Tetrahedron Letters 53 (2012) 1587–1591

Contents lists available at SciVerse ScienceDirect

Tetrahedron Letters

journal homepage: www.elsevier.com/locate/tetlet

New spin probes starting from 4-amino-2,2,6,6-tetramethylpiperidine-1-yloxyl

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ARTICLE INFO

Article history:
Received 30 December 2011
Revised 15 January 2012
Accepted 17 January 2012
Available online 28 January 2012

Keywords:
Nitroxides
Spin probes
ESR spectroscopy
Ionic liquids

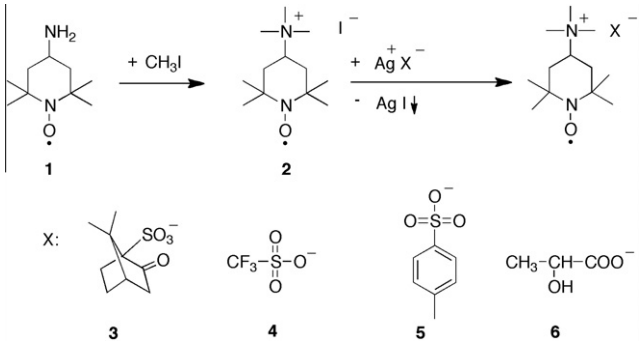
ABSTRACT

This Letter describes four new 4-trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxyls bearing camphorsulfonate, triflate, tosylate, or lactate as counter ions. These spin probes were made by anion metathesis of 4-trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxyl iodide using the corresponding silver salts. The latter is made by the alkylation of 4-amino-2,2,6,6-tetramethylpiperidine-1-yloxyl. Furthermore, the Letter gives an improved synthetic way to 4-sulfonamido-2,2,6,6-tetramethylpiperidine-1-yloxyl using chlorosulfuric acid trimethylsilylester and 4-amino-2,2,6,6-tetramethylpiperidine-1-yloxyl. All the spin probes are highly interesting for the investigation of ionic liquids.

Ionic liquids have received increased attention as solvents and materials in inorganic, organic, and polymer chemistry.[1–4] Although they are composed entirely of ions, the liquid state is below the boiling point of water. Potential applications of ionic liquids are batteries, fuel cells, and solar cells.[5–7] The viscosity of ionic liquids is usually higher compared to traditional organic solvents, and it is strongly dependent on the structure of both the cation and the anion.[2] The mobility of these ions and of the dissolved species is important for the potential applications mentioned above.

Stable radicals, so called spin probes, are useful model compounds for reactive species in ionic liquids because of their definite concentrations in the ionic liquids that facilitate the measurements. Various spin probes have been successfully used for ionic liquid investigation.[8–26] Furthermore, spin probes need only a low concentration for investigation of ionic liquids. Moreover, the color of ionic liquids, which appears sometimes strong by eye although the analysis shows a purity of larger than 99.5%, does not disturb the measurements of spin probes. Therefore, time consuming purification procedures are avoided if spin probes are used for ionic liquid investigation. The spin probes give information about microviscosity and micropolarity of ionic liquids.

2,2,6,6-Tetramethylpiperidine-1-yloxyl derivatives are examples for spin probes, which have been successfully applied for the investigation of ionic liquids.[13,14,16–24] Recently, 2,2,6,6-tetramethylpiperidine-1-yloxyl derivatives have been modified by various substituents to investigate interactions between these model radicals and the individual ions of the ionic liquids.[17–20] Thus, substituents forming hydrogen bonds or ionic substituents are bound at the 4-position of the spin probe resulting in additional interactions with the individual ions of the ionic liquids. These modified compounds are useful as spin probes for the investigation of ionic liquids.[21–23] It is shown that hydrogen bond forming substituents at the 4-position slightly reduce the mobility of the spin probes relative to the 2,2,6,6-tetramethylpiperidine-1-yloxyl. Furthermore, ionic substituents significantly reduce the mobility of the spin probes in the ionic liquids that is caused by additional ionic interactions between the ionic substituent and the individual



