Ionic liquids-assisted ring opening of three-membered hetero-cycles with thio- and seleno-silanes

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Ionic liquids-assisted ring opening of three-membered heterocycles with thio- and seleno-silanes

Damiano Tanini [1], Tommaso Pecchi [1], Nikolai V. Ignat´ev [2,3,*] and Antonella Capperucci [1,*]

[1] University of Florence, Department of Chemistry "Ugo Schiff", Via della Lastruccia 3-13, I-50019 Sesto Fiorentino (Florence), Italy; damiano.tanini@unifi.it (D.T.); antonella.capperucci@unifi.it (A.C.)
[2] Universität Würzburg, Institut für Anorganische Chemie, Institut für nachhaltige Chemie & Katalyse mit Bor (ICB), Am Hubland, Würzburg 97074, Germany. mykola.ignatyev@uni-wuerzburg.de (N.V.I.)
[3] Consultant, Merck KGaA, Darmstadt 64293, Germany. nikolai.ignatiev@external.merckgroup.com (N.V.I.)
* Correspondence: antonella.capperucci@unifi.it; nikolai.ignatiev@external.merckgroup.com

Abstract: Ring opening reactions of strained heterocycles (epoxides, aziridines, thiiranes) by silyl chalcogenides, as thiosilanes and selenosilanes, can be efficiently performed in a variety of ionic liquids, which can behave as reaction media and in some cases also as catalysts. This protocol enables an alternative access to β-functionalized sulfides and selenides under mild conditions.

Keywords: Ring opening reactions; ionic liquids; silyl sulfides; silyl selenides; thiolysis; selenolysis

1. Introduction

It is well known the important role played by organic derivatives of sulfur in numerous fields. Sulfur-containing groups find application in organic chemistry and in a wide range of pharmaceuticals [1,2], foods [3,4], natural compounds [5] and materials [6]. Among the wide variety of sulfurated compounds, β-hydroxy sulfides represent an important class of molecules present in natural products as for example leukotrienes and pteriatoxin A. β-Hydroxy sulfides [7,8] are also used for clinical applications in treating various diseases, *i.e.* heart diseases and hypertension (diltiazem). Catalyzed addition reactions to alkenes or thiolysis of epoxides with thiols or disulfides are the more common methodologies to obtain β-hydroxy sulfides [9-12]. On the other hand, the versatility of silyl nucleophiles as alternative reagents to corresponding proton nucleophiles has been well established [13]. In this context, organothiosilanes are used as synthetic equivalents of thiols for delivery of sulfurated moieties under milder conditions [14-18]. On this matter, we reported the tetrabutylammonium fluoride (TBAF) and tetrabutyl-ammonium phenoxide (PhON^{n}Bu$_4$) catalyzed ring opening reactions of strained heterocycles upon treatment with thiosilanes [15] and more recently with selenosilanes [19,20] to prepare sulfides, thiols, selenides, diselenides and selenols with hydroxyl, amino and mercapto moieties on the β-position. These bifunctionalized compounds represent a class of useful synthons, serving as building blocks to prepare more complex molecules. Thus, the search for new methodologies to access these compounds is still actual, and in particular the development of environmentally friendly protocols is of significant interest. The ionic liquids (ILs) have attracted great attention as alternative reaction media to reduce the application of volatile organic solvents [21-25]. Room temperature ionic liquids (RTILs) are liquids over a wide range of temperatures. RTILs possess valuable properties, such as negligible vapour pressure, thermal and chemical stability, non-inflammability, efficient solvating ability towards organic and inorganic compounds, and recyclability. Additionally, some ionic liquids have demonstrated a catalytic activity towards a variety of organic reaction. [26-31] ILs are composed by posi-

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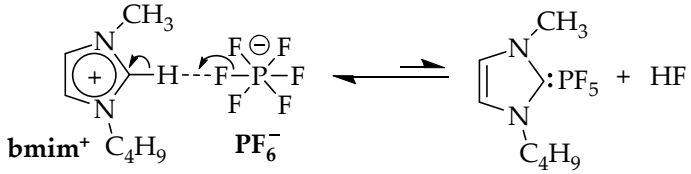
tive and negative ions, whose nature allows tuning ionic liquids properties: by this reason they are defined as "designer solvents".

Ionic liquids comprising stable anion like fap (fap = tris(pentafluoroethyl)trifluoro-phosphate, [$(C_2F_5)_3PF_3$]) or triflate and cation (like bmpl = 1-butyl-1-methylpyrrolidinium) proved to be a useful medium for the reactions with aggressive and dangerous reagents, for instance with elemental fluorine F_2 [32], SF_4 [33] and NaN_3 and HN_3 [34]. Ionic liquids can serve not only as reaction medium but also as catalyst to promote various reactions [35]. In particularly, ILs with [HSO_4]-anion, which are possessing a certain Brønsted acidity, were found to be an advanced medium for dehydration of the alcohols [36]. For example, 1-phenylcyclox-1-ene can be obtained in high yield by heating (80-90 °C, 1 h) of the 1-phenyl-cyclohexan-1-ol in 1-ethyl-3-methyl-imidazolium hydrogensulfate, [emim][HSO_4]. Ionic liquids can be regenerated and reused for several times without losing its activity in this reaction. IL [emim][HSO_4] was successfully used for conversion of mono-, di-, and polysaccharides into furan derivatives, for instance xylose into furfural, fructose and polysaccharide Inulin into 5-(hydroxymethyl)-2-furaldehyde [37] The dehydration of primary alcohols required stronger acidic conditions, which can be achieved by addition of the corresponding acid to ionic liquid. For instance, ionic liquid + Brønsted acid, *i.e.* [emim][HSO_4] + concentrated sulfuric acid, [emim][CF_3SO_3] + Triflic acid, and [emim][$CF_3C(O)O$] + trifluoroacetic acid were successfully used for conversion of the hexan-1-ol into dihexyl ether, cyclohexanol into cyclohexene, and *tert*-butanol into *iso*-butylene [36]. It is interesting to note, that Brønsted acid added to ionic liquid having the same counter anion do not evaporate from this mixture even at the temperature well above the boiling point of pure Brønsted acid [35]. Acidic system ionic liquid + Brønsted acid can be used to carry out cascade reactions. For example, reaction of the 4-brom-3,5-dimethyl-phenol and buten-2-ol in a two-phase system [emim][HSO_4] + H_2SO_4 / Hexane proceeded at low temperature (55–60 °C) and resulted in the formation of the 6-bromo-2,2,5,7-tetramethylchromane in a very short time (15 min) in a good yield (89%). Similar conditions were applied for the synthesis of the vitamin E (D,L-α-tocopherole) [38].

Application of acidic system ionic liquid + Brønsted acid allowed to carry out Schmidt reaction at very mild conditions (40 °C) [34]. Synthesis of tetrazoles can be successfully carried out in acidic IL [emim][HSO_4] without addition of sulfuric acid [39]. 5-Alkyl-2-amino-1,3.4-thiodiazole and α,ω-bis(2-amino-1,3.4-thiodiazol-5-yl)alkane were prepared by interaction of carboxylic acids and thiosemicarbazide in [emim][HSO_4] acidified by addition of sulfuric acid in good to excellent yield. However, application of the [emim][HSO_4] did not allow regeneration and reuse of this catalytic system. Use of hydrophobic ionic liquid [hmim][fap] or [bmpl][fap]) instead of [emim][HSO_4] provided the possibility to regenerate and reuse the catalytic system [hmim][fap] or [bmpl][fap] + H_2SO_4 at least three times [40].

A practical approached to the synthesis of 1-(α-hydroxyalkyl)- or 1-(β-hydroxyalkyl)-2-(aminomethyl)acetylenes was developed in 2012 [41]. Authors used a catalytic system comprising a metallo-catalyst $Cu(OAc)_2$ in combination with acidic IL [emim][HSO_4] diluted with water to promote three components Mannich type reaction of terminals alcohols with formaldehyde and secondary amines. Final products were gained in better yield in comparison to that obtained in conventional organic solvents. It was demonstrated, that catalytic system $Cu(OAc)_2$/ [emim][HSO_4] /H_2O can be recovered and reused for several time without loose in the yield of final product [41].

Acidic properties of N,N-dialkylimidazolium hexafluorophosphate or tetrafluoroborate ILs presumably relates to acidic proton in the position 2 of imidazolium ring. That can result *in situ* generation of HF due to parallel formation of a complex between nucleophilic imidazolium carbene and Lewis acids PF_5 or BF_3 according to equilibrium presented in Scheme 1 [42].



Scheme 1. An equilibrium proposed for *in situ* generation of the HF in [bmim][PF_6] [42]

Acidic properties of [bmim][PF_6] were used to catalyze Johnson-Claisen rearrangement of allylic terpenols. Natural isoprenoid-derived carboxylic esters were prepared in moderate to high yield *via* interaction of allylic terpenols with triethyl orthoacetate (propionate) in the presence of 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF_6] (10 mol%). This convenient protocol allows simple product separation and reuse of the ionic liquid up to ten times without reduction in the product`s yield [42].

Application of of 1-butyl-3-methylimidazolium hexafluorophosphate or tetrafluoroborate ILs to promote von Richter reaction gave the possibility to prepare some compounds, which were inaccessible under literature known conditions [43]. Similarly, Chapman rearrangement of aryl benzimidates to tertiary acyclic amides in [bmim][PF_6] or [bmim][BF_4] proceeded at much milder conditions (at 120-190 °C) in comparison to 220-300 °C typically required for Chapman reaction [44].

Ionic nature of ILs can promote polarization of conjugated system. For example, cations can be attached to the lone pair of the heteroatom and anion coordinate on acidic proton promoting charge separation in the starting compound [45]. This reaction´s mechanism was proposed to explain unprecedent acceleration of the domino reaction between 4-hydroxyalk-3-yonates and amines in ionic liquids yielding 4-aminofuran-2(5*H*)-ones. Ionic liquid [bmim][BF_4] applied for this synthesis can be recycled and reused at list five times without decrease in reaction rate and in product yield. [45] Similar acceleration effect of ionic liquid as reaction medium was observed by fluorocyclization (lactonization) of unsaturated carboxylic acids under action of F-TEDA-BF_4 [46].

