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Dedicated to Professor Luminița Silaghi-Dumitrescu
on the Occasion of Her 75th Anniversary

CATALYTIC SULFOXIDATION REACTIONS OF 1,3-BIS(PARA-TOLYL SULFIDE)-5-TERT-BUTYLBENZENE USING DECAVANADATE DERIVATIVES

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ABSTRACT. Catalytic sulfoxidation of 1,3-bis(*para*-tolyl sulfide)-5-*tert*-butylbenzene in order to obtain sulfones and sulfoxides, was carried out using three decavanadate $(V_{10}O_{28})^{6-}$ containing catalysts. Reaction conditions were varied to evaluate different parameters of the process; the tested procedures followed the guidelines of green chemistry. To align with these principles, reaction parameters were optimized at room temperature using environmentally benign solvents, including methanol, ethanol, *iso*-propanol, water, and ethylene glycol, as well as their mixtures with toluene. In this study we present a fast and environmentally friendly procedure to obtain sulfonyl and sulfinyl containing compounds through sulfoxidation of bis-thioether 1,3-bis(*para*-tolyl sulfide)-5-*tert*-butylbenzene.

Keywords: *catalytic sulfoxidation, bis-thioether, sulfide oxidation, green chemistry*

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INTRODUCTION

Compounds containing sulfonyl (−SO_2−) and/or sulfinyl (−SO−) moieties have a wide variety of applications,[1] for example playing important roles in organic synthesis transformations[2,3,4] or acting as ligands in the synthesis of transition metal complexes.[5] Sulfonyl and sulfinyl containing derivatives can also be found in biologically active compounds[6,7] or in materials with diverse properties.[8] For this reason, the efficient synthesis of such compounds is of interest for the scientific community. The introduction of the sulfonyl and sulfinyl groups can be realized through several well-known strategies,[9] among which one of the most representative being through the oxidation of the corresponding sulfide.[2,10] The sulfoxidation of thioethers is commonly achieved using oxidants like hydrogen peroxide (H_2O_2), meta-chloro-perbenzoic acid (*m*CPBA), oxone, HIO_4, etc. in various solvents.[11] This oxidation can be done through catalytic pathways as well.[12,13] Due to the importance and applicability of the topic, several catalytic derivatives are presented in the literature, with examples for different homogeneous and heterogeneous systems, most commonly employing catalysts based on tungsten, vanadium and titanium.[14,15,16] While there are several examples for sulfoxidation reactions of various sulfide containing substrates[12,13,14,15,16], there are very few examples where the substrates contains two or more sulfide moieties in their structure.

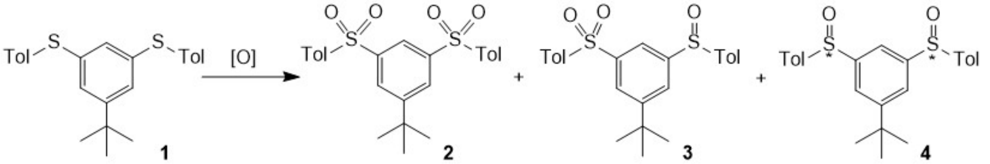
Our research group is also interested in the use of sulfur containing compounds, mainly for their role as pincer-type ligands in various p and d block elements-based derivatives.[17,18,19,20,21] Three compounds containing sulfonyl and sulfinyl groups were designed and used as O,C,O-chelating pincer ligands, one containing two sulfonyl groups,[19] a second one containing a sulfonyl and a sulfinyl group[21] and a third one containing two sulfinyl groups.[18] These sulfone and sulfoxide based compounds were successfully used for the stabilization of low valent group 14 elements and transition metal complexes.[17,18,19,20,21] Thus, we started to explore strategies for the synthesis of the sulfone and sulfoxide-based compounds that are in accordance with the principles of green chemistry. Recently, we presented the potential of decavanadate-containing materials as catalysts in the oxidation of diphenyl sulfide.[22] The obtained results showed that full conversion of the diphenyl sulfide substrate could be reached in a short reaction time (2 h), in solvents like methanol, ethanol, *iso*-propanol, with low catalyst loading (1.5 mol%). Moreover, good results were obtained in the recyclability test of the catalyst as well, observing full conversion of the substrate even after three runs.

