Reaction products of nitronyl nitroxyl radicals with acids

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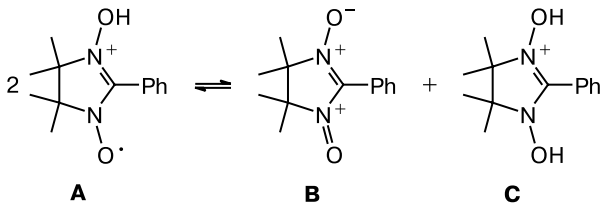
Study of the structures of compounds generated by the reactions of 4,4,5,5-tetramethyl-2-phenyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide with trifluoromethanesulfonic and picric acids demonstrated that these reactions produced salts of disproportionation products of nitronyl nitroxyl.

Key words: nitronyl nitroxyl, disproportionation, triflate, picrate.

It is well known that the classical nitroxyl radical, *viz.*, 2,2,6,6-tetramethylpiperidine-1-oxyl, undergoes rapid disproportionation in the reactions with acids to give the corresponding hydroxylamine and oxoammonium salt.[1] In the presence of the nitroxyl group along with other donor groups in the molecule, the radical can be kinetically more stable. This is attributable to the fact that protonation proceeds at a more basic group to form a radical cation in which the unpaired electron and a positive charge are located on different groups of atoms.[1] This fact has been noted in the pioneering study by Ulman,[2] where kinetically stable nitronyl nitroxyl, *viz.*, 4,4,5,5-tetramethyl-2-phenyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide (NIT-Ph), has been described. Based on the ESR data, it was hypothesized that the treatment of a solution of NIT-Ph in benzene with trifluoroacetic acid (in the absence of water) afforded paramagnetic cation **A**, whereas cation **A** generated in the reaction of NIT-Ph with an aqueous HCl solution underwent disproportionation into cations **B** and **C**. However, the treatment of solutions of NIT-Ph with acids always led to a change in the color of the solution from blue, which is characteristic of NIT-Ph, to orange. Upon subsequent neutralization of these solutions with alkali, NIT-Ph was regenerated in quantitative yield.[2]



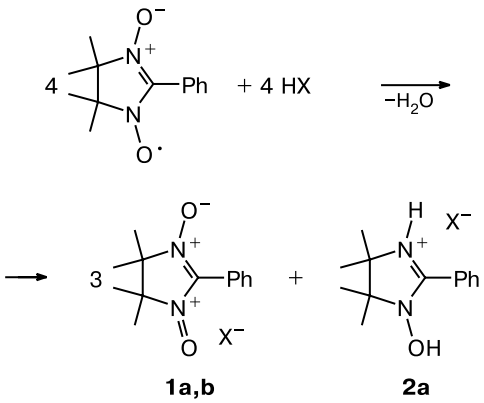
A **B** **C**

We isolated crystalline products produced in the reaction of NIT-Ph with trifluoromethanesulfonic (TfOH) and picric acids and studied their structures.

Results and Discussion

The reaction of NIT-Ph with TfOH in AcOEt resulted in rather rapid precipitation of needle-like orange crystals of **1a**. Storage of the mother liquor after separation of these crystals afforded colorless crystals of **2a** containing an impurity of crystals of **1a**. The crystals of **1a** and **2a** were separated mechanically. Dark-green crystals of **1b** were prepared by the reaction of picric acid with NIT-Ph in EtOH.

X-ray diffraction study demonstrated that compounds **1a** and **1b** are oxoammonium triflate and picrate, respectively. Compound **2a** is triflate of the protonated derivative of the corresponding iminohydroxylamine (Fig. 1). Since the formation of products containing cations of type **A** or **C** was not observed, disproportionation of NIT-Ph in the processes under study can be written as follows



1a,b **2a**

X = CF_3SO_3 (**a**), 2,4,6-$(NO_2)_3C_6H_2O$ (**b**).

