

# Reaction of Nitrosonium Tetrafluoroborate with Nitroxyl Radicals

G. I. Borodkin, I. R. Elanov, M. M. Shakirov, and V. G. Shubin

Vorozhtsov Novosibirsk Institute of Organic Chemistry, Siberian Division, Russian Academy of Sciences, Novosibirsk, 630090 Russia; e-mail: gibor@nioch.nsc.ru

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**Abstract**—It was established by means of multinuclear magnetic resonance method ( $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  and  $^{14}\text{N}$ ) that reaction of 2,2,6,6-tetramethyl-4-R-piperidin-1-oxyl radicals (R = H, OH, OMe, OCOPh, NHCOMe) with nitrosonium tetrafluoroborate gave rise to the corresponding 2,2,6,6-tetramethyl-1-oxo-4-R-piperidinium tetrafluoroborates. Linear correlations were found between the chemical shifts of atoms  $\text{H}^4$ ,  $\text{C}^4$  of cations and respectively  $\sigma_1$ -constants of substituents R and chemical shifts of  $\text{C}^4$  atom calculated from increments of substitution. The conformational features of the generated nitrosonium cations are considered on the grounds of vicinal coupling constants  $J_{\text{HH}}$  and quantum-chemical calculations by AM1 method.

Dialkyloxoammonium (nitrosonium) salts are extensively used in various fields of organic chemistry as oxidants for alcohols [1–13], phenols [2, 14–16], diols [3, 4, 8, 11, 13], ketones [1, 2, 15, 17], amines [2, 15, 16, 18, 19] and N-heterocyclic compounds [2, 16, 20], as active reagents in ketones addition at the oxygen of the oxoammonium group [1, 2, 21], for termination of the cationic polymerization of olefins [22] etc. [14]. Although the oxoammonium ions are very reactive they are highly selective with respect to substrates. For instance, 2,2,6,6-tetramethyl-1-oxopiperidinium ion readily reacts with alcohols [2, 7, 8, 10, 13], phenols [14–16], ketones [2, 15, 17], amines [2, 15, 16, 18, 19], N-heterocyclic compounds [2, 16, 20], and anionic  $\sigma$ -complexes [23], but does not react with ethers, sulfides, sulfones, aldehydes, and olefins [15, 18].

One of the principal methods of oxoammonium ions generation is oxidation of nitroxyl radicals [1, 2, 24, 25]. Taking into consideration that the oxidative potential of the nitroxyl radicals is very high [34, 26–28], their oxidation requires relatively strong oxidants. As oxidants were used molecular chlorine [1, 2, 24, 25, 29, 30], bromine [1, 2, 24, 25, 29, 31, 32],  $\text{NO}_2$  [1, 2, 24, 33],  $\text{ClO}_2$  [34, 35],  $\text{HOCl}$  [36],  $\text{FCIO}_3$  [37, 38],  $\text{XeF}_2$  [2, 24, 39],  $\text{SbCl}_5$  [1, 2, 24, 25, 40–42],  $\text{TiCl}_4$  [1, 2, 43],  $\text{VOCl}_3$ ,  $\text{NbCl}_5$  [43],  $\text{SnBr}_4$  [1, 2, 44],  $\text{SnCl}_4$  [2, 44],  $\text{SnMe}_2\text{Cl}_2$  [2, 44],  $\text{SnPhCl}_3$  [44],  $\text{PdCl}_2$  [2, 45],  $\text{PbO}_2$  [2, 29, 46],  $\text{Cu}(\text{ClO}_4)_2$  [46],  $\text{Ph}_3\text{C}^+\text{ClO}_4^-$  [1, 24, 25, 47],  $\text{Ph}_3\text{C}^+\text{SbCl}_6^-$  [2, 25, 47]. A fair part of these oxidants are gases. Such oxidants are difficult for dosage. In some cases the oxidant should be used in

