

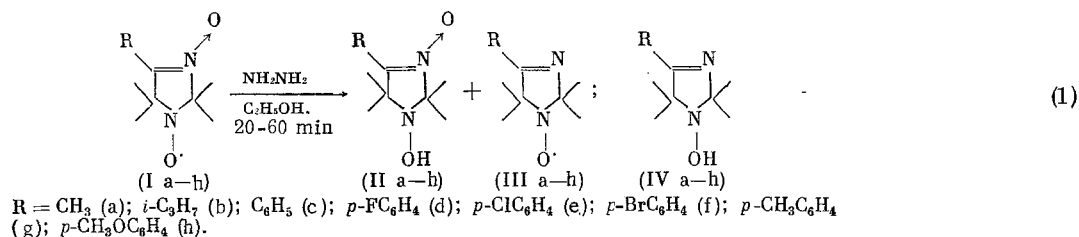
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INFLUENCE OF RADICAL CENTER ON OXIDATIVE
 PROPERTIES OF NITRON GROUP IN REACTION
 OF NITROXYL RADICALS OF 3-IMIDAZOLINE
 3-OXIDE WITH HYDRAZINE

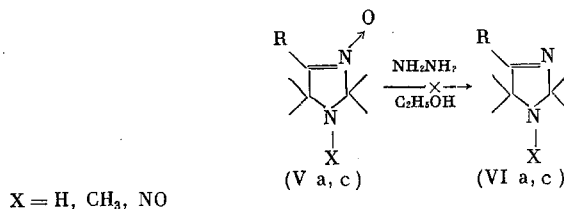
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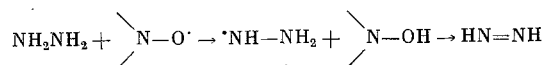
It is known [1, 2] that hydrazine and its derivatives are effective reducing agents of nitroxyl radicals to the corresponding hydroxylamines. During the study of the reduction of nitroxyl radicals of 3-imidazoline 3-oxide (I) by hydrazine hydrate in alcohol at 20°C, we found that in this reaction, besides the usual reduction of the radical center to the hydroxylamino group and formation of diamagnetic product (II), desoxygenation of the nitron group and formation of radical (III) occur in parallel, and radical (III) is further reduced to the diamagnetic product (IV)



The reduction of the nitron group with the formation of product of type (III) takes place under these conditions in the case of the paramagnetic derivatives (I) only. In diamagnetic derivatives (V), with different groups at position 1 of the heterocyclic ring, under similar conditions there is no reduction of the nitron group



Hydroxylamines (II) also do not react with hydrazine in the absence of oxygen. In an alcoholic solution of hydrazine in an argon atmosphere, compound (II) does not change in the course of a month. In a normal atmosphere, where there is always the possibility of oxidation of compounds (II) into radicals (I) by dissolved atmospheric oxygen and the occurrence of process (1), (II) converts into radicals (III), which after 14 days were isolated in yields of 70-80%. This difference in behavior of the diamagnetic and paramagnetic derivatives of 3-imidazoline 3-oxide with respect to hydrazine is probably due to the fact that the nitron group becomes reduced not by the hydrazine itself, but by the products of its partial oxidation with better reducing properties, for example, by diimide [3]

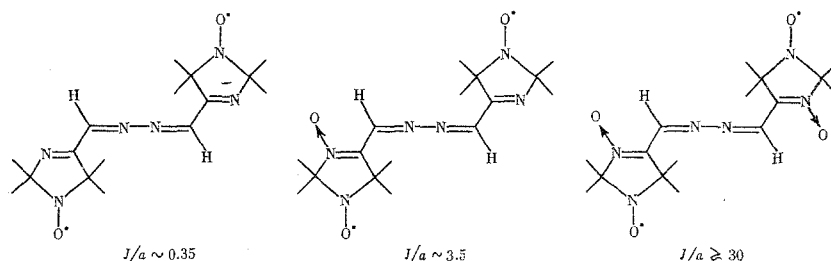


However, when compounds (V) were held with hydrazine in the presence of nitroxyl radicals or Cu^{2+} , able to form diimide or other active particles, products of type (VI) did not form. Thus, the necessary condition for the