Due to its ionic character ionic liquids are good solvent for many organic and inorganic compounds. For instance, dehydration of N-acyl-2-arylethylamines with $POCl_3$ to 3,4-dihydroisoquinolines (Bishler-Napieralski reaction) proceeded in ILs such as [bmim][PF_6], [emim][CF_3SO_3], and [bmpl][CF_3SO_3] under milder condition and better yield in comparison to reaction in conventional solvents [47]. Similarly, high yield of benzofuroxanes was achieved by interaction of the *o*-nitrobenzenes with sodium azide NaN_3 in [empl][BF_4] in the presence of phase transfer catalyst and small quantity of water [48].

However, only few examples are reported on the reaction of epoxides with thiols in ionic liquids. In some cases addition of a catalyst was not necessary, while for some ring opening reactions of epoxides or thiols heating was required [49-52]. The most common ILs consist of dialkylimidazolium cations and [BF_4^-], [Br^-] or [Cl^-] as the counter-anion. The reactions in ILs usually provides good yields and high regioselectivity.

As a continuation of our research dealing with the study of chemical reactivity of thiosilanes and of organoselenosilanes towards electrophiles, targeting the development of mild conditions to functionalize the chalcogen-Si bond, herein we report our results on the interaction of silyl sulfides and silyl selenides with epoxides, aziridines and thiiranes in RTILs. To the best of our knowledge, there is no example on the reactivity of silylated sulfur nucleophiles with these heterocycles in ionic liquids.

Previously, we have found that bis(trimethylsilyl)sulfide reacted efficiently with aldehydes in ionic liquids to afford thioaldehydes [53]. The conversion of the C=O into the C=S group required the use of a suitable catalyst as $CoCl_2{\cdot}6H_2O$ or TfOTMS. 1-R-3-Methyl imidazolium derivatives (R = Et, *n*-Bu, *n*-Hex) with [BF_4^-], [PF_6^-], and [TfO^-]

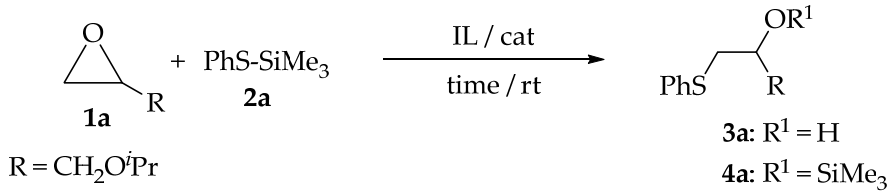
anions were the most efficient in promoting the thionation [53]. On the other hand, when pyrrolidinium based ionic liquids were used, only [bmpl][ntf] allowed to obtain the expected thioaldehydes, while no reaction was observed in [bmpl][$N(CN)_2$]. These results confirm the influence of the cation's and anion's nature on the progress of this reaction. These considerations prompted us to conduct initially a systematic survey on the reaction of thiosilanes with epoxides in ionic liquids.

2. Results

2.1. Reaction of thio- and selenosilanes with epoxides

To find out the best conditions for this reaction, glycidyl isopropyl ether **1a** and (phenylthio)trimethylsilane **2a** were selected as model substrates for the reaction in different ionic liquids. The reaction was performed in the most common ionic liquid [bmim][BF_4] using TBAF· $x H_2O$ or $PhON^nBu_4$ as catalyst, leading to the β-hydroxy phenylsulfide **3a** in fairly good yields (Table 1, entries 1, 2). In the absence of any catalyst, a mixture of sulfides bearing in β-position the hydroxyl (**3a)** or the silylether (**4a)** moiety were isolated in low yield (Table 1, entries 3,4). Formation of hydroxy-derivate (**3a)** is presumably related to presence of acidic impurities in the [bmim][BF_4] applied for this synthesis. This result indicates that ionic liquid [bmim][BF_4] is able to promote the ring opening, though longer reaction time (12 - 48 hours) is required in this case. A similar result was achieved when the epoxide **1a** was reacted in [bmim][PF_6] (Table 1, entries 5,6), giving **3a** in 47% yield when TBAF·$x H_2O$ was employed as catalyst. However, in absence of the catalyst **3a** and **4a** were isolated in low yield (entry 6), though in shorter reaction time of 3 hours in comparison to reaction in [bmim][BF_4]. Presumably, *in situ* hydrolysis of the [bmim][PF_6] by traces of water or equilibrium depicted in Scheme 1 (see above) leaded to generation of the HF, which act as catalyst and proton source in this reaction. Complete desilylation of a mixture of sulfides (**3a)** and (**4a)** was achieved by treating this mixture with TBAF·$x H_2O$ (10%). In all cases, the ring opening occurred with high regioselectivity, allowing isolation of the product deriving from the nucleophilic attack on the less substituted position of the epoxide.

Table 1. Ring opening of glycidyl isopropyl ether by PhSTMS in [bmim][X]

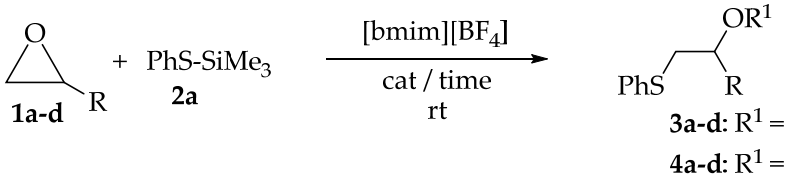


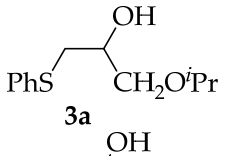
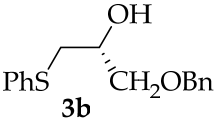
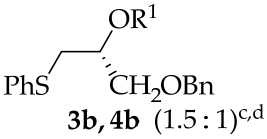
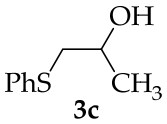
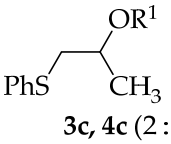
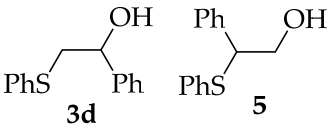
Entry	Ionic liquid	Catalyst	Time	Yield (%)[a]	
				3a	**4a**
1	[bmim][BF_4]	TBAF·$x$$H_2O$ (20%)	2 h	58[b]	-
2	[bmim][BF_4]	PhON^nBu_4 (40%)	4 h	51[b]	-
3	[bmim][BF_4]	--	12 h	10[c]	13
4	[bmim][BF_4]	--	48 h	24[d,e,f]	27
5	[bmim][PF_6]	TBAF·$x$$H_2O$ (20%)	3 h	47[b,e]	-
6	[bmim][PF_6]	--	3 h	28[c,e,f]	22

[a]Isolated yield. [b]Traces of diphenyl disulfide were isolated. [c]24% of $(PhS)_2$. [d]33% of $(PhS)_2$. [e]Unreacted epoxide (ca. 25-30%) was recoverd. [f]ca. 40% after desilylation with TBAF (10%).

The ring opening reaction was extended to various substituted epoxides, such as benzyl glycidyl ether **1b** (*S*-isomer), (±)-propylene oxide **1c** and (±)-styrene oxide **1d**, affording the desired products **3b-d** in good yields in the presence of TBAF·$x$$H_2O$ (Table 2, entries 2,4,6), while without catalysis the yields were much less and longer reaction time was required to complete the reaction (Table 2, entries 3,5). When epoxide **1d** was used as substrate, a mixture of regioisomers **3d** and **5** was obtained (**3d** : **5** = 6 : 1, Table 2, entry 6), similar as it was observed in the organic solvents [17,54].

Table 2. Ring opening of epoxides by PhSTMS in [bmim][BF_4]



Entry	R	Catalyst	Time	Product	Yield (%)[a,b]
1	CH_2O^iPr (±)-**1a**	TBAF·xH_2O (20%)	3 h	 **3a**	58
2	CH_2OBn (*S*)-(+)-**1b**	TBAF·xH_2O (20%)	3 h	 **3b**	63
3	CH_2OBn (*S*)-(+)-**1b**	--	26 h	 **3b, 4b** (1.5 : 1)[c,d]	44
4	CH_3 (±)-**1c**	TBAF·xH_2O (20%)	2 h	 **3c**	39
5	CH_3 (±)-**1c**	--	26 h	 **3c, 4c** (2 : 1)[c,d]	14
6	C_6H_5 (±)-**1d**	TBAF·xH_2O (20%)	3.5 h	 **3d** **5**	61 (**3d**) 11 (**5**)

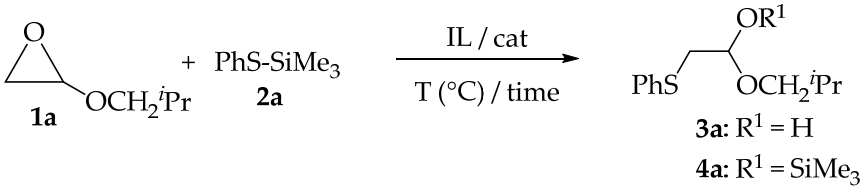
[a]Isolated yield. [b]20-25% of disulfide $(PhS)_2$ was formed. [c]Desilylation with TBAF (10%) was accomplished. [d]Ratio determined by H-NMR.

However, these preliminary results indicate that the reaction of organothiosilanes with epoxides can proceed efficiently also in [bmim][BF_4] as reaction media. Taking into account that the nature of anions and cations has an impact on the properties of ionic liquids, we were interested to test diverse ionic liquids, such as 1-alkyl-3-methyl imidazolium derivatives, bearing alkyl chains of different length, and methyl pyrrolidinium salts in ring opening reactions.

Thus, rection of the epoxide **1a** with PhSTMS in various ionic liquids in absence of catalysts is summarized in Table 3. The desired hydroxyl sulfide **3a** was regioselectively obtained in good yield, alongside the corresponding silyl ether **4a**, in hygroscopic ILs [emim][msu], [emim][atf], and in [bmpl][dca] (Table 3, entries 1-3). The ring opening proceeded less efficiently in [emim][otf] as reaction media (Table 3, entries 4, 5). It is interesting to note that in the absence of catalyst the ratio **3a:4a** is of about 1:9 (total yield is 16%, entry 4), and is reversed to about 9:1 (total yield is 28%, entry 5) when TBAF·xH_2O was used as catalyst. Addition of TBAF·xH_2O or heating (70°C) were necessary to obtain the ring opening products in hydrophobic ILs [hmim][ntf] and [bmpl][ntf] as reaction

media (Table 3, entries 6-8,10,11). A similar result was obtained in the reaction of **1a** with **2a** in [hmim][fap] and [bmpl][fap] (Table 3, entries 9, 12, 13). This could be ascribed to hydrolytic stability and low coordination ability of the [ntf] and [fap] anions in these ionic liquids.

