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Synthesis of 1,3-dialkyl imidazolium ionic liquids containing difunctional and tetrafunctional perfluoroalkylsulfonyl imide anions

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ABSTRACT

Direct methylation of imidazole using methylated difunctional or tetrafunctional perfluorosulfonyl imides renders excellent yields of the corresponding room temperature ionic liquids (RTILs). This methodology provides a simple, halide-free route to several novel RTILs containing multifunctional perfluorosulfonyl imide anions.

1. Introduction

Room temperature ionic liquids (RTILs, mp $\leq$ 100 °C) are attracting considerable attention due to their electrochemical properties, as well as their potential to serve as "green" reaction media [1,2]. These interesting, yet conceptually straightforward, compounds often incorporate the bulky, asymmetric 1,3-dialkylimidazolium cation to preclude good crystal packing. To further decrease interionic interaction the inclusion of an anion with considerable delocalization over the molecular backbone is incorporated and the bis((trifluoromethyl)sulfonyl)imide, $(CF_3SO_2)_2N^-$, is one of the most effective in providing low melting points, as well as high thermal stability [3]. The preparation of ionic liquids typically involves a multi-step synthesis, ending with an anion metathesis reaction. Removal of the metal halide from the ionic liquid can be difficult and often leaves metal halide contaminants.

In this paper we utilize the direct methylation of an alkyl imidazole, as reported by DesMarteau and coworkers in 2003, except here we employ a multifunctional *N*-methylated perfluorosulfonylimide to avoid the anion exchange step [4]. Monofunctional sulfonimides can be methylated with trimethyl orthoacetate or dimethyl sulfate, whereas the multifunctional sulfonimides required methylation with the stronger methylating agent, dimethyl sulfate.

2. Results and discussion

The difunctional RTILs started from the 1,2-bis(chlorosulfonyl)tetrafluoroethane by the method reported in 1998. The difunctional *N*,*N*-perfluorosulfonylimide moiety was synthesized utilizing related literature methods as shown in Schemes 1 and 2 [5–7].

The aforementioned resonance stability, along with the strong electron withdrawing ability of two R_FSO_2 groups on the one nitrogen atom also make the *N*-Me-bis((trifluoromethyl)sulfonyl)imide an excellent candidate for donating a CH_3^+ group to a Lewis base like a 1-alkylimidazole, or possibly a pyridine derivative [4]. Monitoring these reactions is equally straightforward and achieved with both ^{19}F and ^1H NMR. The fluorine atoms adjacent to the sulfonimide moiety exhibit the expected behavior of downfield chemical shifts in going from the sodium salt anion form to the methylated sulfonimide, and then exhibit upfield shifts upon donating the methyl group to the 1-alkylimidazole upon forming the RTIL. The protons on the 1-alkylimidazole ring, most notably the C-2 proton, exhibit a significant downfield shift on going from the 1-alkylimidazole to the 1,3-dialkylimidazolium cation.

All of these salts showed excellent thermal stability with TGA decomposition onset temperatures above 400 °C. DSC data were taken with a heating speed of 10 °C min^{-1} and a cooling rate of 20 °C min^{-1}. The symmetric 1,3-dimethylimidazolium salt had a melting point of 68 °C, and showed no melt upon a second heating. The asymmetric RTILs were liquids at room temperature showing a reproducible glass transition (T_g) effect at −68 °C with a slightly lower T_g of −72 °C upon cooling. Elemental analyses were