Starting from these results, we continued the study in order to employ these catalytic systems in the oxidation of a bis-thioether, a compound that contains two sulfide moieties, namely 1,3-bis(*para*-tolyl sulfide)-5-*tert*-butylbenzene (further named bis-thioether **1**). We aimed to investigate and compare reaction conditions for the oxidation of bis-thioether **1** testing different solvents, catalysts and reaction times, with the purpose of finding a more environmentally friendly procedure.

RESULTS AND DISCUSSION

Based on the results obtained in our previous study for the oxidation of diphenyl sulfide,[22] we investigated the catalytic activity of decavanadate containing compounds in sulfoxidation reactions. Three decavanadate-based materials were used as catalysts to test their activity in oxidation reactions: tetraammonium decaaquadilithium decavanadate $\{Li_2(H_2O)_{10}\}(V_{10}O_{28})(NH_4)_4$ (**Cat.1**),[22] diethylenediammonium diammonium decavanadate tetrahydrate $(NH_4)_2(H_2en)_2\{V_{10}O_{28}\}\cdot 4H_2O$ (**Cat.2**)[23] and triethylenediammonium decavanadate hexahydrate $(H_2en)_3\{V_{10}O_{28}\}\cdot 6H_2O$ (**Cat.3**).[24] Full conversion of diphenyl sulfide was observed even after only two hours in methanol, ethanol, *iso*-propanol, and **Cat.1** showed good results in the recyclability test as well.[22]

These results represented the starting point in the investigation of the oxidation of 1,3-bis(*para*-tolyl sulfide)-5-*tert*-butylbenzene **1** (bis-thioether **1**), in order to obtain 1,3-bis{(4-methylphenyl)sulfonyl}-5-*tert*-butylbenzene (bis-sulfone **2**), 1-(*para*-tolylsulfinyl)-3-tosyl-5-*tert*-butylbenzene (sulfone-sulfoxide **3**) and 1,3-(*para*-tolylsulfinyl)-5-*tert*-butylbenzene (bis-sulfoxide **4**). (**Scheme 1.**)



Scheme 1. Oxidation of 1,3-bis(*para*-tolyl sulfide)-5-*tert*-butylbenzene **1.**

Compounds **2** and **3** can be obtained through different pathways, presented in the literature.[19,20] Bis-sulfone **2** can be synthesized through a palladium catalysed cross-coupling reaction between 1,3-dibromo-5-*tert*-butylbenzene and sodium *para*-toluenesulfinate,[19] while sulfone-sulfoxide

3 can be obtained from 1-bromo-3-(*tert*-butyl)-5-(*para*-tolylsulfinyl)benzene and sodium *para*-toluene sulfinate with a palladium catalyzed coupling reaction.[20] Compounds **2** – **4** can also be obtained by the oxidation of bis-thioether **1** in two ways: one where the oxidation is done in anhydrous acetic acid media with hydrogen-peroxide as oxidant, and a second one using as oxidant *meta*-chloroperoxybenzoic acid (*m*CPBA) in dichloromethane (CH_2Cl_2).[18] In both cases the formation of all three products **2** – **4** can be observed and both oxidation methods have some disadvantages. Among the drawbacks is the use of a large amount of CH2Cl2 for the extraction of the products when oxidation is realized in anhydrous acetic acid with H_2O_2. Another inconvenience is the use of chlorinated solvents and the low atom economy of *m*CPBA in the second case. With the purpose of avoiding these drawbacks, the above-mentioned catalytic conditions, employed previously for the oxidation of diphenyl sulfide, were tested for the oxidation of bis-thioether **1** as well. The major challenge of this process is the presence of two sulfide groups in the molecule, that makes selectivity towards any of the expected compounds difficult to achieve.

In this work the oxidizing reaction of bis-thioether **1** (**Scheme 1.**) was tested with the previously mentioned catalysts **Cat.1-3**. One of the major considerations when selecting the reaction conditions was to comply as much as possible with the recommendations of green chemistry.[25] In the literature there are several guidelines available that help in planning and evaluating the chemical processes in a way to adhere as much as possible to the principles of green chemistry.[26,27,28] In the present case, parameters like atom economy, catalyst use, solvent safety and low energy use were considered.

