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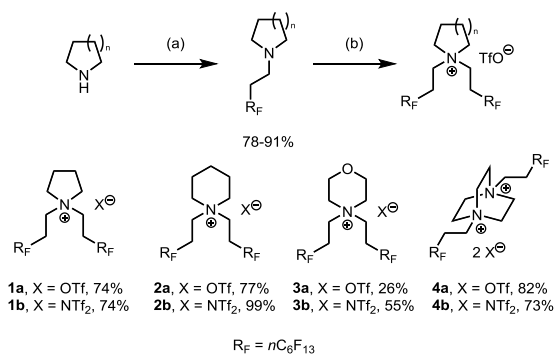
Perfluorinated ammonium, phosphonium and triazolium salts were synthesized by quaternization of amines, phosphanes and triazoles. Subsequent exchange of anions delivered a variety of different salts/ionic liquids.

Introduction

Perfluoroalkyl carboxylic and sulfonic acids with longer carbon chains ($C_nF_{2n+1}CO_2H$ and $C_nF_{2n+1}SO_3H$ with $n > 6$) have found ubiquitous applications for surface treatment. Due to their strong C-F bond they are persistent and accumulate in the biosphere. For this reason they attracted attention as global contaminants. An alternative are shorter chain compounds with C_6F_{13} (R_F) residues. We decided to combine the outstanding characteristics of short chained perfluorinated materials with the advantages of ionic liquids, which are often associated with sustainable processes and green chemistry.

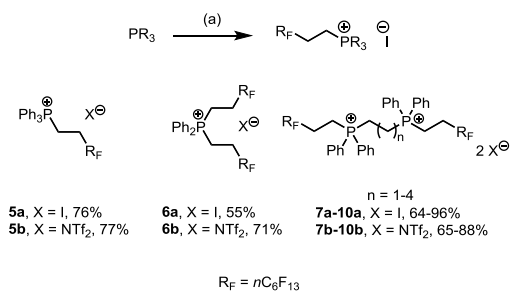
Preparation of ammonium and phosphonium salts^[1]

We have prepared a series of perfluorinated ionic liquids based on cyclic ammonium and phosphonium cations. In the ammonium series we prepared pyrrolidinium **1a**, piperidinium **2a**, morpholinium salts **3a** and DABCO derivatives **4a** over one or two steps resp. Anions were exchanged by using an ion exchange resin.



Scheme 1. Reagents and conditions. a) 1.0 eq. $R_FCH_2CH_2OTf$, 2.0 eq. K_2CO_3 , EtOAc, 70°C, 1 d; (b) 1.0 eq. $R_FCH_2CH_2OTf$, toluene, 130°C, 3 h.

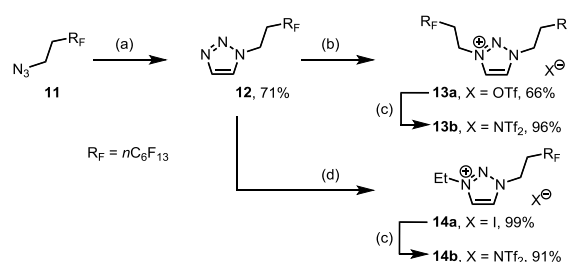
In the phosphonium series mono- and bisperfluorinated phosphonium salts **5a–10a** were obtained in 55–96% yield. After exchange of anions all triflimide salts **5b–10b** can be regarded as ionic liquids with melting points below 100°C.



Scheme 2. Reagents and conditions. a) 1.1–2.5 eq. $R_FCH_2CH_2I$, DMF, 105°C, 17–24 h.

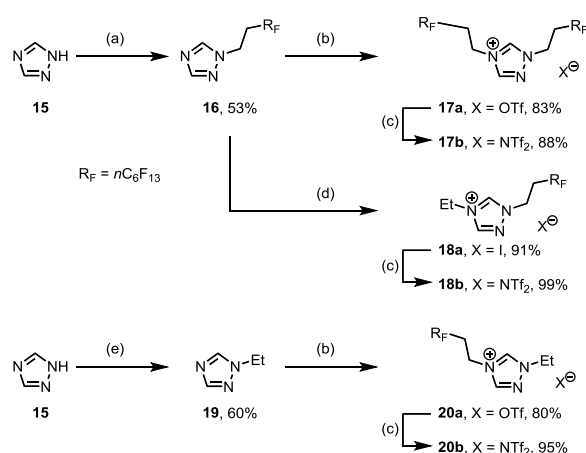
Preparation of triazolium salts^[2]

1,2,3-Triazolium salts **13a–14a** were obtained by copper catalyzed alkyne azide cycloaddition (click reactions) with perfluorinated azide **11** and subsequent alkylation of the triazole **12** in 47–70% yield over two steps.



Scheme 3. Reagents and conditions. (a) 0.02 eq. $CuSO_4$, 0.2 eq. sodium ascorbate, 1.5 eq. $TMSC\equiv CH$, THF, 23°C, 16 h; 3.0 eq. TBAF, THF, 23°C, 6 h; (b) 2.0 eq. $R_FCH_2CH_2OTf$, acetone, 130°C, 3 h; (c) 1. Column of hydroxide loaded Lewatit Mono MP Plus 800, 2. 1.0 eq. $HNTf_2$; (d) 4.0 eq. EtI, acetone, 130°C, 3 h.

In case of 1,2,4-triazolium salts **17a–18a** and **20a** the corresponding unsubstituted 1,2,4-triazole **15** was first mono- **16**, **19** and then dialkylated in 44–48% yield over two steps. All anions (iodide or triflate originated from the syntheses) were changed to the triflimide anion (NTf_2) in 88–99% yield.



Scheme 4. Reagents and conditions. (a) 2.0 eq. $R_FCH_2CH_2OTf$, 2.0 eq. K_2CO_3 , acetone, 23°C, 24 h; (b) 2.0 eq. $R_FCH_2CH_2OTf$, acetone, 130°C, 3 h; (c) 1. Column of hydroxide loaded Lewatit Mono MP Plus 800, 2. 1.0 eq. $HNTf_2$; (d) 2.0 eq. EtI, acetone, 130°C, 3 h; (e) 2.0 eq. EtI, 2.0 eq. K_2CO_3 , acetone, 23°C, 21 h.

Acknowledgement

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[1] T. Alpers, T. W. T. Muesmann, O. Temme, J. Christoffers, *Synthesis* **2018**, *50*, 3531–3539.

[2] T. Alpers, T. W. T. Muesmann, O. Temme, J. Christoffers, *Eur. J. Org. Chem.* **2018**, 4331–4337.