ISSN 1070-4280, Russian Journal of Organic Chemistry, 2011, Vol. 47, No. 6, pp. 869–876. © Pleiades Publishing, Ltd., 2011.
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Mechanism of Autoreduction of 2,2,6,6-Tetramethyl-1,4-dioxopiperidinium Cation in Alkaline Medium

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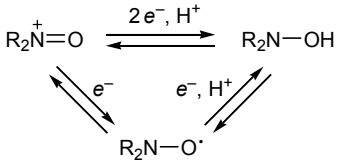
Received April 25, 2010

Abstract—Autoreduction of 2,2,6,6-tetramethyl-1,4-dioxopiperidinium ion to nitroxyl radical in alkaline medium involves a number of parallel and consecutive reactions. The primary products of the reaction of 2,2,6,6-tetramethyl-1,4-dioxopiperidinium with hydroxide ion are three nitroso compounds and *N*-hydroxy-2,2,6,6-tetramethylpiperidine *N*-oxide. Isomerization of the nitroso compounds and elimination of acetone from the *N*-oxide give cyclic hydroxylamines which reduce the initial cation to nitroxyl radical, being oxidized to nitrones.

DOI: 10.1134/S1070428011060066

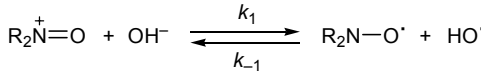
Stable nitroxyl radicals give rise to redox triad consisting of oxoammonium cation $R_2N^+=O$, nitroxyl radical $R_2N–O^{\cdot}$, and hydroxylamine $R_2N–OH$ (Scheme 1), which possesses a unique set of parameters. Properties of two-electron redox couple $R_2N^+=O/R_2N–OH$ and one-electron redox couples $R_2N^+=O/R_2N–O^{\cdot}$ and $R_2N–O^{\cdot}/R_2N–OH$ were utilized in such processes as selective oxidation of alcohols [1–5], design of chemical current sources with improved parameters [6, 7], suppression of oxidative stress in living organisms [8], and even DNA-mediated signaling by base excision repair enzymes [9]. Oxoammonium derivatives of nitroso ureas were found to exhibit a strong antitumor activity [10, 11].

Scheme 1.



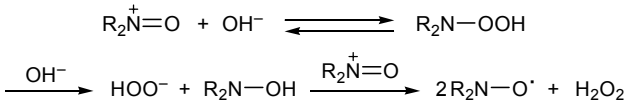
Obviously, stability of compounds in the above triad and the absence of side reactions are necessary conditions for effective utilization of their redox properties. However, even the first study on oxopiperidinium salts [12] revealed their ability to undergo autoreduction in aqueous solution, which is also typical of other strong organic oxidants [13]. Taking into account that the main products of autoreduction of oxoammonium salts are the corresponding nitroxyl radicals, it was presumed [12] that hydroxide ion acts as reducing agent in this reaction. Nevertheless, the equilibrium constant calculated from the reduction potentials of 2,2,6,6-tetramethyl-1-oxopiperidinium ion (0.75 V [14]) and hydroxyl radical $OH^{\cdot}$ (1.89 V [15]) is very small, $K_1 = k_1/k_{-1} \approx 5\times10^{-20}$ (Scheme 2).

Scheme 2.



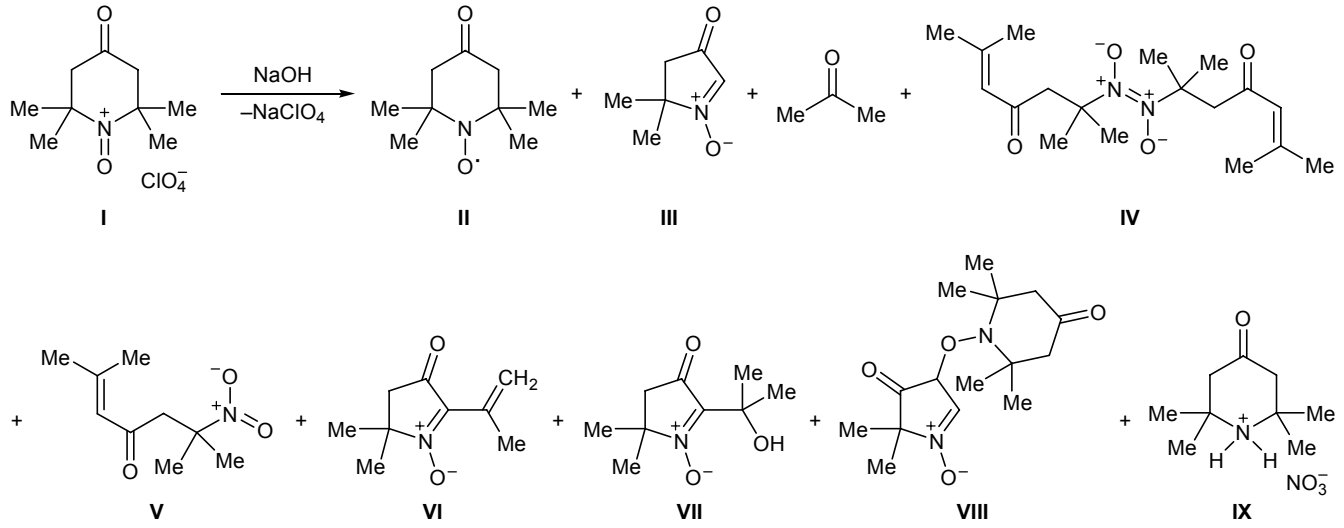
If $k_{-1} \approx 10^{10}$ l mol^{-1} s^{-1}, k_1 should be equal to $\sim5\times10^{-10}$ l mol^{-1} s^{-1}, so that the rate of direct electron transfer from OH^- to the cation will be negligibly low. An alternative mechanism implies that reduction of oxopiperidinium salts involves intermediate formation of amine hydroperoxide R_2NO_2H (Scheme 3).

