state by often-repeated recrystallization from alcohol.

During the oxidation of (VIII), (XII), (XIV), (XVIII), and (XIX) by the action of PbO_2 under the conditions of preparation of radicals (V)-(VII), diamagnetic products, 3,5,6-trisubstituted 1,2,4-triazine 4-oxides (XXIII)-(XXVII), were unexpectedly obtained in yields of 60-80%. During the oxidation, the solution acquired a yellow color, characteristic of solutions of nitroxyl radicals. This color disappeared at the end of the reaction. In the thin-layer chromatographic analysis of the reaction mixture in oxidation of (VIII), besides 1,2,4-triazine N-oxide (XXIII) ($R_f \sim 0.6$ on Silufol in a mixture of $CHCl_3$ and EtOH, 15:1), and the initial (VIII) ($R_f \sim 0.4$), a new yellow compound with $R_f \sim 0.5$ was observed. At the end of the oxidation, only a single compound, 5,6-dimethyl-3-phenyl-1,2,4-triazine 4-oxide (XXIII) was observed in practice. It is possible that the yellow compound, formed as an intermediate during the oxidation of (VIII), is either the radical (A) or (B), or biradical (C)



It could be expected that if a milder one-electron oxidizing agent is used in a homogeneous medium, the formation and recording of the paramagnetic particle (A), (B), or (C) would be possible during the oxidation of (VIII). We used for such an oxidizing agent the nitroxyl radical, 2,2,4,5,5-pentamethyl[d_{15}]-3-[^{15}N]imidazolin-1-[^{15}N]oxyl 3-oxide (XXVIII). The oxidation of (VIII) by radical (XXVIII) was carried out in an ampul of an EPR spectrometer in $CHCl_3$. The isotopic substitution of ^{14}N for ^{15}N in the nitroxyl fragment of radical (XXVIII) was carried out to avoid superposition of the line of this radical on that of the expected radical (A), (B), or biradical (C) in the EPR spectrum. In the EPR spectrum of a solution containing radicals with isotopes of two types (^{14}N and ^{15}N) in the $\diagdown N—\dot{O}$ fragment, the components of the doublet are distributed between middle and edge components of a triplet, and do not overlap. In our experiment it was thus possible to analyze the form of the lines in the EPR spectrum of the expected radical, and to determine the relative equilibrium amount of the formed and initial radicals in the solution. The deuteration of the methyl groups and the isotopic exchange of ^{14}N for ^{15}N at the 3 position of the heterocyclic radical (XXVIII) leads to narrowing of its lines in the EPR spectrum



In the EPR spectrum of a solution initially containing $2.5 \cdot 10^{-3}$ M of (VIII) and $5 \cdot 10^{-4}$ M of (XXVIII) in $CHCl_3$ (Fig. 1), besides the doublet of narrow lines with splitting at 20.2 Oe, a triplet with splitting at $a_{^{14}N}$ = 15.8 Oe, similar to the usual one for the nitroxyl radicals, is also observed [5]. The lines of this triplet have an additional hyperfine structure (hfs). To explain this hfs, we carried out similar experiments with compound (VIII*) in which the bridge ^{14}N atom was substituted for ^{15}N. The isotopic substitution of N led to a change in the additional hfs of the triplet components: The triplet of triplets (Fig. 1a) converts into a triplet of doublets (Fig. 1b) which indicates the formation of type A radical (XXIX*) in the oxidation of (VIII*). The additional

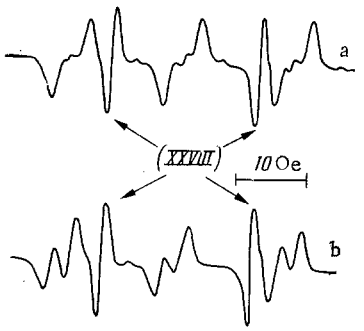
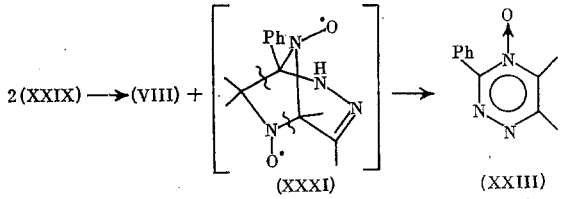