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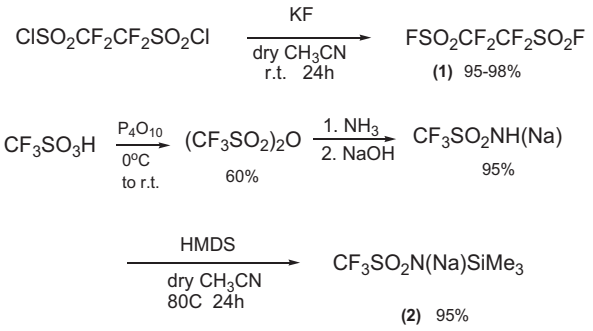
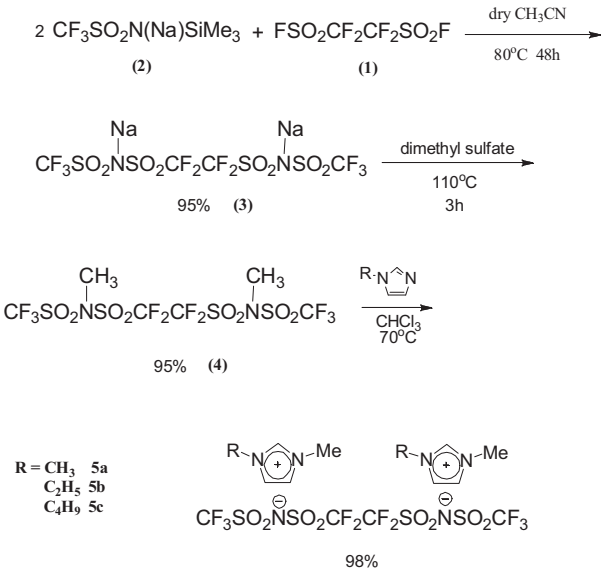


Scheme 1. Preparation of starting materials **1** and **2**.



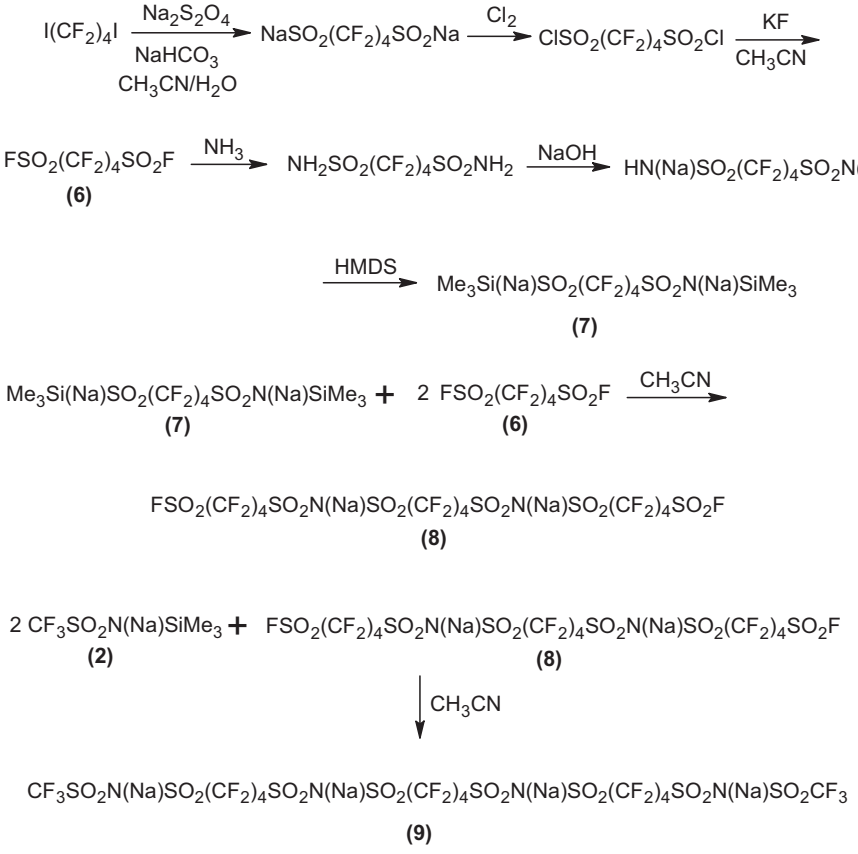
Scheme 2. Preparation of difunctional RTILs.

performed on each RTIL by Atlantic Microlab, Inc. and showed excellent agreement with calculated values.