Scheme 3.



The hypothesis, according to which 4-methoxy-2,2,6,6-tetramethyl-1-oxopiperidinium bromide in alkaline medium is reduced almost quantitatively to the corresponding radical while OH^- is oxidized to H_2O_2 in a high yield, was confirmed in [16]. However, we

Scheme 4.



did not observe formation of H_2O_2 and O_2 in this reaction [17]. In addition, hydrogen peroxide is known [18–20] to be very readily oxidized with oxopiperidinium ions in neutral and alkaline media; therefore, it cannot be formed as final product in reactions of oxopiperidinium salts with alkali. On the other hand, study on the kinetics and products of autoreduction of 2,2,6,6-tetramethyl-1,4-dioxopiperidinium perchlorate (**I**) in acid medium showed [21] that partial (up to ~65%) reduction of 2,2,6,6-tetramethyl-1,4-dioxopiperidinium ion to nitroxyl radical occurs with participation of fragmentation products generated from 1-hydroxy-2,2,6,6-tetramethyl-4-oxopiperidine 1-oxide which is formed in turn via reaction of the cation with water.

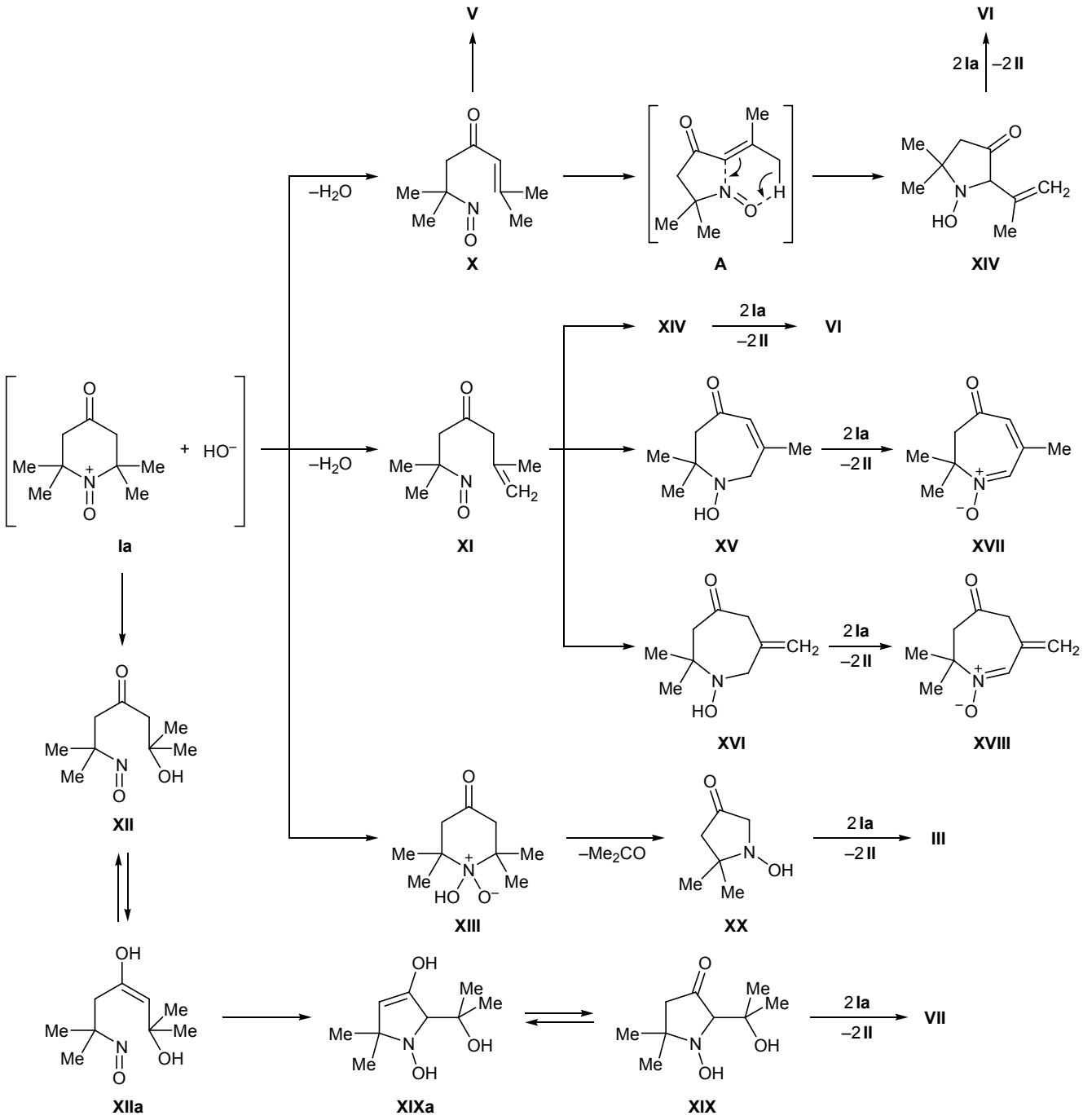
The goal of the present work was to study autoreduction of salt **I** in alkaline medium. When an aqueous suspension of perchlorate **I** was treated with an equimolar amount of alkali at ~20°C, almost complete conversion of the salt was achieved during the time necessary for its dissolution. Analysis of the resulting product mixture by HPLC showed the presence of radical **II** and ~20 more compounds some of which were isolated and identified (Scheme 4). The major products (80–86% on the initial cation) were radical **II**, dihydropyrrole *N*-oxide **III**, diazene *N*,*N*′-dioxide **IV**, and acetone (yield 41, 15, 25, and 15 mol %, respectively). Perchlorate ion is not consumed in the reaction, and it can be recovered completely in the form of $NaClO_4$ or $KClO_4$.