Scheme 1. Synthesis of 4-trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxyl bearing camphorsulfonate (**3**), triflate (**4**), tosylate (**5**) or lactate (**6**) as counter ion by alkylation of 4-amino-2,2,6,6-tetramethylpiperidine-1-yloxyl (**1**) with methyliodide in a first step followed by anion metathesis of the 4-trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxyl iodide (**2**) using the corresponding silver salts in a second step.[27–30]

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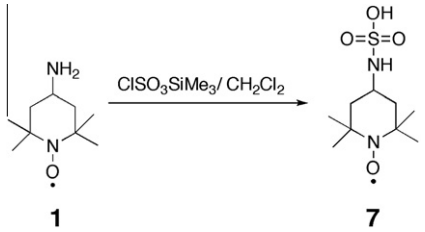
doi:10.1016/j.tetlet.2012.01.063



Scheme 2. Synthesis of 4-sulfonatoamino-2,2,6,6-tetramethylpiperidine-1-yloxyl (**7**) from 4-amino-2,2,6,6-tetramethylpiperidine-1-yloxyl (**1**) and chlorosulfuric acid trimethylsilylester.[31]

ions of the ionic liquids. Moreover, the results of spin probes bearing an ionic substituent show that counter ion exchange occurs with the ionic liquid. The counter ion exchange with the anion of the ionic liquid can be avoided if the spin probe with a cationic substituent has the same anion as the ionic liquid. Some examples of spin probes have been synthesized that contain tetrafluoroborate, hexafluorophosphate or bis(trifluoromethylsulfonyl)imide as counter ion.[18] These spin probes have been successfully used for the investigation of imidazolium based ionic liquids.[21–23] Further spin probes with other typical anions of ionic liquids are necessary for investigation of further ionic liquids in more detail.

In this Letter we describe four new 4-trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxyls bearing camphorsulfonate, triflate, tosylate, or lactate as counter ions. These ions are typical anions in ionic liquids. Investigation of ionic liquids with cationic spin probes bearing the same counter ion as the ionic liquids results in a better understanding of the cation anion interaction because anion exchange is avoided. Furthermore, an improved synthetic way is described for 4-sulfonamido-2,2,6,6-tetramethylpiperidine-1-yloxyl. The latter can form hydrogen bonding with ionic liquids via the sulfonamido group. All spin probes are made from the 4-amino-2,2,6,6-tetramethylpiperidine-1-yloxyl, which has been used for investigation of ionic liquids as well. The spin probes bearing either the cationic substituent or the sulfonamido group are highly interesting for investigation of ionic liquids because they open the possibility to describe interactions of ionic liquids with radicals in more detail.

The new 4-trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxyl compounds **3**–**6** are obtained by the reaction of 4-amino-2,2,6,6-tetramethylpiperidine-1-yloxyl (**1**) with methyliodide forming 4-trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxyl idodide[18] followed by anion metathesis with the corresponding silver salts (Scheme 1).[27–30] Silver iodide is formed during the reaction, it precipitates from the reaction mixture and can be separated by filtration. The new spin probes **3**–**6** formed are isolated from the remaining clear solution by evaporation of the solvent in vacuo and drying under reduced pressure.

Synthesis of 4-sulfonatooxy-2,2,6,6-tetramethylpiperidine-1-yloxyl was successfully carried out by reaction of 4-hydroxy-2,2,6,6-tetramethylpiperidine-1-yloxyl with chlorosulfuric acid trimethylsilylester.[17] Similarly, the 4-sulfonatoamino-2,2,6,6-tetramethylpiperidine-1-yloxyl (**7**) is obtained from 4-amino-2,2,6,6-tetramethylpiperidine-1-yloxyl and chlorosulfuric acid