excess. For instance, whereas the reaction of nitroxyl radicals with chlorine affords oxopiperidinium chlorides [29, 30] and consequently the reaction is carried out with equimolar amounts of the radical and the oxidant, at the use of bromine as a one-electron oxidant arise the corresponding tribromides, and the oxidant is required in excess [31, 32]. An excess of oxidant is also necessary at the use of  $\text{SbCl}_5$  [41]. Thus at a little excess of  $\text{SbCl}_5$  it is impossible to obtain 2,2,5,5-tetramethyl-3-carbamino-1-oxopyrrolidinium hexachloroantimonate, but at the use of  $\text{SbCl}_5$  in a large excess the oxidation occurs readily [25, 41]. The oxidation of radicals from the isoindoline series proceeds in a similar way [42]. A vigorous reaction occurs between nitroxyl radicals and salts of triphenylmethyl cation, but in this case the presence of oxygen is necessary to shift the equilibrium toward formation of the nitrosonium salt: Oxygen reacts with arising triphenylmethyl radical [47]. Among the preparation methods of nitrosonium salts a disproportionation of nitroxyl radicals in acid medium should be mentioned [1, 2, 24, 48]. However here alongside the nitrosonium salt forms hydroxylamine salt. At the use of  $\text{TiCl}_4$  as oxidant for 2,2,6,6-tetramethylpiperidin-1-oxyl radical alongside 2,2,6,6-tetramethyl-1-oxopiperidinium hexachlorotitanate a side product, 2,2,6,6-tetramethylpiperidinoxotitanium trichloride, is obtained [43].  $\text{XeF}_2$  is an efficient oxidant for nitroxyl radicals [39] but it is highly poisonous and expensive.

The target of the present study was an attempt to apply nitrosonium tetrafluoroborate as a convenient and promising oxidant of nitroxyl radicals. To the

**Table 1.**  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra from tetrafluoroborates of ions **IIa-e** in  $\text{CD}_3\text{CN}$  at  $\sim 20^\circ\text{C}$ 

Compd. no.	R	Molar ratio (I): $\text{NO}^+\text{BF}_4^-$	Chemical shifts, $\delta$ , ppm, and coupling constants, Hz (in parentheses) <sup>a</sup>					
			$\text{CH}_3$	$\text{H}^{3,5}$ ( <i>a</i> ) <sup>b</sup>	$\text{H}^{3,5}$ ( <i>e</i> ) <sup>b</sup>	$\text{H}^4$	R	$\text{BF}_4^-$
<b>IIa</b>	H	1:1.02	1.66 s	2.45–2.56 m	2.45–2.56 m	2.31–2.56 m	2.31–2.56 m	149.17
<b>IIb</b>	OH	1:1.15	1.69 s, 1.74 s	2.56 d.d (-14.3, 7.7)	2.79 d.d (-14.3, 4.3)	4.79 t.t (7.7, 4.3)	3.9 br. (OH)	149.38
<b>IIc</b>	OMe	1:1.2	1.68 s, 1.73 s	2.66 d.d (-14.7, 6.6)	2.81 d.d (-14.7, 4.5)	4.29 t.t (6.6, 4.5)	3.46 s (OCH <sub>3</sub> )	149.53
<b>II d</b>	OCOPh	1:1.2	1.77 s, 1.80 s	2.91 d.d (-15.1, 7.3)	3.09 d.d (-15.1, 5.5)	6.00 t.t (7.3, 5.5)	7.53 t (7.5) 7.67 t (7.3) 8.07 d (7.3)	149.30
<b>IIe</b>	NHCOMe	1:1.01	1.52 s, 1.90 s <sup>b</sup>	2.52 d.d (-14.1, 11.9)	2.73 d.d (-14.1, 4.3)	5.09 m (11.9, 7.2, 4.3)	1.97 s <sup>b</sup> (CH <sub>3</sub> ) 6.99 br. (NH, 7.2)	149.30
<b>IIe<sup>c</sup></b>	NHCOMe	1:1.01	1.43 s, 1.90 s <sup>b</sup>	2.43 d.d (-13.9, 12.5)	2.66 d.d (-13.9, 4.1)	5.11 m (12.5, 7.0, 4.1)	1.98 s <sup>b</sup> (CH <sub>3</sub> ) 7.36 br. (NH, 7.0)	
<b>IIe<sup>d</sup></b>	NHCOMe	1:1.01	1.40 s, 1.82 s <sup>b</sup>	2.46 d.d (-16.2, 12.7)	2.59 d.d (-16.2, 4.4)	5.1 m, br. (12.7, 4.4)	1.98 s <sup>b</sup> (CH <sub>3</sub> ) 7.6 br. (NH)	