The formation of a complex mixture of products is the result of a number of parallel and consecutive reactions. Let us consider these reactions separately. In the first step, the following reactions are possible: (1) proton abstraction form the methylene or methyl group in cation **Ia** by the action of hydroxide ion, which leads to nitroso compounds **X** and **XI**, and (2) addition of OH^- ion to cation **Ia** with formation of nitroso compound **XII** and *N*-hydroxypiperidine *N*-oxide **XIII** (Scheme 5).

Preferential formation of nitroso compound **X** is favored by inductive effect of the carbonyl group on the methylene protons in **Ia** and by conjugation in the C=C–C=O bond sequence in molecule **X**; therefore, the amount of **X** is larger by a factor of 28 than the amount of nitroso compound **XI**. At a temperature below 50°C liquid nitroso derivative **X** is converted into colorless stable dimer **IV**. Dimer **IV** and monomer **X** in solution occur in equilibrium with each other. The equilibrium is displaced toward dimer **IV** at a temperature not exceeding 0°C, whereas monomer **X** prevails above 30°C. According to the ^1H NMR data, the equilibrium constant $K = [\mathbf{X}]^2/[\mathbf{IV}]$ in $CDCl_3$ is 1.9×10^{-3} at 0.6°C, 0.57 at 25°C, and 17.8 mol/l at 58°C.

Nitroso compound **X** is unstable both in the liquid state and in solution and is gradually converted into a mixture of products (Scheme 5). Disproportionation of **X** gives nitro compound **V**, and its isomerization leads to *N*-hydroxypyrrolidine **XIV**. The isomerization occurs through intermediate **A** and is accompanied by two-electron reduction of the nitroso group. Analogous isomerization of unsaturated nitroso compounds to cyclic hydroxylamines was reported previously [22]. *N*-Hydroxypyrrolidine **XIV** reduces two cation **Ia** species to radical **II** and is thus oxidized to dihydropyrrole *N*-oxide **VI** as final product.

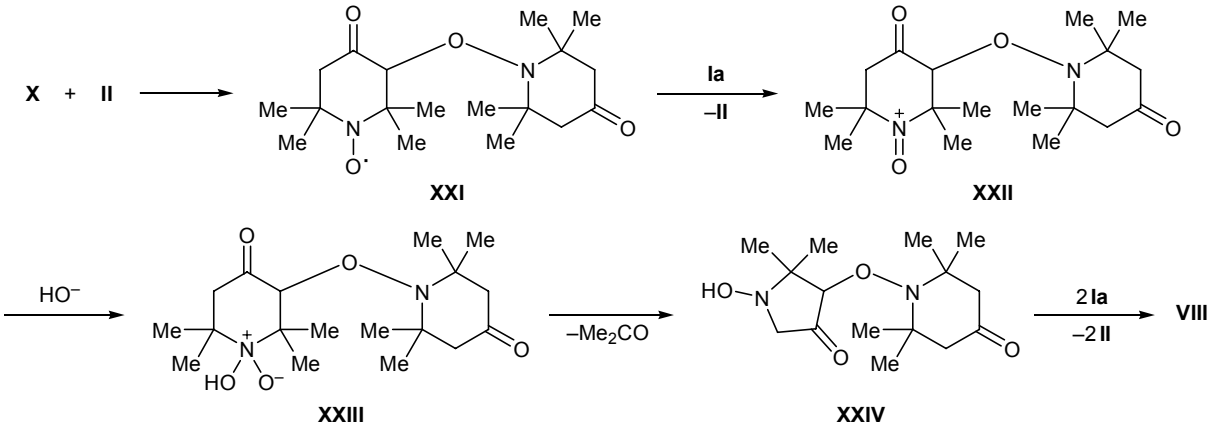
Scheme 5.