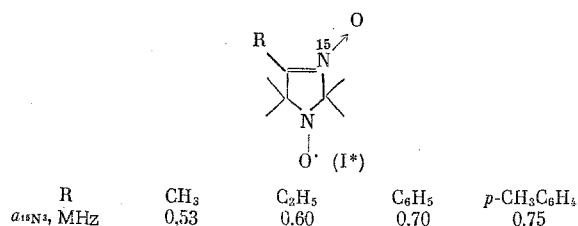
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desoxygenation process under the above conditions in the simultaneous presence of the nitron group and a radical center in (I). We therefore assumed that the radical center in the paramagnetic derivatives (I) can participate not only in the generation of an active reducing particle, but also increases the oxidative ability of the nitron group. Hence, the stronger the interaction between the nitron group and the radical center, the more effectively the desoxygenation of the N-oxide group proceeds in the absence of oxygen.

A study of the spin exchange in the biradicals in the 3-imidazoline series with a rigid system of conjugated bonds showed that the nitron group favors the delocalization of the spin density from the radical center. This is indicated by the increase by one order of magnitude in the value of the exchange integral (J/a) characterizing the degree of delocalization of the spin density over the system of conjugated bonds during indirect exchange, when an N-oxide group is introduced into the imidazoline radical fragment [4]



A direct criterion for characterizing the degree of interaction of the radical center with the nitron group may be the value of the spin density on the nitrogen atom (a_{N^3}) of the nitron group. A study of the influence of the different R groups adjacent to the nitron group in radicals (I*) on the degree of delocalization of the spin density by measuring the value of the isotropic constant a_{15N^3} by the method of spinecho† shows that donor substituents favor the interaction of the nitron group with the radical center



The donor substituents at the para-position of groups R of radicals (I) favor the desoxygenation process and increase in the yield of radical (III) (Table 1). This agrees with the assumption that the nitron group in radicals (I) is reduced more easily when it interacts with the nitroxyl group more strongly, i.e., when its radical character is more marked.

Another influence of the substituents on the reduction of the nitron group, carried out electrochemically, is observed in the series of diamagnetic derivatives (II) [5]. In this case, as expected, the acceptor substituents facilitate reduction, and the donor substituents impede it.

For radicals (VII), (X), and (XIII) with different functional groups at the 2-position of the imidazoline ring, able to exert different steric and electronic influences on both the nitron and the nitroxyl group [6],

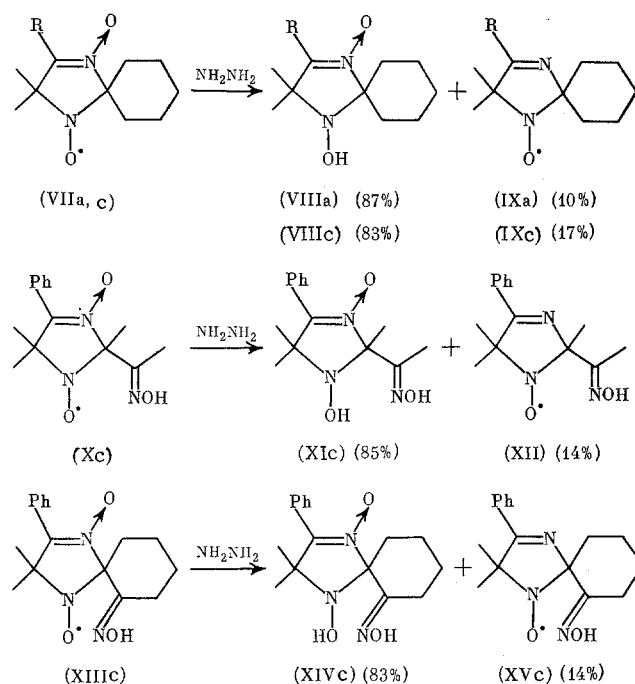
†The procedure and the experimental results will be published in a separate paper.

