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Efficient Oxidation of Sulfides To Sulfoxides and Deoxygenation of Sulfoxides Over Carbonaceous Solid Acid

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EFFICIENT OXIDATION OF SULFIDES TO SULFOXIDES AND DEOXYGENATION OF SULFOXIDES OVER CARBONACEOUS SOLID ACID

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Abstract Carbonaceous Solid Acid (CSA) was found to be a highly efficient, environmentally friendly, recyclable heterogeneous solid acid for the oxidation of sulfides and deoxygenation of sulfoxides, in good to excellent yields under mild reaction conditions.



Keywords Carbonaceous Solid Acid; Hydrogen peroxide; Sulfide; Sulfoxide

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INTRODUCTION

Development of solid acids for fine chemicals synthesis has become a major area of research in both industry and laboratory. Solid acids have many advantages such as easy catalyst separation from the product, simplicity in handling and fewer reactor and plant corrosion problems¹⁻⁹.

Organosulfur compounds, such as sulfoxides and sulfides are valuable compounds for the production of a range of chemically and biologically molecules. For this reason in the recent years the sulfides oxidation to sulfoxides and deoxygenation of sulfoxides has been the subject of many studies¹⁰⁻¹⁵. However, some of these methods still suffer from serious disadvantages like tedious work-up, harsh reaction conditions, intricate procedures and not readily available reagents. Therefore, environmentally benign and convenient procedures for the oxidation of sulfoxides are still required.

Aqueous 30% hydrogen peroxide is a very attractive oxidant, because it is readily available, high effective-oxygen content, formation of water as the only by-product, inexpensive and safely stored¹⁶⁻¹⁹. Nevertheless, oxidation of sulfides with H_2O_2 is slow and therefore various kinds of acids and transition metal based systems have been used to activate hydrogen peroxide²⁰⁻²⁹.

Xuezheng Liang and co-workers reported the synthesis of a heterogeneous strong acid through the copolymerization of p-toluenesulfonic acid (PTSA) and paraformaldehyde using sulfuric acid as catalyst. This carbonaceous solid acid (CSA) has high density of sulfonic acid groups (SO₃H), high thermal and chemical stability^{30, 31}.

In the present study we report oxidation of sulfides to sulfoxides with H_2O_2 and deoxygenation of sulfoxides with NaI ³²⁻³⁴ in the presence of CSA as a heterogeneous solid acid (Scheme 1).

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RESULTS AND DISCUSSION

Oxidation of sulfides

To start with diphenyl sulfide was selected as a model substrate for the optimization and studied its oxidation with 30% H₂O₂ using CSA as catalyst. The results are summarized in Tables 1 and 2.

The effect of various solvents on oxidation of diphenyl sulfide to diphenyl sulfoxide is shown in Table 1. Dichloroethane was found suitable, solvent for reaction at room temperature. However, ethanol as a non-toxic, environmentally benign media and inexpensive solvent was selected for this reaction.

[Insert Table 1]

[Insert Table 2]

Several oxidation reactions were performed with different amounts of hydrogen peroxide, catalyst and without any catalyst in order to find the most adequate condition and optimizing of the oxidation reaction. The yield of oxidation diphenyl sulfide to the corresponding sulfoxide as a function of time is presented in the Table 2. The optimum ratio of sulfide to H_2O_2 (1:1.5 eq.) in the presence of CSA (0.07 g equal to 0.34mmol H⁺) was found to be ideal for complete conversion of sulfides to sulfoxide (Table 2 Entry 5).

The generality of the method was examined using different types of sulfides (Table 3). All the substrates studied were selectively oxidized to their corresponding sulfoxides in good to excellent yields at room temperature. To check the reusability of CSA for the formation sulfoxide, the catalyst was removed by filtration and used for the next experiment under similar

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reaction conditions. This catalyst was reused without significant loss of activities after four runs (Table 3 Entry 1).