As shown previously [23], nitroso compound **XI** is unstable, and it was not isolated as individual substance. The corresponding dimer was detected by HLPC as an impurity in diazene *N*,*N*′-dioxide **IV** (see Experimental). Isomerization of **XI** can give rise to three cyclic hydroxylamines **XIV**–**XVI** which are oxidized to the corresponding cyclic nitrones **VI**, **XVII**, and **XVIII** with cation **Ia**. Among three possible isomers **VI**, **XVII**, and **XVIII**, only the former was detected; dihydropyrrole *N*-oxide **VI** can also be formed from nitroso compound **X** (see above).

Nitroso compound **XII** was not isolated from the reaction mixture, but its formation follows from the isolation of dihydropyrrole *N*-oxide **VII**. The transformation of **XII** into **VII** is likely to follow a path shown in Scheme 5. Enol tautomer of **XII** (nitroso

Scheme 6.



compound **XIIa**) undergoes isomerization into *N*-hydroxydihydropyrrole **XIX** which is oxidized with cation **Ia** to *N*-oxide **VII**. Assuming that all molecules of nitroso compound **XII** are converted into dihydropyrrole *N*-oxide **VII**, the rate of formation of **XII** should be lower by a factor of 18 than the rate of formation of nitroso compound **X**.

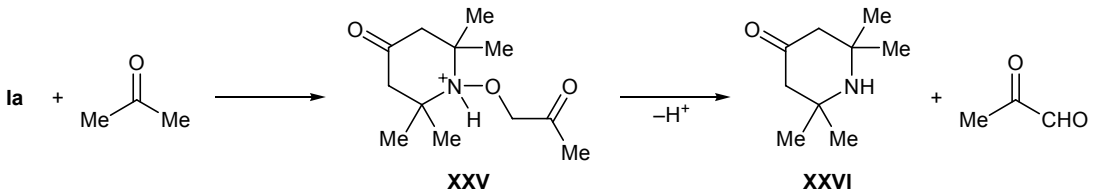
As shown previously [21], *N*-hydroxypiperidine *N*-oxide **XIII** is unstable; it decomposes into acetone and 1-hydroxy-5,5-dimethylpyrrolidin-3-one (**XX**). Oxidation of the latter with cation **Ia** yields dihydropyrrole *N*-oxide **III**. In keeping with the fraction of **III** among autoreduction products of salt **I**, the rate of its formation from **Ia** is lower by a factor of 1.7 than the rate of formation of nitroso compound **X**.

Compounds formed as a result of transformations shown in Scheme 5 may be involved in further reactions with each other. For example, *N*-oxide **VIII** is likely to be formed via reaction of nitroso compound **X** with radical **II** according to Scheme 6. Addition of radical **II** to **X** gives radical **XXI** which was obtained previously by oxidation of **II** with xenon difluoride [23]. Cation **Ia** reversibly oxidizes radical **XXI** to cation **XXII**, and addition of hydroxide ion to the latter gives *N*-oxide **XXIII**. Elimination of acetone molecule from **XXIII** produces hydroxypyrrolidine **XXIV** whose oxidation with **Ia** yields final dihydropyrrole *N*-oxide **VIII**.

As a result of complex processes, cation **Ia** is partly converted into 2,2,6,6-tetramethylpiperidin-4-one (**XXVI**) and nitrate ion. Triacetonamine **XXVI** is formed via four-electron reduction of cation **I** with acetone according to a scheme proposed previously [14, 24] (Scheme 7). Mechanism of four-electron oxidation of the oxoammonium group in **Ia** to NO_3^- ion is not clear. Presumably, precursor of NO_3^- is nitrous acid which can be formed by fragmentation of *N*-oxide **XIII**. By special experiment we found that salt **I** oxidizes $NaNO_2$ to $NaNO_3$, thus being reduced to radical **II**.

The structure of the isolated compounds was determined on the basis of their elemental compositions and ^1H and ^{13}C NMR, IR, UV, and mass spectra (see Experimental). Except for triacetonamine nitrate (**IX**) and dihydropyrrole *N*-oxide **VII**, the mass spectra of all compounds contained the corresponding molecular ion peaks. Salt **IX** displayed no molecular ion peak, but that belonging to triacetonamine, *m*/*z* 155, was present. The molecular ion of *N*-oxide **VII** is unstable and is not observed in the mass spectrum, which is typical of compounds containing a tertiary hydroxy group [25]. Elimination of methyl radical from $[M]^+$ gives fragment ion with *m*/*z* 170. In the mass spectrum of *N*-oxide **VIII**, apart from $[M]^+$ with *m*/*z* 296, ion peaks corresponding to piperidine (*m*/*z* 170) and dihydropyrrole fragments (*m*/*z* 127) were observed.

Scheme 7.



