

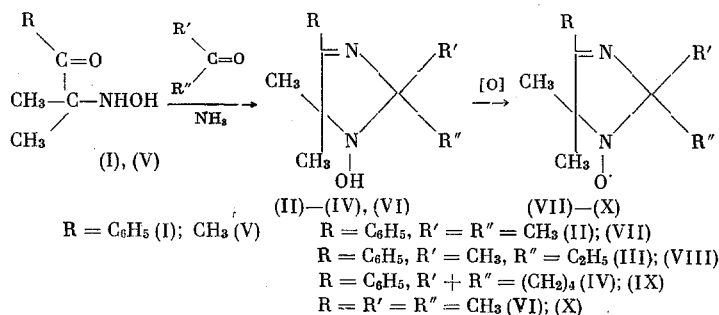
PREPARATION OF STABLE IMINOXYL RADICALS OF  
3-IMIDAZOLINES

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Previously it was shown [1] that the condensation of the anti-isomers of the oximes of  $\alpha$ -hydroxylaminoketones, containing a hydroxylamino group attached to a tertiary carbon atom, with acetone or with its diethyl ketal, leads to the formation of 1-hydroxy-2, 2, 5, 5-tetramethyl-3-imidazoline 3-oxides, the oxidation of which gives stable iminoxyl radicals [2]. In the present paper we attempted to obtain similar compounds without the N-oxide oxygen.

A white crystalline product (II) was formed when N-(1-keto-2-methyl-1-phenyl-2-propyl)hydroxylamine (I) is heated with acetone and  $\text{CH}_3\text{COONH}_4$  (cf. [3]), which in its composition corresponds to the condensation product of compound (I) with acetone and ammonia, which condensation proceeds with the cleavage of two molecules of water. In the IR spectrum of (II) are observed absorption bands at 1620 (C = N) and 3600  $\text{cm}^{-1}$  (OH). In the NMR spectrum of compound (II) are observed a singlet at 8.59 ppm\* (four methyl groups attached to a saturated C atom) and a complex band of five benzene protons, with a center at 2.46 ppm. These data make it possible to assign the structure of 1-hydroxy-2, 2, 5, 5-tetramethyl-4-phenyl-3-imidazoline to product (II). The condensation of  $\alpha$ -hydroxylaminoketone (I) with methyl ethyl ketone and cyclopentanone in the presence of  $\text{CH}_3\text{COONH}_4$  respectively led to the formation of 1-hydroxy-2, 5, 5-trimethyl-2-ethyl-4-phenyl-3-imidazoline (III) and 1-hydroxy-5, 5-dimethyl-2, 2-tetramethylene-4-phenyl-3-imidazoline (IV). The spectral characteristics of compounds (II)-(IV) are close among themselves (Table 1)



It should be mentioned that the condensation of the hydrochloride of N-(3-keto-2-methyl-2-butyl)hydroxylamine (V) with acetone and aqueous  $\text{NH}_3$  could be effected without heating. On the basis of the spectral characteristics (see Table 1) the condensation product (VI) was assigned the structure of 1-hydroxy-2, 2, 4, 5, 5-pentamethyl-3-imidazoline.

The oxidation of compounds (II)-(IV) and (VI) in benzene with either  $\text{PbO}_2$  or atmospheric oxygen led to the quantitative formation of the iminoxyl radicals: 2, 2, 5, 5-tetramethyl-4-phenyl-(VII), 2, 5, 5-trimethyl-2-ethyl-4-phenyl-(VIII), 5, 5-dimethyl-2, 2-tetramethylene-4-phenyl-(IX), and 2, 2, 4, 5, 5-pentamethyl-(X)-3-imidazoline-1-oxyls. Radicals (VII)-(X) are low-melting orange crystals, while compound (X) is a liquid at 20°; in the crystalline state they can be stored at 0° for a long time without decomposition.

\*The chemical shifts are given on the  $\tau$  scale.

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TABLE 1. 1-Hydroxy-3-Imidazolines (II)-(IV), (VI) and 3-Imidazole-1-Oxyls (VII)-(X)

Compound	Mp, °C	Yield, %	Found, %			Empirical formula	Calc. , %			UV spec-trum		IR spec-trum	
			C	H	N		C	H	N	$\lambda_{\max}$ , nm	lg $\epsilon$	C=N	OH
II	152.5-154*	93	71.7	8.3	13.3	C <sub>11</sub> H <sub>16</sub> N <sub>2</sub> O	71.6	8.3	12.8	241	4.0	1620	3600
III	124.5-124†	98	72.9	8.7	12.5	C <sub>11</sub> H <sub>16</sub> N <sub>2</sub> O	72.5	8.7	12.1	239	4.00	1620	3600
IV	130-132‡	80	74.4	8.3	11.6	C <sub>11</sub> H <sub>16</sub> N <sub>2</sub> O	73.8	8.3	11.5	240	4.00	1620	3600
VI	127-128†	60	61.9	10.3	18.0	C <sub>11</sub> H <sub>16</sub> N <sub>2</sub> O	61.5	10.3	18.0	—	—	1660	3600
VII	79.5-81‡	94	72.3	7.9	13.1	C <sub>11</sub> H <sub>17</sub> N <sub>2</sub> O	71.9	7.8	12.9	246	4.10	1620	—
VIII	54-55‡	94	73.0	8.0	12.3	C <sub>11</sub> H <sub>16</sub> N <sub>2</sub> O	72.7	8.3	12.1	246	4.08	1620	—
IX	64-65†	95	74.8	7.9	11.7	C <sub>11</sub> H <sub>16</sub> N <sub>2</sub> O	74.1	7.9	11.5	250	4.10	1610	—
X	—†	80	61.9	10.1	17.5	C <sub>11</sub> H <sub>16</sub> N <sub>2</sub> O	62.0	9.8	18.1	—	—	1650	—

\* Heptane + alcohol.