Having these in mind, we developed a methodology considering the following criteria: the reaction should run at room temperature with the shortest possible reaction time, an easily handled oxidant should be used, solvents should be chosen in adherence to the solvent selection guidelines (factoring in safety, health and environmental effects), and high atom economy should be achieved. Therefore, in our tests, as the oxidizing agent an excess of 35% H_2O_2 solution was used, hydrogen peroxide being one of the most atom-economical choices and easy to handle. According to the selection guide of solvents[27,28] and taking into account the solvents usually used in sulfoxidation reactions, the following solvents were chosen for the experiments: ethanol (EtOH), methanol (MeOH), water (H_2O), ethylene glycol (EG), and isopropanol (*i*-PrOH).[27,28]

The oxidation reactions of bis-thioether **1** were followed using ^{1}H NMR spectroscopy, where compounds **1 – 4** exhibit characteristic signals. (**Figure 1.**)

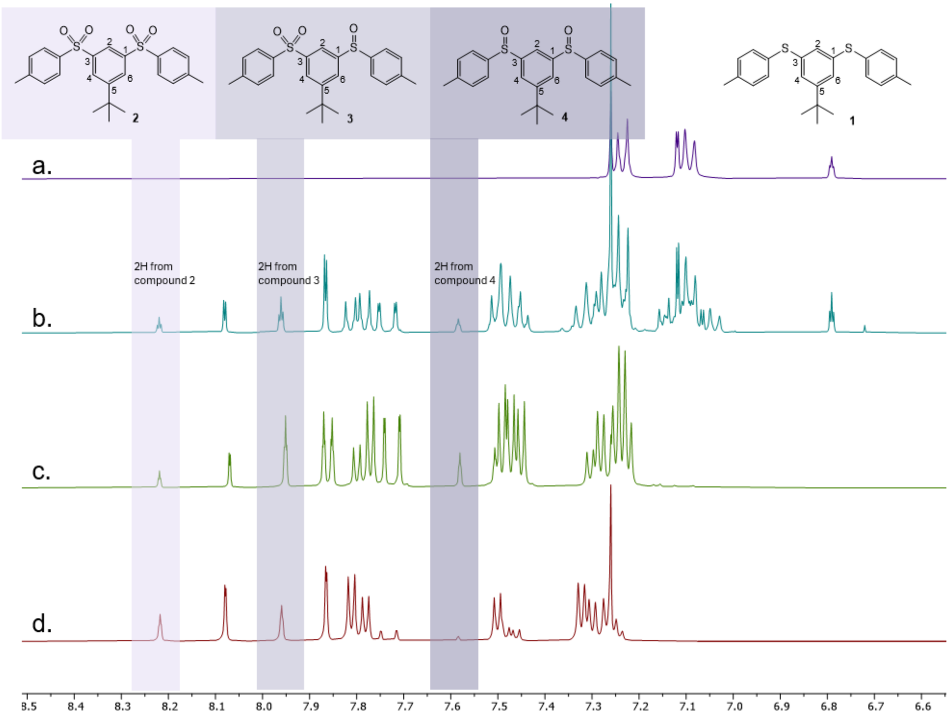


Figure 1. Example for the use of ^{1}H NMR spectroscopy for calculating the conversion and selectivity of the oxidation reactions. a. starting material b. **Cat.1**, EtOH, 48h c. **Cat.2**, H_2O, 48h d. **Cat.3**, *i*-PrOH, 48h ($CDCl_3$, 400.13 MHz)

Specifically, the conversion of the starting material bis-thioether **1** was monitored through the evolution of the distinctive triplet signal at δ 6.79 ppm (t, J = 1.65 Hz). The percentage of this signal, relative to the signals of the oxidation products (8.23 – 7.30 ppm), allowed for the calculation of the conversion. (**Figure 1.**)

The selectivity of the oxidation reaction towards the products bis-sulfone **2**, sulfone-sulfoxide **3**, and bis-sulfoxide **4**, was determined by calculating the percentage ratio of their respective characteristic signals. Using this method, the progress of oxidation, the overall conversion, and the product ratio could be determined. (**Figure 1.**)

The initial tests of sulfoxidation of bis-thioether **1**, after 2 and 24 h reaction time, showed no or very low conversion of the substrate. Thus, the first tests were conducted at 48 h reaction time, and the results are presented in **Table 1**.

