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Moslem Mansour Lakouraj [a] , Hamid Abdi [a] & Vahid Hasantabar [a]
[a] Department of Organic Chemistry, Faculty of Chemistry, University of Mazandaran, Babolsar, 47416, Iran

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Cyanuric chloride promoted oxidation of sulfides to sulfoxides or sulfones in the presence of hydrogen peroxide

Moslem Mansour Lakouraj,* Hamid Abdi and Vahid Hasantabar

Department of Organic Chemistry, Faculty of Chemistry, University of Mazandaran, Babolsar 47416, Iran

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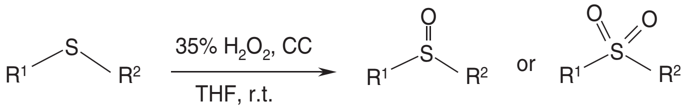
Aromatic and aliphatic sulfides are readily oxidized to sulfoxides or sulfones in high yield with 35% hydrogen peroxide in the presence of cyanuric chloride (CC) as an efficient activator. The oxidation of sulfides proceeds at room temperature and the corresponding sulfoxides or sulfones was selectively obtained by controlling the amounts of H_2O_2 and CC. Various sulfides possessing functional groups such as hydroxyl, methoxy, nitrile, aldehyde and olefinic double bond were successfully and selectively oxidized without affecting sensitive functionalities.



Keywords: cyanuric chloride; oxidation; hydrogen peroxide; sulfones; sulfoxides

1. Introduction

Sulfoxides and sulfones are useful synthetic intermediates for the construction of several important organic molecules (*1*). Moreover, there are many biologically important compounds containing a sulfoxide or sulfone moiety. Sulfoxides and sulfones are generally prepared via oxidation of the corresponding sulfide; however, it is often very difficult to stop the oxidation at the sulfoxide stage and the undesired overoxidation to sulfones is a quite frequent reaction. In general, direct oxidation of sulfides to sulfones is difficult compared with the oxidation of sulfides to sulfoxides (*2*). Moreover, if additional oxidizable functional groups are present, such as C−C double bond and alcohol, a further problem arises from the need to save them during the oxidation process.

So far, aqueous 35% hydrogen peroxide has been utilized as an attractive and environmentally benign oxidant for the oxidation of sulfides, because it is inexpensive, easy to handle, safely stored and produces only water as a side product (*3*). The use of an activator is essential for the success of the reaction because H_2O_2 oxidizes sulfides rather slowly (*4*). Usually hydrogen peroxide can be activated by transition metal (Ti, Mo, Fe, V, W, Re, Ru, Sc, Zr and Mn) compound

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*Corresponding author. Email: lakouraj@umz.ac.ir

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catalysts (*4–13*). Therefore, many efficient metal catalysts have been developed. However, their applications are limited because of difficulties in controlling the reaction at the first oxidation stage, using toxic transition metal compounds, preparation of complex catalyst, removing or recovery of the expensive catalyst and contamination of products (*14, 15*). Hence, there is a need to develop new and environmental friendly catalysts which overcome these drawbacks.

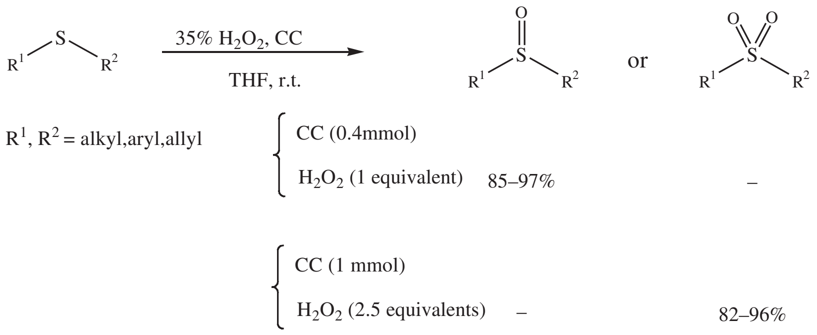
Cyanuric chloride (CC) is a commercially available, environmentally suitable, cheap, easy to handle and stable compound. It has three chlorine atoms which can be substituted by nucleophilic substances such as phenols, alcohols and amines. The stepwise substitution can be controlled at a well-defined temperature. However, the substitution pattern also depends on the structure of the nucleophile, basic strength, steric factors and the nature of the solvent used (*16*). Therefore, in continuation of our study on the activation of hydrogen peroxide to develop an environmentally benign oxidation method, herein we decided to exchange the chlorine atoms of the CC with the hydroperoxy group to prepare an efficient reagent for the conversion of sulfides to sulfoxides or sulfones.

