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Practical And Versatile Oxidation Of Sulfides Into Sulfoxides And Oxidative Coupling Of Thiols Using Polyvinylpolypyrrolidonium Tribromide

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PRACTICAL AND VERSATILE OXIDATION OF SULFIDES INTO SULFOXIDES AND OXIDATIVE COUPLING OF THIOLS USING POLYVINYLPOLYPYRROLIDONIUM TRIBROMIDE

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GRAPHICAL ABSTRACT



Abstract A simple and highly selective oxidation of sulfides to sulfoxides and an oxidative coupling of thiols with polyvinylpolypyrrolidoniume tribromide has been developed. A series of sulfides and thiols was oxidized selectively at room temperature in good to excellent yields.

Keywords Sulfide; sulfoxide; thiol; disulfide; polyvinylpolypyrrolidoniume tribromide

INTRODUCTION

The modern ecological aspect of oxidation research focuses on thereplacement of current toxic and dangerous compounds with ecofriendly oxidants. In this line,

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Scheme 1 Structure of polyvinylpolypyrrolidoniume tribromide (PVP-Br₃). (Color figure available online).

polymer-supported reagents have had much attention in recent years due to their selectivity, stability, and easy handling.^{1–3} They could serve as heterogeneous, clean, and regenerable reagents in the oxidation reactions.

The oxidation of sulfides to sulfoxides and coupling of thiols to disulfides has been the aim of considerable research due to the importance of sulfoxides and disulfides as useful intermediates in various chemically and biologically significant molecules.^{4–7} The chemoselective oxidation of sulfides is also another point of interest.

Various oxidizing reagents used for this purpose include among others: nitric acid, dinitrogen tetroxide, chromic acid, manganese dioxide, ozone, peracids, selenium dioxide, sodium periodate, hypervalent iodine reagents, sodium perborate, halogens, tetrabutylammonium peroxydisulfate,⁸ and cerium(IV) salts,⁹ transition metal oxides,¹⁰ *N*phenyltriazolinedione,¹¹ urea–hydrogen peroxide,¹² halogens,¹³ atmospheric oxygen,¹⁴ H₂O₂,¹⁵ and solvent-free permanganate.¹⁶

However, the reported methods rarely offer the ideal combination of simplicity of method, rapid and selective reactions, and high yields of products, and often suffer from a lack of generality and economic applicability. As a result, the introduction of readily available, safe, and stable reagents for the oxidation research is still a necessity.

RESULTS AND DISCUSSION

As part of our program in environmentally beneficial catalysis and applications of polymeric reagents,^{17–22} we are interested in designing a "green" process to effectively carry out the oxidation reaction. We report herein an inexpensive, safe and environmentally friendly method to oxidize a variety of functional groups under extremely mild conditions.

Polyvinylpolypyrrolidoniume tribromide (Scheme 1) is stable and efficient oxidant that can be prepared *via* the combination of polyvinylpolypyrrolidone with hydrobromic acid followed by the reaction of resulting salt with bromine.²³

Simple work-up and the stability of these reagents make it a safe and convenient source of active bromine in comparison to molecular bromine which is a highly toxic oxidizing agent.

Initially, in order to find appropriate solvent for the oxidation of sulfides and coupling of thiols, we designed separated reactions for these transformations in different organic solvents. Dibenzyl sulfide and 4-bromothiophenol were selected as model substrates to optimize reaction conditions (Scheme 2). The results of the screening process have been summarized in Table 1.

Entry	Substrate	Solvent	Time (min)	Yield (%) ^b 98	
1	4-Br-Thiophenol	CH ₃ CN	8		
2	4-Br-Thiophenol	EtOH	8	99	
3	4-Br-Thiophenol	CH ₃ CH ₂ OAc	27	93	
4	4-Br-Thiophenol	H ₂ O	48h	c	
5	4-Br-Thiophenol	Acetone	10	d	
6	4-Br-Thiophenol	n-Hexane	19	97	
7	4-Br-Thiophenol	CH_2Cl_2	5	e 99 99 93	
8	4-Br-Thiophenol	CHCl ₃			
9	Dibenzyl sulfide	CH ₃ CN	4		
10	Dibenzyl sulfide	<i>n</i> -Hexane	25		
11	Dibenzyl sulfide	CH ₃ CH ₂ OAc	18	99	
12	Dibenzyl sulfide	EtOH	_	f	
13	Dibenzyl sulfide	Acetone	41h	Trace	
14	Dibenzyl sulfide	H ₂ O	24h	g	
15	Dibenzyl sulfide	CH_2Cl_2	_	h	
16	Dibenzyl sulfide	CHCl ₃	5	95	

 a Substrate/PVP-Br₃: 1 mmol/1.2 gr (for oxidation of 4-bromothiophenol) and 1.9 gr (for oxidation of dibenzyl sulfide).

^bIsolated yield.

^{c,g}Reaction did not complete.

d,e,f,hReaction did not complete and impurity was observed on TLC.



Scheme 2 Oxidation of dibenzyl sulfide and 4-bromothiophenol by PVP-Br₃ in different solvents. (Color figure available online).

However, ethanol and ethyl acetate proved to be the best solvent in terms of conversion and selectivity. Under these conditions, dibenzyl sulfide and 4-bromothiophenol were converted to dibenzyl sulfoxide and 1,2-bis(4-bromophenyl) disulfane in 99% isolated yields after 18 and 8 min, respectively (Table 1, entries 2 and 11).