The structure of dihydropyrrole *N*-oxide **VI** was confirmed by the ^{13}C NMR spectrum recorded using DEPT 135 pulse sequence. The spectrum showed the presence of three methyl groups, two methylene groups, and four quaternary carbon atoms in molecule **VI**. Isomeric *N*-oxides **XVII** and **XVIII** were characterized by different ratios of the corresponding carbon atoms. The double C=C bond in molecule **VI** is cross-conjugated with the carbonyl and *N*-oxide moieties; therefore, it displayed in the UV spectrum two strong absorption bands with their maxima at λ 229 and 291 nm. The IR spectrum of a dilute solution of **VII** in carbon tetrachloride lacked absorption band assignable to free hydroxy group, which may be due to formation of strong intramolecular hydrogen bond between the hydroxy proton and oxygen atom of the carbonyl or *N*-oxide group. Compound **VIII** possesses an asymmetric carbon atom and is racemic. In the ^1H NMR spectrum of **VIII** recorded at a temperature below 5°C, all methyl groups and methylene protons in the piperidine fragment gave different signals.

Diazene *N*,*N*′-dioxide **IV** was assigned the structure of *trans* isomer, for its IR spectrum contained a strong absorption band at 1258 cm^{-1} (ε = 460), typical of *trans*-dimers of nitroso compounds [26]. The vinylcarbonyl fragments in nitroso compound **X**, dimer **IV**, and nitro compound **V** have *trans* configuration. This follows from the intensity of the corresponding absorption band in the UV spectra of these compounds, λ_{max} ~240 nm (ε ≈ 15000 l mol^{-1} cm^{-1}). Such intensity is typical of *trans*-vinyl ketones, while the corresponding value for *cis*-vinyl ketones is ε ≈ 8000 l× mol^{-1} cm^{-1} [27].

Thus the results of our studies on the reduction of 2,2,6,6-tetramethyl-1,4-dioxopiperidinium perchlorate (**I**) in alkaline and acid [21] media show that its autoreduction is initiated by hydroxide ion and water. These nucleophiles add to cation **Ia** with formation of *N*-oxide **XIII** and nitroso compound **XII** or abstract a proton from methylene or methyl group in **Ia** with formation of unsaturated nitroso compounds **X** and **XI**. Elimination of acetone molecule from *N*-oxide **XIII** or redox isomerization of nitroso compounds gives cyclic hydroxylamines which reduce cation **Ia** via two-electron transfer process to *N*-hydroxypiperidine [21], thus being oxidized to cyclic nitrones. The reaction of *N*-hydroxypiperidine with cation **Ia** yields radical **II**. The rate of addition of water molecule to the oxoammonium group of cation **Ia** is higher than the rate of proton abstraction by the same nucleophile. Therefore, the main process in acid medium is autoreduction through *N*-oxide **XIII**. By contrast, hydroxide ion better abstracts protons; therefore, autoreduction of **Ia** through nitroso derivatives predominates in alkaline medium. Taking into account high nucleophilicity of hydroxide ion, the rate of reactions with its participation is incomparably higher than the rate of reactions with H_2O as nucleophile. Primary products of the above reactions undergo further transformations leading to numerous products. Such autoreduction mechanism is likely to be general for all oxopiperidinium salts. Stability of the latter to autoreduction is determined by both acidity of the medium and nature of substituents therein.

EXPERIMENTAL

The IR spectra were recorded on a Specord 75 IR spectrometer. The UV spectra were measured on a Specord UV-Vis spectrophotometer. The NMR spectra were recorded from solutions in $CDCl_3$ on a Bruker A III instrument (500 MHz for ^1H). Signals in the NMR spectra were assigned using DEPT pulse sequences and by comparing with the spectra of structurally related compounds. The mass spectra (electron impact, 70 eV) were obtained on a Finnigan GC–MS system. The melting points were determined on a PHMK hot stage. HPLC analysis was performed using a Milikhrom chromatograph equipped with a 2× 64-mm column (Separon C18, 5 μm) and a UV detector (λ 200, 240, and 270 nm); eluent 50% aqueous methanol; retention volumes V_r, μl: **II**, 290; **III**, 210; **IV**, 4400; **V**, 810; **VI**, 480; **VII**, 320; **VIII**, 950; **IX**, 165; **X**, 1450; dimer of **XI**, 3070. 4-Nitrotoluene was used as internal standard for quantitative measurements (V_r = 1280 μl). Preparative separation of components was performed using a 10×250-mm column charged with Separon C18 (7 μm), an HPP-5001 pump, and an LCD-2563 UV detector (λ 254 nm); eluent 50% aqueous methanol; V_r, ml: **II**, 30; **III**, 19.2; **V**, 98.3; **VI**, 54; **VII**, 40; **VIII**, 116; **X**, 182. The amount of liberated acetone was determined by GLC on an LKhM-80 chromatograph equipped with a 3× 1500-mm column (stationary phase Separon BD-1, 100 μm; 159/175°C; carrier gas nitrogen, flow rate 30 ml/min); retention time of acetone 240 s.

2,2,6,6-Tetramethyl-1,4-dioxopiperidinium perchlorate (**I**) was synthesized from 2,2,6,6-tetramethyl-4-oxopiperidin-1-oxyl (**II**) according to the procedure described in [28] and was purified by reprecipitation from acetonitrile with diethyl ether.

