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Application of 1,4-bis(3-methylimidazolium-1-yl)butane ditribromide [bMImB].$(Br_3)_2$ ionic liquid reagent for selective oxidation of sulfides to sulfoxides

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Abstract: 1,4-bis(3-methylimidazolium-1-yl)butane ditribromide [bMImB].$(Br_3)_2$ as an efficient reagent is used for the selective oxidation of dialkyl and alkyl aryl sulfides to the corresponding sulfoxides in high yields under mild conditions. The products can easily be isolated by just washing the highly water soluble of 1,4-bis(3-methylimidazolium-1-yl)butane ditribromide [bMImB].$(Br_3)_2$. The spent reagent can be several times recovered and reused without any significant loss.

Keywords: Ionic liquid, Selective oxidation, Sulfoxide, Bis(3-methylimidazolium-1-yl)butane ditribromide

Owing to their importance as intermediates in organic synthesis[1] and their key role in enzyme activation,[2] organosulfur compounds, such as sulfoxides are much sought after. The oxidation of sulfides is the most straightforward method for the synthesis of sulfoxides. Consequently, the selective oxidation of sulfides to sulfoxides has been a challenge for many years and is a useful transformation in organic chemistry.[3] The results prompted us to verify the possibility of the achievement of a new procedure for the oxidation of sulfides. Since the first reported synthesis of sulfoxides by Maercker in 1865, a number of methods have been developed for the transformation of sulfides to sulfoxides,[4] and therein many reagents are available for the oxidation of sulfides.[5-9]

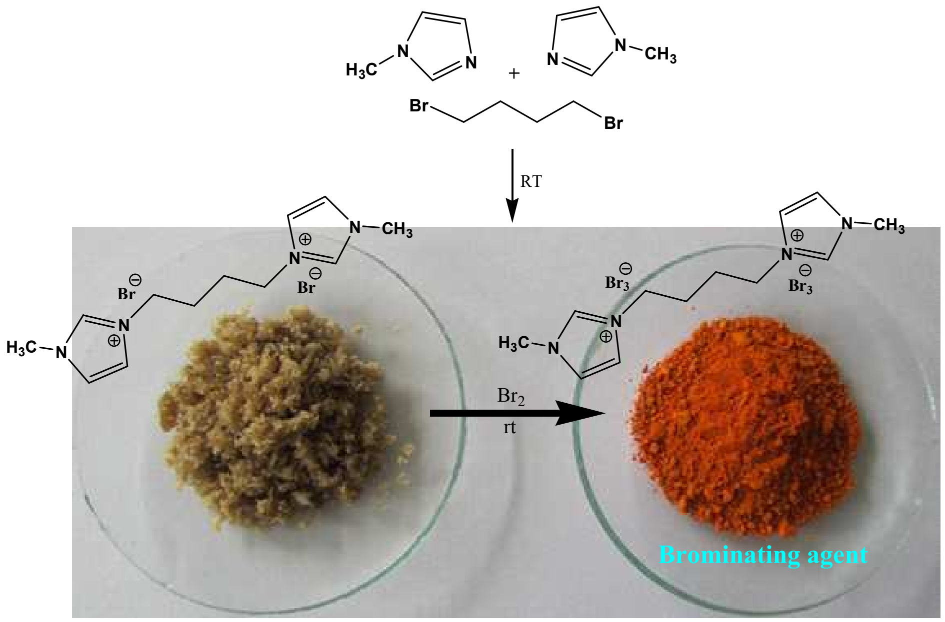
Unfortunately, most of the methods use hazardous, toxic reagents[10] or complex reaction procedures[11], accompanied with overoxidation to sulfone or other unwanted side products.[12,13] Furthermore, that types of reactions in which the catalyst is inherently dissolved in organic phase, require the separation of the expensive catalyst from the product, and consecquently, a chromatographic procedure for the recovery of the catalyst is invariably needed.[14]