<sup>a</sup> Chemical shifts of  $^1\text{H}$  and  $^{19}\text{F}$  are given in ppm from TMS and  $\text{CFCl}_3$  [recalculated with respect to internal references  $\text{CH}_3\text{CN}$  ( $\delta$  1.93) and  $\text{C}_6\text{F}_6$  (162.9 ppm)]. The chemical shifts values of  $^1\text{H}$  and coupling constants were obtained by comparison of calculated and experimental spectra. The values of the geminal constants are negative.

<sup>b</sup> The chemical shift values should probably be reversed.

<sup>c</sup> At  $-50^\circ\text{C}$ .

<sup>d</sup> Temperature  $-80^\circ\text{C}$ , solvent  $\text{CD}_3\text{CN}-\text{CD}_2\text{Cl}_2$ , 1:1 by volume. No multiplicity was observed in the signals of CH and NH groups.

best of our knowledge up till now this oxidant was used in a single instance with a highly strained substrate, nitronylnitroxide radical 2-(4-hydroxy-3,5-di-*tert*-butyl-phenyl)-4,4,5,5-tetramethyl-1*H*-4,5-dihydroimidazol-1-oxyl-3-oxide [46]. As substrates subjected to oxidation we selected 2,2,6,6-tetramethyl-4-*R*-piperidin-1-oxyl radicals (**Ia-e**) with versatile substituents ( $\text{R} = \text{H}, \text{OH}, \text{OMe}, \text{OCOPh}, \text{NHCOMe}$ ), among them also those prone to oxidation.

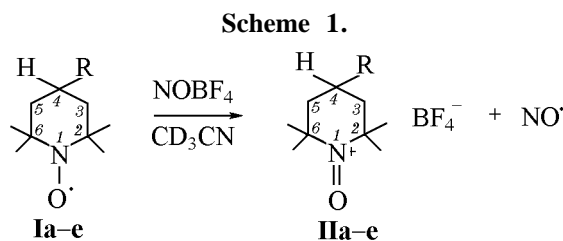
Nitroxyl radicals **Ia-e** in reaction with the salt  $\text{NO}^+\text{BF}_4^-$  in  $\text{CD}_3\text{CN}$  at room temperature were completely converted into the corresponding

2,2,6,6-tetramethyl-1-oxo-4-*R*-piperidinium tetrafluoroborates **IIa-e** (Scheme 1).

The structure of the latter compounds was confirmed by NMR spectra on  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{19}\text{F}$  and  $^{14}\text{N}$  nuclei (Tables 1 and 2).

In the  $^{14}\text{N}$  NMR spectra of ions **IIa, d, e** a relatively wide signal is observed located close to the position of 1-hydroxypyridinium cation ( $-135.7$  ppm) [49] indicating a significant share of the positive charge on the nitrogen of these cations.

In the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of cations **IIb-e** two sets of signals from protons of methyl and methylene groups and also from methyl group carbons are observed due to different magnetic influence of groups *R* on these atoms (Tables 1, 2) (cf. [31, 44, 45, 47, 48]). It was established by X-ray diffraction analysis [50] that cation **IIa** had a form of twisted *boat* (*twist*-form), and the degree of the *boat* twisting is rather high. Our quantum-chemical cal-



\* Note that in [48] the signal of atom  $\text{N}^1$  in the  $^{15}\text{N}$  NMR spectrum of cation **II d** was not observed.

