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Ionic Liquid as Catalyst and Reaction Medium: A Simple, Convenient and Green Procedure for the Synthesis of Thioethers, Thioesters and Dithianes using an Inexpensive Ionic Liquid, [pmIm]Br

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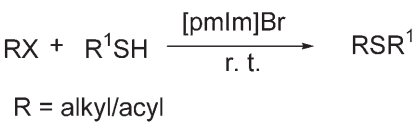
Abstract: An easily accessible and inexpensive room temperature ionic liquid, 1-pentyl-3-methylimidazolium bromide, [pmIm]Br efficiently catalyzes the reaction of alkyl halides or acyl halides with thiols without any solvent at room temperature leading to the synthesis of thioethers and thioesters in high yields. This reaction has also been extended for the preparation of dithianes and transthioetherification. The ionic liquid is recovered and recycled for subsequent runs.

Keywords: dithianes; ionic liquids; thioesters; thioethers; transthioetherification

Introduction

The thioethers and thioesters are very useful building blocks for the synthesis of various organosulfur compounds,[1] and they also play important roles in biological and chemical processes.[2] A variety of the methods for their synthesis is available in the literature.[3] However, the most convenient and direct method involves the conversion of thiols to thioethers or thioesters by the reaction of thiolate anions with organic halides.[1a] The catalysts and reagents used for this reaction are various basic compounds including BuLi,[3a] phase-transfer agents,[3b] palladium(0) complex,[3c] platinum(II) complex,[3d] tellurium complex,[3e] tin sulfides,[3f] other organometallic sulfides,[3g,3h] clay materials,[3i] trifluoroacetic acid,[3j] CSF-celite,[3k] thiomolybdate[3l] and InI.[3 m] The yields of products and reaction conditions depend on the solvent, the catalyst and the acidity of thiols. However, in general these reactions require very long reaction times (reflux/room temperature) and the yields are not always satisfactory. Moreover, many of these catalysts are highly toxic and expensive. Thus, a convenient and efficient procedure involving a simple and environment friendly reagent for the synthesis of thioethers and thioesters is still of high demand.

In recent times room temperature ionic liquids have been the subject of considerable interest in the context of green synthesis.[4] Although ionic liquid was initially introduced as an alternative green reaction medium,[4] today it has marched far beyond showing its significant role in controlling the reaction as catalyst.[5] As a part of our program to explore the potential of ionic liquids in organic synthesis we initiated an investigation to unravel the novel utilities of ionic liquids as catalysts as well as reagents in chemical transformations.[6] We report here the application of a simple ionic liquid [pmIm]Br as catalyst as well as reaction medium for the conversion of thiols to thioethers or thioesters by reaction with alkyl or acyl halides (Scheme 1).

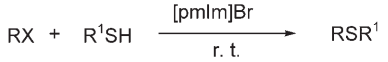


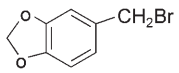
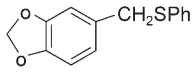
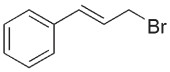
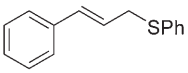
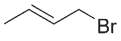
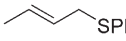
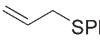
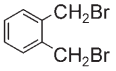
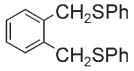
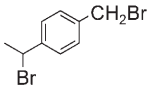
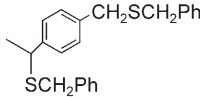
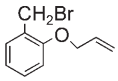
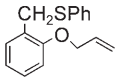
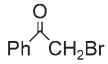
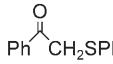
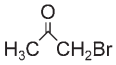
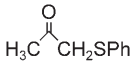
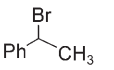
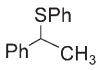
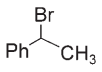
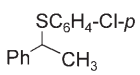
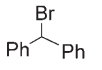
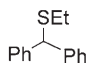
Scheme 1.

Results and Discussion

The experimental procedure is very simple. A mixture of alkyl halide (5 mmol) and thiophenol (5 mmol) is stirred at room temperature in ionic liquid [pmIm]Br (1 g) for a certain period of time (10–60 min) as required to complete the reaction (TLC). The product was isolated by direct distillation of the reaction mixture under reduced pressure. In case of small-scale reactions where distillation is not feasible, the product may be isolated by extraction with ether followed by usual work-up and chromatography. The ionic liquid remaining in the reaction vessel after being washed with ethyl acetate and dried at 80 °C under vacuum for 3–4 h was recycled in subsequent runs.