In the triflate anions, the C—F and S—O distances, as well as the N—O distances in the nitro groups of the

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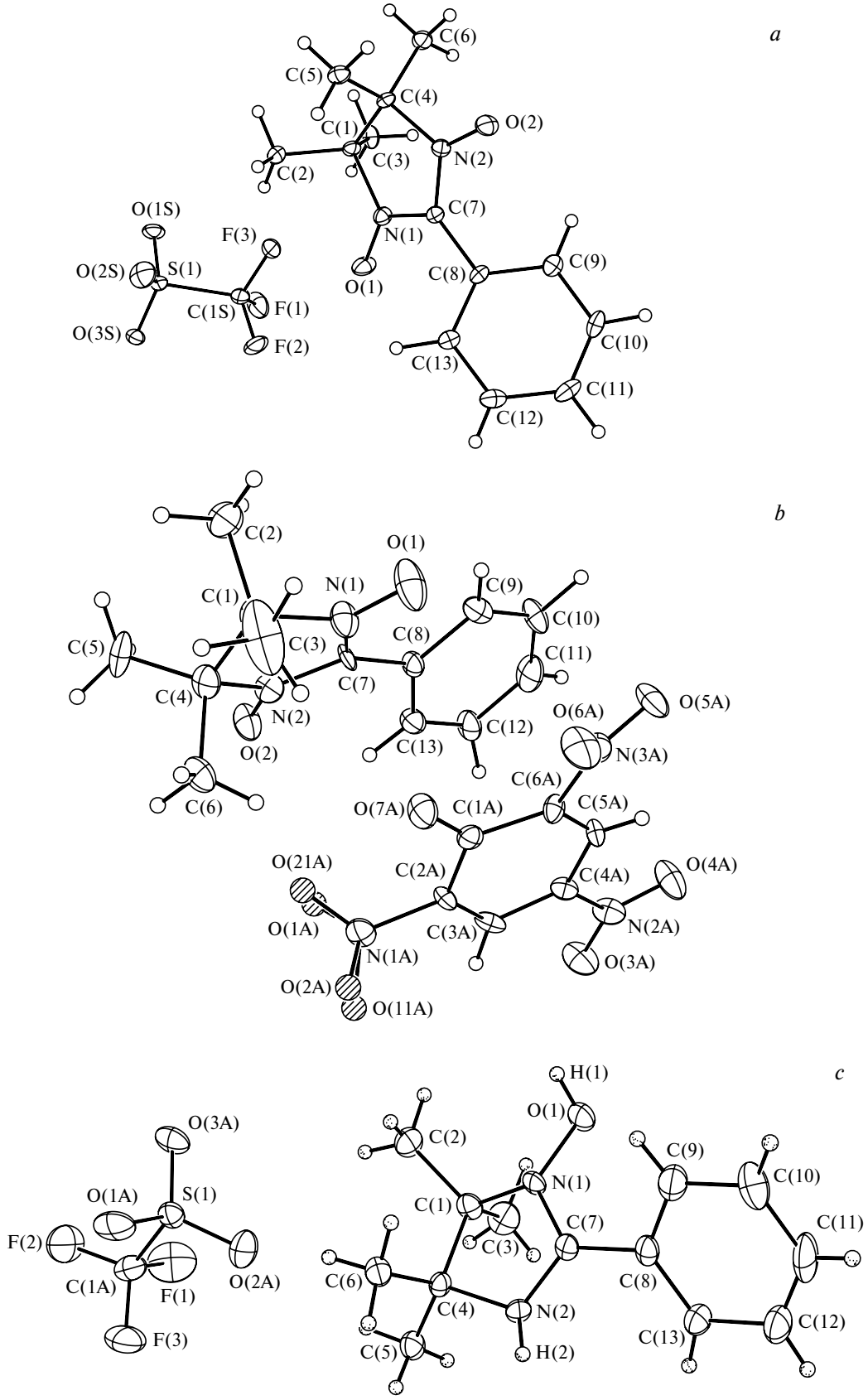

Fig. 1. Structures of the ions in compounds **1a** (*a*), **1b** (*b*), and **2a** (*c*).

