An efficient method for the preparation of symmetrical disulfides using 1-butyl- 3-methylimidazolium hydroxide in aqueous medium

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Abstract- In this study, a one-pot and efficient method is reported for the synthesis of symmetrical disulfides from alkyl halides in the present of sulfur and 1-butyl-3-methylimidazolium hydroxide as a basic reagent and phase transfer catalyst. The reaction proceeded very fast and afforded the desired products in moderate to excellent isolated yields.

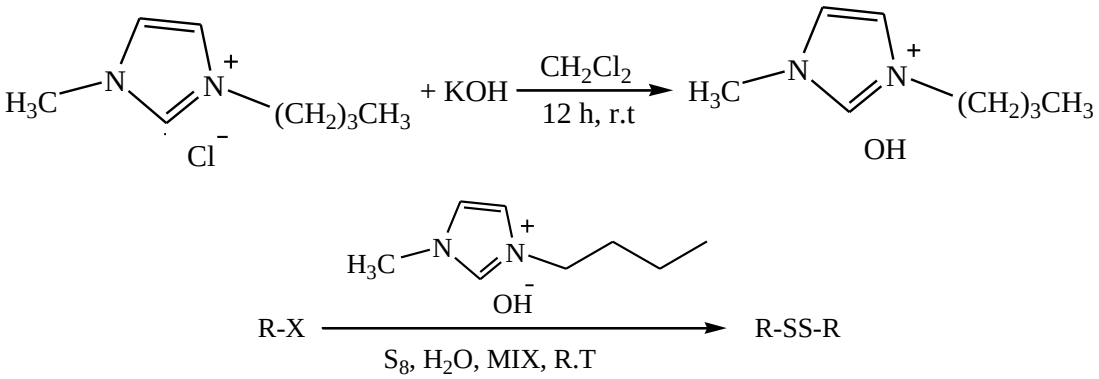
Introduction

Ionic Liquids (ILs) have attracted rising interest in the last decades with a diversified range of applications [1]. The types of ionic liquid available have also been extended to include new families and generations of ionic liquids with more specific and targeted properties. ILs frequently share a number of attractive properties such as low vapor pressure, a wide liquid range, low flammability, high conductivity, excellent stability, a wide electrochemical potential window, and the ability to act as surprisingly good solvents towards many substances, such as asphalt and recalcitrant biopolymers. Because of these favorable properties, ILs are being increasingly studied and tested as solvents or catalysts in a variety of applications including organic catalysis, inorganic and materials synthesis, biocatalysis, electrochemistry, pharmaceutical chemistry, polymerization, and as engineering fluids [2].

From three different kind of IL, acidic, neutral and basic, the last one were used to replace traditional bases such as KOH, NaOH, K_2CO_3, $NaHCO_3$, NaOAc, triethylamine, or tetrabutylammonium acetate. Using the traditional bases generally suffered from disadvantages such as waste production, corrosion and environmental problems [3]. Basic ionic liquid are flexible, nonvolatile, noncorrosive, and immiscible with many organic solvents.

Alkyl disulfides are an important class of organo-sulfur compounds and have received considerable attention in a variety of chemical and biological research fields [4].Although,

there are a number of useful procedures for the synthesis of symmetrical disulfides, the search for a simpleand rapid conversion of alkyl halides to disulfides is still a challenge and an interesting area of research [5-9]. Herein; we describe the application of 1-butyl-3-methylimidazolium hydroxide (BMIM[OH]) as a basic reagent for the synthesis of alkyl disulfide compounds in aqueous media (Scheme 1).



Scheme 1.

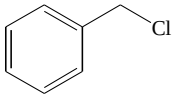
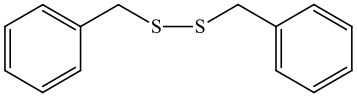
Results and discussion

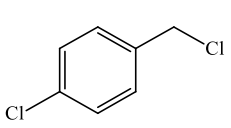
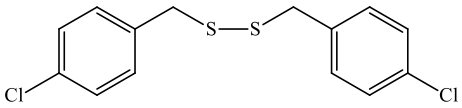
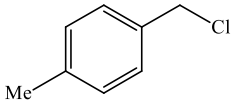
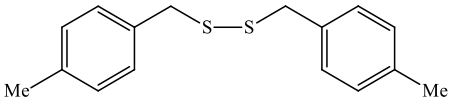
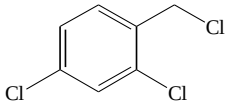
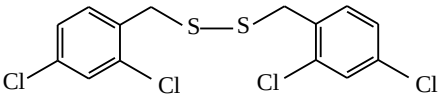
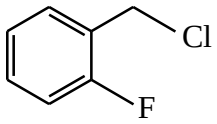
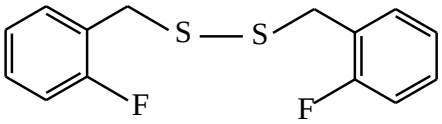
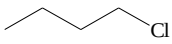
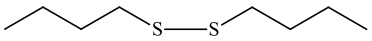
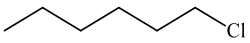
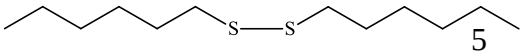
As previously reported, the disulfide dianion (S^{2-}) could be formed from the reaction of a base with S_8. In the second step, the S^{2-}dianion reacts with the respective alkyl halide to produce the corresponding symmetrical disulfide.

We first optimized the reaction with benzyl chloride as a model (Table 1, entry 1) and then applied the conditions for other alkyl halides. Under these conditions, benzyl chloride was converted into diphenyl disulfide in 97% isolated yield after 3 min.

According to the obtained results, application of the basic ionic liquid is very efficient reagent for the synthesis of symmetric dialkyl disulfides from alkyl halides. There action procedure is very simple and includes the generation of the disulfide anion.

Table1 Conversion of alkyl halide into their corresponding symmetric disulfides

Entry	Alkyl halide	Product	Time (min)	Yield[a,b] (%)
1			3	97

2			3	89
4			3	97
5			3	95
6			3	90
7			5	93
8			5	85

[a]All products were identified by comparison of their spectroscopic data with published data

[b] Isolated yields.

Experimental

Synthesis of 1-butyl- 3-methylimidazolium hydroxide

Solid potassium hydroxide (11.2 g, 200 mmol) was added to a solution of1-butyl-3-methylimidazolium chloride (34.72 g, 200 mmol) in dry methylene chloride (15 mL), and the mixture was stirred vigorously at room temperature for 10 h. The precipitated KCl was filtered off, and the filtrate was evaporated to leave the crude 1-butyl- 3-methylimidazolium hydroxide as a viscous liquid .

General procedure for the conversion of alkyl halides into the corresponding disulfides

A mixture of S_8 (1mmol) and the basic ionic liquid (0.5mmol) was mixed in water (5 mL) for 3 min. Subsequently, alkyl halide was added and the resulting mixture was stirred for the appropriate time (Table 1), until consumption of the starting material was complete, as monitored by TLC. Then, the product was extracted with CH_2Cl_2. The solvent was removed under reduced pressure to afford the disulfide in almost pure form. It was further purified by column chromatography on silica gel (hexane/ethyl acetate 9:1).

Acknowledgment

We are grateful to the Islamic Azad University, Omidieh Branch for support of this work.

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