Table 3. Thiolysis of glycidyl isopropyl ether by PhSTMS in different ILs



Entry	Ionic liquid	Catalyst/T(°C)	Time	**3a : 4a**	Yield (%)[a,b]
1	[emim][msu]	-- / rt	2 h	1 : 1.2[c]	73
2	[emim][atf]	-- / rt	2 h	1 : 1.6[c]	78
3	[bmpl][dca]	-- / rt	2 h	1 : 1.6[c]	78
4	[emim][OTf]	-- / rt	4 h	> 1 : 9[c]	16
5	[emim][OTf]	TBAF·xH$_2$O[d] / rt	2 h	> 9 : 1	28
6	[hmim][NTf$_2$]	-- / rt	3 h	> 1 : 9[c]	27
7	[hmim][NTf$_2$]	TBAF·xH$_2$O[d] / rt	2 h	> 9 : 1	66
8	[hmim][NTf$_2$]	-- / 70°C	6 h	1 : 1.4[c]	65
9	[hmim][fap]	TBAF·xH$_2$O[d] / rt	2 h	> 9 : 1	52
10	[bmpl][NTf$_2$]	TBAF·xH$_2$O[d] / rt	1.5 h	> 9 : 1	58
11	[bmpl][NTf$_2$]	-- / 70°C	3 h	1 : 1.7[c]	63
12	[bmpl][fap]	TBAF·xH$_2$O[d] / rt	2 h	> 9 : 1	26
13	[bmpl][fap]	-- / 70°C	6 h	1 : 1.1	37

[a]Total yield. [b]15-20% of diphenyl disulfide was formed. [c]Desilylation was carried out with 10% TBAF.· [d]20% of TBAF was added.

A plausible explanation of the uncatalyzed reactions in the dialkyl imidazolium series could stem from the possible activation of the epoxide by the imidazolium ring, due to a certain acidity of the H2 hydrogen (pK_a=21-23) [25], or by presence of traces HF in case of [BF_4] and [PF_6] ionic liquids.

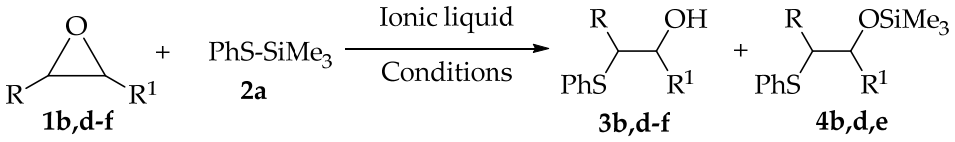
However, the anion can play an important role: [emim] methylsulfate and trifluoroacetate were able to catalyze the NROR (nucleophilic ring opening reaction) better than [emim] trifluoromethylsulfonate (otf), which is a weak nucleophile. [25] Considering the pyrrolidinium series, only [bmpl][dca] behaved as an efficient catalyst (Table 3, entry 3). It seems that nucleophilic dicyanamide $(NC)_2N^-$ [dca]-anion of this ionic liquid is able efficiently functionalize the S-Si bond, enabling the nucleophilic attack on the epoxide. Nonetheless, in case of ionic liquids with weakly coordinating anions [bmpl][ntf] or [bmpl][fap], catalysis with TBAF·xH$_2$O or heating were required, to obtain the products **3a** and **4a**. However, the yield was rather low that confirms the influence of the anion's nucleophily on the progress of ring opening reaction (Table 3, entries 10-13).

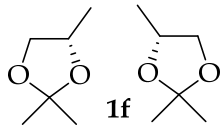
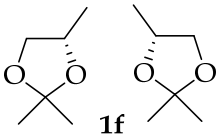
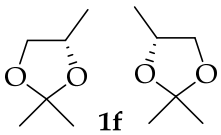
The work up after completion of the reaction was simple. The products were extracted with diethyl ether, except for reactions carried out in [hmim][ntf] and

[hmim][fap], where hexane was employed, and [bmpl][fap] which required extraction with chloroform, since these ionic liquids are miscible or partially miscible with Et_2O.

In order to enlarge the scope of this protocol, the uncatalyzed reaction was extended to other monosubstituted epoxides (Table 4, entries 1-4), showing that the selected ionic liquids with nucleophilic counter anions [msu], [atf], and [dca] were able to perform as reaction medium and as catalysts, enabling formation of the β-substituted phenyl sulfides in good yields.

Table 4. Ring opening reactions of mono- and disubstituted epoxides **1b,d-f**



Entry	R	R^1	Ionic liquid	Conditions	Products	Yield (%)[a,b]
1	CH_2OBn (*R*)-(-)-**1b**	H	[emim][msu]	r.t./2h	**3b:4b**>10:90	62 (59)[c,d]
2	C_6H_5 (±)-**1d**	H	[emim][atf]	r.t./3.5h	(**3d,4d**):(**5,6**)>30:70[e]	59 (58)[f]
3	C_6H_5 (±)-**1d**	H	[bmpl][dca]	r.t./3.5h	(**3d,4d**):(**5,6**)>20:80[e]	67 (65)[f]
4	CH_2OH (*S*)-(-)-**1e**	H	[emim][atf]	r.t./2.5h	**3e:4e**>10:90	60 (57)[c]
5	 **1f**		[emim][msu]	TBAF·xH_2O 70°C/18 h	**3f**	38[c,g]
6	 **1f**		[emim][atf]	TBAF·xH_2O 18 h	**3f**	27[c,h]
7	 **1f**		[bmpl][dca]	TBAF·xH_2O 70°C/18 h	**3f**	<10[c,i]

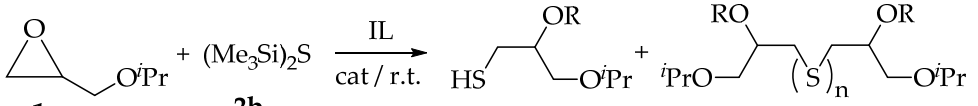
[a]Total isolated yield. [b]In parenthesis yield of **3** after desilylation (TBAF 10%). [c]Ca. 15-20% of $(PhS)_2$. [d]Unreacted epoxide (ca. 15%) was recovered.[e,f]Ratio of regioisomers (**3d,4d**):(**5,6**) = 3:1 and total yields determined by ^1H NMR. [g]Ca.30% of unreacted epoxide. [h]Ca. 50% of unreacted epoxide.[i]Ca. 70% of epoxide.

A high regioselectivity was achieved, except for the styrene oxide which, as already observed [17,54], gave a mixture of regioisomeric β-hydroxy- (**5**) and β-trimethylsilyloxy- (**6**) substituted sulfides (Table 4, entries 2,3). Reaction of chiral non-racemic (*R*)-(-)-benzyl glycidol **1b** and (*S*)-(-)-glycidol **1e** with the thiosilane allowing access to chiral β-hydroxy- or β-OTMS-phenylsulfides (**3b**,**e** or **4b**,**e**, respectively) with retention of stereoselectivity. When the disubstituted epoxide **1f** of D-mannitol was used as substrate, addition of the TBAF or heating and longer reaction time were required in all the ILs used. In spite of a

harder conditions, a low conversion rate for **1f** was observed (Table 4, entries 5-7). These results indicate low reactivity of this disubstituted substrate.

To expand the application of ionic liquids as reaction media in epoxide ring-opening reaction, we tested a more intriguing thiosilane, the bis(trimethylsilyl)sulfide **2b** (hexamethyldisilathiane, HMDST). The interaction of **1a** with HMDST was carried out in selected ionic liquids, as summarized in Table 5. In the absence of catalysis, the ring opening reaction in [bmim][BF_4] resulted in poor conversion and formation of a small quantity of the β-trimethylsilyloxy disulfide **12** (Table 5, entry 1). Conversely, when TBAF was added as catalyst, an almost equimolar mixture of β-mercapto alcohol **7**, β-hydroxy disulfide **11** and β-hydroxy sulfide **9** was obtained within 2 hours of reaction time (Table 5, entry 2).

Table 5. Thiolysis of glycidyl isopropyl ether by HMDST in selected ILs



7 R=H; **8** R=TMS

n=1 **9** R=H; **10** R=TMS

n=2 **11** R=H; **12** R=TMS

Entry	Ionic liquid	Catalyst	Time	Products	Yield (%)[a]
1	[bmim][BF_4]	--	24 h	**12**	8[b]
2	[bmim][BF_4]	TBAF·xH_2O (20%)	2 h	**7:9:11** = 1:1:1[c]	40[c]
3	[emim][msu]	--	5 h	**12:11** > 95:5	28
4	[emim][msu]	TBAF·xH_2O (20%)	2 h	**9:11** = 1:3[c]	36[c]
5	[emim][atf]	--	4 h	**12:9** > 95:5	35
6	[emim][atf]	TBAF·xH_2O (20%)	90 min	**9:11** > 95:5	33[d]
7	[emim][atf]	TBAF·xH_2O (20%)	30 min	**7:(9+11)** > 95:5	56
8	[bmpl][dca]	--	5 h	**12:11** > 95:5	27
9	[bmpl][dca]	TBAF·xH_2O (20%)	3 h	**9:11** = 1:2[c]	35[c]

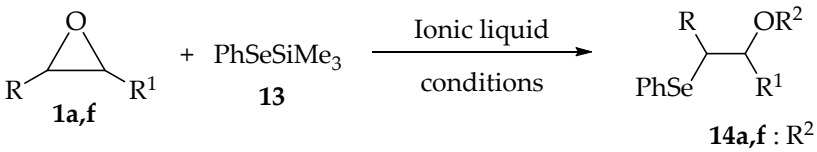
[a]Total yield. [b]Unreacted epoxide (ca. 63%) was recoverd.[c]Yields and products ratio determined by ^{1}H NMR. [d]Epoxide:HMDST 2:1.

On the other hand, the thiolysis of **1a** was achieved without TBAF in [emim][msu], [emim][atf] and [bmpl][dca], leading to the disulfide **12** as the major product, however the yields were low (Table 5, entries 3, 5, 8). The formation of the disulfide or sulfide could be ascribed to the rather long reaction time (4h-5h) required to reach a good conversion. That could favor the oxidation of the thiol intermediate to disulfide **12**, or otherwise its further attack on the epoxide to form the sulfide **9**, as it was observed when an excess of epoxide was reacted under TBAF catalysis (Table 5, entry 6). Application of the TBAF as catalyst allowed to achieve better selectivity by shorter reaction time and, to increase the yield. When the catalyst was used in [emim][msu] and [bmpl][dca], a mixture of products **9** and **11** was obtained (Table 5, entries 4, 9), while the thiol **7** was found to be a major compound by interaction of **1a** with HMDST **2b** after 30 min in [emim][atf] (Table 5, entry 7). Based on these results, we can conclude that thiolysis of epoxides by thiosilanes in ionic liquids occurs under milder conditions in comparison to the reaction with thiols, which need higher temperature (50°-100°C) [49,50].