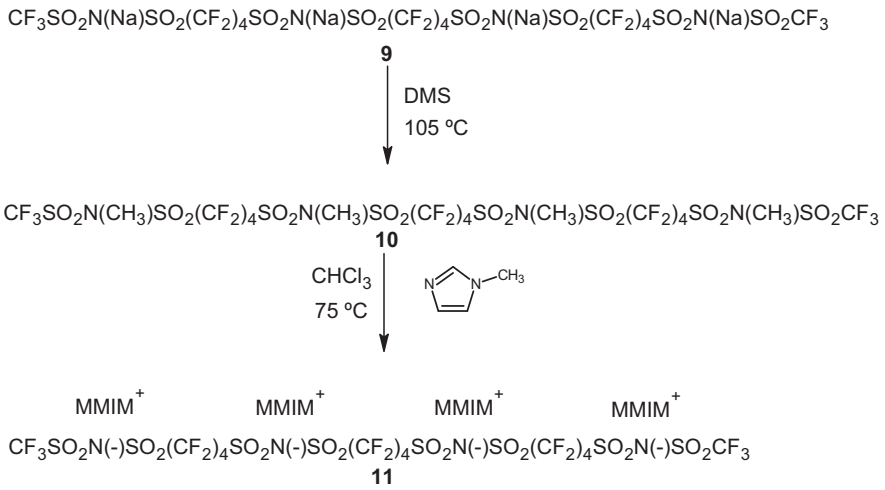
In addition to these three difunctional sulfonylimide ionic liquids, the versatility of these coupling condensation reactions was explored and a 1,3-dimethylimidazolium tetrafunctional perfluorosulfonylimide was also synthesized. However, this compound was synthesized from the starting material, α,ω-diiodooctafluorobutane. Scheme 3 illustrates how straightforward the synthesis of the tetrafunctional anion is.

The α,ω-diiodooctafluorobutane undergoes a deiodo-sulfination with sodium dithionate in a weakly basic acetonitrile/water solution. Without isolating the sodium disulfinate salt chlorine gas is used to form the disulfonyl chloride. The chlorine atom is displaced with KF to form the disulfonyl fluoride. A portion is then converted to the amide using liquid ammonia as solvent and reactant, neutralized with NaOH solution, and then converted to a difunctional silyl derivative with HMDS.

Once the difunctional silyl derivative was formed, an excess of the distillable difunctional sulfonyl fluoride was attached to each end, leaving a sulfonyl fluoride functional group available on the end for further reaction. This was then end capped with the triflouromethyl sulfonamide silyl derivative (**2**) to form a tetrafunctional sulfonyl imide sodium salt. Once the tetrafunctional sulfonimide anion is formed, methylation with dimethyl sulfate proceeds to form **10** (Scheme 4). However isolation of pure **10** is



Scheme 3. Synthesis of a tetrafunctional sodium sulfonimide salt.



Scheme 4. Preparation of a tetrameric RTIL.

more difficult than **4** because **10** cannot be readily sublimed from the sodium methylsulfate byproduct. Compound **10** was subsequently used to methylate 1-methylimidazole forming **11** as carried out with the difunctional sulfonyl imides. The tetrafunctional ionic liquid formed had a glass transition at −43 °C, a melting point at 58 °C, and a decomposition onset at 459 °C.

The preparation of tetra-BMIM$^+$ salt of **9** was also carried out by the more traditional anion metathesis route using the Li salt of **9** and BMIM$^+$Br$^-$ in water. This reaction worked well by extracting the RTIL with CH_2Cl_2 and was more straightforward than the preferred direct alklyation procedure. However the amount of bromide present in the RTIL was not determined. A comparison of samples of **11-**BMIM by both routes would have been desirable, but this was not done.

All the difunctional and tetrafunctional ionic liquids exhibited a high degree of hydrophobicity, but no quantitative data were obtained.

3. Experimental procedure

3.1. General

^{19}F and ^{1}H NMR spectra were obtained on a JEOL ECX 300 NMR using dried CD_3CN as a solvent. $CFCl_3$ was used as the internal reference for fluorine. Chemical shifts (δ_F, δ_H) are in ppm. TGA and DSC were obtained on Perkin Elmer TGA-7 and DSC-7 instruments. Chemicals were obtained from commercial sources and used as received except where noted.