**Table 2.** NMR spectra from ions **IIa–e** in CD<sub>3</sub>CN (<sup>13</sup>C) and sulfolane (<sup>14</sup>N) at ~20°C<sup>a</sup>

Compd. no.	R	Molar ratio (I):NO <sup>+</sup> BF <sub>4</sub> <sup>-</sup>	Chemical shifts, δ <sub>C</sub> , ppm <sup>a</sup>					δ <sub>N</sub> (N <sup>I</sup> )
			CH <sub>3</sub>	C <sup>2,6</sup>	C <sup>3,5</sup>	C <sup>4</sup>	R	
<b>IIa</b>	H	1:1.02	29.44	105.02	41.30	16.85	–	–136 <sub>b</sub>
<b>IIb</b>	OH	1:1.15	30.67, 31.32	103.34	46.94	61.18	–	–
<b>IIc</b>	OMe	1:1.2	30.66, 30.78	103.14	43.29	70.53	56.93	–
<b>IId</b>	OCOPh	1:1.2	29.98, 30.37	102.49	42.42	64.64	130.50 (C <sup>1</sup> ), 129.70 (C <sup>2</sup> ) <sup>c</sup> , 130.39 (C <sup>3</sup> ) <sup>c</sup> , 134.57 (C <sup>4</sup> ) <sup>c</sup> , 166.28 (CO)	–137
<b>IIe</b>	NHCOMe	1:1.01	28.58, 31.38	103.88	44.48	40.18	22.70 (CH <sub>3</sub> ), 171.88 (CO)	–137

<sup>a</sup> Chemical shifts of <sup>13</sup>C are given in ppm from TMS [recalculated with respect to internal reference CD<sub>3</sub>CN (δ 118.2 ppm)]. Chemical shifts of <sup>14</sup>N are given in ppm from external reference CH<sub>3</sub>NO<sub>2</sub> (δ<sub>N</sub>, 0.0 ppm). The negative value of δ<sub>N</sub> means that the signal of <sup>14</sup>N is upfield from the reference.

<sup>b</sup> We failed to observe the signal of <sup>14</sup>N apparently due to the presence of little quantity of the initial nitroxyl radical that was in an equilibrium with the nitrosonium cation.

<sup>c</sup> The chemical shift values should probably be reversed.

**Table 3.** Values of bond lengths (*l*), of bond (φ) and torsional (ω) angles optimized by AM1 method for structures **IIa–e** and calculated mean vicinal coupling constants (*J*<sub>HH</sub>)<sup>a</sup>

Ca-tion	NO	<i>l</i> (Å)			φ, deg	ω, deg				<i>J</i> <sub>calc</sub> , Hz <sup>a</sup>
		NC <sup>2</sup> (NC <sup>6</sup> )	C <sup>2</sup> C <sup>3</sup> (C <sup>5</sup> C <sup>6</sup> )	C <sup>3</sup> C <sup>4</sup> (C <sup>4</sup> C <sup>5</sup> )		H <sup>4</sup> C <sup>4</sup> C <sup>3</sup> H <sup>e</sup>	H <sup>4</sup> C <sup>4</sup> C <sup>3</sup> H <sup>a</sup>	H <sup>4</sup> C <sup>4</sup> C <sup>5</sup> H <sup>e</sup>	H <sup>4</sup> C <sup>4</sup> C <sup>5</sup> H <sup>a</sup>	
<b>IIa</b>	1.163	1.540	1.532	1.511	119.3	25.4	142.0	–89.0	27.7	
		1.540	1.531	1.511						
<b>IIb</b>	1.163	1.538	1.529	1.528	119.4	18.9	135.2	–83.8	33.1	9.1, 4.9
		1.541	1.529	1.524						
<b>IIc</b>	1.163	1.539	1.528	1.526	119.6	25.2	141.4	–89.4	27.3	9.1, 5.4
		1.541	1.529	1.524						
<b>IId</b>	1.163	1.541	1.525	1.524	119.7	23.7	139.1	–87.6	29.0	9.1, 5.2
		1.541	1.530	1.521						
<b>IIe</b>	1.163	1.542	1.526	1.542	118.9	31.4	147.1	–92.9	22.9	9.0, 6.0
		1.538	1.530	1.533						