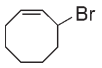
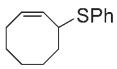
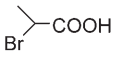
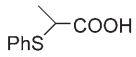
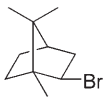
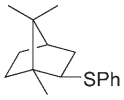
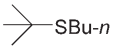
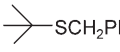
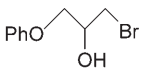
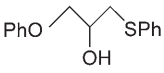
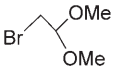
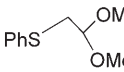
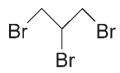
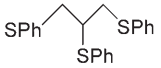
Table 1. Preparation of thioethers from alkyl halides and thiols in [pmIm]Br.



Entry	Alkyl Halide	Thiol	Product	Time [min]	Yield [%][a]	Ref.
1	$PhCH_2Cl$	PhSH	$PhCH_2SPh$	25	90	3m
2	$PhCH_2Br$	PhSH	$PhCH_2SPh$	20	92	3m
3	$PhCH_2I$	PhSH	$PhCH_2SPh$	20	93	3m
4	(*p*-OMe)$C_6H_4CH_2Br$	PhSH	(*p*-OMe)$C_6H_4CH_2SPh$	15	95	3m
5		PhSH		20	96	3m
6		PhSH		17	95	3m
7		PhSH		20	92	3m
8		PhSH		15	93	3m
9		PhSH		100	92	9
10	$PhCH_2Br$	*n*-BuSH	$PhCH_2SBu$-*n*	50	89	10
11	$CH_3(CH_2)_4Br$	*n*-BuSH	$CH_3(CH_2)_4SBu$-*n*	30[b]	82	11
12		PhSH		25	92	
13		$PhCH_2SH$		60	87	
14		PhSH		60	85	
15		PhSH		12	97	3m
16		PhSH		10	98	3m
17	$BrCH_2CO_2Et$	PhSH	$PhSCH_2CO_2Et$	10	98	3m
18	$Br(CH_2)_2CO_2Et$	PhSH	$PhS(CH_2)_2CO_2Et$	15	89	12
19		PhSH		25	89	3m
20		*p*-Cl-C_6H_4SH		25	87	3m
21		EtSH		30	92	13

A wide variety of alkyl halides underwent reactions with thiophenol, ethanethiol and butanethiol by this procedure to produce the corresponding thioethers. The results are summarized in Table 1. Alkyl chlorides, bromides and iodides are equally effective and no marked difference was observed in terms of reaction time and yield. The primary (entries 1–18), secondary (entries 19–27) and tertiary (entries 28–32) halides participate in this reaction without any difficulty. Allylic bromides (entries 6–9) and dibromides (entries 9, 12,

Table 1. (Continued)

22		PhSH		30	85	3m
23		*n*-BuSH		35	95	13
24		PhSH		30[b]	82	3m
25		PhSH		40	90	3m
26		PhSH		80	65	14
27		PhSH		55	92	
28		PhSH		30	82	3m
29		PhSH		40	85	3m
30		PhSH		30	82	3m
31		*n*-BuSH		25[b]	80	15
32		$PhCH_2SH$		50[b]	90	16
33		PhSH		25	92	23
34		PhSH		12	95	24
35		PhSH		120	82[b]	25

[a] Yields refer to isolated pure products unless otherwise stated.
[b] The reaction was carried out under heating at 60 °C.

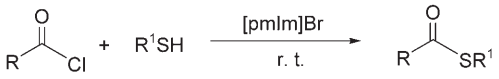
13) are also converted to the corresponding thioethers without any side products. Several sensitive functional groups such as CO_2Et, CO_2H, $COCH_3$, COPh, O-allyl, O-acetal present in the alkyl halides remained unaffected under the reaction conditions. The bromohydrin (entry 33) which is prone to epoxide formation under basic conditions was cleanly converted to the corresponding thioether. This procedure is also efficient for consecutive tris-thioether formation in a single operation (entry 35).