3.2. Typical procedure for 1,1,2,2-tetrafluoro-N,N′-dimethyl-N,N′-bis[(trifluoromethyl)sulfonyl]ethane-1,2-disulfonimide (4)

Into a 25 mL flask under a nitrogen atmosphere, 2.07 g (3.8 mmol) of the sodium sulfonimide salt **3** and 8 mL of dimethyl sulfate were heated to 110 °C for 3 h. Ice was added and the mixture was allowed to stir overnight. Vacuum filtration along with washing with water was done to remove excess DMS and impurities. An extraction was done with ethyl acetate and a $NaHCO_3$ solution. The ethyl acetate layer was dried over Na_2SO_4 and the solvent evaporated. The methylated compound was sublimed under high vacuum at 90 °C yielding a white, flaky solid (1.5 g, 71%). Selected data for **4**: δ_H, 3.55(s); δ_F, 72.5(s, 6F), 104.2(s, 4F).

3.3. Typical procedure for RTIL(5c)

In a 50 mL rb flask with a stir bar, 20 mL of $CHCl_3$ was added followed by 0.40 g (0.72 mmol) of **4**. Then 0.28 g (2.26 mmol) of butylimidazole was added and the mixture was refluxed at 70 °C overnight. The solvent and excess butylimidazole were removed using a vacuum line. The remaining clear liquid was heated overnight at 70 °C under vacuum giving colorless **5c** (0.56 g, 97%). Selected data for **5c**: δ_H 8.39(s, 2H), 7.35(s, 2H), 7.31(s, 2H), 4.10(t, 4H, ^2J = 7.4 Hz), 3.79(s, 6H), 1.72(m, 4H, ^2J = 4.8 Hz), 1.23(m, 4H, ^2J = 7.6 Hz), 0.92(t, 6H, ^2J = 7.3 Hz). T_g = −68 °C, T_d = 441 °C.

5a: ^{19}F same as **5c**, δ_H 8.35 (1H, s), 7.30 (2H, s), 3.80 (6H, s). T_m = 68 °C, T_d = 450 °C.

5b: ^{19}F same as **5c**, δ_H 8.39 (1H, s), 7.37 (2H, s), 4.14 (2H, q, ^3J = 7.3 Hz), 3.80 (3H, s), 1.44 (3H, t, ^3J = 7.3 Hz). T_g = −73 °C, T_d = 446 °C.

3.4. Procedure for 1,1,2,2,3,3,4,4-octafluorobutane-1,4-disulfonyl difluoride (6)

Since the α,ω-diiodo compound is a liquid, the 40.54 g (89.3 mmol) of $I(CF_2)_4I$ was slowly(45 min) added dropwise into a 500 mL round bottom flask containing a solution of 80 mL of acetonitrile and 120 mL water with 30 g $NaHCO_3$ and 39 g $Na_2S_2O_4$ dissolved in it. The flask was placed in a water bath, heated to 40 °C, and allowed to stir overnight. For the chlorination, enough DI H_2O was added to the $NaSO_2(CF_2)_6SO_2Na$ reaction mixture to dissolve the solids. In a 1000 mL 3-neck round bottomed flask cooled in an ice bath at 0 °C, Cl_2 gas was vigorously bubbled into 100 mL H_2O as the $NaSO_2(CF_2)_4SO_2Na$ solution was slowly added dropwise (ca. 30 min.) into the chlorine solution. The $-SO_2Cl$ compound precipitated out and was isolated by vacuum filtration. The white sulfonyl chloride compound was dissolved in CH_2Cl_2, washed with water several times, and then dried over anhydrous Na_2SO_4. Evaporation of the CH_2Cl_2 was done on the vacuum line while keeping the flask containing the $-SO_2Cl$ compound and CH_2Cl_2 at 0 °C. A yield of 28.53 g (80%) was obtained.

