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The design of novel ionic liquid monomers with attractive properties represents a real challenge in the field of poly(ionic liquid)s (PILs). Here, we describe a comparative study of the synthesis of original PIL precursors from various sulfonimides or ketosulfonamides as unprecedented counteranions of imidazolium ILs. These salts were submitted to the Prilezhaev reaction and a first insight into the intrinsic properties of these new epoxy monomers was unveiled, in particular the thermal stability of these advanced epoxy salts by comparison with traditional counterions.

Bis(sulfonyl)imide is a very useful functional group that has greatly contributed to the emergence of ionic liquids in recent years.1 Combined with an imidazolium cation, the anion of bis(trifluoromethanesulfonyl)imide has been widely studied to synthesize various organic salts used as solvents with highly attractive properties, such as excellent thermal and chemical stabilities, low melting point and low viscosity.² These organic salts are usually prepared using efficient anionic metathesis with the commercially available salt LiNTf21d and then employed in many reactions.³ For example, they can be used as a polymerization medium for the development of advanced polymers,^{4,5} doping reagents or additives of polymers.⁶ More recently, they were considered as starting materials for making poly(ionic liquid)s.⁷ In this context, the ion-pair backbone plays a key role and governs the potential applications of the resulting polymer materials.8 Thus, many research groups have prepared quaternary nitrogen-based monomers (ammonium, pyrrolidinium, pyridinium, imidazolium...) and among the wide variety of poly(ionic liquids)s, the imidazolium core is currently the most widespread.9 All of these cations are commonly associated

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Scheme 1 Syntheses of imidazolium salts 2a-b and 3a-c from Im-Br.

and $\eta = 52$ mPa s at 298 K)^{14a} or [emim] NTf₂⁻ ($\rho = 1.52$ g cm³ and $\eta = 34$ mPa s) and [emim] F₃C-SO₂N-CO-CF₃ ($\rho = 1.46$ g cm³ and $\eta = 25$ mPa s at 298 K).^{14b} Ishida *et al.* measured a lower melting point for perfluorinated ketosulfonamide *versus* NTf₂⁻ for ionic liquids with planar chirality and an excellent thermal stability ($T_{decomposition} > 270 \ ^{\circ}$ C) was observed in almost all cases.¹⁵ These encouraging data revealed the real potential of these anions and recent studies have opened easy access to ketosulfonamides¹⁶ or sulfonimides¹⁷ with particularly attractive methodologies from simple substrates. Therefore, the aim of this work was to evaluate these analogs of NTf₂⁻ to confirm the potential of these types of anion as new epoxy precursors and more generally in PILs chemistry.

Firstly, to prepare aliphatic or aromatic ketosulfonamides, we mixed stoichiometric amounts of benzoyl chloride and sulfonamides in the presence of an excess amount of triethylamine (2.5 equiv.). The reaction with methanesulfonamide gave mainly ketosulfonamide which can be isolated without purification in 53% yield. Under the same conditions, we used benzenesulfonamide to prepare a biaryl ketosulfonamide in moderate yield after recrystallization. These yields can be improved by using a substoichiometric amount of iodine.¹⁶ Thereafter, efficient deprotonation of ketosulfonamides by sodium hydride (1.1 equiv.) led to the corresponding anions with hydrogen gas as a sole by-product. At room temperature, these anions reacted as a one-pot sequence with homemade imidazolium Im-Br to afford 1a-b in good yields. Thus, an effective and straightforward route (only two steps) was developed to produce new ionic liquid monomers bearing a terminal alkene avoiding tedious purification from readily accessible reagents.

According to our recent works,¹⁸ imidazolium salts **1a-b** bearing a terminal alkene are promising precursors of epoxy ionic liquid monomers **2a-b**. To date, we have successfully evaluated the epoxidation of several imidazoliums with NTf₂⁻ exclusively (oxidant: *meta*-chloroperoxybenzoic acid "mCPBA" or dimethyldioxirane "DMDO"). As a preliminary study, we extended this recent methodology using other conventional counteranions such as PF_6^- , BF_4^- or Br^- . TGA thermograms of salts **3a-c** (Scheme 1) clearly highlighted the better thermal stability for the NTf₂⁻ salt **3a** compared to **3b** and **3c** (see ESI†). Thus, the thermal stability of these epoxidized salts can be ranked according to the following order: $BF_4^- < PF_6^- < NTf_2^-$. This ranking is consistent with conventional salts without the epoxy group. From a chemical point of view, we detected a