Table 1. Experimental details, conversion and selectivity data for the oxidation reactions of compound **1.**

Nr.	Catalyst	Solvent	Conversion (%)*	Selectivity (%)*		
				2	**3**	**4**
1	**Cat.1**	MeOH	0	0	0	0
2		H_2O	**100**	21	51	28
3		EtOH	97	31	30	39
4		*i*-PrOH	**100**	20	38	42
5		EG	0	0	0	0
6	**Cat.2**	MeOH	0	0	0	0
7		H_2O	**100**	30	58	12
8		EtOH	72	23	47	30
9		*i*-PrOH	41	33	42	25
10		EG	0	0	0	0
11	**Cat.3**	MeOH	0	0	0	0
12		H_2O	**100**	75	25	0.00
13		EtOH	0	0	0	0
14		*i*-PrOH	**100**	36	49	15
15		EG	0	0	0	0
16	none[a,b]	MeOH	20	0	0	0
17	**Cat.3**[c]	MeOH	0	0	0	0

Reaction condition: 50 mg (0.27 mmol) bis-thioether **1**, 3 mL solvent, 1 mL H_2O_2 35% solution, 5 mg catalyst (1.5 mol%), room temperature, 48 hours. [a]no catalyst was used. [a]formation of an unidentified product was observed, based on ^{1}H NMR containing one sulfoxide and one sulfide group [c]no H_2O_2 was used
*without separation from reaction mixture, according to ^{1}H NMR measurements.

The catalytic oxidation efficiency of **Cat.1 – 3** was highly dependent on the reaction solvent. No substrate conversion was detected in either MeOH or EG with any of the catalysts, even after 48 h reaction time. However, complete conversion was achieved in H_2O with all three catalysts **Cat.1 – 3** and *i*-PrOH using catalysts **Cat.1** and **Cat.3** (**Table 1**). Conversions in EtOH were more variable, ranging from undetectable (**Table 1**, entry 14) to nearly quantitative depending on the specific catalyst (**Table 1**, entries 4 and 9). While overall selectivity for products **2 – 4** was generally low across the catalysts and conditions, a notable exception was the 75% selectivity for bis-sulfone **2** observed with **Cat.3** in H_2O (**Table 1**, entry 13). These results are somewhat different compared to the case when using diphenyl sulfide as a substrate in our previous study,[22] where full conversion was obtained every time in MeOH, EtOH, *i*-PrOH, and most of the time in H_2O and EG. This could be explained with the lower solubility of bis-thioether **1** compared to the diphenyl sulfide in the used polar solvents, but also with the presence of the two sulfide groups.

Given that bis-thioether **1** has a lower solubility in the polar solvents chosen for these oxidation reactions, adding an apolar solvent was needed to increase the solubility of the compound. Considering the solubility of compound **1** and the solvent selection guidelines,[19,27,28] toluene proved to be a suitable solvent to be used in the oxidation tests. Thus, toluene was added in a 1:5 ratio to the polar solvents (methanol, water, ethanol, isopropanol and ethylene-glycol) for further reactions. Two different reaction times were tested, 24 and 48 hours. The reactions were followed by ^1H NMR spectroscopy in order to calculate conversion and selectivity, the obtained results being presented in **Table 2**.

Adding toluene in a ratio of 1:5 to the different polar solvents (MeOH, H_2O, EtOH, *i*-PrOH and EG) increased the conversion in most cases, except EG and MeOH (**Table 2.**). In the case of EG and MeOH, although adding toluene helped, full conversion could be reached only with **Cat.1**, after 48 hours (**Table 2.**, entries 1 and 5). When it came to H_2O and *i*-PrOH the conversion was 100% in most cases after 48 hours, no matter what the catalyst was. When the reaction time was 24 hours, full conversion could be observed in toluene and H_2O solvent mixture for all three catalyst **Cat.1 – 3** (**Table 2.**, entries 17, 22, 27), while in toluene and *i*-PrOH **Cat.1** and **Cat.2** (**Table 2.**, entries 19, 24) led to the complete transformation of the substrate.