Organic tribromide reagents (OTBs) are preferable as oxidants, molecular bromine might serve as a good alternative, but its use has been restricted because of being expensive, toxic and enviromentally unfriendly. Also, it contaminates the main product with the formation of side products such as sulfonic acids, sulfinic acids, bromo substituted sulfides and sulfoxides.[15] Extension of the Br_2 oxidation methodology to aromatic sulfides resulted in the competitive aromatic electrophilic substitition of bromine along with electrophilic attack on sulfur, thereby affording unwanted products along with low yields of the target molecules. Several tribromides have been reported, that are, Cetyltrimethylammonium tribromide (CTMATB)[16], 1,8-diazabicyclo [5,4,0]-tetrabutylammonium tribromide[17], pyridin hydrobromide perbromide[18], DABCO-bromine[19], 1,3-di-n-butylimidazolium tribromide[BBIm]Br_3[20], and 1-butyl-3-methylpyridinium tribromide([BMPy]Br_3)[21]. Sodium metaperiodate, $NaIO_4$, might be a good choice for the oxidation of sulfides to sulfoxides[22], but it is prohibitively expensive. Furthermore, the preparation and recycling of the reagent are both very difficult. In view of the above, a protocol is required for the selective oxidation of sulfides to sulfoxides in a clean and cost effective manner under mild conditions. Most relevantly, vanadium bromoperoxidase (VBrPO)[23] oxidizes sulfides to sulfoxides in the presence of hydrogen peroxide wherein the tribromide (Br_3^-) formed in situ has been suggested to be responsible for the sulfide oxidation.

Development of environmentally benign and efficient processes with simple work-up and high purity of the products with high yields is currently receiving considerable attention. Recently, some ionic liquid tribromides (IL-Br_3^-) were reported.[24] In this context, tribromide ionic liquid plays an important role in the process of obtaining sulfoxide derivatives with the ultimate goal of hazard-free and wast-free efficient synthesis of sulfoxides that are valuable intermediates for the construction of various fine chemicals as useful building blocks in asymmetric synthesis.[25] In recent years, there has been considerable interest in the developing green chemistry[26] for organic synthesis due to environmental demand and sustainability. There are various kinds of alkyl imidazolium salts which are commercially available as room temperature ionic liquids (RTILs). (RTILs) have received much attention due to their unique properties, such as negligible volatility, noninflammability, thermal stability, ease of recyclability, broad liquid temperature ranges and the ability to dissolve a wide range of inorganic and organic compounds.[27, 28] The combination of the alkylimidazolium cation with the tribromide anion should therefore lead to RTIL bromine analog.

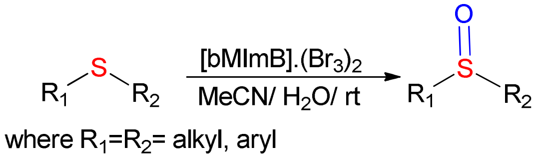
In continuation of our interest in oxidation of sulfides[29], herein, [bMImB].$(Br_3)_2$ that previously synthesized (Scheme 1), and used for bromination[30], we have used for the selective oxidation of sulfides to sulfoxides in very good yields under mild conditions.

[bMImB].$(Br_3)_2$ was easily prepared by treating 1-methylimidazole (2 equiv.) with 1,4-dibromobutane (1 equiv.) at room temperature. The resultant 1,4-bis(3-methylimidazolium-1-yl)butane di(bromide) [bMImB].$(Br)_2$ as light brown crystals was treated with molecular bromine. Then, the orange precipitate of 1,4-bis(3-methyl imidazolium-1-yl)butane ditribromide [bMImB].$(Br_3)_2$ was filtered (96% yield) and recrystallized in acetonitrile to obtain large crystals. The compound was characterized by spectral and analytical data. This crystalline compound is stable for several months at room temperature without loss of its activity.



Scheme1.

To test the oxidation efficiency of this reagent, 1.2 mmol of the reagent 1, 4-bis(3-methylimidazolium-1-yl butane ditribromide [bMImB].$(Br_3)_2$ was added to 1.0 mmol of sulfides in a mixed acetonitrile (2 mL)- water (1 mL). As indicated in Table 1, the reactions are completed within 5-20 minutes in high yields. This procedure works successfully for a number of substrates. All the reactions were quenched by adding water. This caused precipitation of the products, which were readily extracted and then dried. The reaction is generalized through entries 1-14 as shown in Table 1.