significant difference depending on the nature of the counterion with partial hydrolysis of the salt 3c while the ring opening by-product was observed during the epoxidation of the imidazolium bromide. These results clearly confirm the key role of anions on the intrinsic properties of epoxy salts. Thus, we undertook the epoxidation of ketosulfonamide salts 1a-b. Concerning the salt denoted 1a, the use of mCPBA (1 equiv.) showed only unreacted starting alkene by NMR monitoring after 3 h 30 of reaction. The addition of a second equivalent of mCPBA did not afford the expected epoxidized salt while a side compound was detected by NMR. Next, the epoxidation of the salt 1a was investigated by adding DMDO (1 equiv.). After 3 h, the NMR revealed the epoxidation of the alkene up to 70%, and complete oxidation with the further addition of a slight excess of DMDO (0.3 equiv.). Despite this successful oxidation, a side-product was again observed over time. Under similar conditions, epoxidation of salt 1b with DMDO (1 equiv.) showed partial oxidation of the alkene (50%) without by-products. Once again, the reaction was completed with additional DMDO (0.5 equiv.) inducing mainly the oxidation of the alkene but also the appearance of by-products. Although the use of DMDO led to the epoxidation of alkenes, the presence of impurities confirmed the poor stability of these epoxidized salts compared to NTf2⁻. To determine the structure of these side-products, we used saccharin as a cyclic ketosulfonamide counteranion of imidazolium.¹⁹ Thus, we oxidized imidazolium saccharinate 1c with mCPBA (1 equiv.) and minor aromatic impurities appeared by NMR. In the literature, saccharin can react under acidic conditions to give a sulfonic acid and a carboxylic acid or amide.²⁰ In this process of oxidation, the high-resolution mass spectrometry confirmed the presence of the epoxide 2c (m/z =215.1) and side-products 4c and 5b-c which could correspond to the epoxide opened by saccharinate (m/z = 398.1) and derivatives (m/z = 416.1 or 417.1) in accordance with acidic conditions in the presence of mCBA (Scheme 2). To confirm the poor stability of these anions, we checked side reactions for the oxidation of 1a-b using DMDO. Once again, HRMS analyses showed the presence of imidazoliums 4a-b and 5a, which corroborate the slight



Scheme 2 Side-products detected by HRMS after epoxidation of imidazolium ketosulfonamides.

reactivity of the anion of ketosulfonamide towards the epoxide even under neutral conditions (Scheme 2 and ESI[†]).

These oxidations revealed degradation of ketosulfonamide counterions in the presence of strong oxidizing agents such as mCPBA and DMDO. For salts 2a-b, the ketosulfonamide anion is still too nucleophilic towards the epoxide. These results showed the incompatibility of ketosulfonamide anions during the epoxidation of an ionic liquid by mCPBA. Although the epoxidation could be carried out with DMDO, the presence of impurities limits their potential applications. Hence, we continued our investigation by studying the synthesis of the original sulfonimides. The synthesis of these anions required the preparation of sulfonyl chlorides and then sulfonamides which lead potentially to non-symmetrical sulfonimides. We started by the synthesis of symmetrical sulfonimide 8 bearing two p-methoxy aromatic rings (Scheme 3). 4-Methoxybenzenesulfonyl chloride 6 was prepared by the reaction between anisole and chlorosulfonic acid. Sulfonyl chloride 6 was then transformed into sulfonamide 7 in quantitative yield. Under basic conditions, this compound reacted with sulfonyl chloride 6 to afford sulfonimide 8. The anionic metathesis of imidazolium Im-Br with deprotonated sulfonimide 8 gave a salt 9 bearing a terminal alkene. Oxidation of this salt with the most efficient oxidant determined from our previous work, i.e. excess of DMDO, led quantitatively to salt 10 after 7 h in acetone. This epoxidation clearly showed better stability of this anion compared to previous ketosulfonamide salts.

