



Photo-difunctionalization and Photo-oxidative Cleavage of the C– C Double Bond of Styrenes in the Presence of Nanosized Cadmium Sulfide (CdS) as a Highly Efficient Photo-Induced Reusable Nanocatalyst

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Abstract: The synthesis of cyclic dithiocarbonates *via* photodifunctionalization of the C–C double bond of styrene and aryl aldehydes *via* photo-oxidative cleavage of the C–C double bond of styrene was accomplished in the presence of CdS NPs at room temperature in air atmosphere under visible light irradiation without using any external oxidant. Some of the special advantages of these processes can be mentioned the use of CdS NPs as a simple, accessible, safe and visible-light-induced reusable catalyst, air as an easily attainable, inexpensive and harmless oxidant, styrene as a readily accessible substrate and visible-light as a renewable, available and safe energy source.

Introduction

The onset of the 21st century has been accompanied by a significant increase in research in the field of visible light photocatalysis ¹. A combination of visible light and catalysts can be used for developing selective and efficient chemical transformations (like the unrivaled process of photosynthesis in nature) ². Hereon, the organic compounds are synthesized with the minimal environmental impact using mild conditions. So, one of the aims of green chemistry is being achieved. Visible-light can irritate photocatalysts as a safe, easily available, inexpensive, and renewable energy source³. The light absorbent photocatalysts such as organic dyes, metal complexes, and semiconductors can operate as an initiator for the chemical transformations. Whenever organic dyes and metal complexes are used as photocatalysts, the environmental pollutions challenges are inescapable.

In the last decade, many organic reactions have been accomplished with expensive and toxic metal complexes such as Au, Pd, Ni, Ir, Cu, Rh, and Ru in the presence of light ⁴. The synthesis of these metal complexes is confronted with problems such as toxicity, expensive, time-consuming, and the preparation of them are difficult ⁵. Therefore, the use of semiconductors without the need for modification is more important (such as Metal oxides and metal sulfides) ⁶. However, semiconductors as photocatalyst alone are rarely used in important organic reactions for several reasons such as non-absorption of visible light, the fast recombination of electron and hole, and lack of suitable redox potential for the interaction with organic substrates. So usually, the direct use of them is not possible and requires modifications to increase the photocatalytic effect ⁷. Morphological, structural, optical and electric properties of metal oxides and sulfides can be tailored through doping with anions ⁸ or cations ⁹. Most of the

usual doping processes are time-consuming, costly, and/or faced with environmental pollution (For example, doping is done with toxic heavy metals such as Pd, Au, Ni, Ag, etc, ...)⁹. Hence, the use of visible light absorbent semiconductors without requires modifications is very important ¹⁰. The most important properties of CdS as a good photocatalyst can be mentioned as appropriate bandgap, efficient visible light absorption, high surface area, and suitable redox potential for the interaction with organic compounds ^{10c, 11}.

Styrenes as readily accessible substrates can easily trap the radicals, hence, it can perform important chemical transformations via cleavage or difunctionalization of the C-C double bond. The structure of styrenes allows adding two functional groups at the same time and in a single step. Moreover, several studies have been reported for the oxidative cleavage of a C-C double bond ¹² and the difunctionalization of styrenes Interestingly, carbonyl products obtained from cleavage of alkenes applied for the synthesis of biologically active and natural compounds¹⁴. They are also used as important precursors for the synthesis of many organic compounds 15. Many processes have been reported to perform this momentous transformation. The most famous of them are ozonolysis and oxidation reactions using OsO4, RuO4, KMnO4, peracids, peroxides, and other oxidizing reagents in combination with a transition metal catalyst ¹⁶⁻¹⁸. Besides, investigations have been done into equivalent oxygen and oxidants in combination with organic molecules ¹⁹ and electrochemical alternatives ²⁰. The use of homogeneous, expensive or toxic metals catalysts and excess amounts of poisonous oxidants along with the production of great quantities of by-products are the main disadvantages of these processes, which pose safety hazards and environmental pollution. In the past decade, chemists have centralized more on the synthesis of organic compounds via photochemical methods Unfortunately, there are few reports in the field of photochemical cleavage of C-C double bonds ²³. Although these methods are superior to other methods, however, this process suffers from the challenges of low selectivity, solvent and catalyst toxicity, costly catalyst, contamination, and homogeneity of the photocatalyst.

Dithiocarbonates are the principal backbone of numerous bioactivities and natural compounds. They demonstrate antibacterial, neuroprotective, antifungal, and tuberculostatic activities and have applications in the materials science and also used in the organic synthesis as a versatile radical source and intermediates for the preparation of thiols, alkenes, alkanes, photosensitizers, and S-activated carbanions ^{24, 25}. The most popular strategy for the synthesis of five-membered cyclic dithiocarbonates is based on the nucleophilic attack of carbon disulfide salt (such as O-methyl carbonodithioate salt) on the oxiranes in the presence of a base catalyst. For instance,

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pyridine-based organocatalysts, tertiary amines, alcoholates, or alkali metals halides under the non-photochemical conditions have been reported ²⁶. These methods restrain their synthetic utilization on the causes of the organization of regioisomeric products, high catalyst loading, low efficiency, the requirement of high pressure and harsh reaction conditions.

In 2016, the Yadav and co-workers have published the first photochemical approach for the synthesis of 1,3-oxathiolane-2-thiones in the presence of eosin Y *via* the difunctionalization of styrenes (Scheme 1) ²⁷. The drawback of this report is the use of eosin Y as a homogeneous organic photocatalyst but the prefunctionalization of styrenes is superior to the ring-opening of oxiranes.



Scheme 1. The report published in the synthesis of 1,3-oxathiolane-2-thiones under the photochemical approach.

According to the aforementioned topics and our experience in the use of CdS NPs as visible-light-induced reusable catalysts ⁶, we attempted to introduce the photo-oxidative cleavage and the photo-difunctionalization of the C–C double bond of styrenes for the synthesis of aryl aldehydes and 1,3-oxathiolane-2-thiones, respectively. These processes are easily accomplished in the presence of CdS as a visible-light-induced nano photocatalyst under blue LEDs or sunlight in the air atmosphere at room temperature without the use of any external oxidants (Scheme 2). It is worth mentioning that the C–C double bond of styrenes for the synthesis of aryl aldehydes occurred in solvent-free conditions. According to the literature review, there is not any report based on using the photo-induced catalyst in solvent-free conditions for the synthesis of organic compounds, except that our research team has recently published ⁶.