Considering the selectivity of the reactions, in most cases no clear majority was observed for either one of the products. However, in some examples, the formation of bis-sulfone **2** was preferred, after 24 hours using **Cat.1** in H_2O or **Cat.2** in *i*-PrOH. (**Table 2**, entries 17, 24) However, this could not be observed with the increased 48 hours reaction time. This difference can be explained with the stability of the catalytic systems in the alcoholic media.

Table 2. Experimental details, conversion and selectivity data for the oxidation reactions of compound **1** for 48 h and 24 h reaction time.

Nr.	Catalyst	Solvent	Reaction time (h)	Conversion (%)*	Selectivity (%)*		
					2	**3**	**4**
1	**Cat.1**	tol:MeOH	48	**100**	27	44	29
2		tol:H_2O		**100**	69	31	0
3		tol:EtOH		37	33	40	27
4		tol:*i*-PrOH		**100**	59	41	0
5		tol:EG		**100**	16	46	38
6	**Cat.2**	tol:MeOH	48	40	0	0	100
7		tol:H_2O		**100**	15	49	36
8		tol:EtOH		89	27	39	34
9		tol:*i*-PrOH		**100**	35	57	8
10		tol:EG		0	0	0	0
11	**Cat.3**	tol:MeOH	48	20	48	52	0
12		tol:H_2O		**100**	42	47	11
13		tol:EtOH		**100**	28	41	31
14		tol:*i*-PrOH		**100**	14	39	47
15		tol:EG		0	0	0	0
16	**Cat.1**	tol:MeOH	24	0	0	0	0
17		tol:H_2O		**100**	100	0	0
18		tol:EtOH		5[a]	0	0	0
19		tol:*i*-PrOH		**100**	23	49	27
20		tol:EG		**100**	23	62	25
21	**Cat.2**	tol:MeOH	24	37	0	47	53
22		tol:H_2O		**100**	29	48	18
23		tol:EtOH		33	11	30	59
24		tol:*i*-PrOH		**100**	100	0	0
25		tol:EG		20	60	18	22
26	**Cat.3**	tol:MeOH	24	49	0	0	4
27		tol:H_2O		**100**	29	48	23
28		tol:EtOH		18	0	0	100
29		tol:*i*-PrOH		74	12	32	56
30		tol:EG		0	0	0	0

Reaction condition: 50 mg (0.27 mmol) bis-thioether **1**, 3 mL solvent (toluene and polar solvent in a 1:5 ratio), 1 mL H_2O_2 35% solution, 5 mg catalyst (1.5 mol%), room temperature, 24 or 48 hours.

*without separation from reaction mixture, according to ^{1}H NMR measurements.

[a] formation of an unidentified product was observed, based on ^{1}H NMR containing one sulfoxide and one sulfide group

A reaction time of 2 hours was also tested. The calculated conversion and selectivity results are presented in **Table 3**.

Table 3. Experimental details, conversion and selectivity data for the oxidation reactions of compound **1** for 2 h reaction time

Nr.	Catalyst	Solvent	Conversion (%)*	Selectivity (%)*		
				2	**3**	**4**
1	**Cat.1**	tol:MeOH	0	0	0	0
2		tol:H_2O	**100**	38	36	26
3		tol:EtOH	15	33	56	12
4		tol:*i*-PrOH	10	0	29	71
5		tol:EG	0	0	0	0
6	**Cat.2**	tol:MeOH	0	0	0	0
7		tol:H_2O	**100**	38	57	5
8		tol:EtOH	34	0	20	80
9		tol:*i*-PrOH	31	0	21	79
10		tol:EG	0	0	0	0
11	**Cat.3**	tol:MeOH	35[a]	0	0	0
12		tol:H_2O	**100**	25	60	15
13		tol:EtOH	27[a]	6	10	15
14		tol:*i*-PrOH	50	19	32	49
15		tol:EG	25[a]	0	0	0
16	**Cat.2**[b]	H_2O, 1st run	**100**	17	59	24
17		H_2O, 2nd run	**100**	67	33	0
18		H_2O, 3rd run	**100**	31	56	13

Reaction condition: 50 mg (0.27 mmol) bis-thioether **1** , 3 mL solvent (toluene and polar solvent in a 1:5 ratio), 1 mL H_2O_2 35% solution, 5 mg catalyst (1.5 mol%), room temperature, 2 hours.