Fig. 1. EPR spectrum of a mixture of 8-hydroxy-4,5,7,7-tetramethyl-1-phenyl-2,3,6,8-tetraazabicyclo[3.2.1]oct-3-en-6-oxyl (XXIX) and radical (XXVIII) at 20°C (a) and 8-hydroxy-4,5,7,7-tetramethyl-1-phenyl-2,3,6,8[^{15}N]-tetraazabicyclo[3.2.1]-oct-3-en-6-oxyl (XXIX*) and radical (XXVIII) in $CHCl_3$ at 20°C (b).

splitting is due to isotropic hyperfine coupling (hfc) of the unpaired electron of radical (XXIX*) with the nucleus of ^{15}N of the bridge hydroxylamino group. The constant of the isotropic hfc with this nucleus, obtained from the first and second derivatives of the EPR spectrum, is equal to $a_{^{14}N^8\,^{15}N^8} = 2.35 \pm 0.2$ Oe. Hence, for the ^{14}N nucleus, this constant is equal to $a_{^{14}N^8} = 1.68$ Oe, since the magnetic moment of the ^{14}N nucleus is lower by a factor of 1.4 than that for ^{15}N. Analysis of hfs of triplet components of radical (XXIX) was carried out by using the atlas of EPR spectra [6], assuming that each component of the fundamental triplet consists of three components with the same intensity, and gives the value $a_{^{14}N^8} = 1.63 \pm 0.1$ Oe, which agrees well with the value of the constant, found by using isotopic substitution. Similar results are also obtained during oxidation of compounds (XII)-(XIV), (XVIII), and (XIX) by radical (XXVIII). In the solution ($c \sim 10^{-3}$-10^{-2} M), radicals of type (A) are stable for a long time, and the intensity of the EPR spectral lines remains constant for several weeks.

From the results, it can be concluded that mild oxidation of the 6,8-dihydroxy-4,5,7,7-tetraalkyl-2,3,6,8-tetraazabicyclo[3.2.1]oct-3-en derivatives gives radicals of derivatives of 8-hydroxy-4,5,7,7-tetraalkyl-2,3,6, 8-tetraazabicyclo[3.2.1]oct-3-en-6-oxyl (type (A). Radical of type B is not formed during the oxidation of compound (XX) by the action of PbO_2 or under the above experimental conditions.

During oxidation of a suspension of compound (VIII) by an aqueous solution of 2,2,3,4,5,5-hexamethyl-3-imidazolinium-1-oxyl methyl sulfate (XXX) [7], and continuous extraction with $CHCl_3$, CCl_4, or ether, the organic layer acquires a yellow color, and the aqueous layer becomes decolorized. The TLC of the organic layer shows the formation of radical (XXIX), with an inappreciable admixture of (XXIII). In the IR spectrum of solution of radical (XXIX) in CCl_4, bands of stretching vibrations of the OH and NH groups are observed at 3580 and 3380 cm^{-1}, and the general form of the spectrum is similar to that of the initial (VIII). In an attempt to isolate (XXIX) in a pure state, i.e., by removing the solvent, the residual yellow mass of radical (XXIX) becomes decolorized in the course of a few hours, and triazine N-oxide (XXIII) and compound (VIII) are formed in approximately equal ratios (according to PMR). In this case, disproportionation of radical (XXIX) takes place, apparently through the formation of an unstable biradical (XXXI), converting into (XXIII).



During oxidation of 6,8-dihydroxy-4,5,7,7-tetraalkyl-2,3,6,8-tetraazabicyclo[3.2.1]oct-3-enes by an excess of PbO_2, the reaction is completely shifted in the direction of formation of 1,2,4-triazine 4-oxides.

EXPERIMENTAL

The IR spectra were recorded on a Perkin–Elmer-180 spectrophotometer in KBr (c ~ 0.25 and 0.5%). The UV spectra were run on an SF-16 apparatus in EtOH. The PMR spectra were recorded on a Varian A56-60A apparatus for 7-10% solutions in DMSO-d_6 or CD_3OD with reference to HMDS as internal standard. The ^{13}C NMR spectra were recorded on a Varian XL-200 spectrometer for 10-15% solutions in DMSO-d_6 with reference to the solvent signal (39.6 ppm). The EPR spectra were recorded on an EPR-3 Sibir' apparatus, and the samples were evacuated in vacuo to 10^{-3} torr. The spectral characteristics of the compounds are listed in Tables 1, 3, and 4, and data of elementary analysis in Table 2.