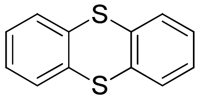
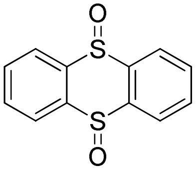
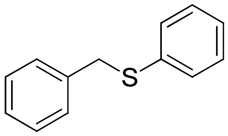
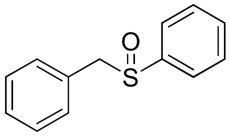
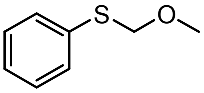
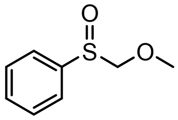
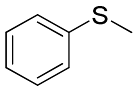
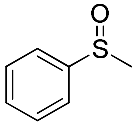
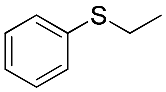
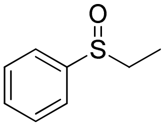
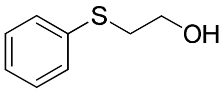
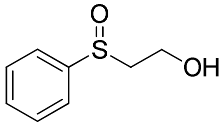
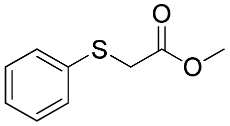
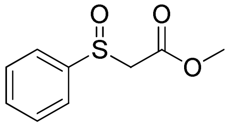
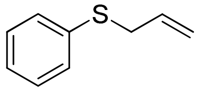
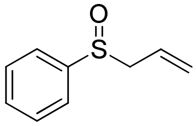
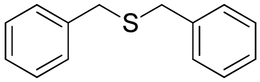
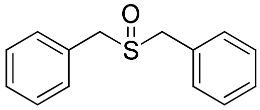
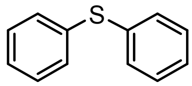
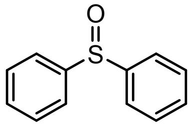
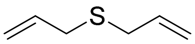
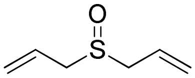
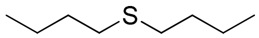
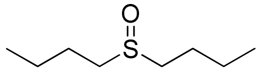


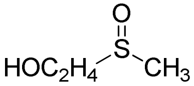
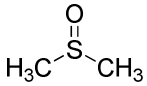
Scheme 2.

The results summarized in Table 1 explains the faster and easier oxidation of dialkyl sulfides (entries 9, 11-14), which are more nucleophilic than alkyl aryl sulfides (entries 2-8). The effect of an alkyl group makes the sulfur atom more nucleophilic and hence comparatively more reactive under the present experimental conditions. Under these conditions functional groups such as hydroxyl and acetate remain unaffected (entries 6-7 and 13).

In order to test the ability of optimized system in the oxidation of selenide compounds, we have used methyl phenyl selenide under same conditions. We observed that no product was formed after 24 h.

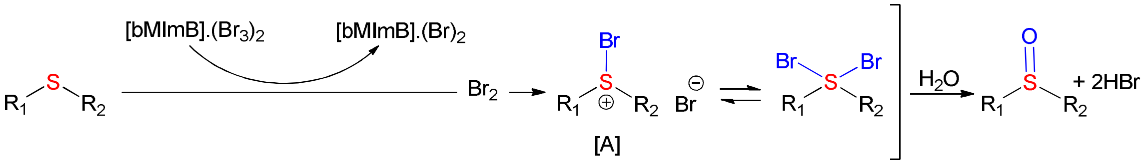
Table 1. Oxidation of sulfides to sulfoxides using [bMImB].$(Br_3)_2$.[a]

Entry	Substrate	Product	Yield (%)	Time (min)	Ref
1			88	18	31
2			95	18	16
3			97	16	16
4			99	15	16
5			90	16	28
6			88	17	28
7			87	19	28
8			86	20	28
9			94	10	16
10			90	20	16
11			93	5	16
12			89	6	28

13	$HOC_2H_4SCH_3$		91	4	32
14	CH_3SCH_3		98	4	16

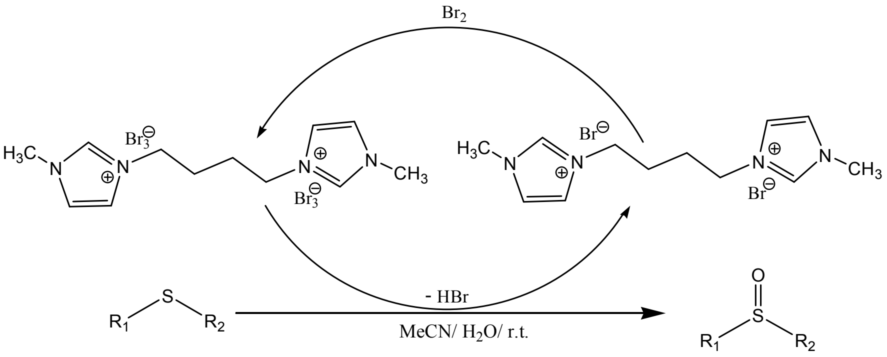
Reaction conditions: 1.2 mmol [bMImB]. (Br$_3$)$_2$, 1 mmol substrate, 3 mL Solvent at 25 °C.