Table 1. Selected bond lengths (d) in compounds **1a**, **1b**, and **2a**

Bond	d/Å		
	1a	**1b**	**2a**
O(1)—N(1)	1.224(3)	1.234(3)	1.392(5)
O(2)—N(2)	1.231(3)	1.233(3)	—
N(1)—C(7)	1.346(3)	1.350(4)	1.312(6)
N(2)—C(7)	1.341(3)	1.358(4)	1.322(6)
F—C	1.316(3)—1.326(4)	—	1.301(7)—1.323(8)
C—S	1.806(3)	—	1.802(7)
S—O	1.419(2)—1.433(2)	—	1.406(4)—1.434(4)
C—O	—	1.238(4)	—
N—O (NO_2)	—	1.197(4)—1.235(4)	—

picrate anion, are equalized (Table 1). In the cations of salts **1a** and **1b**, the N—O distances in the imidazoline fragment are, on the average, 1.227 and 1.233 Å, respectively. These values are close to the bond length (1.225 Å) found in oxoammonium perchlorate (**1**, X = ClO_4^-).[3] The NH and OH groups in **2a** are responsible for the formation of hydrogen bonds with the O atoms of the nearest triflate anions (O(1)—H(1)...O(1A)$^{\#1}$: O—H, 1.16(7) Å; H...O, 1.49(7) Å; O...O, 2.653(5) Å; ∠OHO, 177(6)°; N(2)—H(2)...O(3A)$^{\#2}$: O—H, 0.80(4) Å; H...O, 2.06(4) Å, O...O, 2.843(5) Å, ∠OHO, 168(4)°, the symmetry codes: $^{\#1}(-x + 1, -y + 1, -z)$ and $^{\#2}(-x + 1, y + 1/2, -z + 1/2)$). It should be noted that both oxygen atoms in one of the three NO_2 groups of the picrate anion statistically occupy two positions each with occupancies of 0.85 and 0.15, respectively.

Since oxoammonium salts are strong oxidizing agents,[2] solutions of **1a** and **1b** in alcohols gradually changed to a dark-blue color characteristic of NIT-Ph. This process was accompanied by an increase in the intensity of the ESR signal of nitronyl nitroxyl. The addition of NEt_3 to ethanolic solutions of **1a** and **1b** immediately led to the quantitative (according to the ESR data) regeneration of NIT-Ph. Although being known earlier, the latter fact, to our knowledge, has never been used for solving synthetic problems. In principle, the preliminary transformation of the nitronyl nitroxyl radicals into the corresponding oxoammonium salts can be used as a way of protecting these radicals in reactions proceeding in an acidic medium. After modification of the substituent at position 2, the oxoammonium salt can be readily transformed into nitronyl nitroxyl by the addition of alkali. We plan to carry out such experiments in the nearest future.

To summarize, the study of the single-crystal structures of the compounds generated by the reactions of NIT-Ph with trifluoromethanesulfonic and picric acids demonstrated that these reactions afforded salts of disproportionation products of nitronyl nitroxyl.

Table 2. Crystallographic characteristics of compounds **1a**, **1b**, and **2a**

Parameter	**1a**	**1b**	**2a**
Molecular formula	$C_{14}H_{17}F_3N_2O_5S$	$C_{19}H_{19}N_5O_9$	$C_{14}H_{19}F_3N_2O_4S$
T/K	150	150	295
Molecular weight	382.36	461.39	368.37
Crystal system	Orthorhombic	Monoclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/n$	$P2_1/c$
a/Å	9.494(1)	6.7424(8)	15.627(3)
b/Å	11.028(2)	22.376(3)	11.077(2)
c/Å	15.898(2)	13.720(2)	10.579(2)
α/deg	90	90	90
β/deg	90	97.087(2)	108.878(3)
γ/deg	90	90	90
V/Å^3	1664.5(4)	2054.1(4)	1732.6(5)
Z	4	4	4
d_{calc}/g cm^{-3}	1.526	1.492	1.412
μ/mm^{-1}	0.255	0.121	0.237
θ Scan range/deg	2.25—23.33	2.35—23.26	2.30—23.30
I_{hkl} (measured/independent reflections)	7214/2400	8801/2950	7296/2496
R_{int}	0.0317	0.0404	0.2031
$I_{hkl}/I > 2\sigma(I)$/N*	2400/2278/295	2950/2346/393	2496/1519/294
GOOF	1.101	1.034	0.890
R_1 (for $I > 2\sigma(I)$)	0.0320	0.0546	0.0777
wR_2	0.0716	0.1238	0.1780
R_1 (based on all I_{hkl})	0.0348	0.0724	0.1253
wR_2	0.0731	0.1324	0.2057

Experimental

The IR spectra of samples pressed in pellets with KBr were recorded on a Bruker Vector 22 spectrometer. 4,4,5,5-Tetramethyl-2-phenyl-4,5-dihydro-1*H*-imidazole-1-oxyl 3-oxide was prepared according to a known procedure.[2] Other commercial reagents and organic solvents were used without additional purification.