2-Acetyl-1-hydroxy-2,5,5-trimethyl-4-phenyl-3-imidazoline 3-Oxide Methylhydrazone (II). A solution of 1.65 g of methylhydrazine sulfate in 3 ml of Et_3N and 5 ml of water was added to a solution of 1.5 g of (I) in 30 ml of ethanol. After 5 h, the alcohol was evaporated, and the precipitate was filtered, washed with water, and dried. An additional amount of (II) was isolated by extraction of the filtrate with $CHCl_3$. Compound (II) was recrystallized from ethanol.

2-Acetyl-1-hydroxy-2,5,5-trimethyl-4-phenyl-3-imidazoline 3-Oxide Semicarbazone (III). A solution of 0.68 g of $NH_2CONHNH_2 \cdot HCl$ in 15 ml of water was added to a solution of 1.6 g of (I) in 30 ml of ethanol, and the mixture was left to stand for 12 h. The precipitate of (III) was filtered, washed with water, and recrystallized from ethanol.

2-Acetyl-1-hydroxy-2,5,5-trimethyl-4-phenyl-3-imidazoline 3 oxide thiosemicarbazone (IV) was obtained similarly by the action of $NH_2CSNHNH_2 \cdot HCl$ on (I).

Compounds (II)-(IV) were oxidized into nitroxyl radicals by PbO_2 in acetone [1]. Methylhydrazone (V) was recrystallized from alcohol, semicarbazone (VI) was purified by chromatography on a solumn with SiO_2 (eluent – $CHCl_3$), and thiosemicarbazone (VII) was recrystallized from acetone.

2-Acetyl-1-hydroxy-imidazoline 3-Oxides. The condensation of N-(2-methyl-1-oximino-1-p-tolyl-2-propyl)hydroxylamine [8], N-(2-methyl-1-oximino-p-fluorophenyl-2-propyl)hydroxylamine [8], N-(2-methyl-3-oximino-2-pentyl)hydroxylamine [9], anti-N-(1-oximino-1-phenyl-2-propyl)hydroxylamine [4], and 3-amino-3-methyl-2-oximinobutane [10] with diacetyl was carried out according to [1]. Compounds (IX), (X), and (XVI) were recrystallized from ethanol, and compound (XVII) from acetone. Isomer (XXIa) was obtained after five-fold repeated crystallization of the mixture of (XXIa and b) from ethanol. The mother liquor of the first crystallization was evaporated, and the remaining precipitate recrystallized twice from ethanol. Pure isomer (XXIb) was obtained. The spectral characteristics of (IX), (X), and (XXIa and b) are similar to those of (I), and the characteristics of (XVI) and (XVII) to those of (XV) [1].

2-Acetyl-1-hydroxy-2,5,5-trimethyl-4-phenyl-3[^{15}N]imidazoline 3-Oxide (I*). A solution of 0.23 g of $^{15}NH_2OH \cdot HCl$ (95% content of ^{15}N) in 3 ml of water was added to a solution of 0.36 g of N-(2-methyl-1-oxo-1-phenyl-2-propyl)hydroxylamine [11] in 15 ml of ethanol. The mixture was neutralized by Na_2CO_3, heated for 6 h at 50°C, and left to stand for 24 h at 20°C. The solvent was evaporated, and the precipitate washed with water, filtered, dried (wt. 0.33 g), and condensed with diacetyl according to [1]. In the IR spectrum of (I*), the $\nu C{=}{}^{15}N$ band is shifted by 20 cm^{-1} into the low-frequency region in comparison with the $\nu C = {}^{14}N$ band in (I).

5,5-Dimethyl-1-hydroxy-2-(spirocyclohexan-2-one)-4-phenyl-3-imidazoline 3-Oxide (XI). A 3.5 g portion of cyclohexane-1,2-dione was added to a suspension of 5 g of N-(2-methyl-1-oximino-1-phenyl-2-propyl)-hydroxylamine in 100 ml of MeOH, and the mixture was boiled for 6 h. Methanol was evaporated, the residue was washed by water, and the precipitate of (XI) was filtered and recrystallized from ethanol. The spectral characteristics of (XI) are similar to those of (I).