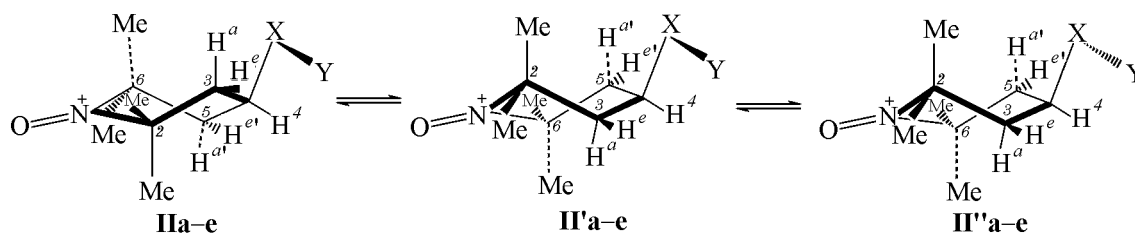
<sup>a</sup> Vicinal coupling constants are calculated by the formula:  $J^{\text{vic}} = 7 - \cos \omega + 5 \cos 2\omega$  [51]. The values of constants are averaged accounting for exchange of proton states  $H^a \rightleftharpoons H^{e'}$ ,  $H^{a'} \rightleftharpoons H^e$  (see Scheme 2).

culations by AM1 method carried out for cations **IIa–e** also suggest the existence of these cations in solution in the *twist*-form, and the cation skeletons have close geometrical parameters. Judging from the <sup>1</sup>H NMR spectra in solutions occurs fast inversion of cations **IIa–e**  $\rightleftharpoons$  **II' a–e** involving rotation of the R (CXY) group; therewith the hydrogen atoms H<sup>3</sup>, H<sup>5</sup> from the pseudoaxial position go into the pseudo-

equatorial one and *vice versa* ( $H^a \rightleftharpoons H^{e'}$ ,  $H^{a'} \rightleftharpoons H^e$ ) (Scheme 2) (cf. [50]).

Note the similarity of vicinal coupling constants values of protons H<sup>3</sup>, H<sup>5</sup> with proton H<sup>4</sup> that evidences the stereochemical uniformity of cations **IIb–e**. The values of these vicinal constants calculated by Karplus formula [51] are listed in Table 3, and

Scheme 2.



they mostly are consistent with the experimental values  $J_{\text{exp}}$  (Table 1)\*.

The difference in values  $J_{\text{calc}}$  and  $J_{\text{exp}}$  observed for cation **IIe** is apparently caused by the difference in the electronegativity of groups OR and NHCOMe. The vicinal coupling constants are known to be affected by the electronegativity of a substituent  $\chi$  [51], and at its decrease the value of the constant  $J^{\text{vic}}$  grows. Comparison of  $\chi$  value of NHCOMe group (3.034) [52] with the  $\gamma$  values of the groups of OR type  $\{\chi(\text{OH}) 3.494, \chi(\text{OMe}) 3.543, \chi(\text{OCOMe}^{**}) 3.510\}$  [52] indicates that the constant  $J^{\text{vic}}$  for R = NHCOMe should be greater.

It is seen from the  $^1\text{H}$  NMR spectra of cation **IIe** that the inversion shown on Scheme 2 is not frozen even at  $-80^\circ\text{C}$  in the solvent  $\text{CD}_3\text{CN}-\text{CD}_2\text{Cl}_2$  revealing the very high rate of inversion *boat*  $\rightleftharpoons$  *boat* in the nitrosonium cations of **II** type. No significant changes in the values of the vicinal coupling constants of protons  $\text{H}^3$  and  $\text{H}^5$  with proton  $\text{H}^4$  occurred at low temperature (Table 1) indicating that the conformation of the cation remained the same.