[Insert Table 3]

In Table 4, we compared our results on the oxidation of diphenyl sulfide with data from some other workers. As shown in table, the previously reported procedures suffer from one or more disadvantages such as elevated reaction temperatures (entry 7, 8, 9), longer reaction times (entry 5, 6), special efforts for the preparation of catalyst (entry 8), using a transition metal (entry 3, 4, 7), no recovery catalyst (entry 10) and the need for volatile and toxic organic solvents (entry 2, 4, 7, 8, 11).

[Insert Table 4]

This procedure offers several major advantages: The use of an available, cheap, and chemically stabile catalyst and oxidant; highly efficient for the oxidation of structurally diverse sulfides to sulfoxides in good to high yields; and the method conforms to several of the guiding principles of green chemistry.

Deoxygenation of sulfoxides

In continuation of this work, we investigated the deoxygenation of sulfoxides. In order to get an insight into the optimum conditions for reduction of sulfoxides to the corresponding sulfide, the reaction of diphenyl sulfoxide by sodium iodide and CSA in ethanol as a model experiment was studied at different solid acid and sodium iodide ratios. Results of these optimization experiments are presented in Table 5.

[Insert Table 5]

The effect of solvent on the deoxygenation efficiency of the reagent was evaluated by carrying out the deoxygenation of diphenyl sulfoxide in ethanol and acetonitrile at room temperature. It was found that reaction in polar aprotic solvent, such as acetonitrile faster than in ethanol (protic solvent), because acetonitrile dissolve salts by ion–dipole interactions and enable formation of naked anions. However ethanol as a non-toxic, environmentally benign media and inexpensive solvent was also investigated for this reaction.

Different types of sulfoxides were subjected to deoxygenation reaction in the presence of sodium iodide and CSA in ethanol. The deoxygenation reactions were performed under mild and heterogeneous conditions at room temperature with good to excellent yields (Table 6).

After the first run, the reusability of the CSA was tested. The recycled solid acid was used for three times. The obtained results demonstrating that CSA can be reused in these deoxygenation reactions (Table 6 Entry 1).

[Insert Table 6]

Table 7 compares the efficiency of this method with the some other method in the deoxygenation of diphenyl sulfoxide to diphenyl sulfide. The data in Table 7 show that some protocols took much longer time (entry 5, 9, 14), using a transition metal (entry 8, 10, 11, 12, 13), reduced isolated yields (entry 7, 9), elevated reaction temperatures and poorly available reagents or harsh conditions (3, 5, 8-14).

[Insert Table 7]

In conclusion, the advantage of this methodology is the availability of the starting materials, simplicity of oxidations and deoxygenation procedure under heterogeneous system, clean, easy

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work-up, high yields, cheapness, safe, eco-friendly, mild condition and recyclability of the solid acid.

EXPERIMENTAL

All chemicals were commercial products. Melting points were measured on an Electrothermal 9100 apparatus. Thin layer chromatography (TLC) was used to monitor all reactions and all yields refer to isolated products. ¹H-NMR spectra were recorded on a Bruker Avance AQS 300 MHz using TMS as an internal standard. The products were purified by column chromatography and were identified by comparison of their m.p and NMR spectra with those reported for authentic samples. GC measurements were carried out on an Agilent 6890 N gas chromatograph.

Synthesis of the Carbonaceous Solid Acid (CSA)

In a typical synthesis, p-TsOH (0.8 g), paraformaldehyde (0.36 g) and sulfuric acid (0.8 mL) was stirred at 80 °C for 24 h and then maintained at 120 °C to form a black solid. The product was washed with boiling distilled water until impurities such as sulfate ions were no longer detected in the wash water³¹. The density of prepared acid (CSA) determined using 0.01 M NaOH as titrant in an acid-base potentiometric titration and the result obtained 4.9 mmol g⁻¹.