To the flask containing the 28.53 g (71.5 mmol) of $ClSO_2(CF_2)_4SO_2Cl$, 150 mL of dry CH_3CN and 25.9 g of dry KF was added. The reaction mixture was stirred at room temperature overnight while under a nitrogen atmosphere. Once complete, the product and CH_3CN were distilled to another flask, away from the salt, with high vacuum and at room temperature. Water was then added to the CH_3CN mixture to separate the product into a separate layer. Compound **6** (25.59 g, 95%) was isolated. Selected data for **6**: δ_F 107.6(t, 4F), +47.7(s, 2F).

3.5. Procedure for $H_2NSO_2(CF_2)_4SO_2NH_2$

For the bis(sulfonamide), in a 100 mL 2-neck round-bottomed flask equipped with a stir bar, approximately 30 mL of ammonia was condensed at −80 °C and vigorously stirred. Then 6.00 g (16.4 mmol) of $(CF_2CF_2SO_2F)_2$ was added dropwise over 5 min. The flask was allowed to come to room temperature overnight so the excess ammonia would evaporate. Then approximately 30 mL of acetone was added and allowed to stir for 2 h. The solution was filtered to remove the NH_4F and the acetone was removed by rotary evaporation. The remaining solid was dried overnight on the vacuum line at 105 °C. A yield of 5.78 g was obtained for a 97% yield. NMR data for the bis(sulfonamide): δ_F 119.4 (t, 4F), 112.8 (t, 4F); δ 6.2 (s) (note: the presence of water in low amounts will shift this signal to near 4.0).

3.6. Procedure for $(Na)HNSO_2(CF_2)_4SO_2NH(Na)$

The sodium salt is obtained by neutralizing the sulfonamide with ca. 1.0 N NaOH solution to a pH of 8.4 and then drying on the vacuum line at 100 °C overnight. NMR data for the disodium salt of the bis(sulfonamide): δ_F 119.3 (t, 4F), 113.5 (t, 4F); $\delta_{H\Psi}$ 4.0 (s).

3.7. Procedure for $Me_3SiN(Na)SO_2(CF_2)_4SO_2N(Na)SiMe_3$ (7)

The disodium salt of the bis(sulfonamide) (3.0 g, 7.4 mmol) was mixed with 40 mL of very dry acetonitrile in a 250 mL heavy-walled flask equipped a Teflon Ace Thread® connection and a reflux jacket with a Teflon-glass valve at the top. Then 20 mL of HMDS was added and the mixture was refluxed in a closed system with vigorous stirring for 4 days. The excess HMDS and solvent were removed under dynamic vacuum and the white solid was dried under dynamic vacuum at 120 °C overnight. A 100% yield is assumed for the next step. Selected data for 7: δ_F 119.2 (t, 4F), 113.4 (t, 4F); δ_H 2.0 (s).

3.8. Procedure for $FSO_2(CF_2)_4SO_2N(Na)SO_2(CF_2)_4SO_2N(Na)SO_2(CF_2)_4SO_2F$ (8)

Very dry acetonitrile (75 mL) was vacuum transferred into the flask above containing **7** (4.1 g, 7.4 mmol). The difluoro compound **6** (18 g, 25 mmol) was dried over P_4O_{10} and freshly distilled before use. It was then vacuum transferred into the flask. The reaction mixture was slowly brought to room temperature and slowly heated to reflux. The clear solution was kept at 120 °C for 7 days. The solvent and excess **6** were distilled out under dynamic vacuum. The remaining off-white sold was dried at 120 °C under dynamic vacuum overnight. The isolated yield of **8** was 94%, 7.6 g. Selected data for **8**: ^{19}F NMR (CD_3CN, ppm) δ_F 106.5(m, 4F), 112.3(m, 8F), 119.3(m, 12F), +46.6(s, 2F).

3.8.1. Preparation of tetramer sodium salt $CF_3SO_2N(Na)SO_2(CF_2)_4SO_2N(Na)SO_2(CF_2)_4SO_2N(Na)SO_2(CF_2)_4SO_2N(Na)SO_2CF_3$ (9)

To the 250 mL heavy-walled flask containing compound **8** (7.6 g, 6.5 mmol) $CF_3SO_2N(Na)Si(CH_3)_3$ (3.4 g, 14.0 mmol) was added while inside a dry box. Dry acetonitrile (ca. 50 mL) was vacuum transferred to the flask using a vacuum line. The mixture was then heated at 100 °C for 4 days. The acetonitrile and product trimethylsilyl fluoride were then removed under dynamic vacuum at 100 °C and the white solid was dried at 100 °C under dynamic vacuum for 4 h. Selected data for **9**: δ_F 78.6(s, 6F), 112.2 (s, 12F), 119.3 (s, 12F).