4,4,5,5-Tetramethyl-1-oxo-2-phenyl-4,5-dihydro-1*H*-imidazol-1-ium 3-oxide trifluoromethanesulfonate (1a) and 3-hydroxy-4,4,5,5-tetramethyl-2-phenyl-4,5-dihydro-3*H*-imidazol-1-ium trifluoromethanesulfonate (2a). Sodium triflate (256 mg) and three drops of 36% HCl were added to a solution of NIT-Ph (344 mg, 1.5 mmol) in AcOEt (20 mL), which led to a change in the color of the solution from blue to orange. The precipitate that formed within a few minutes was washed with AcOEt and dried in air. Compound **1a** was prepared in a yield of 189 mg (34%) as orange needle-like crystals, m.p. 135—137 °C. Found (%): C, 43.7; H, 3.8; F, 14.7; N, 7.3. $C_{14}H_{17}F_3N_2O_5S$. Calculated (%): C, 44.0; H, 4.5; F, 14.9; N, 7.3. IR, ν/cm^{-1}: 515, 548, 573, 640, 689, 714, 734, 890, 1031, 1159, 1191, 1225, 1255, 1311, 1385, 1438, 1462, 1602, 3015, 3072. The mother liquor was stored at ~20 °C for one day. The precipitate that formed was filtered off, washed with AcOEt, and dried in air. Compound **2a** was prepared in a yield of 115 mg (20%) as thin (thickness was no more than 0.05 mm) colorless platelet-like crystals, m.p. 131—133 °C. Found (%): H, 5.4; F, 15.6; N, 7.2. $C_{14}H_{19}F_3N_2O_4S$. Calculated (%): H, 5.2; F, 15.5; N, 7.6. IR, ν/cm^{-1}: 516, 638, 692, 762, 1029, 1109, 1172, 1234, 1289, 1377, 1402, 1455, 1470, 1490, 1550, 1582, 1612, 2947, 2986, 3204.

4,4,5,5-Tetramethyl-1-oxo-2-phenyl-4,5-dihydro-1*H*-imidazol-1-ium 3-oxide trinitrophenoxide (1b). A solution of picric acid (46 mg, 0.20 mmol) in 95% EtOH (2 mL) was added to a warm solution of NIT-Ph (47 mg, 0.20 mmol) in 95% EtOH (2 mL). After storage of the reaction mixture at 0 °C for one day, the precipitate that formed was filtered off, washed with cold benzene, and dried in air. Compound **1b** was prepared in a yield of 44 mg (47%) as thin (the size of the cross-section was ~0.04 mm) dark-green needle-like crystals. Upon heating to 114—116 °C, compound **1b** decomposed to give gaseous products. Found (%): C, 49.9; H, 4.1; N, 15.6. $C_{19}H_{19}N_5O_9$. Calculated (%): C, 49.5; H, 4.2; N, 15.2. IR, ν/cm^{-1}: 708, 747, 914, 1078, 1165, 1192, 1270, 1313, 1365, 1385, 1400, 1441, 1467, 1490, 1517, 1557, 1613, 1632, 2980, 3070.

X-ray diffraction analysis. X-ray data sets were collected from single crystals of the compounds on an automated Bruker AXS SMART APEX diffractometer according to a standard procedure using Mo radiation. The structures were solved by direct methods and refined by the full-matrix least-squares method with anisotropic and isotropic thermal parameters for non-hydrogen and hydrogen atoms, respectively. The positions of the H atoms were located from difference electron density syntheses. All calculations were carried out using the SHELX97 program package. The principal crystallographic characteristics of the compounds and details of X-ray diffraction study are given in Table 2.

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