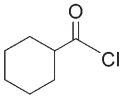
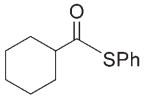
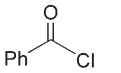
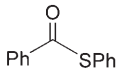
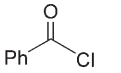
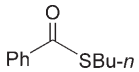
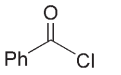
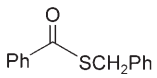
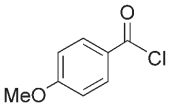
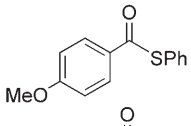
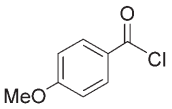
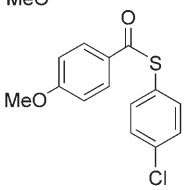
Following the same procedure when acyl halides were used in place of alkyl halides, the corresponding thioesters were obtained. The results are presented in Table 2. Aliphatic as well as aromatic acid chlorides react with both aromatic and non-aromatic thiols by this procedure.

By simple manipulation of the strategy when *geminal* or *vicinal* dihalides were reacted with ethanedithiol or propanedithiol under heating a variety of dithianes of different ring size were obtained. The results are reported in Table 3. These reactions do not proceed at room temperature; however the reactions went very cleanly at 60 °C during 5–7 h although the reaction of 1,2-dichoroethane required microwave heating. Presumably, higher energy (heat) is required because of the relatively weak nucleophilicity of the dithiol compared to the thiol and involvement of simultaneous inter- and intra-C–S bond formations. The dithianes are very useful intermediates in organic synthesis[7] and this procedure makes an easy access to these compounds.

Recently we have developed a convenient procedure for bromination of alcohols to the corresponding alkyl

Table 2. Preparation of thioesters from acid chlorides and thiols in [pmIm]Br.



Entry	Acid Chloride	Thiol	Product	Time [min]	Yield [%][a]	Ref.
1	CH_3COCl	PhSH	CH_3COSPh	12	96	3m
2		PhSH		12	97	3m
3		PhSH		10	98	3m
4		*n*-BuSH		15	97	17
5		$PhCH_2SH$		10	95	18
6		PhSH		10	98	3m
7		*p*-Cl-C_6H_4SH		12	98	3m

[a] Yields refer to isolated pure products unless otherwise stated.

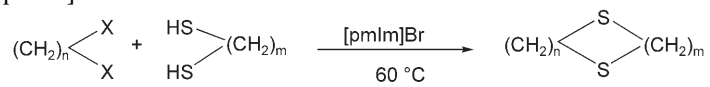
bromides using *tert*-butyl bromide in the same ionic liquid [pmIm]Br.[6g] Thus, combining this protocol with the present one an alcohol is directly converted to a thioether by a one-pot reaction with *tert*-butyl bromide and a thioalcohol at 60 °C in [pmIm]Br. This combined operation did not go at all at room temperature. Although the bromination of many alcohols at 60 °C with *t*-BuBr/[pmIm]Br was not very clean[6g] this combined reaction proceeded well at 60 °C. This reaction may also be carried out under sonication as tested by us for three substrates. A wide range of structurally varied alcohols underwent reactions with thiophenol or butanethiol to provide the corresponding thioethers by this procedure. The results are reported in Table 4. The same procedure has also been successfully applied for transthioetherification of ethers (Table 5). Both aromatic and non-aromatic thiols take part in this reaction. On the other hand, cyclic as well as open chain benzylic and allylic ethers are transthioetherified; however simple aliphatic dialkyl ethers remained inert. In the case of open chain ethers, although two products are formed, the lower boiling one such as methyl thioether (or methyl bromide when it is formed by initial bromination) was eliminated during the distillation or work-up process.

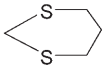
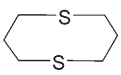
In general, all the reactions are clean, high yielding and reasonably fast. The products are of high purity (^{1}H and ^{13}C NMR) irrespective of whether they are obtained by direct distillation or solvent extraction. No tedious purification is required either way. The products are easily characterized by spectroscopic data (IR, ^{1}H and ^{13}C NMR). The recovered ionic liquid may be recycled for five runs without any loss of efficiency. After five runs 50% fresh ionic liquid was mixed with it to maintain equal efficiency.

Conclusion

In conclusion, the present procedure using a neutral and inexpensive ionic liquid, [pmIm]Br, provides an efficient and convenient procedure for the synthesis of thioethers, thioesters and dithianes by a simple reaction of alkyl halides and thiols. This method is also applied for direct conversion of alcohols to thioethers and trans-

Table 3. Preparation of dithianes from dihalides and dithiols in [pmIm]Br.



