

Synthesis of 4-trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxy with various anions for investigation of ionic liquids

Veronika Strehmel^{a,*}, Hans Rexhausen^a, Peter Strauch^b

^a University of Potsdam, Institute of Chemistry, Applied Polymer Chemistry, Karl-Liebknecht-Str. 24-25, D-14476 Potsdam-Golm, Germany

^b University of Potsdam, Institute of Chemistry, Inorganic Chemistry, Karl-Liebknecht-Str. 24-25, D-14476 Potsdam-Golm, Germany

Received 16 February 2008; revised 11 March 2008; accepted 17 March 2008

Available online 20 March 2008

Abstract

A new synthetic way is described to prepare 4-trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxy bearing tetrafluoroborate, hexafluorophosphate or bis(trifluoromethylsulfonylimide) by an anion metathesis of 4-trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxy iodide using the corresponding silver salts. 4-Trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxy iodide is obtained by the methylation of 4-amino-2,2,6,6-tetramethylpiperidine-1-yloxy with methyl iodide. The new spin probe 4-trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxy bistrifluoromethylsulfonylimide and the spin probes containing tetrafluoroborate or hexafluorophosphate may be useful for an effective investigation of ionic liquids with similar anions.

© 2008 Elsevier Ltd. All rights reserved.

Keywords: Spin probes; ESR spectroscopy; Nitroxides; Ionic liquids

Ionic liquids are new solvents distinguishing from traditional solvents by their higher viscosity and their tunability of solvent properties just by the variation of the cation or the anion structure resulting in the name ‘designer solvents’. Furthermore, ionic liquids are interesting for various applications, such as in electrochemical devices, as solvents for extractions and for reactions in organic, inorganic, and polymer chemistry.^{1–7} The specific structure of ionic liquids composed of cations and anions, and their interactions with solutes may cause advantages of ionic liquids compared to molecular solvents. However, the knowledge about the properties of ionic liquids on a molecular level and their interactions with solutes can be considered as rare. Spin probes are a versatile tool to explore molecular properties of these designer solvents in the molecular domain.^{8–16} Positively or negatively charged spin probes are crucial for the investigation of ionic liquids because they directly interact with the individual ions of the ionic

liquids. Recently, we described an improved synthesis for potassium 4-sulfonatoxy-2,2,6,6-tetramethylpiperidine-1-yloxy and sodium 4-sulfonatoxy-2,2,6,6-tetramethylpiperidine-1-yloxy.¹⁶ These spin probes open the possibility to study especially interactions with the cation of the ionic liquid. This Letter describes the synthesis of 4-trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxy salts bearing either bistrifluoromethylsulfonylimide, tetrafluoroborate or hexafluorophosphate as anions, which can also function as anions in ionic liquids. The selection of spin probes with similar counter ions as ionic liquids will improve the solubility of the spin probes in these ionic liquids and it will eliminate the counter ion exchange of charged spin probes dissolved in ionic liquids. Therefore, spin probes containing a similar counter ion as the investigated ionic liquid will increase the efficiency of the investigation of ionic liquids with spin probes.

4-Trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxy iodide can be obtained by the methylation of 4-dimethylamino-2,2,6,6-tetramethylpiperidine-1-yloxy or 4-amino-2,2,6,6-tetramethylpiperidine-1-yloxy with methyl iodide.^{17–19} The latter¹⁹ cites a further reference, where

* Corresponding author. Tel.: +49 331 977 5224; fax: +49 331 977 5036.
E-mail address: vstrehme@uni-potsdam.de (V. Strehmel).

the formation of another trimethylammonio substituted radical is described by the reaction of a primary amino substituted radical with methyl iodide.²⁰ Nevertheless, the information about the experimental conditions to obtain 4-trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxy iodide is rare in the literature.

Furthermore, exchange of the iodide can be done by using KPF_6 to obtain 4-trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxy hexafluorophosphate.²¹ However, no experimental details are given for this anion exchange in the literature. Anion exchange is important to tailor-made spin probes for the investigation of ionic liquids. Therefore, we developed an improved procedure for anion exchange of 4-trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxy iodide to obtain 4-trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxy derivatives bearing similar counter ions as ionic liquids, such as bistrifluoromethylsulfonylimide, tetrafluoroborate, and hexafluorophosphate.

