SHORT PAPER

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Synthesis of organic sulfides from disulfides using a $Zn/AlCl_3$ system in aqueous media[†]

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A convenient procedure for the synthesis of organic sulfides from different alkyl halides and aryl disulfides by a $Zn/AlCl_3$ system in aqueous media is presented.

Sulfides are a class of important synthetic reagents and intermediates in organic synthesis.[1] Several procedures for the preparation of sulfides have been reported including, desulfurization of disulfides, reduction of sulfoxides and sulfones, aryllithium or organocuprate addition to thiocarbonyl compounds;[2,3] treatment of alkyl halides with sodium sulfide,[4] thiourea,[5] or thiocarbonate;[6] the use of electrophilic sulfur species;[7] the use of bis(tributyltin) sulfide as a sulfur transfer agent;[8] the reaction of halides with thiosilanes;[9] nucleophilic displacement of aryl halides by thiolate ion;[10] treatment of thiols and alkyl halides with DBU.[11] Recently Kannan and coworkers reported montmorillonite-3-aminopropyltriethoxysilane as a catalyst for synthesis of sulfides from thiols.[12] Also, an organosamarium reagent reacts with disulfides to afford allyl sulfides.[1] In a recent study Lu and Zhang reported the formation of benzyl sulfides and selenides from the reaction of benzyl bromide with disulfides and diselenides promoted by $Sm/BiCl_3$ system in aqueous media.[13] Such reactions in aqueous media offer numerous advantages over common reactions in organic solvents.[13] To our knowledge no sulfide formation mediated by a $Zn/AlCl_3$ system in aqueous media has been reported. Here we introduce a simple and convenient method for the synthesis of sulfides by the reaction between alkyl halides and aryl disulfides in the presence of such a system in aqueous media (Scheme 1). There are some major limitations to the synthesis of sulfides by S–S bond cleavage in disulfides, among them are: (a) loss of half unit of disulfide, (b) strong base catalysis, (c) the need for anhydrous organic solvents and (d) the necessity to prepare an organometallic complex.[13,14] S–S bond cleavage in disulfides by a $Zn/AlCl_3$ system, however, circumvents these problems. This paper describes a convenient method for the synthesis of organic sulfides in excellent yields.

As seen in Table 1 , a series of symmetrical aryl disulfides were treated with various alkyl halides in a $Zn/AlCl_3$ system in $DMF\text{-}H_2O$ mixed solvent to afford sulfides in excellent yields. While aryl disulfides react well with benzyl bromides and primary alkyl bromides, tertiary alkyl halide (entry 9, Table 1) does not give the expected sulfide even after 27h.

$$\mathrm{ArSSAr + RX \xrightarrow[DMF/H_2O]{Zn/AlCl_3} ArSR}$$

Table 1 Reaction conditions and yields of sulfides[a]

Entry	Ar	RX	Time (h)	Yield (%)	Ref.[d]
1	Ph	$PhCH_2Br$	13	90[b]	13
2	p-MeC_6H_4	$PhCH_2Br$	11	94[b]	15
3	p-ClC_6H_4	$PhCH_2Br$	15	90[b]	12
4	m-MeC_6H_4	$PhCH_2Br$	12	94[b]	16
5	Ph	p-$NO_2C_6H_4CH_2Br$	12	95[b]	17
6	p-MeC_6H_4	p-$NO_2C_6H_4CH_2Br$	10.5	93[b]	18
7	p-MeC_6H_4	$CH_3(CH_2)_4CH_2Br$	16	99[b]	19
8	p-ClC_6H_4	$CH_3(CH_2)_4CH_2Br$	18	100[b]	19
9	p-MeC_6H_4	Me_3CCl	27	0	–
10	p-ClC_6H_4	p-$NO_2C_6H_4CH_2Br$	14	85[b]	20
11	p-MeC_6H_4	$CH_3(CH_2)_2CH_2Br$	17	95[c]	21

[a]All products were identified by their IR and ^1H NMR sepctra and/or comparison of their b.p. or m.p. with authentic samples. [b]Yields of isolated product. [c]Yields based on GC analysis. [d]Published physical and spectroscopic properties.

Experimental

Typical procedure: A mixture of diphenyl disulfide (109 mg, 0.5 mmol), zinc powder (130 mg, 2 mmol), aluminum chloride (133 mg, 1 mmol), DMF (10 ml), and water (2.5 ml) was stirred at 65°C for 1h until the zinc powder disappeared; benzyl bromide (256 mg, 1.5 mmol) was then added at once to the solution and stirring was continued at that temperature for 13h in air . After completion of the reaction, the solution was filtered and washed with ether. The combined ether/DMF solutions were then washed with water and dried over anhydrous sodium sulfate. The solvent was evaporated in vacuo to give benzyl phenyl sulfide which was recrystallized from ethanol (180 mg, 90 %); m.p. 41-43°C (Lit.[13] 40–42°C).

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

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