Scheme 2. The synthesis of 1,3-oxathiolane-2-thiones and aryl aldehydes in the presence of CdS as a visible-light-induced nano photocatalyst.

Results and Discussion

In the beginning, CdS NPs were prepared according to our previously reported method 6 (see supporting information).

To find the best reaction conditions, styrene (1.0 mmol) and carbon disulfide salt (1.0 mmol) were chosen as model compounds for the synthesis of 5-phenyl-1,3-oxathiolane-2-thione (**3a**) (Scheme 3).

According to the proposed mechanism, the solvent should have both good nucleophilic character and be a good leaving group, which will be discussed in the following pages. Therefore, an attempt was made to replace methanol with ethanol when the cesium carbonate was present as a base. Unfortunately, the yield was reduced due to the low solubility of cesium carbonate and cesium methyl xanthate salt (A) in EtOH. (Table 1, Entry 2). By using a mixture of water and ethanol to increase the solubility, but it did not help (Table 1, Entry 3). A batch of bases including K₂CO₃, K₃PO₄, NaHCO₃, NaH, and NaOMe was replaced (Table 1, Entries 4-8). As it can be perused in Table 1, Cs₂CO₃ acts more effectively to produce the desired product. Furthermore, different amounts of Cs₂CO₃ and methanol were also applied (Table 1, Entries 1, 11-14). Using less than 3 mL of MeOH and 1 eq of Cs₂CO₃ were reduced efficiency. Investigation of other photocatalysts such as ZnO and TiO₂ were revealed the special performance of CdS for the synthesis of 1,3-oxathiolane-2-thiones (Table 1, Entries 15, 16).



Scheme 3. The synthesis of 5-phenyl-1,3-oxathiolane-2-thione (3a) as a model reaction under different conditions.

Table	1:	The	effect	of	various	solvents,	bases,	and	photocatalysts	for	the
synthesis of 5-phenyl-1,3-oxathiolane-2-thione (3a).											

yrn	nulesis of 5-phenyl-1,5-oxatilolarie-2-tillone (Ja).									
	Entry	Solvent	Base	Photocatalyst	Yield (%)					
	1	MeOH	Cs ₂ CO ₃	CdS	86					
	2	EtOH	Cs ₂ CO ₃	CdS	25					
	3	EtOH/H2O (2:1)	Cs ₂ CO ₃	CdS	25					
	4	MeOH	K2CO3	CdS	76					
	5	MeOH	K₃PO₄	CdS	30					
	6	MeOH	NaHCO₃	CdS	15					
	7	MeOH	NaH	CdS	20					
	8	MeOH	NaOMe	CdS	40					
	9	CH₃CN	NaOMe	CdS	35					
	10	Solvent-Free	NaOMe	CdS	30					
	11	MeOH	Cs ₂ CO ₃	CdS	40 ^a					
	12	MeOH	Cs ₂ CO ₃	CdS	30 ^b					
	13	MeOH	Cs ₂ CO ₃	CdS	50°					
	14	MeOH	Cs ₂ CO ₃	CdS	87 ^d					
	15	MeOH	Cs ₂ CO ₃	ZnO	Trace					
	16	MeOH	Cs ₂ CO ₃	TiO ₂	Trace					

Reaction conditions: CS_2 (1 mmol) and base (1.0 mmol) in the solvent (3 mL) were taken in a closed test tube and stirred at room temperature for 3 hours after that styrene (2a, 1 mmol) and photocatalyst (0.015 g) were added to the open test tube and the reaction mixture was exposed under withe LEDs 12 W lamp for 12 hours in the air atmosphere at room temperature. ^a Cs₂CO₃ (0.5 mmol), ^b MeOH (1.0 mmol), ^c MeOH (2 mL), ^d MeOH (4 mL).

As discussed in Table 1, the reaction proceeds very well in the presence of CdS NPs and Cs₂CO₃ (1.0 mmol) in methanol (3 mL) (Table 1, Entry 1). Next, the amount of CdS, wavelength of light, and the atmosphere were examined. There is an insignificant difference between 10-20 mol% of CdS (Table 2, Entries 1-3), whereas less than 10 mol% was decreased the yield (Table 2, Entry 4) and no product was formed in the absence of CdS NPs (Table 2, Entry 5). Also, no product was formed in the dark which confirms the photocatalytic ability of CdS NPs for the reaction progression (Table 2, Entry 6). A comparison of different wavelengths showed that the reaction under blue LEDs light and sunlight has made the best progress (Table 2, Entries 3, 7-10). According to the UV-visible spectrum, this implies a maximum absorption of CdS in the range of 400-480 nm (blue light range). In other studies, reactions were carried out under argon and oxygen gas, in which the formation of the trace amounts of the desired product under the argon was proved that oxygen plays a key role in the reaction (Table 2, Entries 11, 12).

Table 2: The effect of diverse amounts of photocatalyst, different wavelengths of light, and atmospheres for the synthesis of 5-phenyl-1,3-oxathiolane-2-thione (3a)

Entry	Amount of photocatalyst (mol%)	Light	Yield (%)
1	CdS (20)	White	87
2	CdS (15)	White	86
3	CdS (10)	White	86
4	CdS (5)	White	73
5	Catalyst-Free	White	0
6	CdS (10)	Dark	0
7	CdS (10)	Red	65
8	CdS (10)	Green	76
9	CdS (10)	Blue	89
10	CdS (10)	Sun	90
11	CdS (10)	Blue	Trace ^a
12	CdS (10)	Blue	90 ^b

Reaction conditions: CS2 (1.0 mmol) and CS2CO3 (1.0 mmol) in MeOH (3 mL) were taken in a closed test tube and stirred at room temperature for 3 hours after that styrene (2a, 1.0 mmol) and CdS (10 m0l%) was added to the open test tube and the reaction mixture was exposed under LEDs 12 W lamp for 12 hours in the air atmosphere at room temperature. ^a Argon balloon, ^b oxygen balloon.