The alcohols and amides are known to afford with nitrosonium cation nitrites and nitrosoamides respectively [56]. However oxidation of radicals **Ib**, **e** with nitrosonium tetrafluoroborate at equimolar amounts of reagents almost did not affect the functional OH and NHCOMe groups. It is evidenced by the presence in the  $^1\text{H}$  NMR spectra of signals from OH and NHCOMe groups of an appropriate integral

\* According to quantum-chemical calculations by AMI method in the *chair* conformation of ions **IIb-e** the substituent R is located predominantly in equatorial position, and therewith the vicinal constants  $J[\text{H}^4-\text{H}^{3e(5e)}]$  calculated by Karplus formula (see note to Table 3) amount to 3.2–3.3 and 5.4 Hz. For cation **IIe** more favorable is the *chair* conformation with an axial position of NHCOMe substituent, and the calculated vicinal constants  $J[\text{H}^4-\text{H}^{3e(5e)}]$  equal to 3.4 and 13.0 Hz.

\*\* To the best of our knowledge the  $\chi$  value for OCOPh group is lacking in the literature [52–55].

intensity and also by linear correlations that we revealed between the chemical shift values of  $\text{H}^4$  proton ( $\delta_{\text{H}^4}$ ) and  $\sigma_{\text{F}}$ -constants of substituents R [57]:

$$\delta_{\text{H}^4} = (2.51 \pm 0.42) + (8.0 \pm 1.5)\sigma_{\text{F}}, \quad r \ 0.953, \quad s \ 0.5, \quad n \ 5$$

This is additionally confirmed by correlation existing between experimental values of the chemical shifts of  $\text{C}^4$  atom and the shifts calculated using the increments of R substituents determined for 1-R-cyclohexanes [58]\*:

$$\delta_{\text{C}^4}^{\text{exp}} = (-2.31 \pm 0.76) + (1.13 \pm 0.02)\delta_{\text{C}^4}^{\text{cal}}, \\ r \ 0.9997, \quad s \ 0.6, \quad n \ 5$$

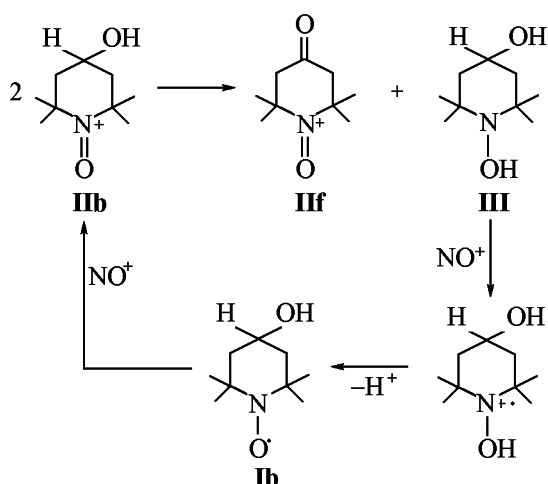
These data show that the nitroxyl radicals are faster oxidized with  $\text{NO}^+$  cation providing the corresponding **IIa-e** ions than this cation might react with the functional groups OH and NHCOMe (cf. [56]).

At increased ratio  $\text{NO}^+ \text{BF}_4^-$ -radical **Ib** from 1.2:1 to 1.5:1 or 2:1 and after keeping the solution for 24 h in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra appear signals corresponding to 2,2,6,6-tetramethyl-1,4-dioxopiperidinium cation **IIIf**:  $\{^1\text{H}$  NMR spectrum ( $\text{CD}_3\text{CN}$ ),  $\delta$ , ppm: 1.75 s ( $\text{CH}_3$ ), 3.53 s ( $\text{CH}_2$ );  $^{13}\text{C}$  NMR spectrum ( $\text{CD}_3\text{CN}$ ),  $\delta$ , ppm: 29.53 ( $\text{CH}_3$ ), 101.43 ( $\text{C}^{2,6}$ ) 49.36 ( $\text{C}^{3,5}$ ), 198.29 (CO) (cf. [31])\}. Taking into account the data of [7] the presumable mechanism of this conversion may be represented by Scheme 3. It follows from the scheme that the excess of salt  $\text{NO}^+ \text{BF}_4^-$  is necessary for oxidation of arising 1-hydroxypiperidine (**III**) and nitroxyl radical **Ib**.