Reaction of 2,2,6,6-tetramethyl-1,4-dioxopiperidinium perchlorate (I) with sodium hydroxide.

A mixture of 2.3 g (8.53 mmol) of perchlorate **I** and 90 ml of water was stirred for 4 min at ~20°C, and 90 ml of aqueous sodium hydroxide (c = 0.1 M) was added to the resulting suspension. The originally yellow mixture instantaneously turned light green, and a blue emulsion (nitroso compounds) separated. After addition of a few crystals of dimer **IV**, the emulsion solidified to colorless crystals. The mixture was stirred for ~15 min at ~20°C and was left to stand for ~3 h in a refrigerator for complete crystallization. The precipitate, 342 mg, was filtered off, washed with water, and dried. According to the HPLC data, it contained 325 mg (22.5 mol % calculated on the initial cation **Ia**) of dimer **IV**, 2 mg (0.1 mol %) of nitro compound **V**, and 11 mg (0.8 mol %) of (assumingly) nitroso compound **XI** dimer.

The aqueous phase contained (HPLC) 590 mg (40.6 mol %) of radical **II**, 33 mg (2.3 mol %) of nitroso compound **X**, 159 mg (14.7 mol %) of *N*-oxide **III**, and 72 mg (14.5 mol %) of acetone. The aqueous solution was extracted with chloroform (5×15 ml), and the extract was dried over Na_2SO_4 and evaporated under reduced pressure to obtain 1.05 g of a mixture of products as a dirty green liquid which was dissolved in 45 ml of diethyl ether. The solution was left to stand for 24 h at ~20°C, and 32 mg (1.7 mol %) of triacetonamine nitrate (**IX**) was filtered off. The filtrate was evaporated, and the residue was subjected to chromatography in a 10×250-mm column charged with Separon C18 (5 μm). A ~200-mg portion was separated at once using first 300 ml of 30% MeOH and then 50% MeOH as eluent. As a result we obtained 550 mg (38 mol %) of radical **II**, 154 mg (14 mol %) of *N*-oxide **III**, 14 mg (1 mol %) of nitroso compound **X**, 22 mg (1.5 mol %) of *N*-oxide **VI**, 8 mg (0.5 mol %) of nitro compound **V**, 32 mg (1.3 mol %) of *N*-oxide **VIII**, and 21 mg (1.4 mol %) of *N*-oxide **VII**.

2,6,6,9,9,13-Hexamethyl-7,8-diazatetradeca-2,7,12-triene-4,11-dione 7,8-dioxide (IV) (dimer of nitroso compound **X)** was formed in the reaction of salt **I** with sodium hydroxide (see above). Yield 25%, colorless plates (from aqueous acetonitrile), mp 91.5–92°C; published data: mp 86°C [29], 92°C [23]. UV spectrum (MeCN), λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 238.4 (28400), 296 (7800). IR spectrum, ν, cm^{-1} (ε, l× mol^{-1} cm^{-1}): in $CHCl_3$: 1622 (500) and 1692 (390) [C=C–C=O], 1258 (460) and 1280 (390) [O–N=N–O]; in mineral oil: 1630 and 1688 [C=C–C=O], 1249 and 1258 [O–N=N–O]. ^{1}H NMR spectrum (25°C), δ, ppm: 1.60 s (12H, CH_3), 1.86 d (6H, CH_3, J = 0.9 Hz), 2.10 d (6H, CH_3, J = 0.98 Hz), 3.26 s (4H, CH_2), 6.03 m (2H, CH). ^{13}C NMR spectrum (25°C), δ_C, ppm: 20.69 (C^1, C^{14}), 24.57 (6-CH_3, 9-CH_3), 27.72 (2-CH_3, 13-CH_3), 50.61 (C^5, C^{10}), 76.57 (C^6, C^9), 123.97 (C^3, C^{12}), 155.31 (C^2, C^{13}), 196.32 (C^4, C^{11}). Mass spectrum, m/z (I_{rel}, %): 338 (0.2) $[M]^+$, 335 (1.0), 285 (1.1), 235 (1.1), 169 (6.2) $[\mathbf{X}]^+$, 147 (2.0), 119 (1.5), 97 (2.0), 84 (5.4), 83 (100).

2,6-Dimethyl-2-nitrosohept-5-en-4-one (X) was formed upon melting of dimer **IV**. Light blue liquid. UV spectrum (MeCN), λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 240 (15400), 322 (72), 670 (26). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1621 and 1688 (C=C–C=O), 1566 (N=O). ^{1}H NMR spectrum (58°C), δ, ppm: 1.26 s (6H, CH_3), 1.86 d (3H, CH_3, J = 0.9 Hz), 2.08 d (3H, CH_3, J = 0.8 Hz), 3.00 s (2H, CH_2), 6.00 m (1H, CH). ^{13}C NMR spectrum (58°C), δ_C, ppm: 20.70 (C^7), 21.42 (C^1, 2-CH_3), 27.57 (6-CH_3), 50.31 (C^3), 96.92 (C^2), 124.0 (C^5), 155.95 (C^6), 197.10 (C^4).