With optimization outcomes in hand, in order to appraise the scope of 1,3-oxathiolane-2-thiones (3) through photodifunctionalization of the C-C double bond, diverse styrenes as starting materials were used (Scheme 4). The obtained outcomes are summarized in Table 3. Besides the 1,3-oxathiolane-2-thione derivatives, relevant aldehydes were also formed in small amounts (trace or less than 5%).



Scheme 4. The synthesis of 1,3-oxathiolane-2-thione derivatives (3) in the presence of CdS NPs





Reaction conditions: CS2 (1.0 mmol) and Cs2CO3 (1.0 mmol) in MeOH (3 mL) were taken in a closed test tube and stirred at room temperature for 3 hours after that styrene derivative (2, 1.0 mmol) and CdS (10 mol%) were added to the open test tube and the reaction mixture was exposed under Blue LEDs 12 W lamp for 12 hours in the air atmosphere at room temperature. $^{\rm a}$ The precursors were a mixture of 1-(chloromethyl)-ortho-vinylbenzene and 1-(chloromethyl)-para-vinylbenzene, so the products have also obtained a mixture 5-(4-(chloromethyl)phenyl)-1,3-oxathiolane-2-thione 5-(2and (chloromethyl)phenyl)-1,3-oxathiolane-2-thione. ^b trans-stilbene precursor was used and the products have obtained a mixture of (trans)-4,5-diphenyl-1,3-

oxathiolane-2-thione and (cis)-4,5-diphenyl-1,3-oxathiolane-2-thione (The HNMR spectrum of the reaction mixture shows that the trans-product (~65%) is 3.33 times as much as cis-product (~28%)).

In continuation, to explore optimal conditions for the synthesis of aryl aldehydes through the photo-oxidative cleavage of the styrene C-C double bond, styrene (2a) was elected as a model compound (Scheme 5). After examining a series of reaction parameters, it has been found that CdS NPs (10 mol%) as a photocatalyst, blue LED light, solvent-free conditions, air atmosphere, and at room temperature were the most appropriate options for the establishment of the benzaldehyde (4a) formation.

To find a suitable media for the reaction, various solvents such as H₂O, EtOH, CH₃CN, MeOH, EtOAc, acetone, CH₂Cl₂, CHCl₃, DMF, DMSO, THF, dioxane, and solvent-free condition were examined (Table 4, Entries 1-12) and the best consequences were captured under the solvent-free condition (Table 4, Entry 13). Investigation of other photocatalysts such as ZnO and TiO₂ reveals the special performance of CdS NPs for the synthesis of benzaldehyde (4a) under the solvent-free condition (Table 4, Entries 14, 15).



(2a)

Scheme 5. The synthesis of benzaldehyde (3a) from styrene (2a) as a model reaction under different conditions.

Table 4	4:	The	effect	of	various	solvents	and	different	photocatalysts	for the
synthes	sis	of be	enzalde	ehy	de (4a) f	from the s	styrer	ne (2a).		

or benzaidenyde (4a) from the styrene (2a).								
Entr	y Solvent	Photocatalyst	Yield (%)					
1	H ₂ O	CdS NPs	5					
2	EtOH	CdS NPs	40					
3	CH₃CN	CdS NPs	80					
4	MeOH	CdS NPs	40					
5	EtOAc	CdS NPs	5					
6	Acetone	CdS NPs	30					
7	CH ₂ Cl ₂	CdS NPs	35					
8	CH₃CI	CdS NPs	30					
9	DMF	CdS NPs	40					
10	DMSO	CdS NPs	0					
11	THF	CdS NPs	45					
12	Dioxane	CdS NPs	Trace					
13	Solvent-Free	CdS NPs	90					
14	Solvent-Free	ZnO	Trace					
15	Solvent-Free	TiO ₂	Trace					

Reaction conditions: The reaction of styrene (2a, 1 mmol) in the presence of photocatalyst (0.015 g) under the air atmosphere under the solvent at room temperature for 12 h

Table 5: The effect of diverse amounts of CdS NPs, wavelengths of light, and atmo

ospheres for the synthesis of benzaidenyde (4a).								
	Entry	Amount of photocatalyst (g)	Light	Yield (%)				
	1	CdS (0.020)	White	92				
	2	CdS (0.015)	White	90				
	3	CdS (0.010)	White	90				
	4	CdS (0.005)	White	82				
	5	Catalyst-Free	White	0				
	6	CdS (0.010)	Red	68				
	7	CdS (0.010)	Green	81				
	8	CdS (0.010)	Blue	95				
	9	CdS (0.010)	Sun	95				
	10	CdS (0.010)	Dark	0				
	11	CdS (0.010)	Blue	Trace ^a				
	12	CdS (0.010)	Blue	97 ^b				

Reaction conditions: The reaction of styrene (2a, 1 mmol) in the presence of CdS NPs under air atmosphere and solvent-free conditions at room temperature for 12 h. a Argon balloon, b oxygen balloon.

After discovering CdS NPs a more efficient photocatalyst and the solvent-free as the most appropriate reaction media, diverse amounts of photocatalyst (Table 5, Entries 1-5), various wavelengths of light (Table 5, Entries 6-10) and different atmospheres (Table 5, Entries 8, 11, 12) were tested. As it can be observed in Table 5, the best results were similar to the optimal

conditions for the synthesis of 1,3-oxathiolane-2-thiones (3). Therefore, aldehyde derivatives can be synthesized with high yields in the presence of CdS NPs (10 mol%) under blue LED 12 W or sunlight and solvent-free conditions at room temperature under the air atmosphere.

In the subsequent step, various styrene derivatives bearing both electron releasing (ERG) and electron-withdrawing groups (EWG) were used (Scheme 6). The photo-oxidative cleavage of the C–C double bond of styrene derivatives having electron releasing groups (ERG) carried out easier compared with those bearing electron-withdrawing groups (EWG), probably due to the stability of the intermediate radical cation. Obtained outcomes are summarized in Table 6. Also, relevant benzoic acids were formed in small amounts (less than 5%).