Reaction of 2-Acyl-3-imidazoline 3-Oxides (I), (IX)-(XI), (XV)-(XVII), (XXIa), (XXIb) with Hydrazine Hydrate. A 2 ml portion of hydrazine hydrate was added to a solution of 1.5 g of 2-acyl-3-imidazoline 3-oxide in 70 ml of ethanol, and the mixture was left to stand for 6-10 h. The solvent was evaporated, and the precipitate of the 2,3,6,8-tetraazabicyclo[3.2.1]oct-3-ene derivative was filtered, washed with water, dried and recrystallized from ethanol. Compound (VIII*) was obtained similarly from (I*).

Oxidation of 2,3,6,8-Tetraazabicyclo[3.2.1]oct-3-ene Derivatives. A 2 g portion of PbO_2 was added to a suspension of 0.65 g of (VIII) in 30 ml of acetone, and the mixture was stirred for 10 h. The mixture was filtered, the filtrate was evaporated, and the residue chromatographed on a column with SiO_2 (eluent – $CHCl_3$), and recrystallized from heptane. The melting point and the spectral characteristics of (XXIII) were identical with those given in [12]. Similarly, compounds (XXIV)-(XXVIII) were obtained from (XII)-(XIV), (XVIII), and

(XIX), respectively. 5,6-Dimethyl-3-p-tolyl-1,2,4-triazine 4-oxide (XXIV): UV spectrum (λ_{max}, nm): 262 (log ε 4.43). PMR spectrum (in CCl_4, δ, ppm): 2.37 s (3 H, $CH_3C_6H_4$), 2.49 s and 2.70 s (3 H and 3 H, 5,6-CH_3), 7.27 d (2 H, m-C_6H_4, J = 8 Hz), 8.22 d (2 H, o-C_6H_4, J = 8 Hz). 3-Phenyl-5,6,7,8-tetrahydrobenzo[e]1,2,4-triazine 4-oxide (XXV): UV spectrum (λ_{max}, nm): 260 (log ε 4.33). PMR spectrum ($CDCl_3$): 1.66-2.05 m and 2.67-3.22 m (4 H and 4 H, $4CH_2$), 7.25-7.55 m and 8.05-8.35 m (3 H and 2 H, C_6H_5). 3,5,6-Trimethyl-1,2,4-triazine 4-oxide (XXVI), yield 60%. Melting point and spectral characteristics are similar to those described in [13]. 5,6-Dimethyl-3-ethyl-1,2,4-triazine 4-oxide (XXVII) was purified by sublimation. UV spectrum (λ_{max}, nm): 226 (log ε 4.20), 272 (3.94). PMR spectrum ($CDCl_3$): 1.37 t (3 H, CH_3CH_2), 2.44 s and 2.64 s (3 H and 3 H, 5,6-CH_3), 3.08 q (2 H, CH_3CH_2).

The synthesis of radical (XXVIII) will be reported in a separate article.

CONCLUSIONS

1. Reaction of 2-acyl-1-hydroxy-3-imidazoline 3-oxides with monosubstituted hydrazines leads to monosubstituted hydrazones, derivatives of 2-acyl-1-hydroxy-3-imidazoline 3-oxide, which on oxidation give stable nitroxyl radicals of the imidazoline series.

2. In the reaction between 2-acyl-3-imidazoline 3-oxides and hydrazine, an intramolecular cyclization takes place with the formation of a new heterocyclic system, 2,3,6,8-tetraazabicyclo[3.2.1]oct-3-ene.

3. The oxidation of 6,8-dihydroxy-4,5,7,7-tetraalkyl-1-R-2,3,6,8-tetraazabicyclo[3.2.1]oct-3-enes leads to bicyclic nitroxyl radicals, 8-hydroxy-4,5,7,7-tetraalkyl-1-R-2,3,6,8-tetraazabicyclo[3.2.1]oct-3-en-6 oxyls, which on oxidation give 1,2,4-triazine 4-oxides.

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