The functionalization of oxiranes with silyl chalcogenides was extended to selenosilanes, providing access to seleno-derivatives, which are applicable in different fields, such as: organic synthesis [55-57], materials [58], medicinal and food chemistry [59-63]. Reaction of the epoxide **1a** with (phenylseleno)trimethylsilane **13** in selected ionic liquids resulted in the formation of the β-hydroxy- (**14a)**, or β-silyloxy-phenylselenide (**15a)** in good yields (Table 6, entries 1-5). Addition of the catalyst to reaction mixture was not required to complete the reaction in a short time. It seems that all ionic liquids used in this reaction act as efficient catalysts, enabling nucleophilic addition of the selenosilane to epoxide. The Se-Si compounds, as expected, is more reactive than the substances containing S-Si bond: in fact the nucleophilic ring opening with seleno-derivatives was achieved without catalysis in ILs with weakly nucleophilic anion, *i.e.* in [hmim][ntf] and [bmpl][ntf], while for completing the reaction with corresponding thiosilane **2a** heating or addition of TBAF was necessary (Table 3).

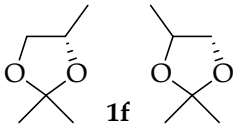
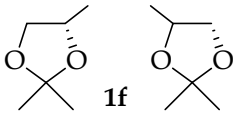
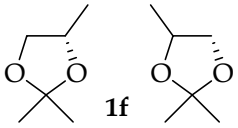
The disubstituted epoxide **1f** was also tested in the reaction with PhSeTMS in ionic liquids used for the interaction with PhSTMS. However, no reaction was evidenced without addition of a catalysis. After addition of TBAF, the disubstituted β-hydroxy phenylselenide **14f** was isolated from the reaction mixture, albeit in very low yields (Table 6, entries 6,7). Presence of significant amount of unreacted epoxide was detected in this case. No increase in yield was observed after heating in [emim][msu] and [emim][atf], while in [bmpl][dca] formation of small quantity of product **14f** was observed after prolonged heating (Table 6, entry 8). These results indicate that, despite the higher reactivity expected for silyl selenides, the disubstituted epoxide show very poor reactivity towards these reagents.

Table 6. Ring opening of epoxides by PhSeTMS in selected ILs



14a,f : R^2 = H

15a : R^2= $SiMe_3$

Entry	R	R^1	Ionic liquid	Conditions	**14 : 15**	Yield (%)[a]
1	CH_2O^iPr **1a**	H	[emim][msu]	r.t./90min	1 : 1	72[b,c]
2	CH_2O^iPr **1a**	H	[hmim][NTf_2]	r.t./90min	2 : 1	70[b,c]
3	CH_2O^iPr **1a**	H	[hmim][fap]	r.t./90min	2 : 1	58[b,c]
4	CH_2O^iPr **1a**	H	[bmpl][NTf_2]	r.t./90min	2 : 1	64[b,c]
5	CH_2O^iPr **1a**	H	[bmim][PF_6]	r.t./90min	1.5 : 1	72[b,c]
6	 **1f**		[emim][msu]	TBAF·xH_2O r.t./18h	>99:1	16[d,e]
7	 **1f**		[emim][atf]	TBAF·xH_2O r.t./18h	>99:1	12[d,e]
8	 **1f**		[bmpl][dca]	70°C/18h	>99:1	<10[e]

[a]Total yield. [b]25-30% of diphenyl diselenide was obtained. [c]Desilylation with TBAF (10%) led to **14a** in quantitative yields.[d]60% of TBAF was added portionwise. [e]Ca. 55% of unreacted epoxide and 20% of $(PhSe)_2$ were detected.

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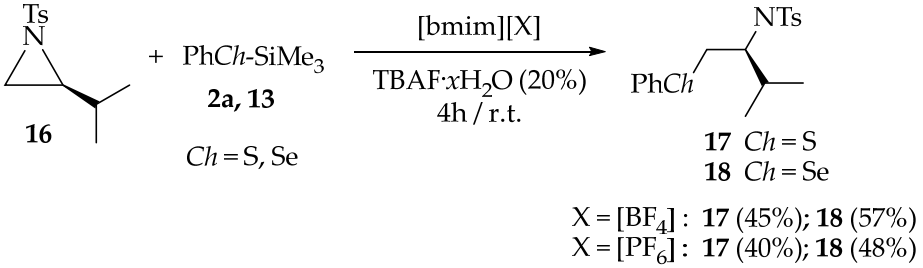
2.2. Reaction of thio- and selenosilanes with aziridines

Aiming to evaluate the scope and limitations of the proposed protocol, the reaction of thiosilanes was extended to aziridines. Aziridines represent a versatile class of compounds, being employed as useful building blocks in organic synthesis, to prepare more complex molecules, with various biological properties, as well as with a variety of applications in organic chemistry [64]. In this context, the nucleophilic ring opening in aziridines is a well-established method to prepare nitrogen containing bifunctional intermediates. The reactivity of aziridines is influenced by substituent on the nitrogen: electron withdrawing groups, such as sulfonyl or carbonyl, tend to favour the ring opening comparing to aziridines, bearing N-H, N-Alk or N-Aryl groups. Only a few examples of reaction of aziridines with chalcogen nucleophiles in ionic liquids are reported in the literature. For example, interaction of N-H aziridines with thiols proceeded efficiently in [bmim][X] (X = Cl, Br) in the absence of any catalyst [65]. β-Seleno amines can be prepared by heating aziridines with diselenides in presence of CuO nanoparticles [66] or by use of stable zinc selenolate (PhSeZnBr) [67]. However, to the best of our knowledge, no examples dealing with the application of silyl-chalcogenides in reaction with aziridines are reported in the literature.

First, we have tested the reactivity of the *N*-tosyl aziridine **16**, prepared from L-valine, towards PhSTMS **2a** in [bmim][BF_4] and [bmim][PF_6]. Despite the activation by the Ts-group, no ring opening was observed without catalysis, while in the presence of TBAF·*x*H_2O (20%) a regioselective formation of the chiral β-thio *N*-Ts-amine **17** was achieved (Scheme 2). Reaction of the silyl-selenide **13** with aziridine **16** under TBAF catalysis led to the formation of the β-seleno amine **18**, together with diphenyl diselenide (ca. 30%) (Scheme 2).

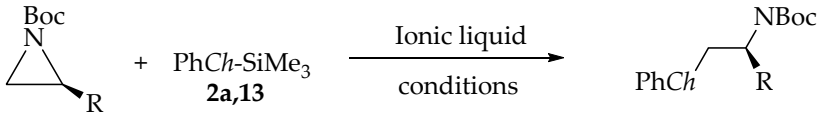


Scheme 2. Ring opening of *N*-Ts aziridine by Ph*Ch*$SiMe_3$ in [bmim][X]

In the next step we focused on testing of the reactivity of *N*-Boc aziridines, considering that Boc deprotection is generally more practical than removal of the tosyl group. Preliminary investigations showed that the reaction of *N*-Boc aziridines with silyl chalcogenides (Ph*Ch*$SiMe_3$) in THF, under TBAF catalysis, yielded expected β-phenylchalcogenated derivatives [68]. Use of HMDST **2b** and HMDSS in this reaction led to the formation of the *N*-Boc amino thiols and the mixture of amino selenides and diselenides, respectively [19,69].

Like the interaction of the *N*-tosyl aziridine **16** (Scheme 2), the reaction of the *N*-Boc aziridine **19a,** obtained from methionine, with PhSTMS in the absence of catalyst in [bmim][PF_6] resulted in the formation only a small quantity (13%) of ring opening product. Mainly unreacted aziridine was recovered (65%). Addition of TBAF·*x*H_2O (20%) to the reaction mixture enabled the formation of **20a** in 48% yield, together with diphenyl disulfide (30%) (Table 7, entry 1). Application of [emim][atf] and [bmpl][dca] as reaction media allowed obtaining **20a** in satisfactory yield without use of any catalyst (Table 7, entries 2, 3). Formation of the β-amino phenylsulfide **20a** in other ionic liquids with less nucleophilic anions was achieved only after addition of TBAF·*x*H_2O (20%) to the reaction mixture (Table 7, entries 4-9).

Table 7. Reaction of Ph*Ch*SiMe$_3$ with *N*-Boc aziridines **19a,b**



19a R = $(CH_2)_2SMe$ **20a,b** *Ch* = S
19b R = ^{i}Pr **21a,b** *Ch* = Se

Entry	R	Ch	Ionic liquid	Conditions	Products	Yield (%)[a]
1	$(CH_2)_2SMe$	S	[bmim][PF_6]	TBAF·*x*H_2O/r.t./6 h	**20a**	48[b]
2	$(CH_2)_2SMe$	S	[emim][atf]	r.t./3 h	**20a**[c]	57
3	$(CH_2)_2SMe$	S	[bmpl][dca]	r.t./3 h	**20a**	54
4	$(CH_2)_2SMe$	S	[emim][OTf]	TBAF·*x*H_2O/r.t./2 h	**20a**	63
5	$(CH_2)_2SMe$	S	[hmim][fap]	TBAF·*x*H_2O/r.t./2 h	**20a**	56
6	$(CH_2)_2SMe$	S	[emim][msu]	TBAF·*x*H_2O/r.t./3 h	**20a**	61
7	$(CH_2)_2SMe$	S	[hmim][NTf_2]	TBAF·*x*H_2O/r.t./3 h	**20a**	49
8	$(CH_2)_2SMe$	S	[bmpl][NTf_2]	TBAF·*x*H_2O/r.t./3 h	**20a**	65
9	$(CH_2)_2SMe$	S	[bmpl][fap]	TBAF·*x*H_2O/r.t./3 h	**20a**	43
10	$(CH_2)_2SMe$	Se	[bmim][PF_6]	TBAF·*x*H_2O/r.t./4 h	**21a**[c,d]	45
11	$(CH_2)_2SMe$	Se	[emim][msu]	r.t./3 h	**21a**	54
12	$(CH_2)_2SMe$	Se	[hmim][fap]	r.t./3 h	**21a**	42
13	$(CH_2)_2SMe$	Se	[bmpl][NTf_2]	r.t./3 h	**21a**	68
14	*i*-Pr	S	[bmim][PF_6]	TBAF·*x*H_2O/r.t./4 h	**20b**	48
15	*i*-Pr	S	[emim][atf]	r.t./3 h	**20b**[c,d]	55
16	*i*-Pr	S	[bmpl][dca]	r.t./6 h	**20b**	59[e]
17	*i*-Pr	S	[hmim][NTf_2]	70°C/10 h	**20b**	47
18	*i*-Pr	S	[bmpl][NTf_2]	TBAF·*x*H_2O/r.t./3 h	**20b**	38[f]
19	*i*-Pr	S	[hmim][fap]	TBAF·*x*H_2O/r.t./2 h	**20b**	46
20	*i*-Pr	Se	[bmim][PF_6]	TBAF·*x*H_2O/r.t./3 h	**21b**	47

[a]Isolated product. [b]Without catalysis 65% of unreacted aziridine was recovered. [c]Minor regioisomer Ph*Ch*CH(R)CH_2NHBoc (10%) was observed. [d]20% of the minor regioisomer. [e]10% of unreacted aziridine. [f]45% of unreacted aziridine.