TABLE 1. Yields of Products (II) and (III) in Reaction (1)

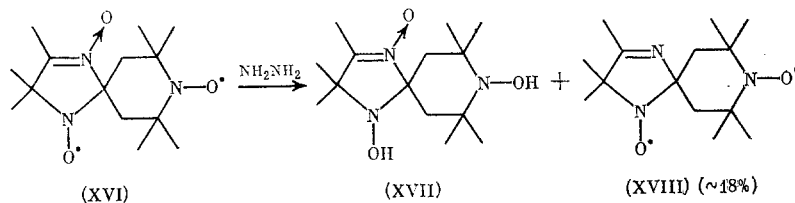
Radical	R	Yield, %		Radical	R	Yield, %	
		(II)	(III) *			(II)	(III) *
(Ia)	CH ₃	87	9	(Ie)	<i>p</i> -ClC ₆ H ₄	86	13
(Ib)	<i>i</i> -C ₃ H ₇	85	12	(If)	<i>p</i> -BrC ₆ H ₄	85	13
(Ic)	C ₆ H ₅	85	14	(Ig)	<i>p</i> -CH ₃ C ₆ H ₄	81	17
(Id)	<i>μ</i> -FC ₆ H ₄	86	13	(Ih)	<i>p</i> -CH ₃ OC ₆ H ₄	80	18

*The yields are given for kinetically controlled reaction (1). On multiple repetition, the reproducibility of the results for radicals (Ic-h) is $\pm 1\%$, and for radicals (Ia, b) it is $\pm 3\%$.

the fraction of desoxygenation products (IX), (XII), and (XV) is determined mainly by the nature of the substituents at the nitron group and corresponds to the situation observed for radicals (I).



The following can serve to confirm the conclusion that the ability of the nitron group in derivatives of 3-imidazoline 3-oxide to be reduced by hydrazine is determined by its radical character: On transition from monoradical (Ia) to biradical (XVI), which also has a methyl-nitron group, the yield of desoxygenation product (XVIII) almost doubles.



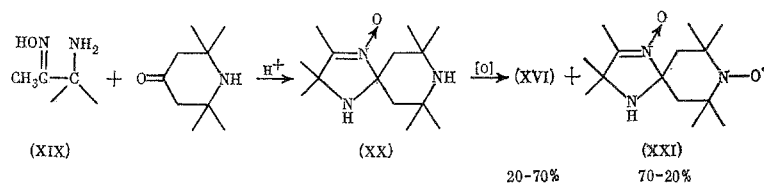
The radical center in nitroxyl radicals of 3-imidazoline 3-oxide thus increases the oxidative properties of the nitron group in the same molecule of the radical, compared with similar diamagnetic derivatives of 3-imidazoline 3-oxide. This is probably due to the presence of a spin density on the nitron group as the result of its interaction with the not directly bound nitroxyl group.

EXPERIMENTAL

Synthesis of Nitroxyl Radicals of 3-Imidazoline 3-Oxide (Ia-h). Radicals (Ia-h) were obtained by the oxidation of compounds (IIa-h) by PbO_2 or MnO_2 in acetone by the method in [7]. The synthesis of hydroxylamines (IIa-d, g) has been described in [8]. Hydroxylamines (IIe, f, h) were synthesized by the method described in [8] from the corresponding α -hydroxylaminooximes [9].

The synthesis of radicals (VIIa, c) has been described in [10], and of radicals (Xc) in [11]. 5,5-Dimethyl-1-hydroxy-2-(2-oximinospirocyclohexane)-4-phenyl-3-imidazoline 3-oxide (XVIc) was obtained by the method in [11] from 5,5-dimethyl-1-hydroxy-2-(spirocyclohexan-2-one)-4-phenyl-3-imidazoline 3-oxide [12]. 5,5-Dimethyl-2-(2-oximinospirocyclohexane)-4-phenyl-3-imidazoline-3-oxide-1-oxyl (XIIIc) was obtained by oxidation of (XIVc) according to [11].