2. Results and discussion

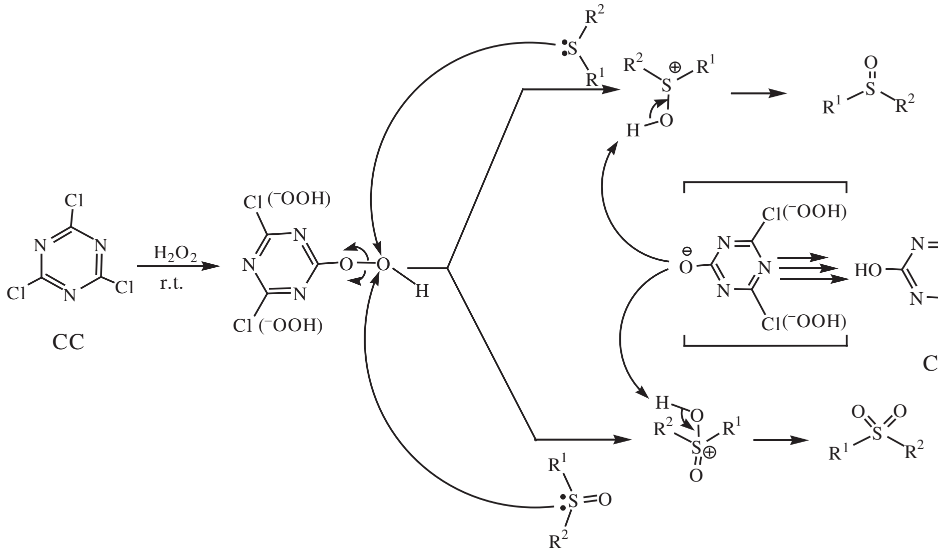
According to the empirical observations, it is expected that monosubstitution of a chlorine atom in the hydrolysis of CC occurs below or at 273.15 K, disubstitution at room temperature (r.t.) and trisubstitution above 333.15 K (*16*). Therefore, cyanuric hydroperoxide can be formed *in situ* on treatment of hydrogen peroxide with CC. The CC/H_2O_2 system offers an ideal combination for the chosen oxidations. The oxidation byproduct, cyanuric acid (CA), is classified as essentially nontoxic. In fact, cyanuric acid is widely used for the manufacture of *N*-chlorinated isocyanurates, which are employed as disinfectants in swimming pool, bleaches, cleaners and sanitizers. CA serves as a stabilizer of available chlorine in swimming pools. In concentrations of 20–40 ppm, it reduces the deactivation rate of chlorine by a factor of 5–10. CA is approved in ruminant feed as a source of nitrogen (*17*).

In this work, the activation of hydrogen peroxide is accomplished upon simple treatment of CC with commercial (35%) hydrogen peroxide. The chemoselective oxidation of sulfides to sulfoxides or sulfones with H_2O_2 was achieved in the presence of a catalytic amount of CC by controlling the amount of H_2O_2 (Scheme 1).

In an extended experiment to optimize the reaction conditions, the oxidation of methyl phenyl sulfide using 35% H_2O_2 in the presence of CC was attempted in different solvents. When the reaction was carried out in the solvent that constitutes a heterogeneous solvent system with aqueous hydrogen peroxide such as diethylether, dichloromethane and *n*-hexane, no reaction was observed with methyl phenyl sulfide even after 8 h. However, it was found that in the solvents



Scheme 1. Selective oxidation of sulfides.



Scheme 2. Proposed mechanism for the oxidation of sulfide to sulfoxides or sulfones.