*without separation from reaction mixture, according to ^{1}H NMR measurements

[a] formation of an unidentified product was observed, based on ^{1}H NMR containing one sulfoxide and one sulfide group

[b] scale-up to 500 mg substrate and catalyst recyclability test

It was shown that, when using toluene and H_2O as solvent mixture, even after a 2 hours reaction time, full conversion can be obtained for all three catalyst **Cat.1 – 3**. When using other solvents (MeOH, EtOH, *i*-PrOH, EG) the conversion was usually lower than with the reaction time of 24 or 48 hours. When considering the selectivity, no clear preference towards products **2 – 4** was observed, all three being obtained in all cases.

A scale-up and catalyst recyclability test was carried out as well with **Cat.2**. Using 500 mg bis-thioether **1** in the toluene and H_2O solvent mixture full conversion of the substrate could be observed even after 3 runs, thus showing a robust, environmentally friendly and fast procedure to obtain the targeted compounds **2 – 4**.

CONCLUSIONS

In this study an efficient and environmentally benign method for the catalytic oxidation of bis-thioether **1** to its corresponding sulfone and sulfoxide derivatives was successfully developed using three decavanadate-based catalysts (**Cat.1**, **Cat.2**, **Cat.3**). The results of the present research indicate that using a mixture of toluene and water, full conversion of the substrate was obtained within two hours at room temperature, with a low catalyst loading and H_2O_2 as oxidant.

This methodology aligns with the principles of green chemistry by employing non-toxic solvents and H_2O_2 as oxidant, and represents a significant advancement over traditional oxidation techniques, which frequently rely on hazardous organic solvents and oxidants with low atom economy. The ability of the system to maintain high activity in aqueous-organic mixtures validates the feasibility of using water as a primary medium for oxidation of sulfides, aligning with the principles of green chemistry. Furthermore, this system proved to be scalable, and the catalyst displayed potential for recyclability.

The method described in this work is highly effective for achieving full conversion of a substrate containing two sulfide groups, even if selectivity towards any of the products is not observed. Future investigations will focus on tailoring the catalyst and the catalytic system to reach selectivity towards either sulfoxides or sulfones.

EXPERIMENTAL SECTION

General considerations

Compounds bis-thioether **1**[18] and catalysts **Cat.1 – 3** were prepared according to literature procedures.[22,23,24] All other chemicals were purchased from usual chemical suppliers and used as received. NMR spectra were recorded in deuterated chloroform on Bruker Avance 400 spectrometer (operating frequency of 400.13 MHz for ^{1}H). Chemical shifts are given in ppm relative to the solvent residual peak for the ^{1}H NMR spectra.

General procedure for catalytic oxidation

In a typical experiment 50 mg bis-thioether **1**, 3 mL solvent, 1 mL 35% H_2O_2 solution and 5 mg catalyst were added to a 25 mL one-necked round bottom flask and stirred at room temperature for different time periods (2, 24 or 48 hours). After adding 3 mL water, the phases were extracted with 5 mL ethyl-acetate two times. The organic phases were dried under vacuum and analyzed by ^{1}H NMR spectroscopy using $CDCl_3$ as solvent. Conversion was calculated in MestReNova software considering the sum of the integral for H2 of bis-thioether **1** (**Figure 1**), bis-sulfone **2**, sulfone-sulfoxide **3** and bis-sulfoxide **4** (**Figure 1**) 100, then using the normalized values as percentage of each signal, thus each compound. In a similar fashion, when calculating the selectivity, the sum of the integrals corresponding to H2 in compounds **2 – 4** (**Figure 1**) was set to 100.

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