2,2,6,6-Tetramethylpiperidine-1-oxyl-4-spiro-2-(4',5',5'-trimethyl-3'-imidazoline 3'-Oxide-1'-oxyl) (XIV) was synthesized according to the following scheme



a)* A 0.05-mole portion of aminooxime (XIX) [10] and 3 ml of 15% HCl were added at 120-130°C to a melt of 0.15 mole of triacetoneamine, and the mixture was left to stand at this temperature for ~ 5 h. To

*The synthesis was carried out by V. V. Martin.

TABLE 2. Data of Elemental Analysis and Melting Points of Compounds Synthesized

Compound	mp, °C	Found/Calculated, %				Empirical formula
		C	H	N	Hal	
(Ib)	123-125	60,7 60,3	9,6 9,6	14,4 14,1	—	C ₁₀ H ₁₉ N ₂ O ₂
(Id)	99-104	62,4 62,1	6,5 6,3	11,0 11,1	7,6 7,6	C ₁₃ H ₁₆ FN ₂ O ₂
(Ie)	132-133	58,6 58,5	5,6 6,0	10,1 10,5	13,3 13,3	C ₁₃ H ₁₆ ClN ₂ O ₂
(If)	129-130	50,3 50,0	5,1 5,1	8,6 9,0	25,5 25,6	C ₁₃ H ₁₆ BrN ₂ O ₂
(Ig)	108-110	68,2 68,0	7,7 7,7	11,6 11,3	—	C ₁₄ H ₁₉ N ₂ O ₂
(Ih)	117-119	63,6 63,9	7,2 7,2	10,6 10,6	—	C ₁₄ H ₁₉ N ₂ O ₃
(IIe)	151-152	58,1 58,0	6,4 6,3	10,2 10,4	13,7 13,2	C ₁₃ H ₁₇ ClN ₂ O ₂
(IIIf)	132-134	49,5 49,8	5,3 5,4	8,7 8,9	25,1 25,6	C ₁₃ H ₁₇ BrN ₂ O ₂
(IIh)	183-185	63,7 63,6	7,6 7,6	10,4 10,6	—	C ₁₄ H ₂₀ N ₂ O ₃
(IIIb)	65-66	66,0 65,5	10,1 10,4	14,9 15,3	—	C ₁₀ H ₁₉ N ₂ O
(IIIId)	66-68	66,7 66,4	6,8 6,8	12,1 11,9	8,0 8,1	C ₁₃ H ₁₆ FN ₂ O
(IIIe)	85-87	62,2 62,1	6,7 6,5	11,0 11,1	14,1 14,1	C ₁₃ H ₁₆ ClN ₂ O
(IIIIf)	84-86	53,1 52,8	5,5 5,4	9,2 9,5	26,6 27,1	C ₁₃ H ₁₆ BrN ₂ O
(IIIg)	74-76	72,3 72,7	8,1 8,2	11,9 12,1	—	C ₁₄ H ₁₉ N ₂ O
(IIIh)	95-97	68,0 68,0	7,5 7,7	11,2 11,3	—	C ₁₄ H ₁₉ N ₂ O ₂
(IVb)	117-119	65,6 65,2	10,6 10,9	15,6 15,2	—	C ₁₀ H ₂₀ N ₂ O
(IVd)	162-163	65,6 66,1	7,1 7,2	11,6 11,8	7,6 8,0	C ₁₃ H ₁₇ FN ₂ O
(IVg)	129-131	72,7 72,4	8,7 8,6	11,9 12,1	—	C ₁₄ H ₂₀ N ₂ O
(IVh)	149-151	67,7 67,7	8,4 8,1	11,0 11,3	—	C ₁₄ H ₂₀ N ₂ O ₂
(IXc)	95-97	75,0 74,8	8,0 8,2	10,7 10,9	—	C ₁₆ H ₂₁ N ₂ O
(XIIc)	111-113	64,4 64,6	7,1 6,9	15,9 16,2	—	C ₁₄ H ₁₈ N ₃ O ₂
(XIIIc)	116-120	63,4 63,6	6,4 6,6	13,7 13,9	—	C ₁₆ H ₂₀ N ₃ O ₃
(XIVc)	168-170	63,6 63,4	6,6 6,9	14,2 13,9	—	C ₁₆ H ₂₁ N ₃ O ₃
(XVc)	127-130	66,8 67,2	6,8 7,0	14,3 14,7	—	C ₁₆ H ₂₀ N ₃ O ₂
(XVI)	107-109	59,4 59,4	8,7 8,8	14,8 14,8	—	C ₁₄ H ₂₅ N ₃ O ₃
(XX)	148-150	66,4 66,4	11,0 10,7	16,6 16,6	—	C ₁₄ H ₂₇ N ₃ O
(XXI)	104-106	62,3 62,7	9,6 9,7	15,4 15,7	—	C ₁₄ H ₂₆ N ₃ O ₂