General Experimental Procedure for the Preparation of Sulfoxides

In a typical reaction, a mixture of CSA (0.07 g equal to 0.34mmol H^+), diphenyl sulfide (1 mmol), hydrogen peroxide (aq. 30%, 1.5mmol) and ethanol (5 mL) was stirred at r.t. for 240 min. The progress of reaction was monitored by TLC method. At the end of the reaction, catalyst

was removed by filtration and the resulting solution was concentrated under reduced pressure. Then, residue was purified by column chromatography on silica gel (n-hexane – ethyl acetate 1 : 5) to afford 0.192 g (93%) of diphenyl sulfoxide as a white solid. The resulting products were determined by their ¹H-NMR spectra and compared with the authentic samples^{21,35}.

General Experimental Procedure for the Deoxygenation of Sulfoxides

A mixture of diphenyl sulfide (1 mmol), NaI (2.5 mmol), and CSA (0.45 g equal to 2.2 mmol H^+) and ethanol (5 mL) was stirred at r.t. for 210min. The progress of the reaction was monitored by TLC. When the starting sulfoxide had completely disappeared, the mixture was neutralized by adding NaOH solution. The product was extracted with EtOAc (3× 5 mL). The combined extracts were washed with 10% aq Na₂S₂O₃. The organic layer dried over MgSO₄. The filtrate was evaporated, and then residue was purified by column chromatography on silica gel.

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Entry	Solvent	Reaction time	Viald $(0/)^{a}$	
Entry	Solvent	(min)	T ICIG (70)	
1	1,2-Dichloroethane	80	95	
2	Acetonitrile	150	90	
3	Xylene	360	60	
5	Ethanol	240	93	

Table 1 The effect of various solvents on oxidation of diphenyl sulfide to diphenyl sulfoxide

^aIsolated yield.

Table 2 Optimization of the amounts of H_2O_2 and CSA for the oxidation of diphenyl sulfide todiphenyl sulfoxide in Ethanol.

Entry	H_2O_2 (eq.)	CSA	Time (min)	Vield $(\%)^a$
Lintry	11202 (04.)	$(mmol H^+)$	Time (mm)	1 ioid (70)
1	1.5	0	1440	60
2	0.5	0.24	350	60
3	0.5	0.34	300	65
4	1.0	0.34	300	90
5	1.5	0.34	240	93
6	2.5	0.34	210	90 (5) ^b

^aIsolated yield.

^bdiphenyl sulfone. Conversion was determined by GC.

Table 3 Oxidation of sulfides to sulfoxides with hydrogen peroxide in the presence

Of CSA in Ethanol

	Substrate	Time (min)	Yield (%) ^a	ref
1 ^b	Diphenyl sulfide	240	93,90,95,91	21
2	Methyl phenyl sulfide	80	91	21
3	p-Nitrophenyl methyl sulfide	160	89	35a
4	Benzyl phenyl sulfide	170	93	35b
5	Benzyl phenyl sulfide	65	90	35b
6	Dibenzyl sulfide	90	93	35b
7	Di n-butyl sulfide	65	90	21
8	Tetrahydrothiophene	65	95	35c
9	Ethyl phenyl sulfide	90	90	35b
10	Allyl phenyl sulfide	90	92	35d
11	p-Bromophenyl methyl sulfide	120	90	35b
12	Dibenzothiophene	240	85	35e

^aIsolated yield.

^bThe same reagent was used for each of the four runs.