Entry	Dihalide	Dithiol	Dithiane	Time [h]	Yield [%][a]	Ref.
1	CH_2I_2			5.5	92	19
2	CH_2I_2			6	94	20
3				5.5	92	20
4				8 [min][b]	81	20
5				7	80	20

[a] Yields refer to isolated pure products unless otherwise stated.
[b] The reaction was carried out under microwave irradiation.

thioetherification of ethers. The significant advantages offered by this method are: (a) general applicability to all types of alkyl halides and thioalcohols, (b) clean reactions and high yields, (c) mild and neutral reaction condition tolerable to sensitive functional groups, (d) reusability of catalyst and cost-effectiveness. Another important feature of this methodology is the use of ionic liquid as catalyst as well as reaction medium and avoidance of hazardous organic solvent. Thus we believe, this simple and green procedure will provide a practical and better alternative to the existing procedures.[3]

Experimental Section

NMR spectra were recorded on Bruker DPX-300 instrument at 300 MHz for ^{1}H and 75 MHz for ^{13}C NMR in $CDCl_3$ solutions. IR spectra were measured on a FT-8300 Shimadzu spectrometer as neat samples. All liquid substrates were distilled before use. Ionic liquid [pmIm]Br was prepared by the reaction of 1-methylimidazole and pentyl bromide following a reported procedure.[8]

Conversion of Benzyl Bromide to 1-Thiophenyl-1-phenylmethane; Typical Procedure for Conversion of Alkyl halides to Thioethers (entry 2, Table 1)

A mixture of benzyl bromide (855 mg, 5 mmol) and thiophenol (550 mg, 5 mmol) in the ionic liquid 1-pentyl-3-methylimidazolium bromide, [pmIm]Br was stirred at room temperature (25–30 °C) for 15 min until completion of reaction was indicated by TLC. The product was then directly distilled out from the reaction vessel under reduced pressure to furnish 1-thiophenyl-1-phenylmethane as a colorless oil (low melting solid, m.p. 42 °C); yield: 920 mg, (92%); $R_f = 0.80$; IR: $\nu = 1581$, 1479, 1438, 1024 cm^{-1}; ^{1}H NMR: $\delta = 7.53–7.55$ (m, 1H), 7.23–7.37 (m, 9H), 4.15 (s, 2H); ^{13}C NMR: $\delta = 138.0$, 137.0, 130.8 (2C), 129.4 (4C), 129.0 (2C), 127.7, 126.8, 39.5. These values are in good agreement with the reported data.[3m]

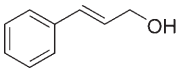
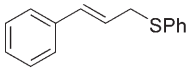
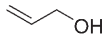
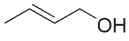
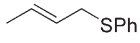
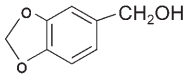
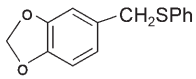
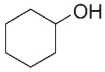
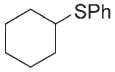
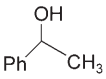
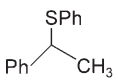
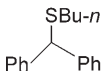
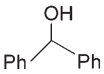
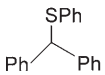
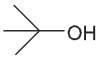
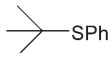
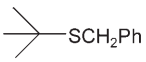
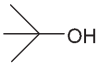
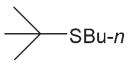
When the reaction was carried out with 1 mmol or smaller amounts the product was isolated by extraction with ethyl acetate followed by column chromatography. The residual ionic liquid was washed with small amount of ethyl acetate, dried under vacuum at 80 °C for 4 h and recycled.

This procedure is followed for the conversion of all the alkyl halides into thioethers listed in Table 1, acyl halides into thioesters in Table 2 and dihalides to dithianes in Table 3. All the products except four (entries 12, 13, 14, 27 in Table 1) are known compounds (references in Tables 1–5) and were identified by comparison of their spectroscopic data with those reported. The new compounds were properly characterized by their spectroscopic data (IR, ^{1}H and ^{13}C NMR) and elemental analysis. These values are reported below.