avoid resinification, the reaction was carried out in an argon current. After the mixture was cooled, excess of triacetoneamine was distilled in vacuo, and the residue was purified chromatographically on Al_2O_3 by chloroform. The yield of 2,2,6,6-tetramethylpiperidine-4-spiro-2-(4',5',5'-trimethyl-3'-imidazoline 3'-oxide) (XX) was 20-30%. IR spectrum (ν , cm^{-1}): 1605 (C=N), 3260, 3320 (NH), UV spectrum (λ_{max} , nm, log ϵ): 232 (4.02).

b) Oxidation of compound (XX) by H_2O_2 by method in [10] leads to a different ratio of biradical (XVI) and 2,2,6,6-tetramethylpiperidina-1-oxyl-4-spiro-2-(4',5',5'-trimethyl-3'-imidazoline 3'-oxide) (XXI), depending on the time of holding. Compounds (XVI) and (XXI) were separated by chromatography on silica gel, using chloroform as eluent. Biradical (XVI): IR spectrum (ν , cm^{-1}): 1600 (C=N), 1340 shoulder (N-O \cdot). UV spectrum (λ_{max} , nm, log ϵ): 236 (4.12), 274 (3.07), 410 (1.15). The EPR spectrum has a form characteristic of biradicals of this type [13].

Monoradical (XXI): IR spectrum (ν , cm^{-1}): 1600 (C=N), 1340 (N-O \cdot), 3300 (NH). UV spectrum (λ_{max} , nm, log ϵ): 234 (4.13). The presence of the radical center in the piperidine ring and not in the imidazoline ring is proved by the presence in the IR spectrum of a stretching vibrations band of $\text{>N-O}\cdot$ in the region characteristic of six-membered nitroxyl radicals [14], and also by the value of the HFI [hyperfine interaction] constant $a_N = 15.3$ Oe (chloroform) in the EPR spectrum, which is characteristic of radicals in the piperidine series ($a_N = 15.3 \pm 0.2$ Oe). In the EPR spectra of radicals (I) in $CHCl_3$, $a_N = 14.4 \pm 0.2$ Oe.