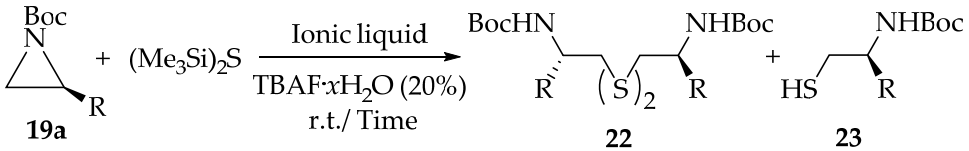
Similarly, PhSeTMS **13** reacted with aziridine **19a** in [bmim][PF_6] under TBAF catalysis yielding **21a** (Table 7, entry 10). Interestingly, when other ionic liquids were used (Table 7, entries 11-13), no addition of catalyst was necessary to isolate the ring-opening product **21a**.

The reaction's conditions described above was also applied to the TBAF catalyzed interaction of aziridine **19b**, derived from valine, with PhSTMS **2a** and PhSeTMS **13** (Table 7, entries 14, 20) in [bmim][PF_6], as well as in other ionic liquids (Table 7, entries 18, 19). In all cases the yield of *N*-Boc amino thiol **20b** and amino selenide **21b** was moderate (38-47%). Heating of reactants in [hmim][ntf] leaded to the formation of the amino thiol **20b** in 47% yield (Table 7, entry 17). Application of the catalyst TBAF is not required in this case. Similarly, reaction of the of aziridine **19b** with PhSTMS **2a** in [emim][atf] and

[bmpl][dca] can be carried out without application of the catalyst (Table 7, entries 15, 16). This observation confirms that ionic liquid with nucleophilic anions can induce the nucleophilic substitution by **2a** in the absence of any catalyst. The results presented in Table 7 highlight that ionic liquids are suitable reaction media to promote the ring opening reaction of less activated aziridines by silyl-chalcogenides under mild conditions. Furthermore, the reactions proceeded under high regiocontrol, enabling the isolation of the products arising from the attack on less hindered side of aziridine. Only when reactions of the aziridines **19a** and **19b** with PhSTMS **2a** were carried out in [emim][atf] (Table 7, entries 2, 15), the regio-isomers (PhSCH(R)CH_2NHBoc, R = $(CH_2)_2$SMe, *i*-Pr) derived from the attack on more substituted side of the aziridine was detected in the reaction mixture as minor products. Moreover, the formation of minor regio-isomer was observed in the reaction between aziridine **19a** whith the selenated nucleophile PhSeTMS **13** in [bmim][PF_6] (Table 7, entry 10).

The reaction of aziridine **19a** with bis(trimethylsilyl)sulfide HMDST **2b** did not proceed without catalyst in selected ionic liquids. Addition of TBAF to the reaction mixture initiated the ring opening reaction leading to the formation of the β-amino disulfide **22** as major product, together with the amino thiol **23** in somewhat lower yields (Table 8).

Table 8. Ring opening of *N*-Boc aziridine **19a** by HMDST in selected ILs



R = $(CH_2)_2SCH_3$

Ionic liquid	Time	Products	Yield %[a]
[bmim][PF_6]	5 h	**22**	28
[emim][atf]	3 h	**22** : **23** = 4 : 1	48[b,c]
[bmpl][dca]	1.5 h	**22** : **23** = 4 : 1	52[b,c]
[emim][msu]	3 h	**22** : **23** = 3 : 1	61[b,c]

[a]Isolated yield. [b]Total yield of **22** and **23** (not separated). [c]Ratio determined by NMR

2.3. Reaction of thio- and selenosilanes with thiiranes

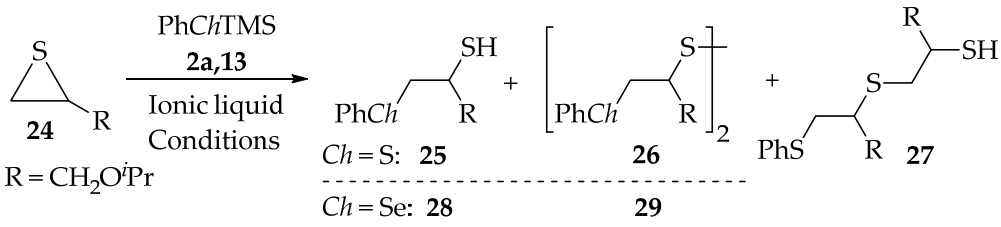
Among strained heterocycles, thiiranes also represent interesting building blocks and intermediates in different organic transformations to prepare a variety of molecules, including sulfurated heterocycles, through ring expansion routes [70]. Nevertheless, thiiranes have received less attention, probably due their lower stability in comparison to other three membered derivatives discussed above. In fact, in the presence of strong nucleophiles they are subjected to desulfurization to the corresponding alkenes, while the reaction with weak nucleophiles leads to polymerization resulting in polysulfides [71]. Moreover, the nucleophilic ring opening gives thiols, whose high tendency to oxidation to disulfides is well known. Thiols are identified to play an important role in some biochemical transformations due to their capability to be oxidized and then regenerated, such as in sugar derivatives [72], and to be a noteworthy intermediates for development novel spice compounds and aromas [73]. Therefore, a mild and straightforward method for ring opening of thiiranes to prepare the corresponding thiol-containing derivatives is

highly desirable. Several methods dealing with the reaction of thiiranes with thiols, or thiolates to obtain mercapto sulfides through a S_N2 ring opening reaction in the presence of suitable catalysts have been reported. It was observed that the product's distribution pattern depends on the reaction conditions, such as: the type of the nucleophile, the solvent polarity, the concentration, and the reaction temperature [74,75].

It was obeyed to investigate the reaction of thiiranes with thiosilanes in ionic liquids. To the best of our knowledge, no ring opening of thiiranes with any nucleophile in these reaction media have been reported. At first, the interaction of the 2-(isopropoxymethyl)thiirane **24** with thiosilane **2a** was carried out in [bmim][PF_6], but no reaction was observed. After addition of TBAF·$x$$H_2O$ (20%) to the reaction mixture and stirring for 6 h, the major isolated compound was the disulfide **26** (Table 9, entry 1). The disulfide **26** was generally the major compound obtained in all reactions listed in the Table 9 together with small quantity of the β-phenylthio thiol **25**, except the reaction in [bmpl][dcn], in which the mixed sulfide **27** was isolated in low yield as the only product. The reaction carried out in [emim][atf], [bmpl][fap] and [emim][OTf] required the addition of TBAF to achieve the thiirane ring opening (Table 9, entries 3,7,9). In [bmpl][fap] a similar result was obtained when the reaction mixture was heated at 50°C for 4 hours (Table 9, entry 7, footnote 'g'). Mixed sulfide **27** was identified by GC-MS, even if in rather low amount, in the reaction mixture obtained in [emim][otf] (Table 9, entry 9). Presumably, compound **27** resulted from nucleophilic attack of the thiol moiety of **25** on a second molecule of the thiirane. As can be observed, the uncatalyzed ring opening was obtained in several ionic liquids (Table 9, entries 2, 4-6, 8), leading to a similar distribution of products.

Fluoride induced ring opening of episulfide was also observed with the Se-nucleophile **13**. The β-phenylseleno disulfide **29** was formed as major product in this reaction together with small quantity of the β-mercaptoselenide **28** (Table 9, entry 10).

Table 9. Reaction of thioglycidyl isopropyl ether **24** with $PhSSiMe_3$ and $PhSeSiMe_3$



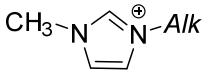
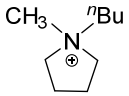
Entry	Ionic liquid	Conditions	Products	Yield (%)[a,b]
1	[bmim][PF_6]	TBAF·$x$$H_2O$/r.t./6 h	**26**	52
2	[emim][msu]	r.t./2h30min	**25, 26**	56[c,d]
3	[emim][atf]	TBAF·$x$$H_2O$/r.t./4 h	**25, 26**	54[c,d]
4	[hmim][NTf_2]	r.t./3 h	**25, 26**	59[c,d]
5	[bmpl][NTf_2]	r.t./2h30min	**25, 26**	48[c,d]
6	[hmim][fap]	r.t./2h30min	**25, 26**	45[d,e]
7	[bmpl][fap]	TBAF·$x$$H_2O$/r.t./4 h	**25, 26**	49[d,f,g]
8	[bmpl][dcn]	r.t./2 h	**27**	30[f]
9	[emim][OTf]	TBAF·$x$$H_2O$/r.t./2 h	**25,26,27**	57[f,h,i]
10	[hmim][fap]	TBAF·$x$$H_2O$/r.t./3h	**28, 29**	42[l,m]

[a]Isolated product. [b]10-15% of $(PhS)_2$ was formed (except entry 10). [c]Total yield of **25** and **26** (not separated; ca. 1:4 by NMR). [d]10-15% of **27** was detected (GC/MS and NMR). [e]Total yield of **25** and **26** (ca. 1 : 6 by NMR). [f]Polysulfides were detected by mass spectra. [g]Comparable result was achieved at 50°C/5h. [h]Total yield (by NMR). [i]**25**:(**26**+**27**)= 1:2 (by NMR). [l]Total yield of **28**:**29** (not separated; ca. 1:8 by NMR). [m]5% of $(PhSe)_2$ was formed.