1,2-Di(methylthiophenyl)benzene (entry 12, Table 1): Viscous liquid; $R_f = 0.80$; IR: $\nu = 1585$, 1570, 1479, 1454, 1436, 730, 716 cm^{-1}; ^{1}H NMR: $\delta = 7.14–7.32$ (m, 14H), 4.23 (s, 4H); ^{13}C NMR: $\delta = 136.5$ (2C), 135.8 (2C), 130.8 (2C), 130.7 (4C), 129.2 (4C), 128.0 (2C), 126.9 (2C), 37.0 (2C); anal. calcd. for $C_{20}H_{18}S_2$: C 74.49, H 5.63; found: C 74.35, H 5.65.

2-Oxyallyl-1-(methylthiophenyl)benzene (entry 14, Table 1): Colorless viscous liquid; $R_f = 0.75$; IR: $\nu = 1581$, 1479, 1454, 1436, 730, 716, 688 cm^{-1}; ^{1}H NMR: $\delta = 7.33–7.36$ (m, 2H), 7.19–7.27 (m, 5H), 6.83–6.86 (m, 2H), 6.00–6.06 (m, 1H), 5.25–5.47 (m, 2H), 4.24–4.56 (m, 2H), 4.19 (s, 2H); ^{13}C NMR: $\delta = 156.2$, 137.0, 133.3, 130.3, 129.8 (2C), 128.7 (2C),

Table 4. One-pot synthesis of thioethers from alcohols.

Entry	Alcohol	Thiol	Product	Time [h]	Yield [%][a]	Ref.
1	$PhCH_2OH$	PhSH	$PhCH_2SPh$	1.25	92	3m
2	$PhCH_2OH$	*n*-BuSH	$PhCH_2SBu$-*n*	2	85	10
3	$CH_3(CH_2)_4OH$	PhSH	$CH_3(CH_2)_4SPh$	3	72	3m
4		PhSH		1.5	87	3m
5		PhSH		2	75	3m
6		PhSH		2.5	79	3m
7	*p*-MeO-$C_6H_4CH_2OH$	PhSH	*p*-MeO-$C_6H_4CH_2SPh$	1	95	3m
8		PhSH		1.25	93	3m
9		PhSH		2.5	82	16
10		PhSH		2	85	3m
11		*n*-BuSH		2.5	83	13
12		PhSH		2	87	3m
13		PhSH		1.5	92	3m
14		$PhCH_2SH$		1.5	83	16
15		*n*-BuSH		2.5	75	15

[a] Yields refer to isolated pure products unless otherwise stated.

128.4, 126.3, 126.1, 120.6, 117.2, 111.4, 68.9, 33.5; anal. calcd. for $C_{16}H_{16}OS$: C 74.96, H 6.29; found: C 74.83, H 6.30.

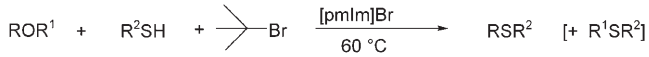
1-Methylthiophenyl-4-(1-methyl-1-thiobenzylmethylene benzene (entry 13, Table 1): Colorless viscous liquid; $R_f = 0.80$; IR: $\nu = 1586, 1572, 1480, 1452, 1435, 736\ cm^{-1}$; ^1H NMR: $\delta =$ 7.27–7.35 (m, 14H), 3.66 (s, 2H), 3.63 (s, 4H), 3.61 (q, $J =$ 13.5 Hz, 1H), 1.57 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR: $\delta = 142.6$, 142.5, 138.2, 136.9, 129.1 (2C), 129.0 (2C), 128.8 (3C), 128.4 (3C), 127.6 (2C), 127.4, 126.8, 43.2, 35.7, 35.6, 35.3, 22.2; anal. calcd. for $C_{23}H_{24}S_2$: C 75.77, H 6.64; found: C 75.65, H 6.67.