Reaction of Radicals (I) with Hydrazine. A 5-ml portion of a solution of hydrazine hydrate in alcohol (in 20 ml of the solution - 2 ml of 85% hydrazine hydrate) was added to a solution of 4 mmoles of radical (I) in 15 ml of alcohol, and the mixture was left to stand for 0.5-1h at $\sim 20^\circ C$. The end of the reaction was indicated by the disappearance of the initial radical during TLC of the reaction mixture on Silufol in a $CHCl_3-C_2H_5OH$ 20:1 system ($R_f \sim 0.5$ (I), 0.3 (II), 0.6 (III), 0.4 (IV)). The mixture was then evaporated to dryness, dissolved in acetone, and oxidized by PbO_2 or MnO_2 to complete oxidation of compounds (II) and (IV) into radicals (I) and (III), respectively (according to TLC). The solution was filtered from the oxidant, the filtrate was evaporated, and radicals (I) and (III) were separated by chromatography on silica gel, using $CHCl_3$ as eluent. The yields are shown in Table 1 and in the text. We should note that compounds (II) and (IV) are oxidized into the corresponding radicals in quantitative yields, and therefore the yields of radicals (I) and (III) after oxidation and separation by column chromatography correspond to the yields of products (II) and (III) in reaction (1), respectively, and the sum total amounts to 96-100%.

The radicals (IIIa, c) were identified by comparing the spectral characteristics, chromatographic behavior, and melting points with the same characteristics of compounds synthesized by the methods in [15]. Biradical (XVIII) has spectral characteristics and melting point identical with those described in [13]. The structure of the newly synthesized compounds was established from the analytical and spectral data. The data on the elemental analysis and melting points of the compounds synthesized are listed in Table 2. The IR and UV spectra of the compounds obtained are similar to the spectra of analogous compounds described in [16, 17]. The PMR spectra of the diamagnetic compounds (II), (IV), (XIVc) and (XX) correspond to the assigned structures.

CONCLUSIONS

1. The influence of the radical center on the reactivity of the functional group in derivatives of 3-imidazoline 3-oxide not bound directly to it has been discovered.
2. In the reaction of nitroxyl radicals of a series of 3-imidazoline 3-oxides with hydrazine, two parallel processes take place: Reduction of the radical center to a hydroxylamino group and reduction of the nitron group to an amino group.
3. The desoxygenation process of the nitron group by hydrazine in alcohol at $20^\circ C$ proceeds in the case of paramagnetic derivatives of 3-imidazoline 3-oxide only.

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SUBSTITUTION REACTION WITH PARTICIPATION
OF ORGANOALUMINUM COMPOUNDS
3.* CROSS-COMBINATION OF ALLYL ACETATES
WITH TRIALKYLALANES

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547.256.2

In continuation of our studies on the synthesis of allenes from acetates of tertiary acetylenic alcohols [1], we investigated the reaction of alkylalanes with allyl acetates. In reaction of this type, Mg and Li compounds are actively used as organometallic reagents [2, 3].

Possible allylation of alkylalanes by allyl acetates was shown in the reactions of acetates of geraniol and *cis*, *trans*-carveols with organoaluminum compounds (OAC) of type R_3Al ($R = Me, Et, i-Bu$) [4, 5]. The reactions proceeded under mild conditions ($-78^\circ C$) and led to alkylation products in a yield of 66-85%. We extended this method to other allyl substrates, and compared the behavior in this reaction of primary and secondary allyl acetates, and also acetates containing electron-donor substituents at the γ -position of the leaving group. As starting compounds, we selected allyl (I), crotyl (II), cinnamyl (III), sorbyl (IV), 2,7-octadienyl (V), 2-pentenyl (VI), 2-cyclohexenyl acetates (VII), and trialkylalanes R_3Al ($R = Et, i-Bu, n-C_6H_{13}$).

The reaction conditions were selected using as an example the reaction of OAC with acetate V, which is interesting in synthesis, since 1,6-alkadienes based on it can be used in the synthesis of several pheromones [6]. It was found that the optimal molar ratio of the reagents is $ROAc : R_3Al = 1 : 2$. The reaction proceeds in hexane or in CH_2Cl_2 at $\sim 20^\circ C$ for several hours. In ether and in THF, the reaction products are formed after 24 h in trace amounts. The experimental data (Table 1) show that the ratio between the two competing paths, i.e., alkylation and nucleophilic attack by alkyl on the carbon atom of the carbonyl group, is appreciably dependent

*For article 2, see [1].