Against the backdrop of the reagent acting as a brominating agent[33] for aromatics and olefins as well as a deprotecting agent[34, 35] for dithioacetals and thiols, and as a protecting/deprotecting agent for carbonyl-1, 3-oxathiolane interconversion, it is believed that the active species in these reactions is molecular bromine generated in situ, which in turn acts as an electrophile. Importantly, the amount of the active species can be tuned by regulating the amount of reagent, an operation that is rather difficult in the direct use of liquid bromine or a bromine solution. An electrophilic attack of bromine on sulfur then leads to the intermediate [A], which is then hydrolyzed by water to give the corresponding sulfoxide as shown in Scheme 3.



Scheme 3. Proposed mechanism for the oxidation of sulfide to the corresponding sulfoxide with [bMImB].(Br$_3$)$_2$.

An interesting feature of this reagent is that it can be regenerated at the end of the reaction by the extraction with water and can be used several times without losing its activity. The aqueous phase containing highly water-soluble IL was easily concentrated *in vacuo* to recycle [bMImB].(Br)$_2$, which then could be used to regenerate [bMImB].(Br$_3$)$_2$ with bromine (Scheme 4). Regeneration and reusability are two significant features of ionic liquids.[36] The effectiveness of ionic liquid, their recyclability and regeneration processes were observed for the oxidation of methyl phenyl sulfide and found to be effective up to 6 cycles (Figure 1).



Scheme 4.

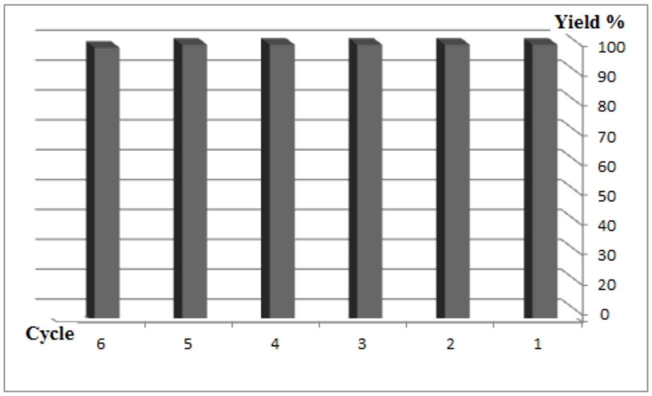


Fig. 1 Recyclability of the catalyst.

For showing the practical applicability of the catalyst, we have scaled up the reaction of methyl phenyl sulfide up to 10 mmol with 12 mmol [bMImB].$(Br_3)_2$ under the optimized reaction conditions. Results indicated that reaction performed effectively and desired product obtained in 97% isolated yield.

In summary, we have developed an efficient and versatile method for the oxidation of sulfides to sulfoxides using 1,4-bis(3-methylimidazolium-1-yl)butane ditribromide, based on the oxidation of bromide by a peroxometal intermediate. The byproduct [bMImB].$(Br)_2$ can be recycled to give [bMImB].$(Br_3)_2$, thereby rendering the protocol economic. The mild reaction conditions, simple experimental procedure, rapid conversion, good yields, and reusability of the reagent are notable advantages of the method.