2,6-Dimethyl-2-nitrohept-5-en-4-one (V). Dimer **IV**, 169 mg, was dissolved on heating in 10 ml of acetonitrile, and the light blue solution was left to stand for 3 days at 36°C. The solution was evaporated, and the residue was passed through a 30×50-mm chromatographic column charged with silica gel L (63–70 μm) using chloroform–hexane (1:4) as eluent to remove tars. A fraction containing nitro compound **V** was collected. It was evaporated to obtain 80 mg of a mixture of nitro and nitroso compounds. The mixture was subjected to chromatography on a 10×250-mm column (Silasorb 600, 7 μm; chloroform–hexane, 1:4); V_r 21 ml (**X**), 30 ml (**V**). As a result, we isolated 42 mg of nitro compound **V** as colorless crystals with mp 40–40.5°C. UV spectrum (MeCN), λ_{max}, nm (ε, l× mol^{-1} cm^{-1}): 240 (15000), 317 (64). IR spectrum ($CHCl_3$), ν, cm^{-1}: 1696, 1628 (C=C–C=O); 1550, 1366 (NO_2). ^{1}H NMR spectrum, δ, ppm: 1.67 s (6H, CH_3), 1.90 d (3H, CH_3, J = 1.15 Hz), 2.13 d (3H, CH_3, J = 1.1 Hz), 3.09 s (2H, CH_2), 6.02 m (1H, CH). ^{13}C NMR spectrum, δ_C, ppm: 20.9 (C^7), 26.5 (C^1, 2-CH_3), 27.8 (6-CH_3), 52.2 (C^3), 85.1 (C^2), 123.2 (C^5), 157.8 (C^6), 195.1 (C^4). Mass spectrum, m/z (I_{rel}, %): 185 (0.8) $[M]^+$, 149 (0.5), 138 (1.9), 123 (1.6), 110 (4.9), 83 (100). Found, %: C 58.15; H 8.25; N 7.49. $C_9H_{15}NO_3$. Calculated, %: C 58.36; H 8.16; N 7.56. M 185.

Nitro compound **V** formed in the reaction of salt **I** with NaOH (see above) was identical in the melting point and spectral parameters to a sample of **V** synthesized from dimer **IV** as described above.

2,2,6,6-Tetramethyl-4-oxopiperidinium nitrate (IX). Triacetonamine **XXVI**, 1 g, was dissolved in

4 ml of water, and the solution was neutralized with dilute (1:4) nitric acid. The mixture was evaporated to dryness under reduced pressure, and the residue was recrystallized from acetonitrile. Yield 1.12 g (80%), colorless crystals; the product sublimes above 150°C and decomposes without meting above 200°C. UV spectrum (H_2O), λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 200 (12300), 278 sh (19). IR spectrum (mineral oil), ν, cm^{-1}: 2300–2800 (N^+–H), 1731 (C=O), 1595 (δNH_2), 1376, 826, 712 (NO_3). ^{1}H NMR spectrum, δ, ppm: 1.59 s (12H, CH_3), 2.75 s (4H, CH_2), 8.93 s (2H, NH_2). ^{13}C NMR spectrum, δ_C, ppm: 28.23 (CH_3), 50.46 (C^3, C^5), 60.53 (C^2, C^6), 202.86 (C^4). Mass spectrum, *m*/*z* (I_{rel}, %): 155 (3.2) [**XXVI**]$^+$, 140 (48.1), 112 (3.9), 98 (15.9), 83 (60.4), 58 (80.5), 56 (15.0), 55 (23.9), 46 (32.4), 42 (100). Found, %: C 49.26; H 8.17; N 12.57. $C_9H_{17}NO\cdot HNO_3$. Calculated, %: C 49.53; H 8.31; N 12.84. *M* 218.

Salt **IX** formed in the reaction of salt **I** with NaOH (see above), was identical in the melting point and spectral parameters to a sample of **IX** synthesized from compound **XXVI**.

5,5-Dimethyl-4,5-dihydro-3*H*-pyrrol-3-one 1-oxide (III) was formed in the reaction of salt **I** with NaOH (see above). Yield 14%, colorless crystals, mp 42°C (from hexane); published data [21]: mp 41–42°C. ^{1}H NMR spectrum, δ, ppm: 1.58 s (6H, CH_3), 2.82 s (2H, CH_2), 7.08 s (1H, CH). ^{13}C NMR spectrum, δ_C, ppm: 26.56 (CH_3), 48.74 (C^4), 75.58 (C^5), 131.89 (C^2), 195.69 (C^3).