Scheme 6. The synthesis of aryl aldehyde derivatives (4) from styrenes (2a-I) in the presence of CdS NPs.

Table 6: The synthesis of aryl aldehyde derivatives (4) from styrenes (2a-I) in the presence of CdS NPs.



Reaction conditions: styrene derivatives (**2**, 1.0 mmol) and CdS (10 mol%) were added to the open test tube and the reaction mixture was exposed under blue LEDs 12 W lamp and the solvent-free conditions for 12 hours in the air atmosphere at room temperature. ^a The precursors were a mixture of 1-(chloromethyl)-ortho-vinylbenzene and 1-(chloromethyl)-para-vinylbenzene, so the products were also obtained a mixture of ortho-(chloromethyl)benzaldehyde and para-(chloromethyl)benzaldehyde.

To establish the reusability of CdS as a heterogeneous nano photocatalyst, the model reactions for the synthesis of 5-phenyl-1,3-oxathiolane-2-thione (**3a**) and benzaldehyde (**4a**) (Scheme 3 and 5) were surveyed in the presence of the recovered nano photocatalyst under optimal conditions. After the completion of the reaction, EtOH (3 mL) was added to the reaction mixture and stirred for 3-5 min. The insoluble CdS NPs were separated from the solution by centrifuge, washed by EtOH (2 mL, 2 times), dried at 50 °C, and re-used. The recovered nano photocatalyst

was re-used five times without any remarkable efficiency reduction. The results are summarized in Figure 1.



Time (h) Yield (%)

Figure 1. (A): The recovered CdS NPs for the synthesis of 5-phenyl-1,3-oxathiolane-2-thione (3a). (B): The recovered CdS NPs for the synthesis of benzaldehyde (4a)

A possible mechanism for the synthesis of 1,3-oxathiolane-2-thiones (3) and aryl aldehyde (4) is proposed in Scheme 7. Based on our knowledge, CdS acts as a visible-light-induced photocatalyst. With the visible light collision to the CdS nanoparticles surface, the electrons are transferred from the valence band (VB) to the conduction band (CB). Therefore, holes in the VB and electrons in the CB are created. Two paths can be suggested for the preparation of 1,3-oxathiolane-2-thiones 3. It is speculated that electron transfer from styrene 2 and cesium methyl xanthate A to the holes in the VB, intermediates B and C are generated, respectively. Radical intermediate C could be reacted with styrene 2 (it causes intermediate formation D) or traps radical cation B (it causes intermediate formation E). On the other hand, oxygen could be received an electron from the CB of CdS to generate superoxide radical anion (O_2^{-1}) . Through path a: superoxide radical anion (O_2^{-1}) , can couple with intermediates **D** or E to form F or G, respectively, which ultimately, intermediate H forms 1,3-oxathiolane-2-thiones (cyclic dithiocarbonates, 3) through an intramolecular cyclization ²⁸. Through path b: after the formation of intermediates **D** and **E**, the more probable pathway is to perform an intramolecular cyclization reaction to create intermediates (I) and (J). Ultimately with interference superoxide radical anion, the desired cyclic dithiocarbonates (3) are formed.

Whereas, in the absence of cesium methyl xanthate **A** oxygen radical anion accomplishes [2+2] cycloaddition with radical cation **B** for the synthesis of 3-phenyl-1,2-dioxetane **K**. Then, 3-aryl-1,2-dioxetane compound **I** perform the oxidative cleavage of a C-C and O-O bonds for the synthesis of desired aryl aldehyde (**4**) (Scheme 7).

Based on the results obtained during optimization reactions for the synthesis of 5-phenyl-1,3-oxathiolane-2-thione **3a** and benzaldehyde **4a**, the necessity of photocatalysts (Table 2, Entry 5 and Table 5, Entry 5), light (Table 2, Entry 10 and Table 5, Entry 10), and oxygen (Table 2, Entry 11 and Table 5, Entry 11) for the progression of the reaction were obvious. Besides these, to confirm the proposed mechanism, some supplementary control experimental studies were also performed. Accordingly, the model reactions (Scheme 3 and 5) were accomplished in the

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presence of the hole and radical scavengers to prove the creation of hole/electron pairs and also a radical pathway of the reaction (Scheme 8).



Scheme 7. The proposed mechanism for the synthesis of 1,3-oxathiolane-2thiones (3) and aryl aldehyde (4) in the presence of CdS nanoparticles as a photocatalyst and air atmosphere.

The study of the model reaction (Scheme 3) in the presence of TEMPO (1 equivalent) as a radical scavenger demonstrated that only 15% of 5-phenyl-1,3-oxathiolane-2-thione 3a and 35% of benzaldehyde 4a was formed, respectively. Probably, the electron transfer from both reactants (cesium methyl xanthate A and styrene 2a) is taken place into the photocatalytic hole. Undoubtedly, TEMPO can traps both radical cation **B** and radical methyl xanthate C, respectively. Radical methyl xanthate C is mostly inhibited by TEMPO because it has a faster rate of formation than radical cation **B**. The efficiency of the product **3** is decreased compared to byproduct 4, due to the increase in the efficacious collisions and contacts between the C and TEMPO caused by the enhancement in the concentration of C (Scheme 8, A1). Consequently, 2 equivalents of TEMPO traps both radical cation B and radical methyl xanthate C, and both products 3 and 4 were obtained in trace (Scheme 8, A2). The model reaction (Scheme 3) in the presence of triethylamine (TEA, 1 equivalent) as a hole scavenger under optimized conditions demonstrated that only 10% of 5-phenyl-1,3-oxathiolane-2-thione (3a) is formed, whereas trace amount of benzaldehyde (4a) is produced. Probably, cesium methyl xanthate A has been able to compete slightly with TEA in electron transfer to the photocatalyst hole (Scheme 8, B1). Increasing the concentration of TEA (2 equivalent) leads to a decrease in the efficiency of the product (3a, 5%) (Scheme 8, B₂).