3. Materials and Methods

3.1. Instruments and Reagents

All reactions were carried out in an oven-dried glassware under inert atmosphere (N_2). All commercial products were purchased from Merck-Sigma-Aldrich and used as received, without further purification. The ionic liquids used were prepared ([bmim][BF_4], [bmim][PF_6]) according to reported methods, or gently provided by Merck ([emim][otf], [emim][msu], [emim][atf], [hmim][fap], [hmim][ntf][, [bmpl][ntf], [bmpl][dcn], [bmpl][fap]). Ionic liquids were maintained under high-vacuum for 30 minutes prior to use. Thin layer chromatography was performed with TLC plates Silica gel 60 F_{254}, which was visualised under UV light, or by staining with an ethanolic acid solution of *p*-anisaldehyde followed by heating. Mass spectra were determined by ionization potential (EI, 70 eV) and by ESI. NMR spectra (^1H and ^{13}C) were recorded in $CDCl_3$ using Varian Gemini 200 or a Mercury 400 operating at 200 or 400 MHz for ^1H and 50 or 100 MHz for ^{13}C. ^{77}Se NMR spectra were recorded using a Bruker 400 Ultrashield spectrometer, operating at 76 MHz. NMR signals were referenced to nondeuterated residual solvent signals (7.26 ppm for ^1H, 77.0 ppm for ^{13}C). Diphenyl diselenide $(PhSe)_2$ was used as an external reference for ^{77}Se NMR (δ=461 ppm). Chemical shifts (δ) are given in parts per million (ppm), and coupling constants (J) are given in Hertz (Hz), rounded to the nearest 0.1 Hz. Multiplicity is reported as s = singlet, d = doublet, t = triplet, ap d = apparent doublet, m = multiplet, dd = doublet of doublet, bs = broad singlet, bd = broad doublet. Line separation = ls.

Abbreviations of ionic liquids	*Full name*	*Anions*	*Cations*
[bmim][BF_4]	1-Butyl-3-methylimidazolium tetrafluoroborate	[BF_4^-]	 (*Alk = n-Butyl, Ethyl, n-Hexyl*)
[bmim][PF_6]	1-Butyl-3-methylimidazolium hexafluorophosphate	[PF_6^-]	
[emim][otf]	1-Ethyl-3-methylimidazolium trifluoromethanesulfonate	[$CF_3SO_3^-$]	
[emim][msu]	1-Ethyl-3-methylimidazolium methylsulfate	[$CH_3OSO_3^-$]	
[emim][atf]	1-Ethyl-3-methylimidazolium trifluoroacetate	[CF_3COO^-]	
[hmim][fap]	1-Hexyl-3-methylimidazolium tris(pentafluoroethyl)trifluorophosphate	[$(C_2F_5)_3PF_3^-$]	
[hmim][ntf]	1-Hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide	[$N(CF_3SO_2)_2^-$]	
[bmpl][ntf]	1-Butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide	[$N(CF_3SO_2)_2^-$]	
[bmpl][dcn]	1-Butyl-1-methylpyrrolidinium dicyanamide	[$N(CN)_2^-$]	
[bmpl][fap]	1-Butyl-1-methylpyrrolidinium tris(pentafluoroethyl)trifluorophosphate	[$(C_2F_5)_3PF_3^-$]	

3.2. Experimental Method

*3.2.1. General Procedure for the ring opening of epoxides **1** by (phenylthio)trimethylsilane **2a** and (phenylseleno)trimethylsilane **13***

A mixture of epoxide (1 eq.) and silyl nucleophile (PhSTMS **2a** or PhSeTMS **13**) (1.2 eq.) in the ionic liquid (0.5 mL) was stirred at room temperature. The progress of the reaction was followed by TLC (typically: hexanes/ethyl acetate 9:1) upon extraction with diethyl ether of a small amount of the reaction mixture. After completion, the reaction mixture was extracted with diethyl ether (3x2mL) or hexanes (depending on the miscibility of the ionic liquid with the organic solvent). The combined organic extracts were dried over Na_2SO_4 and then concentrated under vacuum to obtain the crude product. The ionic liquid can be reused after drying under vacuum to eliminate traces of the extraction solvent.

When required, following the previously described procedure, TBAF·$x$$H_2O$ (20%) was added to the reaction mixture of the epoxide (1 eq.) and the silyl nucleophile (1.2 eq.) in 0.5 mL of the ionic liquid. When the reaction was performed without catalyst, a mixture of alcohol (**3** or **14**) and silyl ether (**4** or **15**) was obtained. Treatment of the crude product with 10% TBAF (1M in THF) afforded the deprotected β-hydroxy-phenyl sulfide **3** or selenide **14**.

1-Isopropoxy-3-(phenylthio)propan-2-ol, **3a**

Yellowish oil, yield: see Tables 1-4. ^{1}H NMR (200 MHz, $CDCl_3$), δ (ppm): 1.15 (d, 6H, *J* = 6.2 Hz); 2.43 (br s, 1H, OH), 3.05-3.11 (m, 2H), 3.40-3.63 (m, 2H + 1H), 3.81-3.92 (m, 1H), 7.18-7.41 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$), δ (ppm): 22.1, 37.6, 69.2, 70.3, 72.3, 126.2, 128.9, 129.5, 135.1. MS, *m*/*z* (%): 226 (M^+, 58), 135 (63), 123 (69), 109 (68), 99 (100).

[(1-Isopropoxy-3-(phenylthio)propan-2-yl)oxy]trimethylsilane, **4a**

Yellow oil, yield: see Tables 1-3. ^{1}H NMR (200 MHz, $CDCl_3$), δ (ppm): 0.11 (s, 9H), 1.15 (d, 6H, *J* = 6Hz), 2.98 (dd, $1H_A$, *J* = 6.6 Hz, 13.6 Hz), 3.19 (dd, $1H_B$, *J* = 4.8 Hz, 13.6 Hz), 3.45 (app dd, 2H, *J* = 4.6 Hz, 5.3 Hz), 3.49-3.64 (m, 1H), 3.94 (app quint, 1H, *J* = 5.2 Hz), 7.38-7.42 (m, 5H). MS, *m*/*z* (%): 298 (M^+, 10), 225 (17), 135 (82), 117 (65), 99 (76), 73 (100).

(*R*)-1-(benzyloxy)-3-(phenylthio)propan-2-ol, **3b**

Light yellow oil, yield: see Tables 2,4. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 2.61 (br d, 1H, *J* = 4.5 Hz), 3.02 (dd, $1H_A$, *J* = 7.3 Hz, 14.1 Hz), 3.14 (dd, $1H_B$, *J* = 4.9 Hz, 14.1 Hz), 3.50 (dd, $1H_A$, *J* = 5.7 Hz, 10.0 Hz), 3.59 ($1H_B$ dd, *J* = 4.3 Hz, 10.0 Hz), 3.84-3.96 (m, 1H), 4.53 (br s, 2H), 7.18-7.38 (m, 10H). ^{13}C NMR (50 MHz, $CDCl_3$), δ (ppm): 37.5, 68.9, 72.3, 73.4, 127.4, 127.7, 128.2, 128.5, 128.9, 129.6, 135.3, 137.7. MS, *m*/*z* (%): 274 (M^+, 4), 135 (19), 123 (22), 109 (16), 91 (100).

[(1-(Benzyloxy)-3-(phenylthio)propan-2-yl)oxy]trimethylsilane, **4b**

Yellow oil, yield: see Tables 2,4. ^{1}H NMR (200 MHz, $CDCl_3$), δ (ppm): 0.09 (s, 9H), 2.99 (dd, $1H_A$, *J* = 6.7 Hz, 13.5 Hz), 3.21 (dd, $1H_B$, *J* = 5.6 Hz, 13.5 Hz), 3.49-3.59 (m, 2H), 3.90-4.06 (m, 1H), 4.52 (br s, 2H), 7.20-7.40 (m, 10H). MS, *m*/*z* (%): 346 (M^+, 3), 135 (44), 91 (100), 73 (68).

1-(Phenylthio)propan-2-ol, **3c**

Light yellow oil, yield: see Table 2. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 1.27 (d, 3H, *J* = 6.2 Hz), 1.88 (br s, 1H), 2.84 (dd, $1H_A$, *J* = 8.8 Hz, 13.6 Hz), 3.13 (dd, $1H_B$, *J* = 3.9 Hz, 13.6 Hz), 3.79-3.87 (m, 1H), 7.16-7.41 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$), δ (ppm): 22.0, 43.7, 65.6, 127.4, 128.9, 130.1, 135.0. MS, *m*/*z* (%): 168 (M^+, 29), 124 (63), 109 (20), 91 (39), 45 (100).

Trimethyl[(1-(phenylthio)propan-2-yl)oxy]silane, **4c**

Yellow oily liquid, yield: see Table 2. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 0.09 (s, 9H), 1.26 (d, 3H, *J* = 6.0 Hz), 2.89 (dd, $1H_A$, *J* = 6.3 Hz, 13.1 Hz), 3.06 (dd, $1H_B$, *J* = 5.9 Hz, 13.1 Hz), 3.94 (br sext, 1H, *J* = 6.2 Hz), 7.12-7.40 (m, 5H). MS, *m*/*z* (%): 240 (M^+, 12), 117 (91), 73 (100).

1-Phenyl-2-(phenylthio)ethan-1-ol, **3d**

Yellow oil, yield: see Tables 2,4. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 2.81 (br s, 1H), 3.09 (dd, $1H_A$, *J* = 9.2 Hz, 13.8 Hz), 3.34 (dd, $1H_B$, *J* = 3.8 Hz, 13.8 Hz), 4.73 (dd, 1H, *J* = 3.8 Hz, 9.2 Hz), 7.24-7.45 (m, 10H). ^{13}C NMR (50 MHz, $CDCl_3$), δ (ppm): 43.9, 71.8, 126.1, 126.8, 128.1, 128.7, 129.3, 133.2, 138.1. MS, *m*/*z* (%): 230 (M^+, 9), 124 (100), 107 (37), 91 (15), 77 (33).