3.8.2. Preparation of methylated tetramer salt $CF_3SO_2N(CH_3)SO_2(CF_2)_4SO_2N(CH_3)SO_2(CF_2)_4SO_2N(CH_3)SO_2(CF_2)_4SO_2N(CH_3)SO_2CF_3$ (10)

The sodium sulfonimide salt **9** (6.00 g, 4.29 mmol) was placed in a 25 mL flask equipped with a stopcock adapter under a nitrogen atmosphere. Then 15 mL of freshly distilled dimethyl sulfate was syringed and injected into the flask. The reaction was heated to 105 °C in an oil bath overnight and a 19F NMR spectrum was taken to determine completion of the reaction.

Cold DI water was added and the mixture was allowed to stir overnight to decompose the excess DMS. After 12 h a light brown solid was removed by filtration and then 10 mL of ethyl acetate and a $NaHCO_3$ solution was used to separate and dry the compound. After separation the ethyl acetate was removed by vacuum. This product would not sublime as the other monofunctional and difunctional methylated sulfonimides did in previous experiments. The compound was a very light tan color. The yield was 75% for a total of 4.40 g. Selected data for **6**: δ_F 73.7(s, 6F), 107.0 (s, 12F), 119.9 (s, 12F); δ_H 3.65 (s).

3.8.3. Preparation of tetramer $RTILCF_3SO_2N(MMIM)SO_2(CF_2)_4SO_2N(MMIM)SO_2(CF_2)_4SO_2N(MMIM)SO_2(CF_2)_4SO_2N(MMIM)SO_2–CF_3$(11)

In a 50 mL round bottom flask with a stir bar, 30 mL of $CHCl_3$ was added with 3.00 g (2.2 mmol) of the methylated tetramer. Then 0.87 g (10.5 mmol) of methyl imidazole was added. The mixture was refluxed at 75 °C overnight. The $CHCl_3$ was decanted and the IL was dried under dynamic vacuum line for14 h at 75 °C to remove excess methyl imidazole and moisture. The yield was 98% for a total of 3.65 g. Selected data for **11**: δ_F 78.6 (s, 6F), 112.2 (s, 12F), 119.4 (s, 12F); δ_H 8.35 (1H, s), 7.30 (2H, s), 3.80 (6H, s). T_g = −43 °C, T_m = 58 °C, T_d = 459 °C.

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Appendix A. A bit of history

Diplomatic relations between China and the US were established in early 1979. Prior to this historic event, there were many activities in anticipation of increased scientific exchange. In 1977, I learned that one of the last US educated PhD in Chemistry was Prof. Huang Wei-Yuan who received his degree at Harvard in 1952 and returned to China in 1955, where he began work in fluorochemicals (*C&EN*, May 16, 1977, p. 30). As part of improved scientific exchange the American Chemical Society was planning to have a Chinese delegation attend the ACS-Japan Chemical Society meeting in Hawaii in April 1979 as the first Chinese to attend an ACS meeting. I was Co-chair of the 4th ACS Winter Conference on Fluorine Chemistry to be held in January 1979 in Daytona Beach, FL. I began correspondence in 1978 to invite Prof. Huang Wei-Yuan to this meeting and make the ACS Fluorine Division the first to have Chinese participants at an ACS sponsored meeting. My efforts were successful and three scientists from the Shanghai Institute of Organic Chemistry, deputy director Huang Wei-Yuan, research fellow Chen Ching-Hun and deputy chief engineer Feng Yun-Kung attended (*C&EN*, Jan. 29, 1979, p. 8). As part of their visit to the US, they also visited several industrial and academic laboratories in the US including my university, Kansas State University (see picture). It was the beginning of an excellent scientific and personal relationship.

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