In a further study, the model reaction (Scheme 5) was carried out in the presence of a hole and radical scavengers (Scheme 8, C, and D). The lack of target molecule formation (4a) by TEMPO (Scheme 8, C) as well as TEA (Scheme 8, D) was confirmed the hole-electron formation and radical pathway.

There was an assumption for the formation of 1,3oxathiolane-2-thione compounds **3** that, the radical cation **B** is converted to oxirane **L** in the presence of oxygen. Accordingly, the opening of the oxirane ring is occurred by the nucleophilic attack of the cesium methyl xanthate **A** and is eventually formed the desired product **3** *via* intramolecular cyclization (Scheme 8, E). But the Scheme 8 / Test F shows that radical cation **B** was not converted to oxirane **L** in the presence of oxygen, whereas, along with cesium methyl xanthate **A**, 1,3-oxathiolane-2-thione compound **3a** was prepared. In other words, in the absence of cesium methyl xanthate **A**, the oxidation of styrene to 2-phenyloxirane **L** did not occur, whereas, the oxidative cleavage of a C-C double bond of styrene has mainly undergone for the synthesis of benzaldehyde (Scheme 8, F).



Scheme 8. The mechanism studies: The model reaction for the synthesis of 5phenyl-1,3-oxathiolane-2-thione (3a) (Scheme 5) under optimization conditions: (A) In the presence of TEMPO as a radical scavenger (^{A1} TEMPO 1 eq, ^{A2} TEMPO 2 eq). (B) In the presence of TEA as hole scavenger (^{B1} TEA 1 eq, ^{B2} TEA 2 eq). The model reaction for the synthesis of benzaldehyde (4a) (Scheme 7) under optimized conditions: (C) In the presence of TEMPO (^{C1} TEMPO 1 eq, ^{C2} TEMPO 2 eq). (D) In the presence of TEA. (E) The mechanism of preparation of 1,3-oxathiolane-2-thiones (3a) through the formation of oxirane. (F) The oxidation of styrene in the presence of CdS in the MeOH solvent. (G) The synthesis of 5-phenyl-1,3-oxathiolane-2-thione (3a), when all the reagents were added at the concurrent.

In another study, to ensure that 1,3-oxathiolane-2-thiones synthesis is not dependent on 2-phenyloxirane L formation, the reaction between styrene and CS2 in the presence of CdS and Cs₂CO₃ under blue LEDs in MeOH was investigated simultaneously (all the reagents were added at the concurrent). It was observed that 1,3-oxathiolane-2-thiones 3a was formed with low efficiency and benzaldehyde was a major product (Scheme 8, G). As it is shown in scheme 7, it was speculated that electron transfer from cesium methyl xanthate A and styrene 2a to the photocatalytic holes have also occurred. When initially, the styrene 2a concentration is more than the carbon disulfide salt A, styrene undergoes the oxidative cleavage of a C-C double bond leads to the formation of benzaldehyde and the concentration of styrene or radical cation B to interact with the radical intermediate C is reduced. Correspondingly, the efficiency of 5-phenyl-1,3oxathiolane-2-thione 3a formation is reduced. Nevertheless, the reaction between carbon disulfide (1, 1.0 mmol), cesium carbonate (1.0 mmol), and methanol (3 mL) were taken in a closed test tube and stirred at room temperature for 3 hours to perfect the formation of cesium methyl xanthate salt A. In the next step, CdS (10 mol%) and styrene (2a, 1.0 mmol) were added to the open test tube and the reaction mixture was exposed under blue LEDs 12 W lamp for 12 hours under the air atmosphere at room temperature. Interestingly, the efficiency of 5-phenyl-1,3oxathiolane-2-thione 3a formation is greatly increased. Indeed, cesium methyl xanthate A wins in competition with styrene for the electron transfer to the photocatalyst hole, or simultaneously with styrene conducts electron to the photocatalyst hole (the formation of intermediates **B** and **C**).

Conclusion

So briefly, we have successfully presented the oxidant-free process for the synthesis of cyclic dithiocarbonate and aryl aldehyde derivatives. photo-oxidative cleavage and photodifunctionalization of C-C double bonds have occurred in the presence of CdS nanoparticles as a visible-light-induced reusable nanocatalyst at room temperature under air and blue LEDs or sunlight irradiation. The present work is the second report of a photo-difunctionalization process for the synthesis of desired compounds and is superior to the previous report. Also, this work is the first report of a photo-oxidative cleavage in the solvent-free conditions along with a milder and superior process. Furthermore, direct use of styrene as a readily accessible substrate, excellent regioselectivity, greatly decreasing the byproducts, improving the reaction efficiency, reaction safety, photocatalyst recyclability, and operational simplicity represented prominent advantages of the presented method.

Experimental Section

General procedure for the synthesis of cadmium sulfide nanoparticles (CdS NPs)

The CdS NPs were readied according to the previously reported method by our research group ⁶. Accordingly, sodium sulfide hexahydrate and *N*-cetyl *N*, *N*, *N*-trimethylammonium bromide were dissolved in deionized water and cadmium nitrate tetrahydrate was added dropwise. The mixture was stirred for 1 hour at room temperature. Then, the reaction temperature was raised to the reflux temperature for 36 hours. Finally, CdS

nanoparticles (yellow solid) were gathered and laundered with deionized water and ethanol and dried at 50 $^{\rm o}C$ for 24 hours.

General procedure for the synthesis of cyclic dithiocarbonate derivatives (1,3-oxathiolane-2-thione derivatives)

In a test tube equipped with a magnetic stir, the bar was added Cs₂CO₃ (1.0 mmol) and MeOH (3 mL), and the obtained mixture was stirred until the complete dissolving of Cs₂CO₃. CS₂ (1.0 mmol) was added into the obtained solution and the test tube was completely sealed and the reaction mixture was magnetically stirred for 3 hours at room temperature until the production of cesium methyl xanthate (A). In the next step, CdS NPs (10 mol%) and styrene (1.0 mmol) were added. The open test tube containing the reaction mixture was placed under irradiation of blue LEDs (12 W, in the distance about 6 cm) or sunlight and was permitted to stir at room temperature under the air atmosphere for 12 hours. The reaction progress was controlled by thin-layer chromatography (TLC). After the completion of the reaction, EtOAc (3 mL) and H₂O (5 mL) were added to the reaction mixture and insoluble CdS NPs were separated by centrifuge, washed with EtOAc (2 mL, 2 times), dried under the vacuum and reused. The organic phase (EtOAc) was separated, dried over Na₂SO₄ and evaporated under reduced pressure. The raw products were purified using silica gel column chromatography to afford pure cyclic dithiocarbonates (1,3-oxathiolane-2-thiones).