Table 1. Optimization of the amounts of H_2O_2 and CC for the selective oxidation of methyl phenyl sulfide to methyl phenyl sulfoxide or methyl phenyl sulfone.[a]

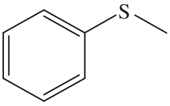
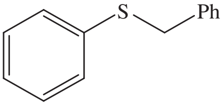
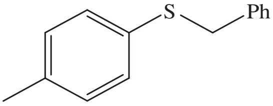
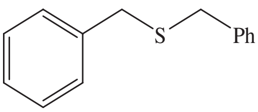
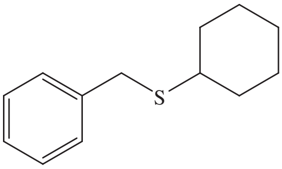
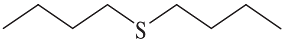
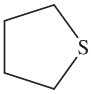
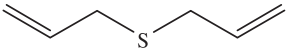
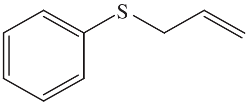
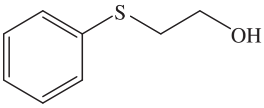
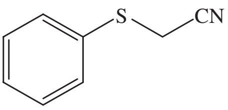
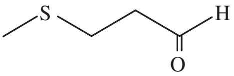
Entry	H_2O_2 (equivalent)	CC (mmol)	Time	Yield (%)[b] Sulfoxide	Yield (%)[b] Sulfone
1	0.5	0.4	30 min	50	–
2	**1**	**0.4**	**10 min**	**100**	–
3	1	0	24 h	60	–
4	1	0.1	30 min	40	–
5	1	0.2	30 min	56	–
6	1.75	1	60 min	–	60
7	**2.5**	**1**	**15 min**	–	**100**
8	2.5	0	24 h	55	8
9	2.5	0.5	60 min	–	55
10	2.5	0.75	60 min	–	75

Notes: The bold numbers show the selected reaction conditions.
[a] Reactions were performed with methyl phenyl sulfide (1 mmol) at r.t.
[b] Conversions determined by GC.

that are miscible with hydrogen peroxide such as tetrahydrofuran (THF) and acetonitrile, methyl phenyl sulfide was efficiently oxidized to the corresponding sulfoxide or sulfone (Schemes 1 and 2). The results show that THF is generally the best of the solvents examined in terms of yield, time and economy.

In addition, we evaluated the influence of different amounts of hydrogen peroxide and CC on the oxidation of methyl phenyl sulfide in THF at r.t. The results are summarized in Table 1. As seen in Table 1 (Entries 3 and 8), the reaction was incomplete in the absence of a catalyst even after 24 h. When CC was added, the times were reduced considerably and the yield increased to 100%. H_2O_2 (1 equivalent) in the presence of CC (0.4 mmol) was found to be ideal for the quantitive conversion of sulfides to sulfoxides. The use of excess H_2O_2 (2.5 equivalents) in the presence of CC (1 mmol) leads to the corresponding sulfone in a clean reaction. In each case, after the consumption of CC, the formed CA is separated from the mixture by simple filtration.

Table 2. Selective oxidation of sulfides to sulfoxides or sulfones using H_2O_2/CC.

		Sulfoxide[a]			Sulfone[b]		
Entry	Substrate	Time (min)	Isolated yield (%)	Reference	Time (min)	Isolated yield (%)	Reference
1		10	96	(*26a*)	15	93	(*26b*)
2		20	90	(*26b*)	25	89	(*26b*)
3		15	97	(*26a*)	20	96	(*26e*)
4		10	94	(*26b*)	20	91	(*26b*)
5		15	95	(*26a*)	20	96	(*26f*)
6		20	90	(*26a*)	65	82	(*26c*)
7		20	92	(*26a*)	55	90	(*26e*)
8		15	93	(*26a*)	30	91	(*26c*)
9		25	87	(*26b*)	35	90	(*26b*)
10		35	96	(*26a*)	45	85	(*26c*)
11		30	90	(*26d*)	35	92	(*26d*)
12		40	85	(*26a*)	55	86	(*26a*)

Notes: [a]Reaction conditions: sulfide (1 mmol), 35% H_2O_2 (1 equivalent), CC (0.4 mmol), r.t.
[b]Reaction conditions: sulfide (1 mmol), 35% H_2O_2 (2.5 equivalents), CC (1 mmol), r.t.

Table 3. Comparison of the potential activity of CC with reported catalysts in the oxidation of methyl phenyl sulfide.