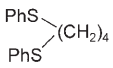
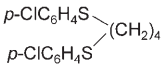
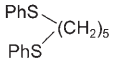
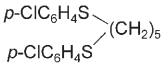
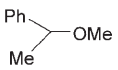
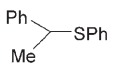
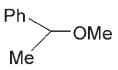
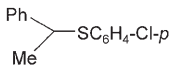
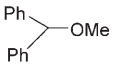
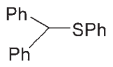
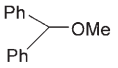
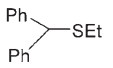
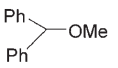
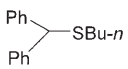
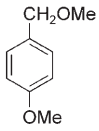
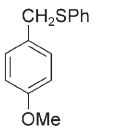
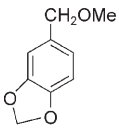
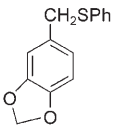
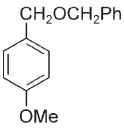
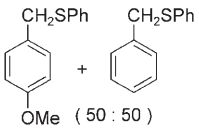
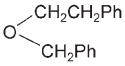
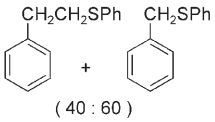
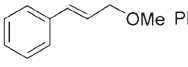
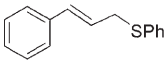
1,7,7-Trimethyl-2-phenylsulfanyl-bicyclo[2.2.1]heptane (entry 27, Table 1): Viscous liquid; $R_f = 0.80$; IR: $\nu = 2950$, 1454, 1436, 1022 cm^{-1}; ^1H NMR: $\delta = 7.56$–7.65 (m, 2H), 7.25–7.31 (m, 3H), 3.40 (dd, $J_1 = 9.1$ Hz, $J_2 = 5.8$ Hz, 1H), 2.21–2.25 (m, 1H), 2.10 (dd, $J_1 = 14.1$ Hz, $J_2 = 8.5$ Hz, 2H), 1.69–1.80 (m, 4H), 1.15 (s, 3H), 1.03 (s, 3H), 0.86 (s, 3H); ^{13}C NMR: $\delta = 132.9$ (2C), 131.6, 129.3 (2C), 127.0, 54.9, 50.0, 47.9, 46.4, 41.3, 38.5, 27.5, 20.6, 20.2, 15.7; anal. calcd. for $C_{16}H_{22}S$: C 77.99, H 9.00; found: C 77.92, H 8.98.

Conversion of Benzyl Alcohol to Benzyl Thiophenyl Ether; Typical Procedure (entry 1, Table 4):

A mixture of benzyl alcohol (540 mg, 5 mmol) and *tert*-butyl bromide (1.02 g, 7.5 mmol) in ionic liquid [pmIm]Br (500 mg) was heated at 60 °C with a cold water circulating condenser for 1.5 h. The excess *tert*-butyl bromide was then removed from the reaction flask under reduced pressure and thiophenol (550 mg, 5 mmol) was added. The reaction mixture was then heated again at 60 °C for 20 min (TLC). The product benzyl thiophenyl ether was isolated by distillation under reduced

Table 5. Transthioetherification of Ethers.



Entry	Ether	Thiol	Product	Time [h]	Yield [%][a]	Ref.
1		PhSH		1.5	95	21
2		*p*-Cl-C_6H_4SH		1.5	92	21
3		PhSH		1.3	94	21
4		(*p*-Cl)C_6H_4SH		1.5	90	21
5	$PhCH_2OCH_2Ph$	PhSH	$PhCH_2SPh$	1.6	91	3m
6	$PhCH_2OCH_2Ph$	*n*-BuSH	$PhCH_2SBu$-*n*	2	85	10
7	$PhCH_2OMe$	PhSH	$PhCH_2SPh$	2	88	3m
8	$PhCH_2OMe$	*n*-BuSH	$PhCH_2SBu$-*n*	2	87	10
9		PhSH		1.5	90	3m
10		*p*-Cl-C_6H_4SH		1.5	91	3m
11		PhSH		1.8	89	3m
12		EtSH		2	85	13
13		*n*-BuSH		2	87	13
14		PhSH		1.6	92	3m
15		PhSH		1.5	90	3m
16		PhSH		1.8	93	3m ,3m
17		PhSH		2	87	22, 3m
18		PhSH		2	92	3m

[a] Yields refer to isolated pure products unless otherwise stated.

pressure as in earlier procedure (alternatively, it was obtained by extraction with benign solvent for relatively small scale reactions) as a colorless liquid (low melting solid); yield: 920 mg (92%). The product was identified by comparison of its spectra (^{1}H and ^{13}C NMR) with those of an authentic sample prepared earlier. The ionic liquid was recycled in the same way as in earlier experiment.

This procedure was followed for the conversion of all alcohols into the corresponding thioethers listed in Table 4. All the products are known compounds and were easily identified by comparison of their spectra with those of authentic samples.

This procedure was also followed for the transthioetherification of ethers listed in Table 5 using 3 equivalents of *tert*-butyl bromide and 2 equivalents of thiophenol for one equivalent of ether. All the products in this series are also known compounds and were easily identified by comparison of their spectroscopic data with those of authentic samples.

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