General procedure for the synthesis of aryl aldehydes

In an open test tube armed with a magnetic stir bar, styrene (1.0 mmol) and CdS NPs (10 mol%) were added. After that, the open test tube was placed under irradiation of blue LEDs (12 W, in the distance about 6 cm) or sunlight and was permitted to stir at room temperature under the air atmosphere for 12-24 hours under solvent-free conditions. The reaction progress was controlled by thin-layer chromatography (TLC). After the completion of the reaction, EtOH (3 mL) was added to the reaction mixture and insoluble CdS NPs were separated by centrifuge, washed with EtOH (2 mL, 2 times), dried under the vacuum and reused. The ethanol solvent was evaporated under reduced pressure. The raw products were purified using silica gel column chromatography to afford pure aryl aldehydes.

Characterization of compounds

5-Phenyl-1,3-oxathiolane-2-thione (3a) ^{26b}: Yellow solid, Yield: 89%, M.P = 116-117 °C (115-117 °C). IR (KBr) v_{max} 1604, 1559, 1478, 1432, 1396, 1086 cm⁻¹. ¹HNMR (^r00 MHz, CDCl₃) δ (ppm); 3.95 (dd, 1H, *J* = 12.0, 5.7, Hz), 4.10 (dd, 1H, *J* = 12.0, 10.5 Hz), 5.57 (dd, 1H, *J* = 10.5, 5.7 Hz), 7.32-7.37 (m, 3H), 7.42 (dd, 2H, *J* = 8.1, 1.5 Hz). ¹³CNMR (75 MHz, CDCl₃), δ (ppm); 49.79, 64.24, 127.53, 129.24, 129.28, 135.15, 2^τV.^Υ°. Anal. Calcd for C₁H_ΔOS₂: C 55.07, H 4.11. Found: C 54.89, H 4.23.

5-Methyl-5-phenyl-1,3-oxathiolane-2-thione (3b): Yellow viscous liquid, Yield: 92%. IR (KBr) v_{max} 1613, 1521, 1453, 1417, 1406, 1105 cm⁻¹. ¹HNMR (250 MHz, CDCl₃) δ (ppm); 2.04 (s, 3H), 3.58 (d, 1H, *J* = 12.0 Hz), 4.03 (d, 1H, *J* = 12.0 Hz), 7.26-7.35 (m, 3H), 7.46-7.50 (m, 2H). ¹³CNMR (75 MHz, CDCl₃), δ (ppm); 29.38, 48.29, 68.15, 128.19, 128.32, 129.02, 141.87, 227.24. Anal. Calcd for C₁₀H₁₀OS₂: C 57.11, H 4.79. Found: C 57.02, H 4.82.

5-(4-Methoxyphenyl)-1,3-oxathiolane-2-thione (3c) ²⁷: Yellow viscous liquid, Yield: 85%. IR (KBr) v_{max} 1702, 1651, 1486, 1394, 1289, 1129 cm⁻¹. ¹HNMR (250 MHz, CDCl₃) *δ* (ppm); 3.84 (s, 3H), 3.96 (dd, 1H, *J* = 12.1, 5.7 Hz), 4.12 (dd, 1H, *J* = 12.0 Hz), 5.57 (dd, 1H, *J* = 10.5, 5.7 Hz), 6.98 (d, 2H, *J* = 7.0 Hz), 7.78 (d, 2H, *J* = 7.0 Hz). ¹³CNMR (75 MHz, CDCl₃), *δ* (ppm); 49.84, 55.49, 64.45, 114.55, 127.86, 135.89, 160.33, 227.13. Anal. Calcd for C₁₀H₁₀O₂S₂: C 53.07, H 4.45. Found: C 53.19, H 4.38.

5-(4-(Chloromethyl)phenyl)-1,3-oxathiolane-2-thione and 5-(2-(Chloromethyl)phenyl)-1,3-oxathiolane-2-thione (3d): The

precursors were a mixture of 1-(chloromethyl)-ortho-vinylbenzene and 1-(chloromethyl)-para-vinylbenzene, so the products were also obtained a mixture of 5-(4-(chloromethyl)phenyl)-1,3-5-(2-(chloromethyl)phenyl)-1,3oxathiolane-2-thione and oxathiolane-2-thione. Yellow viscose liquid, Yield: 83%. IR (KBr) v_{max} 1684, 1651, 1631, 1618, 1465, 1448, 1362, 1310, 1216, 1178, 1127, 1085 cm⁻¹. ¹HNMR (250 MHz, CDCl₃) δ (ppm); 4.24 (s, 2H, overlapped), 4.25 (s, 2H, overlapped), 5.11-5.17 (m, 2H), 5.58-5.67 (m, 2H), 6.52-6.63 (m, 2H), 7.12-7.26 (m, 8H). ¹³CNMR (100 MHz, CDCl₃), δ (ppm); 40.44, 40.45, 40.60, 40.61, 60.09, 60.10, 125.44, 126.39, 126.89, 128.44, 128.78, 129.23, 134.97, 135.71, 136.90, 137.90, 214.70, 214.72. Anal. Calcd for $C_{10}H_9CIOS_2$: C 49.07, H 3.71. Found: C 48.95, H 3.86.