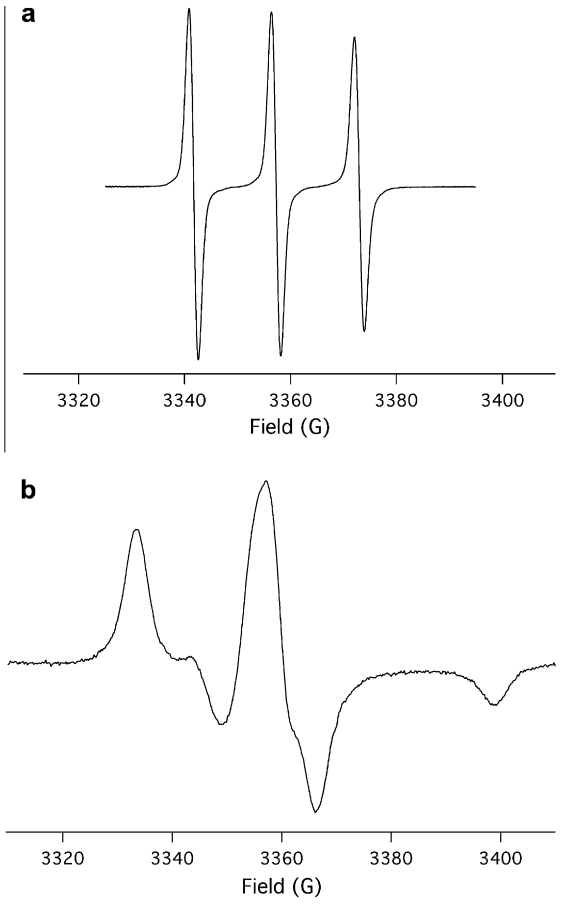


Figure 1. ESR spectrum of 4-trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxyl bearing camphorsulfonate as anion (**3**) in (a) dimethylsulfoxide at 295 K ($A_{iso}(^{14}N)$ = 15.6 G; τ = 0.6 ns) and (b) 1-butyl-3-methylimidazolium camphorsulfonate at 296 K (τ = 207.9 ns).

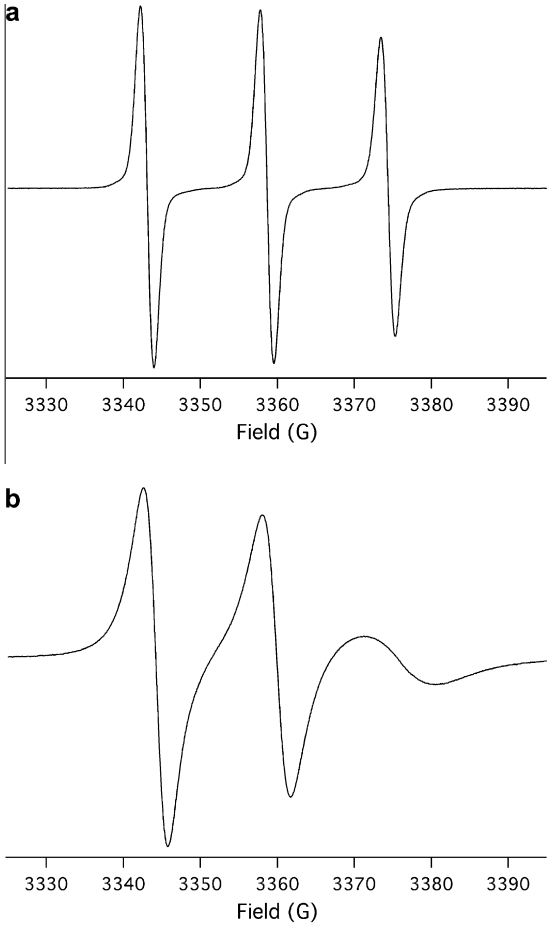


Figure 2. ESR spectrum of 4-trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxyl bearing triflate (**4**) as counter ion in (a) dimethylsulfoxide at 295 K ($A_{iso}(^{14}N)$ = 15.6 G; τ = 0.1 ns) and (b) 1-butyl-3-methylimidazolium triflate at 292 K (τ = 12.8 ns; $A_{iso}(^{14}N)$ = 15.6 G).