Experimental

Preparation of 1,4-bis(3-methylimidazolium-1-yl)butane ditribromide [bMImB].$(Br_3)_2$

In a fume cupboard, molecular bromine (1.0 mL, 2.0 mmol) was added dropwise over 10 min to 1, 4-bis (3-methylimidazolium-1-yl)butane dibromide (0.380 g, 1.0 mmol) under stirring and cooling in an ice-bath affording a deep orange solid [bMImB].$(Br_3)_2$ ionic liquid, and stirring was continued for 2 h. The orange precipitate was recrystallized from acetonitrile to yield 1.77 g (96% yield) of 1, 4-bis (3-methylimidazolium-1-yl)-butane ditribromide [bMImB].$(Br_3)_2$. Melting point: 132 ^{o}C. UV (CH_3CN) 267 nm. IR (KBr) 3158, 3136, 3086, 2966, 2856, 1635,1595, 1570, 1556, 1464, 1400, 1162, 1103, 837, 742, 617 cm^{-1}.^{1}H NMR (D_2O) (ppm) d: 8.83 (s, 2H, CH imidazolium); 7.55 (m, 4H, CH imidazolium); 4.33 (t, 4H, NCH_2); 3.96 (s, 6H, NCH_3); 1.99 (m, 4H, CH_2CH_2). ^{13}C NMR ($CDCl_3$) (ppm) d: 123.7, 123.6 and 122.0 (CH imidazolium); 48.6 (NCH_2); 35.8 (NCH_3); 26.0 (CH_2). Anal. calcd for $C_{12}H_{20}Br_6N_4$: C, 20.60; H, 2.88; N, 8.01; Br, 68.51. Found: C, 20.10; H, 2.19; N, 7.65; Br, 67.87%.

General procedure for the oxidation of sulfides to sulfoxides

Methyl phenyl sulfide (1 mmol) in a mixed acetonitrile (2 mL)-water (1 mL) solvent reacted with [bMImB]. $(Br_3)_2$ (1.2 mmol) under stirring at room temperature for 15 min. The reaction was monitored by TLC and no overoxidation detected. On completion of the reaction, acetonitrile was removed under reduced pressure and water added. The product was extracted with ethyl acetate, dried over Na_2SO_4 and then evaporated to dryness, while the aqueous layer was retained for recovery of [bMImB].$(Br)_2$. Methyl phenyl sulfoxide was isolated in 99% yield. The aqueous layer containing [bMImB].$(Br)_2$ was concentrated by evaporation until a crystallin compound obtained. The [bMImB].$(Br)_2$ thus recovered and was recycled to [bMImB]. $(Br_3)_2$ following the described procedure.

Regeneration of Ionic Liquid

After the addition of water into the reaction mixture, the water soluble ionic liquid 1,4-bis(3-methylimidazolium-1-yl)butane dibromide [bMImB].$(Br)_2$ was recovered by evaporation of the aqueous solution and washing with diethyl ether in each case. The recovered ionic liquid [bMImB].$(Br)_2$ was dried at 40 ºC for 12 h, and treated with molecular bromine (2 mmol) under stirring and cooling in an ice-bath for 2 h to regenerate 1,4-bis(3-methylimidazolium-1-yl)butane ditribromide [bMImB].$(Br_3)_2$ ionic liquid and reused for the subsequent reaction without loss of activity.