After the successful synthesis of epoxy ionic liquid **10** bearing a symmetrical biaryl sulfinimide counterion, we were interested in the preparation of non-symmetrical anions (Scheme 4). Due to the important contribution of fluorine atoms on the final properties of ionic liquids, we used triflamide in the presence of various aromatic sulfonyl chlorides. Firstly, an ether group was kept on the aromatic sulfonyl chlorides to give salt **11a**, possibly to incorporate a perfluorinated chain if necessary. We also prepared the fluorinated sulfonamide salts **11b** and **11c** according to the previous strategy from an arylsulfonyl chloride and triflamide in the presence of an excess of NaH. The sulfonamide salts **11a–c** were directly engaged in anionic metathesis with imidazolium **Im–Br** to give products **12a–c** with good yields. All ionic liquids were quantitatively oxidized with DMDO (2.4 equiv.) in 2 h at room temperature. Worthy of note,







the oxidation of **12b-c** with mCPBA (2 equiv.) required 24 h at 40 $^{\circ}$ C to give **13b** and **13c** in 89% and 68% yield, respectively (Scheme 4).

The fluorinated sulfonimide of salt 13c is fairly similar to the NTf_2^{-} anion with the presence of a phenyl moiety as a unique difference. Thus, a comparison of the thermal behavior can be carried out between these salts 10, 13a-c and a similar imidazolium salt incorporating the NTf2⁻ as a counteranion (Im-NTf₂) (see ESI[†]). For this epoxidized salt Im-NTf₂, high thermal stability (up to 310 °C) was observed with a maximal degradation temperature between 410 and 460 °C. For imidazolium combined with symmetrical biaryl sulfinimide anion 10, two degradation peaks have been revealed at 110 °C (14 wt%) and 320 °C (50 wt%), respectively. The analysis of monoaryl salt 13a showed two decomposition temperatures at 120 °C (16 wt%), followed by a maximal degradation temperature at around 379-414 °C. Consequently, the monoaryl sulfonimide salt 13a appears more stable which may be due to the presence of fluorine atoms whereas the steric effects and the rigidity of the biaryl counterion destabilize salt 10. Finally, the TGA of salt 13b exhibits better thermal stability compared to salt 13c. In fact, salt 13b had thermal stability of up to 300 °C with a mass loss of only 4%. The maximum degradation of salt 13b was noticed at high temperature from 350 °C to 420 °C, which was close to the values of the reference Im-NTf₂ (410-460 °C). These results showed the great potential of sulfonimides to synthesize tailor-made ionic liquid monomers and their superiority over ketosulfonamides with a better chemical and thermal stability. In addition, these anions are easily adjustable without reducing their potential for polymerization at processing temperatures of epoxy networks.

Finally, we synthesized ionic liquids carrying two epoxides from sulfonimide salts **11b-c**, which led to the best results in the thermal analysis of salts **13b-c**. The sequence was slightly different from our previous study, the synthesis of salts **15a-b** required anionic metathesis with imidazolium **diIm-Br** to give **14a** and **14b** in 63% and 48% yield, respectively. In both cases, the oxidation of the two alkenes was carried out with 3.3 equivalents of DMDO to quantitatively obtain the corresponding diepoxides **15a** and **15b** (Scheme 5).

The TGA curves of diepoxides **15a** and **15b** have a similar appearance to the monoepoxides **13b** and **13c** (see ESI[†]). A first



Scheme 5 Synthesis of diepoxidized sulfonimidate salts 15a-b.

degradation peak was observed at 100 °C with a maximum degradation close to 410 °C for **15a** and 400 °C for **15b**. Although the overall thermal stability of these new epoxidized salts is low compared to the same diepoxidized imidazolium salt with NTf₂⁻ as a counteranion, the thermal behaviors of **15a-b** are sufficient to envisage the preparation of new epoxy networks with possible applications requiring high hydrophobicity (anti-corrosion coatings). The preparation of these new cationic poly(ionic liquid)s from an epoxy monomer incorporating a sulfonimide counterion is currently under progress in our laboratory.

Conclusions

In this study, we prepared various sulfonimides and ketosulfonamides as counteranions to the imidazolium. These new salts were evaluated during an epoxidation reaction in order to compare their chemical stability. The salts bearing ketosulfonamide anions were particularly sensitive to this reaction and will not be suitable for further uses. Conversely, the salts bearing sulfonimides lead to epoxy salts with good to excellent thermal stability. Epoxidized salts represent a new family of very exciting monomers. Henceforth, we will consider their use in the polymerization processes and study their behavior. These original sulfonamide salts are still unexploited in this field and represent a real opportunity for the preparation of tailor-made PILs with novel properties.

Conflicts of interest

There are no conflicts to declare.

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