5-(4-Chlorophenyl)-1,3-oxathiolane-2-thione (3e) 27: Yellow viscose liquid, Yield: 77%. IR (KBr) vmax 1684, 1642, 1433, 1308, 1145, 1088 cm⁻¹. ¹HNMR (250 MHz, CDCl₃) δ (ppm); 3.98 (dd, 1H, J = 12.1, 5.7 Hz), 4.138 (dd, 1H, J = 12.0, 10.5 Hz), 5.60 (dd, 1H, J = 10.5, 5.7 Hz), 7.40 (d, 2H, J = 7.7 Hz), 7.55 (d, 2H, J = 7.7 Hz). ¹³CNMR (75 MHz, CDCl₃), δ(ppm); 49.99, 44.43, 128.49, 130.10, 133.52, 138.90, 227.24. Anal. Calcd for C₉H₇ClOS₂: C 46.85, H 3.06. Found: C 47.03, H 3.17.

5-(4-Bromophenyl)-1,3-oxathiolane-2-thione (3f) 27: Yellow viscous liquid, Yield: 80%. ¹HNMR (250 MHz, CDCl₃) δ (ppm); IR (KBr) v_{max} 1697, 1651, 1486, 1394, 1289, 1129 cm⁻¹. 4.01 (dd, 1H, J = 12.0, 6.0 Hz, 4.16 (dd, 1H, J = 12.0, 10.5 Hz), 5.63 (dd, 1H, J = 10.5, 6.0 Hz), 7.39 (d, 2H, J = 8.2 Hz), 7.65 (d, 2H, J = 8.2 Hz). ¹³CNMR (75 MHz, CDCl₃), δ(ppm); 50.00, 64.52, 121.33, 130.02, 131.98, 138,95, 227.33. Anal. Calcd for C₉H₇BrOS₂: C 39.28, H 2.56. Found: C 38.96, H 2.49.

(Trans)-4,5-diphenyl-1,3-oxathiolane-2-thione (3g) ^{26b}: Yellow solid, Yield: 93%, M.P = 126-128 °C (127-129 °C). IR (KBr) v_{max} 1691, 1638, 1444, 1322, 1195, 1047 cm⁻¹. ¹HNMR (400 MHz, CDCl₃) δ (ppm); 4.27 (d, 1H, J = 5.6 Hz), 4.81 (d, 1H, J = 5.6 Hz), 7.04-7.07 (m, 2H), 7.08-7.11 (m, 3H), 7.16-7.19 (m, 2H), 7.19.7.22 (m, 3H). ¹³CNMR (100 MHz, CDCl₃), δ (ppm); 57.89, 88.33, 127.74, 128.23, 128.50, 128.60, 128.72, 128.80, 138.00, 141.00, 227.01. Anal. Calcd for $C_{15}H_{12}OS_2$: C 66.14, H 4.44. Found: C 66.30, H 4.33

5,5'-(1,4-Phenylene)bis(1,3-oxathiolane-2-thione) (3h): Yellow solid, Yield: 83%, M.P = 133-135 °C. IR (KBr) v_{max} 1613, 1575, 1469, 1422, 1342, 1123 cm⁻¹. ¹HNMR (300 MHz, CDCl₃) δ (ppm); 3.97 (dd, 2H, J = 12.0, 5.7 Hz), 4.13 (dd, 2H, J = 12.0, 10.5 Hz), 5.77 (dd, 2H, J = 10.5, 5.7 Hz), 7.38 (s, 4H). ¹³CNMR (75 MHz, CDCl₃), δ (ppm); 49,96, 65.59, 125.12, 135.86, 217.39. Anal. Calcd for C₁₂H₁₀O₂S₄: C 45.84, H 3.21. Found: C 45.96, H 3.10. 5,5'-(1,3-Phenylene)bis(1,3-oxathiolane-2-thione) (3i): Yellow solid, Yield: 76%, M.P = 128-130 °C. IR (KBr) v_{max} 1620, 1543, 1451, 1418, 1342, 1201 cm⁻¹. ¹HNMR (300 MHz, CDCl₃) δ (ppm); 3.98 (dd, 2H, J = 12.0, 5.7 Hz), 4.12 (dd, 2H, J = 12.0, 10.5 Hz), 5.59 (dd, 2H, J = 10.5, 5.7 Hz), 7.48 (t, 1H, J = 8.4 Hz), 7.56 (s, 1H), 7.68 (dd, 2H, J = 8.7, 0.7 Hz). ¹³CNMR (75 MHz, CDCl₃), δ (ppm); 49.84, 64.50, 127.41, 128.34, 128.87, 135.32, 226.99. Anal. Calcd for C12H10O2S4: C 45.84, H 3.21. Found: C 46.07, H 3.29.

Benzaldehyde (4a) and (4b) 23a: Colorless liquid, Yield 4a: 95%, Yield 4b: 88%, IR (KBr) v_{max} 1756, 1620, 1543, 1451, 1418, 1342, 1201 cm⁻¹. ¹HNMR (300 MHz, CDCl₃) δ (ppm); 7.54 (t, 2H, J = 7.8 Hz), 7.54 (t, 1H, J = 6.9 Hz), 7.89 (t, 2H, J = 7.8 Hz), 10.03 (s, 1H). ¹³CNMR (75 MHz, CDCl₃), δ (ppm); 128.99, 129.74, 134.47, 136.37, 192.42. Anal. Calcd for C8H8O: C 79.23, H 5.70. Found: C 78.94. H 5.88

Acetophenone (4c) ^{19e}: Colorless liquid, Yield: 93%, ¹HNMR (300 MHz, CDCl₃) δ (ppm); 2.61 (s, 3H), 7.64 (t, 2H, J = 7.5 Hz), 7.57 (t, 1H, J = 7.5 Hz), 7.96 (d, 2H, J = 7.5 Hz). ¹³CNMR (75 MHz, CDCl₃), δ (ppm); 26.63, 128.29, 128.56, 133.11, 137.07, 198.16. Anal. Calcd for C₈H₈O: C 79.97, H 6.71. Found: C 80.14, H 6.59. 4-Methoxybenzaldehyde (4d) ^{19e}: Colorless liquid, Yield: 90%, ¹HNMR (300 MHz, CDCl₃) δ (ppm); 3.88 (s, 3H), 7.00 (dd, 2H, J = 7.2, 1.5 Hz), 7.84 (dd, 2H, J = 7.3, 1.5 Hz), 9.88 (s, 1H). ¹³CNMR (75 MHz, CDCl₃), δ (ppm); 55.58, 114.30, 129.91, 131.98, 164.5, 190.83. Anal. Calcd for C₈H₈O₂: C 70.58, H 5.92. Found: C 70.32, H 6.11.