Table 4 Comparison of the activity of various catalysts in the oxidation of diphenyl sulfide using H_2O_2

Entry	catalyst	Conditions	Time	Yield	ref
1	CSA	EtOH, rt	240 min	93	This work
2	Silica sulfuric acid	CH ₃ CN, rt	30 min	95	26
3	MoO_2Cl_2	Acetone, rt	25 min	89	24
4	TaCl ₅	CH ₃ CN	30 min	93.8	35d
5	Amberlite IR-400	MeOH,rt	6.5 h	98	36
6	Amberlyst 15	MeOH, rt	7.5 h	98	36
7	$H_5 PMo_{11}Al_{0.5}V_{0.5}O_{40}$	CH ₃ CN, reflux	120 min	100	22
8	CBSA	C ₂ H ₄ Cl ₂ , reflux	10 min	95	27
9	L-proline	CH ₃ CN, reflux	90 min	93	37
10	HNO ₃	EtOH, rt	40 min	92	39
11	NBS	CH ₃ CN 40°C	48 h	60	40

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Entry	NaI (eq.)	$\frac{\text{CSA}}{(\text{mmol }\text{H}^{+})}$	Time (min)	Yield (%) ^a
1	2.0	1.96	300	70-73
2	2.2	1.96	300	79
3	2.5	2.2	210	91
4	2.5	2.45	200	91-93
+	2.5	2.43	200)1-)3

 Table 5 Optimization of the amounts of NaI and CSA for the deoxygenation of diphenyl sulfoxideto diphenyl sulfide in Ethanol.

^a Isolated yield.

		E	thanol	Acetonitrile		
Entry	Substrate	Time	Yield (%) ^a	Time	Yield	ref
		(min)		(min)	(%) ^a	
1 ^b	Diphenyl sulfoxide	210	91,90,93,87	25	95	41a
2	Methyl phenyl sulfoxide	60	95	15	93	41b
3	Benzyl phenyl sulfoxide	80	90	15	90	41c
4	Benzyl methyl sulfoxide	80	88	15	95	41d
5	Dibenzyl sulfoxide	60	91	15	93	41e
6	Di n-butyl sulfoxide	100	93	15	93	41a
7	Tetrahydrothiophene oxide	210	89	25	91	41f
8	Ethyl phenyl sulfoxide	60	96	15	95	41b
9	Allyl phenyl sulfoxide	60	93	15	93	41g
10	p-Bromophenyl methyl	200	93	20	90	14
10	sulfoxide					
11	p-Nitrophenyl methyl	240	92	25	93	41h
	sulfoxide					
12	Dibenzothiophene-5-oxide	300	85	45	87	41f

Table 6 deoxygenation of sulfoxides to sulfides with NaI and CSA in Ethanol and Acetonitrile

^a Isolated yield.

^bThe same reagent was used for each of the four runs.

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Table 7 C	Comparison	of the a	ctivity of	f various	reducing	system	in the	deoxygenat	tion of d	iphenyl
sulfoxide	to diphenyl	sulfide								

Entry	Reaction Conditions	Time	Yield (%)	ref
1	CSA, Ethanol, NaI	210 min	91	This work
2	Silica sulfuric acid, PEG-200, rt	240 min	94	34
3	TABCO, 1,3-Dithiane, CHCl ₃ , rt	55 min	93	41g
4	NBS, 1,3-Dithiane, CHCl ₃ , rt	40 min	94	41g
5	Zn(OTf) ₂ , PhSiH ₃ , toluene ,100 °C	24 h	>99	41f
6	KI-TCT, CH ₃ CN, 25 °C	25 min	96	42a
7	Mg, MeOH, rt	90 min	75	41c
8	Mo(CO) ₆ , EtOH, reflux	120 min	92	42b
9	2,6-dihydroxypyridine, CH ₃ CN, reflux	14 h	24	42c
10	ReIO ₂ (PPh ₃) ₂ , PhSiH ₃ , THF, rt	20 min	97	42d
11	MoO ₂ Cl ₂ (DMF) ₂ , pinacol, 90 °C	240 min	89	42e
12	MoCl ₅ /Gallium, under Ultrasonication, THF, r.t.	10 min	92	42f
13	TiI ₄ , CH ₃ CN, 0 °C	10 min	83	41e
14	Woollins' reagent, toluene, reflux	20 h	99	41a



Scheme 1