		Sulfoxide			Sulfone			
Entry	Catalyst	Conditions	Time (min)	Yield (%)	Conditions	Time (min)	Yield (%)	Reference
1	CC	THF, r.t.	10	96	THF, r.t.	15	93	–
2	β−Cyclodextrin	H_2O, reflux	240	89	H_2O, reflux	240	91	(*18*)
3	Mn(TPPBr$_3$)OAc	CH_2Cl_2, r.t.	2	–	CH_2Cl_2, r.t.	2	100	(*19*)
4	Carbon-based solid acid	CH_2Cl_2, reflux	10	94	CH_2Cl_2, reflux	10	95	(*20*)
5	WO_3/MCM-48	MeOH, r.t.	240	97	MeOH, reflux	720	99	(*21*)
6	UHP	Solid state, reflux	15	80	Solid state, reflux	60	87	(*22*)
7	SiO_2-W_2-Py	MeOH/CH_2Cl_2, 8 °C	150	90.1	MeOH/CH_2Cl_2, 10 °C	300	90.4	(*23*)
8	$(Bu_4N)_3[PMo_{12}O_{40}]$/FAp	Solid state, 4 °C	4320	85	Solid state, r.t.	1440	93	(*24*)

Note: UHP, urea hydrogen peroxide.

Therefore, based on these observations, a plausible mechanistic pathway can be proposed as in Scheme 2.

To extend the scope of the reaction and to generalize the procedure, we investigated the oxidation of a variety of organic sulfides including dibenzyl, alkyl benzyl, dialkyl and heterocyclic sulfides under these optimized reaction conditions and the results are presented in Table 2. The expected products were obtained in short times and in high yields. It is notable that under these conditions, various functional groups including olefin, alcohol, nitrile and aldehyde groups were tolerated (Table 2, Entries 8–12). These substrates selectively underwent oxidation at the sulfur atom without undergoing further structural changes in their functional groups.

In order to show the potential activity of CC in promotion of H_2O_2, we compared our results on the oxidation of methyl phenyl sulfide with some data from the literature (Table 3). As shown in Table 3, the previously reported procedures were not selective or suffer from one or more disadvantages such as elevated reaction temperatures (*18, 19–21*), longer reaction times (*18, 20, 22, 23*), special efforts for the preparation of catalyst (*19, 20, 22–24*) and using a transition metal (*20, 22–24*).

3. Conclusions

This procedure offers several major advantages: (1) the use of a commercially available cheap activator and oxidant; (2) highly efficient for the selective oxidation of structurally diverse sulfides in good to high yields; (3) control over the degree of oxidation offers access to sulfoxides or sulfones; (4) excellent chemoselectivity; (5) the method conforms to several of the guiding principles of green chemistry. We believe the present method to be an improvement with respect to other procedures.

4. Experimental

Chemicals were purchased from Merck, Fluka and Aldrich chemical companies. A number of sulfides were prepared using the standard synthesis method (*25*). All sulfoxides were separated and purified by chromatographic techniques and also identified by comparison of their mp, IR and NMR with those reported in the literature (*26*).

4.1. *General procedure for the oxidation of sulfides to sulfoxides*

In a 25 ml round-bottom flask, to a solution of sulfide (1 mmol) in THF (4 ml), 35% H_2O_2 (1 equivalent) and CC (0.4 mmol) were added successively and the mixture was stirred magnetically at r.t. for the time indicated in Table 2. The progress of the reaction was monitored by TLC. After completion of the reaction, solid CA precipitate was filtered and washed with diethyl ether. The filtrate was neutralized by adding (10%) $NaHCO_3$. The product was extracted with diethyl ether (3 × 5 ml) and the combined extracts were dried (Na_2SO_4). The solvent was removed under reduced pressure to give the corresponding pure sulfoxide. Further purification was achieved by short-column chromatography on silica gel with EtOAc/*n*-hexane (1:2) as the eluent.

4.2. *General procedure for the oxidation of sulfides to sulfones*

In a 25 ml round-bottom flask, to a solution of sulfide (1 mmol) in THF (6 ml), 35% H_2O_2 (2.5 equivalents) and CC (1 mmol) were added successively and the mixture was stirred magnetically at r.t. for the time indicated in Table 2. The progress of the reaction was monitored by TLC. After completion of the reaction, solid CA precipitate was filtered and washed with diethyl ether. The combined filtrates were neutralized by adding (10%) $NaHCO_3$. The product was extracted with diethyl ether (3 × 5 ml) and the combined extracts were dried (Na_2SO_4). Evaporation of the solvent under reduced pressure gave the corresponding pure sulfone in most cases. Further purification was achieved by recrystallization from EtOH.

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