Para-(chloromethyl)benzaldehyde and Ortho (chloromethyl)benzaldehyde (4e) 29: The precursors were a mixture of 1-(chloromethyl)-ortho-vinylbenzene and (chloromethyl)-para-vinylbenzene, so the products were also obtained a mixture of ortho-(chloromethyl)benzaldehyde and para-(chloromethyl)benzaldehyde. Colorless liquid, Yield: 88%, IR (KBr) v_{max} 2865, 2843, 2771, 2738, 1707, 1692, 1612, 1596, 1509, 1488 cm⁻¹. ¹HNMR (300 MHz, CDCl₃) δ (ppm); 4.56 (s, 2H), 4.57 (s, 2H), 4.44-7.50 (m, 3H), 7.59 (d, 1H, J = 7.5 Hz), 7.75-7.83 (m, 4H), 9.94 (s, 1H), 9.95 (s, 1H). ¹³CNMR (75 MHz, CDCl₃), δ (ppm); 45.26, 45.28, 129.13, 129.48, 129.54, 129.80, 130.13, 134.47, 136.13, 136.76, 138.60, 143.84, 191.70, 191.82. Anal. Calcd for C₈H₇CIO: C 62.16, H 4.56. Found: C 62.31, H 4.63.

4-Chlorobenzaldehyde (4f) ^{23a}: White solid, Yield: 85%, M.P. 46-48 °C. ¹HNMR (300 MHz, CDCl₃) δ (ppm); 7.53 (dd, 2H, J = 6.9, 1.8 Hz), 7.84 (dd, 2H, J = 6.9, 1.8 Hz), 10.00 (s, 1H). ¹³CNMR (75 MHz, CDCl₃), δ (ppm); 129.45, 130.90, 134.69, 140.96, 190.87. Anal. Calcd for C7H5CIO: C 59.81, H 3.59. Found: C 58.74, H 3.66.

4-Bromobenzaldehyde (4g) ^{23a}: White solid, Yield: 87%, M.P = 56-58 °C. ¹HNMR (300 MHz, CDCl₃) δ (ppm); 6.72 (d, 2H, J = 8.4 Hz), 7.77 (d, 2H, J = 8.4 Hz), 10.00 (s, 1H). ¹³CNMR (75 MHz, CDCl₃), δ (ppm); 129.81, 130.99, 132.45, 135.03, 191.13. Anal. Calcd for C₇H₅BrO: C 45.44, H 2.72. Found: C 45.61, H 2.68.

4-Fluorobenzaldehyde (4h) 30: Pale yellow liquid, Yield: 82%, ¹HNMR (300 MHz, CDCl₃) δ (ppm); 7.21 (dd, 2H, J = 8.7, 8.1 Hz), 7.91 (dd, 2H, J = 8.4, 5.4 Hz), 9.97 (s, 1H). ¹³CNMR (75 MHz, CDCl₃), δ (ppm); 116.33 (d, J = 22.3 Hz), 132.22 (d, J = 9.6 Hz), 132.95 (d, J = 2.0 Hz), 166.50 (d, J = 255.0 Hz), 190.49. Anal. Calcd for C7H5FO: C 67.74, H 4.06. Found: C 67.88, H 4.13.

4-Nitrobenzaldehyde (4i) 23a: Yellow solid, Yield: 69%, 104-106 °C. ¹HNMR (300 MHz, CDCl₃) δ (ppm); 8.10 (d, 2H, J = 8.7 Hz), 8.41 (d, 2H, *J* = 8.7 Hz), 10.18 (s, 1H). ¹³CNMR (75 MHz, CDCl₃), δ (ppm); 124.31, 130.49, 140.03, 151.12, 190.29. Anal. Calcd for C₇H₅NO₃: C 55.64, H 3.34. Found: C 55.53, H 3.28.

Isonicotinaldehyde (4j) ³¹: Yellow liquid, Yield: 64%, ¹HNMR (300 MHz, CDCl₃) δ (ppm); 7.66 (dd, 2H, J = 4.5, 1.8 Hz), 8.84 (dd, 2H, J = 4.5, 1.2 Hz), 10.04. ¹³CNMR (75 MHz, CDCl₃), δ (ppm); 122.08, 141.33, 151.19, 191.51. Anal. Calcd for C₆H₅NO: C 67.28, H 4.71, N 13.08. Found: C 66.98, H 4.86, N 13.22.

Terephthalaldehyde (4k) 32: White solid, Yield: 83%, M.P = 116-118 °C. ¹HNMR (300 MHz, CDCl₃) δ(ppm); 8.05 (s, 4H), 10.13 (s, 2H). ¹³CNMR (75 MHz, CDCl₃), δ(ppm); 130.12, 139.98, 191.52. Anal. Calcd for C₈H₆O₂: C 71.64, H 4.51. Found: C 71.59, H 4.62. Isophthalaldehyde (4I) ³³: White solid, Yield: 77%, M.P = 89-91 °C. ¹HNMR (300 MHz, CDCl₃) δ (ppm); 7.67 (t, 1H, J = 7.8 Hz), 8.10 (dd, 2H, J = 7.5, 1.5 Hz), 8.32 (s, 1H), 10.05 (s, 2H). ¹³CNMR (75 MHz, CDCl₃), δ (ppm); 129.20, 131.01, 134.64, 136.98, 198.10. Anal. Calcd for C₈H₆O₂: C 71.64, H 4.51. Found: C 71.80, H 4.69.

Keywords: cyclic dithiocarbonate • aryl aldehyde • CdS nanoparticles • photo-induced catalyst • photo-difunctionalization photo-oxidative cleavage

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FULL PAPER

Key Topic

Photo-oxidative Cleavage

Table of Contents

Nanosized cadmium sulfide as an efficient visible lightinduced reusable nano-catalyst was designed for the photodifunctionalization and photo-oxidative cleavage of the C-C double bond of styrene in mild conditions.