In a first step the commercially available 4-amino-2,2,6,6-tetramethylpiperidine-1-yloxy is converted into 4-trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxy iodide by reaction with methyl iodide (Fig. 1).²² Then, anion metathesis of the iodide occurs when 4-trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxy iodide is stirred with silver bistrifluoromethylsulfonylimide, silver tetrafluoroborate or silver hexafluorophosphate in acetone.²³ High yields on the new spin probe 4-trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxy bistrifluoromethylsulfonylimide (**3**, mp 229–248 °C dec), 4-trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxy tetrafluoroborate (**4**, mp 259–268 °C dec), and 4-trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxy hexafluorophosphate (**5**, mp 250–256 °C dec) are obtained because silver iodide precipitates, and it can be easily separated from the reaction mixture by the filtration resulting in the crystalline 4-trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxy salts after the evaporation of acetone in vacuo (Fig. 1).²³

In principle, **3** can be obtained from **2** and lithium bistrifluoromethylsulfonylimide as well. However, purification is difficult in this case, and a paste-like product is obtained. The significant decrease in the melting point of **3** may be

attributed to the presence of a small amount of the lithium salt. Therefore, anion metathesis using silver bistrifluoromethylsulfonylimide is preferred because the formed silver iodide precipitates, and it can be easily removed resulting in **3** with a higher purity.

The spin probes are well soluble in dimethylsulfoxide. The ESR spectrum of **3** dissolved in dimethylsulfoxide consists of the expected three lines (Fig. 2), which are characteristic for 2,2,6,6-tetramethylpiperidine-1-yloxy derivatives. Examples for ESR spectra of **3–5** dissolved in 1-butyl-3-methylimidazolium salts containing similar anions as the spin probes are depicted in Figure 2 as well. The ESR spectra of the spin probes in the ionic liquids show line broadening and changes in the habitus in comparison with the ESR spectrum of **3** in dimethylsulfoxide due to the stronger interactions between the spin probes and the individual ions of the ionic liquids and the higher viscosity of the ionic liquids. Furthermore, the observed differences between the ESR spectra of the spin probes in the ionic liquids may be attributed to the viscosity of these ionic liquids that increase in the order 1-butyl-3-methylimidazolium bistrifluoromethylsulfonylimide < 1-butyl-3-methylimidazolium tetrafluoroborate < 1-butyl-3-methylimidazolium hexafluorophosphate.^{24,25} This is also mirrored in the rotational correlation times (τ) of the spin probes (figure caption of Fig. 2) determined using the method of Budil et al.²⁶ The τ values increase in the same order as the solvent viscosity: dimethylsulfoxide < 1-butyl-3-methylimidazolium bistrifluoromethylsulfonylimide < 1-butyl-3-methylimidazolium tetrafluoroborate < 1-butyl-3-methylimidazolium hexafluorophosphate.^{24,25,27} Moreover, slight distinct values are obtained for the isotropic hyperfine coupling constant ($A_{iso}(^{14}N)$) of the spin probes dissolved in dimethylsulfoxide and in ionic liquids.

We can conclude from the synthetic work that anion metathesis of 4-trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxy iodide using silver bistrifluoromethylsulfonylimide, silver tetrafluoroborate and silver hexafluorophosphate is an efficient way to obtain the corresponding 4-trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxy salts in a high yield. This new method opens the possibility to make further ammonio substituted spin probes with anions, which can be also found as the

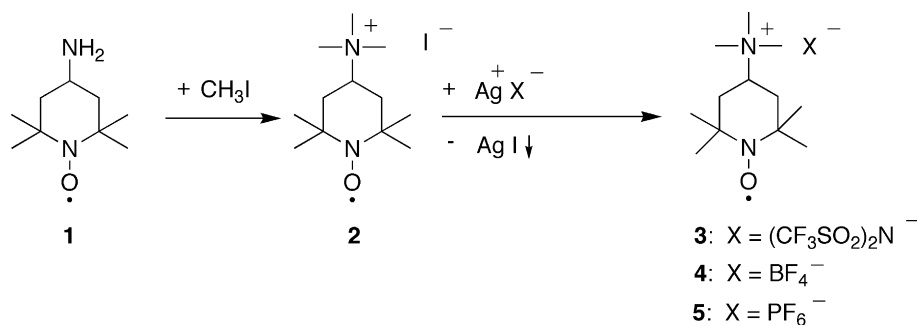


Fig. 1. Formation of 4-trimethylammonio-2,2,6,6-tetramethylpiperidine-1-yloxy iodide (**2**) by the methylation of 4-amino-2,2,6,6-tetramethylpiperidine-1-yloxy (**1**) with methyl iodide²² and anion metathesis using silver salts resulting in the cationic spin probes **3–5**.²³

Download English Version:

<https://daneshyari.com/en/article/5281658>

Download Persian Version:

<https://daneshyari.com/article/5281658>

[Daneshyari.com](https://daneshyari.com)