2-Phenyl-2-(phenylthio)ethan-1-ol, **5**

Yellow oil, yield: see Tables 2. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 2.02 (br s, 1H), 3.89-3.98 (m, 2H), 4.31 (t, 1H, *J* = 3.8 Hz), 7.23-7.35 (m, 10H). ^{13}C NMR (50 MHz, $CDCl_3$), δ (ppm): 55.6, 67.2, 127.3, 127.6, 128.0, 128.5, 128.8, 134.6, 137.4. MS, *m*/*z* (%): 230 (M^+, 43), 199 (78), 121 (97), 110 (99), 103 (76), 91 (100).

(*R*)-3-(Phenylthio)propane-1,2-diol, **3e**

Light yellow oil, yield: see Table 4. ^{1}H NMR (200 MHz, $CDCl_3$), δ (ppm): 2.73 (br s, 2H), 2.99 (dd, 1H, *J* = 7.8 Hz, 13.7 Hz), 3.13 (dd, 1H, *J* = 4.8 Hz, 13.7 Hz), 3.54-3.63 (m, 2H), 3.73-3.81 (m, 1H), 7.21-7.42 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$), δ (ppm): 37.6, 65.1, 69.9, 126.6, 129.0, 129.2, 134.9. MS, *m*/*z* (%): 135 (M^+,-49, 27), 123 (38), 110 (100), 109 (55), 91 (29), 77 (34), 65 (48), 45 (61).

(*R*)-1-(Phenylthio)-3-[(trimethylsilyl)oxy]propan-2-ol, **4e**

Yellow oily liquid, yield: see Table 4. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 0.11 (s, 9H), 1.87 (br s, 1H), 2.88-3.10 (m, 2H), 3.56-3.68 (m, 2H), 3.82-3.87 (m, 1H), 7.24-7.46 (m, 5H).

2-[(*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl]-1-[(*S*)-2,2-dimethyl-1,3-dioxolan-4-yl]-2-(phenylthio)-ethan-1-ol, **3f**

Following the general procedure, 1 eq. of D-mannitol epoxide (**1f**) and 1.2 eq. of the thiosilane **2a** were added with 0.6 eq. of TBAF·*x*H_2O in 0.5 mL of the ionic liquid. Pale yellow oil, yield: see Table 4. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 1.36 (s, 3H), 1.37 (s, 3H); 1.43 (s, 3H), 1.47 (s, 3H), 2.76 (b s, 1H), 3.19 (app t, 1H, *J* = 3.6 Hz), 3.72-3.78 (m, 1H), 3.81-3.87 (m, 1H), 3.92-3.96 (m, 1H), 4.06-4.18 (m, 2H), 4.35-4.46 (m, 2H), 7.23-7.44 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$), δ (ppm): 25.4, 25.6, 26.3, 26.8, 54.6, 65.8, 66.5, 67.2, 72.0, 75.4, 109.4, 109.6, 127.0, 129.0, 131.2, 135.3. MS, *m*/*z* (%): 354 (M^+, 10), 339 (8), 281 (6), 236 (9), 123 (12), 110 (16), 109 (14), 101 (100).

1-Isopropoxy-3-(phenylselanyl)propan-2-ol, **14a**

Yellow orange oil, yield: see Table 6. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 1.15 (d, 6H, *J* = 6.2 Hz), 2.60 (bs, 1H), 3.03 (dd, 1H, *J* = 12 Hz, 6.6 Hz), 3.10 (dd, 1H, *J* = 12 Hz, 5.8 Hz), 3.39-3.63 (m, 3H), 3.84-3.96 (m, 1H), 7.21-7.30 (m, 5H). ^{13}C NMR ($CDCl_3$, 50 MHz), δ (ppm): 22.1, 31.9, 69.6, 70.7, 72.2, 126.9, 128.9, 129.7, 132.5. ^{77}Se NMR ($CDCl_3$, 38.1 MHz), δ (ppm): 242.9. MS *m**z* (%): 274 ($M^{+\cdot}$, 26), 272 (11), 201 (8), 183 (30), 158 (31), 99 (59), 73(48), 57 (100).

[1-Isopropoxy-3-(phenylselanyl)propan-2-yl)oxy]trimethylsilane**, 15a**

Yellow orange liquid, yield: see Table 6. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 0.10 (s, 9H), 1.12 (b d, 3H, *J* = 6.4 Hz), 1.14 (b d, 3H, *J* = 5.8 Hz), 3.01 (dd, 1H, *J* = 12.7 Hz, 6.4 Hz), 3.17 (dd, 1H, *J* = 12.7 Hz, 5 Hz), 3.38-3.62 (m, 3H), 3.92-4.15 (m, 1H), 7.21-7.30 (m, 5H).

2-[(*R*)-2,2-Dimethyl-1,3-dioxolan-4-yl]-1-[(*S*)-2,2-dimethyl-1,3-dioxolan-4-yl]-2-(phenylselanyl)-ethan-1-ol, **14f**

Yellow orange liquid, yield: see Table 6. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 1.35 (s, 6H), 1.38 (s, 3H); 1.46 (s, 3H), 2.86 (b s, 1H), 3.15 (app b t, 1H, *J* = 4.5 Hz), 3.67-3.78 (m, 1H), 3.88-4.00 (m, 2H), 4.15-4.21 (m, 2H), 4.42-4.53 (m, 2H), 7.26-7.39 (m, 5H). ^{13}C NMR (50 MHz, $CDCl_3$), δ (ppm): 25.4, 25.6, 26.3, 26.8, 54.6, 65.8, 66.5, 67.2, 72.0, 75.4, 109.4, 109.6, 127.0, 129.0, 131.2, 135.3. MS, *m*/*z* (%): 314 (M^+-88, 29), 312 (20), 310 (13), 234 (17), 232 (8), 157 (62), 155 (30), 154 (34), 153 (19), 77 (100), 51 (76).

3.2.2. General procedure for the reaction of epoxides with bis(trimethylsilyl)sulfide ***2b***

A mixture of glycidyl isopropyl ether **1a** (1 mmol) and HMDST **2b** (1.2 mmol) in the ionic liquid (0.4 mL) was stirred at room temperature (when required 0.2 mmol of TBAF·*x*H_2O was added). The progress of the reaction was followed by TLC (typically: hexanes/ethyl acetate 5:1) upon extraction of a small amount with diethyl ether. After completion, the reaction mixture was treated with citric acid (50% aq. solution) and extracted with diethyl ether. The organic phase was then washed with citric acid (20% aq. solution) and dried over Na_2SO_4. Evaporation of the solvent gave the crude product, as variable mixture of β-hydroxy-thiol, -sulfide and -disulfide.

571
572 1-Isopropoxy-3-mercaptopropan-2-ol, **7**
573 Yellowish oil, yield: see Table 5. ^{1}H NMR (200 MHz, $CDCl_3$), δ (ppm): 1.16 (d, 3H, *J* =
574 6.2 Hz), 1.18 (d, 3H, *J* = 6.2 Hz), 1.48 (app t, 1H, *J* = 8.8 Hz), 1.93 (b s, 1H), 2.62-2.75 (m, 2H),
575 3.45-3.67 (m, 3H), 3.74-3.83 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$), δ (ppm): 22.1, 28.2, 70.0,
576 71.3, 72.2.
577 MS *m**z* (%): 151 (M^++1, 0.3), 117 (6), 99 (28), 91 (11), 73 (35), 61 (22), 57 (100).
578
579
580 3-Isopropoxy-2-[(trimethylsilyl)oxy]propane-1-thiol, **8**
581 Bright yellow oil, yield: see Table 5. ^{1}H NMR (200 MHz, $CDCl_3$), δ (ppm): 0.15 (s,
582 9H), 1.14 (d, 6H, *J* = 6.0 Hz), 1.4 (b t, 1H, *J* = 8.4 Hz), 2.46-2.78 (m, 2H), 3.40 (b d, 2H, *J* = 6.6
583 Hz), 3.58 (sept, 1H, *J* = 6.0 Hz), 3.79-3.87 (m, 1H). ^{13}C NMR (50 MHz, $CDCl_3$), δ (ppm):
584 22.1, 28.2, 70.0, 71.3, 72.2.
585
586 3,3'-Thiobis(1-isopropoxypropan-2-ol), **9**
587 Pale yellow oil, yield: see Table 5. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 1.17 (d, 12H,
588 *J* = 6.4 Hz), 2.67 (dd, 2H, *J* = 13.4, 7.2 Hz), 2.77 (dd, 2H, J = 13.4, 4.6 Hz), 3.10 (b s, 2H),
589 3.39-3.56 (m, 4H), 3.63 (sept, 2H, *J* = 6.4 Hz), 3.79-383 (m, 2H). ^{13}C NMR ($CDCl_3$, 50
590 MHz), δ(ppm): 22.1, 36.5, 36.6, 69.7, 69.8, 70.6, 72.3. MS m\z (%): 248 (M^+-18, 2), 99 (30),
591 73 (19), 57 (90), 43 (100).
592
593 3,3′-Disulfanediylbis(1-isopropoxypropan-2-ol), **11**
594 Pale yellow oil, yield: see Table 5. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 1.16-1.20 (m,
595 12H), 2.20 (bs, 2H), 2.82-2.91 (m, 4H), 3.38-3.65 (m, 6H), 3.99-4.07 (m, 2H). ^{13}C-NMR
596 ($CDCl_3$, 50 MHz), δ (ppm): 22.1, 22.2, 42.5, 42.6, 69.4, 69.5, 70.4, 72.3. MS m/z (%): 298
597 (M^+, 4), 207 (3), 99 (21), 89 (12), 73 (34), 57 (100).
598
599 *3.2.3. General Procedure for the reaction of N-Ts-aziridine **16** with silyl nucleophiles **2a** and*
600 ***13***
601
602 *N*-Ts-aziridine **16** (1 eq.) in 0.5 mL of [bmim][BF_4] (or [bmim][PF_6]) is added with 1.1
603 eq. of $PhSSiMe_3$ **2a** (or PhSeTMS **13)** and TBAF·*x*H_2O (0.2 eq.). The progress of the reaction
604 was followed by TLC (hexanes/ethyl acetate 4:1 or 5:1) upon extraction with diethyl ether
605 of a small amount of the reaction mixture. At the end of the reaction, diethyl ether was
606 added and the organic phase was washed with brine and dried over Na_2SO_4. Evaporation
607 of the solvent afforded the crude product **17**(or **18**).
608
609 *(S)*-4-Methyl-N-(3-methyl-1-(phenylthio)butan-2-yl)benzenesulfonamide, **17**
610 Pale yellow solid, yield 45%, [bmim][BF_4]; 40%, [bmim][PF_6]. Recorded spectro-
611 scopic data matched those previously reported in the literature [76].
612
613 *(S)*-4-Methyl-N-(3-methyl-1-(phenylselanyl)butan-2-yl)benzenesulfonamide, **18**
614 Yellowish solid, yield 57%, [bmim][BF_4]; 48%, [bmim][PF_6]. Spectroscopic data
615 matched those previously reported in the literature [76].
616
617 *3.2.4. General Procedure for the reaction of N-Boc aziridines with (phenyl-*
618 *thio)trimethylsilane **2a** and (phenylseleno)trimethylsilane **13***
619
620 To a mixture of *N*-Boc-aziridine (1 mmol) in the ionic liquid (0.5 mL), 1.2 mmoL of
621 $PhSSiMe_3$ **2a** (or PhSeTMS **13**) were added. Depending on the used ionic liquid (see Table
622 7) TBAF·*x*H_2O (0.24 mmol) or heating were required.
623 The progress of the reaction was followed by TLC (hexanes/ethyl acetate 4:1 or 5:1)
624 upon extraction with diethyl ether (or chloroform) of a small amount of the reaction

mixture. At the end of the reaction, diethyl ether (or $CHCl_3$) was added (3x2mL) and the organic phase was washed with brine and dried over Na_2SO_4. Evaporation of the solvent afforded the crude product.