† Heptane.

‡ Hexane.

\*\* Liquid, bp 160-165° (decompn.) (according to Sivolobov).

The ESR spectra of compounds (VII)-(X) represent a triplet with a hyperfine splitting constant of ~14.5 Oe, which is characteristic for iminoxyl radicals [2]. In the transition to the radicals the IR spectra exhibit little change, and specifically the bands of the OH group at 1000-1040 and 3600 cm<sup>-1</sup> disappear. In the UV spectra of radicals (VII)-(IX) is observed a bathochromic shift of the band at 240 nm and an increase in its intensity (see Table 1); judging by the NMR spectra, the radicals do not contain diamagnetic impurities.

Mention was made previously of the absence of direct methods for the preparation of sterically hindered hydroxylamine derivatives - the starting compounds for the generation of iminoxyl radicals under mild conditions [2]. The reaction of  $\alpha$ -hydroxylaminoketones, containing a tertiary hydroxylamino group, with ketones and ammonia is a simple method for the preparation of such hydroxylamines.

#### EXPERIMENTAL

The IR spectra were taken on a UR-10 instrument as KBr pellets (concentration 0.25%, thickness 1 mm) and in CCl<sub>4</sub> solution, while the UV spectra were taken on a Unicam-SP-700 C instrument in alcohol. The NMR spectra were taken in CD<sub>3</sub>OD solution (3-5%) on a Varian A-56-60A instrument, using HMDS as the internal standard. The yields, melting points, analysis data and spectral characteristics of condensation products (II)-(IV) and (VI), and of radicals (VII)-(X), are given in Table 1. The hydrochloride of  $\alpha$ -hydroxylaminoketone (V) was obtained by the hydrolysis of N-(3-oximino-2-methyl-2-butyl)hydroxylamine in conc. HCl solution [4], mp 145-146° (alcohol-ether).

Condensation of  $\alpha$ -Hydroxylaminoketones with Ketones and Ammonia. To 1.0 g of  $\alpha$ -hydroxylaminoketone (I) in 15 ml of acetone was added 0.65 g CH<sub>3</sub>COONH<sub>4</sub> and the mixture was refluxed for 1 h. The solution was evaporated, and the crystalline residue was treated with water, filtered, and dried to give 1.12 g of compound (II). Under analogous conditions, the condensation of (I) with CH<sub>3</sub>COONH<sub>4</sub> and methyl ethyl ketone led to the formation of compound (III). NMR spectrum: singlets at 8.66, 8.64, and 8.53 ppm (2, 5, 5- (3 CH<sub>3</sub>)), a quartet at 8.26 ppm (J 7.0 Hz) and a triplet at 9.10 ppm (CH<sub>2</sub>CH<sub>3</sub>), and a complex band at 2.46 ppm (C<sub>6</sub>H<sub>5</sub>). The analogous reaction with cyclopentanone in alcohol for 20 min led to the formation of (IV). NMR spectrum: singlet at 8.64 ppm (gem-(CH<sub>3</sub>)<sub>2</sub>), complex bands at 8.24 and 7.71 ppm [(CH<sub>2</sub>)<sub>4</sub>], and a complex band at 2.50 ppm (C<sub>6</sub>H<sub>5</sub>).

To a suspension of 1.8 g of the hydrochloride of  $\alpha$ -hydroxylaminoketone (V) in 10 ml of acetone was added 10 ml of conc. NH<sub>4</sub>OH and the mixture was allowed to stand at 20°. A crystalline precipitate of compound (VI), weighing 1.12 g, deposited after partial evaporation of the solution. NMR spectrum: singlets at 8.78 and 8.72 ppm [2 gem-(CH<sub>3</sub>)<sub>2</sub>], and a singlet at 8.08 ppm (CH<sub>3</sub>).

Oxidation of 1-Hydroxy-3-imidazolines (II)-(IV) and (VI). A suspension of 0.65 g of compound (II) and 7.0 g of PbO<sub>2</sub> in 50 ml of benzene was stirred at 20° for 3 h and then filtered. Evaporation of the benzene solution gave orange crystals of compound (VII). The oxidation of 3-imidazolines (II), (IV), and (VI) under the same conditions led to the formation of 3-imidazole-1-oxyls (VIII)-(X). Radical (X) was purified by chromatographing on Al<sub>2</sub>O<sub>3</sub>, followed by elution with a 1:1 petroleum ether (40-60°)-ether mixture. The passage of air through a suspension of compound (II) in benzene for a day gave an orange solution, the evaporation of which gave radical (VII).

## CONCLUSIONS

1. The condensation of  $\alpha$ -hydroxylaminoketones, containing a hydroxylamino group attached to a tertiary carbon atom, with ketones and ammonia led to the formation of 1-hydroxy-2, 2, 5, 5-tetrasubstituted 3-imidazoline derivatives.
2. The oxidation of the 1-hydroxy-2, 2, 5, 5-tetrasubstituted 3-imidazolines gave stable iminoxyl radicals.

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