The NMR spectra data for compounds

Entry 1 (Thioxanthen-9-one-10-oxide): M. p. 202-204 $^{\circ}$C. ^{1}H NMR ($CDCl_3$): 7.22– 7.26 (dd, 4H), 7.41– 7.51 (m, 4H).
Entry 2 (Benzyl phenyl sulfoxide): M. p. 122-124 $^{\circ}$C. ^{1}H NMR ($CDCl_3$): 4.18 (s, 2H), 7.24– 7.25 (m, 2H), 7.29– 7.31 (m, 3H), 7.32-7.38 (m, 5H).
Entry 3 (n-Butyl phenyl sulfoxide): Oil. ^{1}H NMR ($CDCl_3$): 0.9 (t, J = 7.0 Hz, 3H); 1.25– 1.53 (m, 4H), 2.78 (t, J = 7.0 Hz, 2H); 7.36 – 7.5 (m, 3H); 7.89 – 7.91 (m, 2H).
Entry 4 (Methyl phenyl Sulfoxide): ^{1}H NMR ($CDCl_3$): 2.73 (s, 3H, -CH3), 7.55 (m, 3H, aromatic), 7.64 (m, 2H, aromatic).
Entry 5 ((Ethylsulfinyl)benzene): ^{1}H NMR ($CDCl_3$): 1.18 (3H, t); 2.76 (2H, q); 7.53 (2H, dd); 7.58 (2H, d); 7.62 (1H, t).
Entry 6 (2-(Phenylsulfinyl)ethanol): ^{1}H NMR ($CDCl_3$): 7.54-768 (m, 5H), 2.8-3.25 (m, 2H), 3.9-4.25 (m, 2H).
Entry 7 (Methyl 2-(phenylsulfinyl)acetate): ^{1}H NMR ($CDCl_3$): 3.63 (3H, s, CH methyl); 3.78 (2H, s); 7.47 (2H, dd); 7.51 (2H, d); 7.71 (1H, t).
Entry 8 (Allyl phenyl sulfoxide): Oil. ^{1}H NMR ($CDCl_3$): 3.80-3.82 (m, 2H), 5.16-5.22 (m, 1H), 5.30-5.33 (m, 1H), 5.78-5.80 (m, 1H), 7.50-7.53 (m, 3H), 7.80-7.86 (m, 2H).
Entry 9 (Dibenzyl sulfoxide): M. p. 132-134 $^{\circ}$C. ^{1}H NMR ($CDCl_3$): 3.81 (s, 2H), 3.92(s, 2H), 7.10-7.50(m, 10H).
Entry 10 (Diphenyl sulfoxide): ^{1}H NMR ($CDCl_3$): 7.65-7.63 (m, 4H), 7.47-7.43 (m, 6H).
Entry 11 (Diallyl sulfoxide): Oil. ^{1}H NMR ($CDCl_3$): 3.57 (d, J = 7.1 Hz, 4H), 5.24– 5.38 (m, 4H), 5.72– 5.96 (m, 2H).
Entry 12 (Dibutyl sulfoxide): M. p. 34-35 $^{\circ}$C. ^{1}H NMR ($CDCl_3$): 0.94 (t, J =7.2), 1.40– 1.47 (m), 1.59-1.63(m), 2.52 – 2.55 (t).
Entry 13 (2-(methylsulfinyl)ethanol): ^{1}H NMR ($CDCl_3$): 1.94 (s, 3H), 2.50 (t, 2H), 3.48(s, 1H), 3.55 (t, 2H).
Entry 14 ((Methylsulfinyl)methane): ^{1}H NMR(CDCl3): 2.62 (s, 6H).

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Graphical Abstract

Application of 1,4-bis(3-methylimidazolium-1-yl)butane ditribromide [bMImB].$(Br_3)_2$ ionic liquid reagent for selective oxidation of sulfides to sulfoxides

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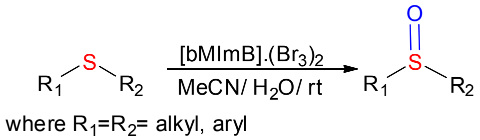

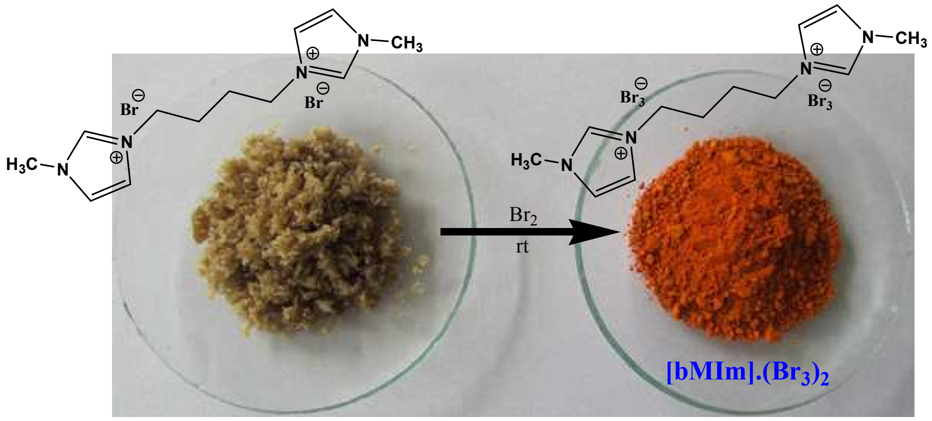

1,4-bis(3-methylimidazolium-1-yl)butane ditribromide [bMImB].$(Br_3)_2$ as an efficient reagent is used for the selective oxidation of dialkyl and alkyl aryl sulfides to the corresponding sulfoxides in high yields under mild conditions