The ratio of cations **IIb:IIIf** within 24 h attains a value of  $\sim 4:1$  and grows further apparently because of subsequent transformations of cation **IIIf**. Note that in the absence of excess  $\text{NO}^+ \text{BF}_4^-$  no cation **IIIf** was

\* The increment value for substituent NHCOMe ( $\Delta\delta$  20.96 ppm) we obtained by comparison of the chemical shifts of the  $\text{C}^1$  atom in 1-acetylamino-cyclohexane ( $\text{CDCl}_3$ ,  $\delta_{\text{C}^1}^1$  47.96) and in cyclohexane ( $\text{CDCl}_3$ ,  $\delta_{\text{C}^1}^4$  27.0 ppm [58]).

Scheme 3.



detected even at heating the solution of ion **IIIb** tetrafluoroborate in MeCN for 3 h at 70°C.

Judging from the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of solution obtained at the ratio **Ie** :  $\text{NO}^+ \text{BF}_4^-$  of 1:10 after keeping the mixture for 24 h forms ion **IV** [ $^1\text{H}$  NMR spectrum ( $\text{CD}_3\text{CN}$ ),  $\delta$ , ppm: 1.68 s, 1.74 s ( $\text{CH}_3$ ), 3.12 d.d ( $J$  4.5 and 1.4 Hz) ( $\text{CH}_2$ ), 6.13 d.t (10.3 and 1.4 Hz), 6.27 d.t ( $J$  10.3 and 4.5 Hz) ( $\text{CH}$ );  $^{13}\text{C}$  NMR spectrum ( $\text{CD}_3\text{CN}$ ),  $\delta$ , ppm: 27.46, 30.70 ( $\text{CH}_3$ ), 39.35 ( $\text{CH}_2$ ), 124.00, 130.24 ( $\text{CH}$ )]\*. The ratio of ions **IIIe**:**IV** was ~10:1. The presumable mechanisms of ion **IV** formation are presented in Scheme 4.

Thus nitrosonium tetrafluoroborate is efficient oxidant for nitroxyl radicals; therewith if the initial

radicals contain groups capable to react with nitrosonium cation the resulting oxoammonium salts have a structure unlike that of the initial nitroxyl radical.

## EXPERIMENTAL

NMR spectra were registered on spectrometers Bruker WP-200-SY, AC-200, AM-400 ( $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$ ), and DRX-500 ( $^{14}\text{N}$ ). As internal references for registering  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{19}\text{F}$  NMR spectra were used  $\text{CD}_3\text{CN}$  ( $\delta_{\text{H}}$  1.93,  $\delta_{\text{C}}$  118.2 ppm) and  $\text{C}_6\text{F}_6$  ( $\delta_{\text{F}}$  162.9 ppm), and  $^{14}\text{N}$  spectra were registered with an external standard  $\text{MeNO}_2$  ( $\delta_{\text{N}}$  0.0 ppm).

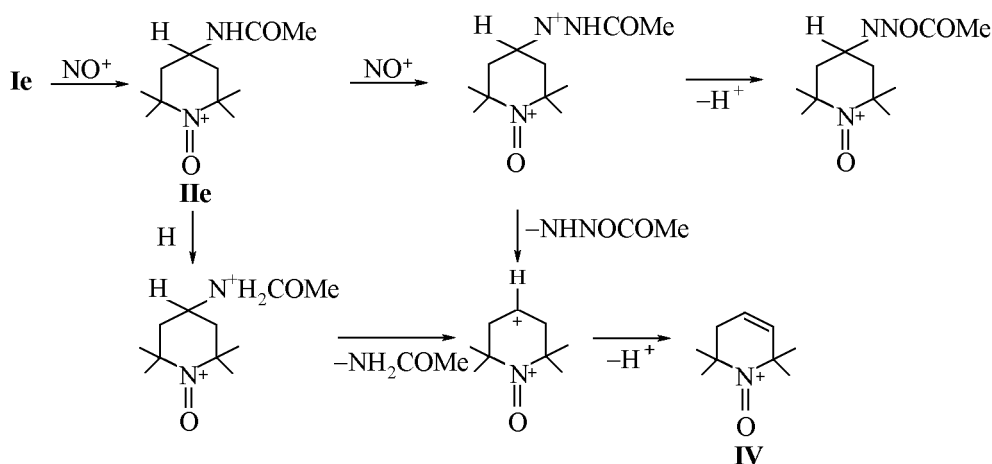
The calculated  $^1\text{H}$  NMR spectra of fragments  $\text{C}^4\text{H}$  and  $\text{CH}_2$  ( $\text{AA}'\text{BB}'\text{X}$  system) and also  $\text{C}^4\text{H}$ ,  $\text{CH}_2$  and  $\text{NH}$  ( $\text{AA}'\text{BB}'\text{XZ}$  system) were obtained using the program SpinWork 1.3. Quantum-chemical calculations were carried out by AM1 method [59] with full optimization of cations geometry.