tert-Butyl (*S*)-(4-(methylthio)-1-(phenylthio)butan-2-yl)carbamate, **20a**

Pale yellow oil, yield: see Table 7. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 1.42 (s, 9H), 1.68-1.97 (m, 2H), 2.08 (s, 3H), 2.46-2.55 (m, 2H), 3.12 (b d, 2H, ls = 5.1 Hz), 3.86-3.99 (m, 1H), 4.60-4.63 (b s, 1H), 7.18-7.45 (m, 5H). ^{13}C-NMR ($CDCl_3$, 50 MHz), δ (ppm): 15.1, 28.1, 30.7, 33.4, 39.4, 49.8, 79.8, 126.2, 128.9, 129.6, 135.9, 155.2. MS *m*/*z* (%): 327 (M^+, 5), 254 (4), 218 (9), 211 (5), 204 (11), 148 (32), 124 (25), 104 (51), 57 (100).

tert-Butyl (*S*)-(4-(methylthio)-1-(phenylselanyl)butan-2-yl)carbamate, **21a**

Orange-yellow oil, yield: see Table 7. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 1.41 (s, 9H), 1.71-1.92 (m, 2H), 2.06 (s, 3H), 2.44-2.53 (m, 2H), 3.11 (b d, 2H, *J* = 5.4 Hz), 3.83-4.02 (m, 1H), 4.61-4.72 (m, 1H), 7.24-7.88 (m, 3H), 7.48-7.52 (m, 2H). ^{13}C-NMR ($CDCl_3$, 50 MHz), δ (ppm): 15.6, 28.1, 30.4, 32.3, 33.6, 52.4, 79.3, 126.9, 129.0, 132.3, 155.2. ^{77}Se NMR ($CDCl_3$, 38.1 MHz), δ (ppm): 239.9. MS *m**z* (%): 375 (M^+, 2), 259 (4), 162 (25), 118 (26), 91 (11), 70 (22), 61(54), 57 (100).

tert-Butyl (*S*)-(3-methyl-1-(phenylthio)butan-2-yl)carbamate, **20b**

Yellowish oil, yield: see Table 7. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 0.90 (d, 3H, *J* = 6.8 Hz), 0.92 (d, 3H, *J* = 6.8 Hz), 1.43 (s, 9H), 1.92 (app sext, 1H, *J* = 6.8 Hz), 3.07 (b d, 2H, *J* = 5.6 Hz), 3.59-3.71 (m, 1H), 4.52-4.60 (m, 1H), 7.17-7.53 (m, 5H). ^{13}C-NMR ($CDCl_3$, 50 MHz), δ (ppm): 19.4, 19.6, 28.4, 30.9, 37.7, 55.3, 79.2, 126.1, 127.4, 128.9, 136.9, 156.1. MS *m*/*z* (%): 295 (M^+, 4), 179 (4), 172 (17), 152 (3), 135 (5), 123 (17), 116 (36), 110 (6), 72 (70), 57 (100).

tert-Butyl *(S)*-(3-methyl-1-(phenylselanyl)butan-2-yl)carbamate, **21b**

Yellow oil, 47% yield. ^{1}H and ^{13}C NMR data matched those previously reported in the literature. [76]. ^{77}Se NMR ($CDCl_3$, 38.1 MHz), δ (ppm): 244.1.

*3.2.5. Reaction of aziridine **19a** with bis(trimethylsilyl)sulfide **2b***

A mixture of *N*-Boc-methionine **19a** (1 mmol) in the ionic liquid (0.5 mL) and HMDST (1.2 mmoL) was added with TBAF·*x*H_2O (0.24 mmol) and stirred at room temperature. The progress of the reaction was followed by TLC (hexanes/ethyl acetate 5:1) upon extraction with diethyl ether of a small amount, and, after completion, the reaction mixture was treated with citric acid (50% aq. solution) and extracted with diethyl ether. The organic phase was then washed with citric acid (20% aq. solution) and dried over Na_2SO_4. Evaporation of the solvent gave the crude product, which was purified on TLC (hexanes/ethyl acetate 5:1) to afford β-amino-disulfide **22** (major) and β-amino-thiol **23** (minor).

d

di-*tert*-Butyl [(*2S,2'S*)-disulfanediylbis(4-(methylthio)butane-1,2-diyl)]dicarbamate, **22**

Yellow oil, yield: see Table 8. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 1.44 (s, 18H), 1.66-1.75 (m, 4H), 1.85-1.94 (m, 2H), 2.11 (s, 6H), 2.48-2.58 (m, 4H), 2.68 (dd, 2H, *J* = 13.2 Hz, 6 Hz), 2.75 (dd, 2H, *J* = 13.2 Hz, 5.8 Hz), 3.78-3.90 (m, 2H), 4.64-4.72 (m, 2H). ^{13}C NMR ($CDCl_3$, 50 MHz), δ (ppm): 15.3, 28.4, 30.7, 33.6, 38.2, 49.6, 79.6, 155.3. MS *m*/*z* (%): 351 (M^+-149, 3), 250 (5), 194 (11), 162 (10), 148 (16), 104 (34), 101 (40), 57 (100).

tert-Butyl (*S*)-(1-mercapto-4-(methylthio)butan-2-yl)carbamate, **23**

Yield: see Table 8. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 1.31 (t, 1H, *J* = 8.8 Hz, SH). Most of the other proton signals are overlapped with those of the disulfide **22**. ^{13}C NMR ($CDCl_3$, 50 MHz), δ (ppm): 15.6, 28.4, 29.5, 30.7, 32.6, 50.9, 79.6, 155.4.

3.2.6. General Procedure for the ring opening of thiirane ***24***

2-(Isopropoxymethyl)thiirane **24** (1 equiv.) in 0.4 mL of the appropriate ionic liquid was treated with (phenylthio)trimethylsilane **2a** (1.2 equi.) or (phenylthio)trimethylsilane **13** (1.2 equiv.). Depending on the ionic liquid, TBAF·*x*H_2O (0.24 mmol) was added (see Table 9). Progress of the reaction was monitored by TLC (hexanes:ethyl acetate 7:1). At the end, the reaction mixture was treated with citric acid (50% aq. solution) and extracted with diethyl ether. The organic phase was washed with citric acid (20% aq. solution) and dried over Na_2SO_4. Evaporation of the solvent gave the crude product, as mixture of products (**25**, **26**, **27** and **28, 29**), which can be purified on silica gel.

1-Isopropoxy-3-(phenylthio)propane-2-thiol, **25**

Yellow oil, yield: see Table 9. H-NMR signals partially overlapped with disulfide **26**. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 1.13 (d, 6H, *J* = 6.0 Hz), 2.11 (d, 1H, *J* = 7.9 Hz), 3.13-3.34 (m, 3H), 3.41-3.46 (m, 1H), 3.53 (dd, 1H, *J* = 9.2 Hz, 5.2 Hz), 3.66 (dd, 1H, *J* = 9.2 Hz, 4.8 Hz), 7.20-7.43 (m, 5H). ^{13}C NMR ($CDCl_3$, 50 MHz), δ (ppm): 22.1, 39.4, 39.9, 70.8, 72.2, 126.2, 128.8, 129.5, 135.7. MS *m*/*z* (%): 242 (M^+, 31), 149 (5), 123 (12), 109 (26), 73 (23), 57 (100).

1,2-Bis(1-isopropoxy-3-(phenylthio)propan-2-yl)disulfane, **26**

Yellow oil, yield: see Table 9. ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm) : 1.15 (d, 12H, *J* = 6.2 Hz), 2.82-3.12 (m, 6H), 3.56-3.75 (m, 6H); 7.22-7.54 (m, 10H). MS *m*/*z* (%): 405 (M^+-77, 4), 328 (11), 273 (19), 242 (100), 196 (24), 142 (21), 99 (22), 73 (20), 57 (44).

1-Isopropoxy-3-(phenylselanyl)propane-2-thiol**, 28**

Not isolated (see Table 9), characteristic data. ^{1}H NMR ($CDCl_3$, 200 MHz), δ (ppm): 2.18 (d, 1H, *J* = 8.0 Hz, SH). The other signal are overlapped with the disulfide **29.**

1,2-bis(1-isopropoxy-3-(phenylselanyl)propan-2-yl)disulfane, **29**

Pale orange oil, yield: see Table 9. ^{1}H NMR ($CDCl_3$, 200 MHz), δ (ppm): 1.15-1.25 (m, 12H), 2.99-3.29 (m, 6H), 3.43-3.77 (m, 6H), 7.23-7.61 (m, 10H). ^{77}Se NMR ($CDCl_3$, 38.1 MHz), δ (ppm): 282.8, 284.9.

5. Conclusions

In conclusion, we have found that the ring opening of strained heterocycles by thiosilanes and selenosilanes can be efficiently carried out in various RTILs. Thus, ionic liquids are able to act as alternative reaction media, and in some cases also as catalysts. This synthetic protocol allows to prepare β-disubstituted sulfides and selenides bearing different substituents as hydroxyl-, *N*-Ts- or *N*-Boc amino- and sulfurated groups under mild conditions with high regiocontrol.

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