5,5-Dimethyl-2-(prop-1-en-2-yl)-4,5-dihydro-3*H*-pyrrol-3-one 1-oxide (VI) was formed in the reaction of salt **I** with NaOH (see above). Yield 1.5%, colorless crystals, mp 53°C (from hexane). UV spectrum (MeCN), λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 229 (14000), 291.4 (10700). IR spectrum (CCl_4), ν, cm^{-1} (ε, l× mol^{-1} cm^{-1}): 1711 (540) (C=O), 1597 (15) (C=C), 1519 (360) (C=N–O). ^{1}H NMR spectrum, δ, ppm: 1.56 s (6H, CH_3), 2.15 d.d (3H, CH_3, *J* = 0.9, 1.55 Hz), 2.75 s (2H, CH_2), 5.51 m (1H, CH, *J* = 1.55, 1.7 Hz), 6.31 m (1H, CH, *J* = 0.9, 1.7 Hz). ^{13}C NMR spectrum, δ_C, ppm: 20.38 ($C^{3'}$), 26.77 (CH_3), 47.64 (C^4), 72.67 (C^5), 122.76 ($C^{1'}$), 130.51 ($C^{2'}$), 139.30 (C^2), 195.51 (C^3). Mass spectrum, *m*/*z* (I_{rel}, %): 167 (38.8) $[M]^+$, 152 (21.4) $[M - CH_3]^+$, 150 (3.5) $[M - OH]^+$, 111 (10.1), 83 (100). Found, %: C 64.73; H 7.71; N 8.21. $C_9H_{13}NO_2$. Calculated, %: C 64.65; H 7.84; N 8.38. *M* 167.

2-(1-Hydroxy-1-methylethyl)-5,5-dimethyl-4,5-dihydro-3*H*-pyrrol-3-one 1-oxide (VII) was formed in the reaction of salt **I** with NaOH (see above). Yield 1.4%, colorless crystals, mp 49–50°C (from hexane). UV spectrum (H_2O), λ_{max}, nm (ε, l mol^{-1} cm^{-1}): 271.6 (17300), 334 sh (75). IR spectrum (CCl_4), ν, cm^{-1} (ε, l mol^{-1} cm^{-1}): 3431 (OH), 1714 (430) (C=O), 1537 (380) (C=N–O). ^{1}H NMR spectrum, δ, ppm: 1.53 s (6H, CH_3), 1.55 s (6H, CH_3), 2.73 s (2H, CH_2), 5.62 s (1H, OH). ^{13}C NMR spectrum, δ_C, ppm: 25.95 ($C^{1'}$, $C^{3'}$), 26.44 (5-CH_3), 47.90 (C^4), 70.03 ($C^{2'}$), 73.17 (C^5), 145.73 (C^2), 194.25 (C^3). Mass spectrum, *m*/*z* (I_{rel}, %): 170 (70) $[M - CH_3]^+$, 142 (53) $[M - CH_3 - CO]^+$, 114 (12), 99 (8), 86 (42), 83 (78), 72 (9), 59 (86), 55 (50), 43 (100). Found, %: C 58.11; H 8.43; N 7.64; O 25.77. $C_9H_{15}NO_3$. Calculated, %: C 58.36; H 8.16; N 7.56; O 25.91. *M* 185.

2,2-Dimethyl-4-(2,2,6,6-tetramethyl-4-oxopiperidin-1-yloxy)-3,4-dihydro-2*H*-pyrrol-3-one 1-oxide (VIII) was formed in the reaction of salt **I** with NaOH (see above). Yield 1.3%, colorless crystals, mp 104°C (from hexane). UV spectrum (MeCN): λ_{max} 275.6 nm (ε = 20000 l mol^{-1} cm^{-1}). IR spectrum ($CHCl_3$), ν, cm^{-1} (ε, l mol^{-1} cm^{-1}): 3123 (=C–H), 1719 (790) (C=O), 1548 (1380) (C=N–O). ^{1}H NMR spectrum (–5°C), δ, ppm: 1.13 s, 1.15 s, 1.24 s, and 1.43 s (3H each, 2′-CH_3, 6′-CH_3); 1.59 s and 1.61 s (3H each, 2-CH_3), 2.18 m and 2.21 m (1H each, 3′-H, 5′-H); 2.66 d (1H, 3′-H or 5′-H, *J* = 13.3 Hz); 2.76 d (1H, 5′-H or 3′-H, *J* = 13.5 Hz), 4.47 s (1H, 4-H), 7.11 s (1H, 5-H). ^{13}C NMR spectrum (24°C), δ_C, ppm: 19.02 (CH_3), 26.90 (CH_3), 53.55 ($C^{3'}$, $C^{5'}$), 77.23 (C^2), 79.26 ($C^{2'}$, $C^{6'}$), 85.89 (C^4), 130.55 (C^5), 194.47 (C^3), 207.09 ($C^{4'}$) (primed numbers refer to the piperidine ring). Mass spectrum, *m*/*z* (I_{rel}, %): 296 (1.7) $[M]^+$, 281 (3.4) $[M - CH_3]^+$, 199 (3.2), 170 (22.7) $[C_9H_{16}NO]^+$, 127 (7.7) $[C_6H_9NO_2]^+$, 115 (6.3), 114 (100). Found, %: C 60.92; H 8.27; N 9.27. $C_{15}H_{24}N_2O_4$. Calculated, %: C 60.79; H 8.16; N 9.45. *M* 296.

The authors thank A.V. Chernyak for recording the NMR spectra.

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