The following reagents were used in the study:  $\text{NO}^+ \text{BF}_4^-$  (Lancaster), sulfolane of "pure" grade additionally purified as in [51], 2,2,6,6-tetramethyl-4-R-piperidin-1-oxyl radicals ( $\text{R} = \text{H}, \text{OH}, \text{OMe}, \text{OCOPh}, \text{NHCMe}$ )\*\* produced at the Pilot Plant of Vorozh-tsov Novosibirsk Institute of Organic Chemistry.

$\text{CD}_3\text{CN}$  was dried on molecular sieves 4 Å preliminary calcined for 6 h at 460–480°C.  $\text{CH}_3\text{CN}$  of "pure" grade was stirred with  $\text{KMnO}_4$  for 26 h and then distilled in succession over  $\text{P}_2\text{O}_5$  (cf.[60]) and calcium hydride (cf. [51]) and was stored on molecular sieves 4 Å.

## Solution of 2,2,6,6-tetramethyl-1-oxopiperidinium tetrafluoroborate in $\text{CD}_3\text{CN}$ . To a salt $\text{NO}^+ \text{BF}_4^-$

Scheme 4.



\* In the  $^{13}\text{C}$  NMR spectrum was not observed the signal from atoms  $\text{C}^{2,6}$  apparently due to low concentration of ion **IV**.

\*\* The authors gratefully acknowledge the kindness of M. A. Voinov who placed at our disposal compound **Ie**.

(0.51 mg, 0.4 mmol) was added under argon atmosphere a solution of 2,2,6,6-tetramethylpiperidinoxyl (67 mg, 0.43 mmol) in 0.6 ml of anhydrous  $\text{CD}_3\text{CN}$ . In several minutes the solution obtained was transferred into an NMR tube and immediately spectra were registered. Solutions of cations **Ib–e** were prepared in a similar way. The ratios radical **I**: $\text{NO}^+\text{BF}_4^-$  are mentioned in Tables 1, 2, and in the text of the paper. The generation of cations **IIf** and **IV** was performed directly in NMR tubes.

**Solution of 4-acetamido-2,2,6,6-tetramethyl-1-oxopiperidinium tetrafluoroborate in  $\text{CD}_3\text{CN}-\text{CD}_2\text{Cl}_2$ .** To a solution of ion **Ie** tetrafluoroborate prepared as described above was added an equal volume of  $\text{CD}_2\text{Cl}_2$ , the solution was mixed, and the NMR spectra were registered.

**Solution of 2,2,6,6-tetramethyl-1-oxopiperidinium tetrafluoroborate in sulfolane.** A solution of ion **Ia** tetrafluoroborate was prepared as described above from 2,2,6,6-tetramethylpiperidinoxyl (122 mg, 0.78 mmol) and  $\text{NO}^+\text{BF}_4^-$  (96 mg, 0.82 mmol) in  $\text{CH}_3\text{CN}$  (1.5 ml). The solvent was evaporated in a high vacuum, the solid residue was dissolved in 1 ml of sulfolane, the solution was filtered, and NMR spectra were registered. The solutions of cations **Ib–e** were prepared similarly.

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