Scheme 3 Oxidation of sulfides and thiols into sulfoxides and disulfides using PVP-Br₃ at room temperature. (Color figure available online).

After optimizing the conditions, all reactions with other sulfides and thiols were carried out in ethyl acetate and ethanol using polyvinylpolypyrrolidoniume tribromide as oxidizing agent at room temperature (Scheme 3); the substrates and the yields of products are listed in Table 2.

All oxidation reactions were performed under completely heterogeneous conditions at room temperature with good to excellent yields. In some cases, lower yields were obtained because of the loss of the volatile products during their isolation. There are several advantages of these reactions over other methods in the literature. The reactions were very clean, gave excellent reproducible yields, and excellent selectivity was obtained from these reactions. Thus, this method can be considered as a relatively green technology having more advantages and wider applicability compared to the conventional oxidation reagents.

A possible mechanism for these transformations is depicted in Scheme 4, based on previously reported works.^{28–32}

CONCLUSION

In conclusion, an environmentally benign and polymer-supported reagents has been reported for safe preparation of disulfides and sulfoxides. Rapid reaction, operational simplicity, good yield, and high purity of products are attractive features of this protocol.

EXPERIMENTAL

The chemicals and solvents were purchased from Fluka, Merck, and Aldrich chemical companies without further purifications. All products are known and were characterized by comparison of their spectral and physical data with authentic samples.

Oxidation of sulfides (general procedure): In a 25 mL round-bottom flask, to a solution of sulfide (1 mmol) in ethyl acetate (5 mL), 1.9 gr of polyvinylpolypyrrolidoniume tribromide was added successively and the mixture was stirred magnetically at room temperature for the indicated time in Table 2 (the progress of the reaction monitored by TLC). After completion of the reaction, the pure product was isolated by passing of reaction

Entry	Substrate	Product	Time (min)	Yield ^b (%)	Solvent	M.p found (°C)	M.p Reported (°C)
1	Br	Br S-S Br	8	99	EtOH	91–93	89–92 [22]
2	SH	S-S C	7	97	EtOH	45	39–42 [22]
3	CCC-SH	CCC ^{S-S} CCC	15	99	EtOH	143–144	141–144 [22]
4	SH	C) ^{S-S} C)	6	95	EtOH	56–57	55–58 [24]
5	N SH N		8	94	EtOH	160–162	164–166 [22]
6	нѕ∕соон	HOOC^S-S^COOH	40	90	EtOH	Oil	Oil [24]
7	нѕ∕∽_ОН	но _{~~s-s} ~_он	9	99	EtOH	Oil	Oil [24]
8	СССООН	COOH COOH	90	99	EtOH	190–192	273–285 [22]
9	()^s^()	$\bigcirc \bigcirc $	18	99	CH ₃ CH ₂ OAc	138–139	130–134 [25]
10	C-H ₃ (CH ₂) ₁₁ SH	C-H ₃ (CH ₂) ₁₁ S-S- (CH ₂) ₁₁ CH ₃	15	95	CH ₃ CH ₂ OAc	88–89	[26]
11	CH ₃ (CH ₂) ₁₁ SH	CH ₃ (CH ₂) ₁₁ S-S-(CH ₂) ₁₁ CH ₃	105	99°	CH ₃ CH ₂ OAc	31	31 [25]
12	℃ ^S	C) ^S	40	99	CH ₃ CH ₂ OAc	Liquid	Liquid [27]
13	C) ^S	C) S	25	94	CH ₃ CH ₂ OAc	Liquid	Oil [28]
14	S	C S	15	96	CH ₃ CH ₂ OAc	Liquid	Liquid [27]
15	CIS	c. O.S.	12	78	CH ₃ CH ₂ OAc	Liquid	Liquid [25]
16	$\langle \mathbf{s} \rangle$	S o	12	77	CH ₃ CH ₂ OAc	Oil	Oil [25]
17	S 0	° \$ 0	35	99 ^d	CH ₃ CH ₂ OAc	Liquid	Liquid [27]
18	-s	O===	70	99 ^e	CH ₃ CN	126–127	116–120 [25]

Table 2 Oxidation of sulfides and thiols into sulfoxides and disulfides respectively, using PVP-Br $_3$ at room temperature^a

^aSubstrate/PVP-Br₃: 1 mmol/1.2 (for oxidation of thiols)or 1.9 gr (for oxidation of sulfides).

^bIsolated yield.

^{c,d,e}Reaction proceeded in the presence of 2.9, 2, and 2.6 gr of PVP-Br₃, respectively.



Scheme 4 General mechanism for the oxidation of sulfides and thiols. (Color figure available online).

mixture through a short column using dichlromethane and acetone (95:5) as eluent. The filtrate was evaporated and pure sulfoxides were obtained in good to excellent yields.

Oxidative coupling of thiols (general procedure): A 25 mL round-bottom flask was charged with thiol (1 mmol), polyvinylpolypyrrolidoniume tribromide (1.2 gr), and EtOH (5 mL) as solvent. The reaction mixture was stirred at room temperature, and the progress of the reaction was monitored by TLC. After completion of the reaction, corresponding disulfides easily obtained by passing of reaction mixture through a short column using dichlromethane and acetone (95:5) as eluent.

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