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Blue Light induced Coupling of N-Hydroxysulphonamides: An efficient and green Approach to Access Symmetrical Thiosulfonates

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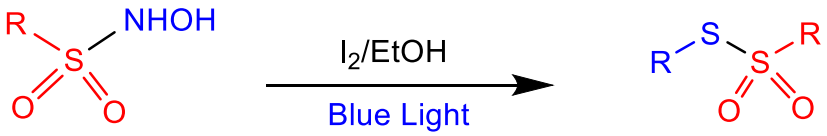
Abstract

The visible light induced, highly efficient, and green protocol has been demonstrated for the synthesis of symmetrical S-Phenyl benzene thiosulfonates by irradiation of N-Hydroxy sulphonamides in the presence of ethanol solvent. The adopted method shows significant advantages such as eco-friendly procedures, short reaction time, cost effectiveness, operational simplicity, excellent yields and use of blue light which is a ubiquitous, making it a genuinely green protocol.



Keywords

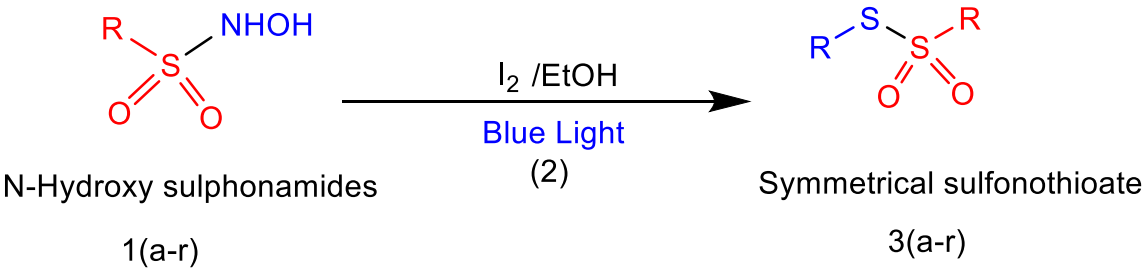
symmetrical thiosulfonates; hydroxy sulphonamides; visible light; green synthesis; Iodine.

Introduction

Organosulfur compounds have attracted great attention due to their potent antimicrobial and fungicidal activities, with considerable attention to agrochemical area in recent years [1]. among them, thiosulfonates are of particular interest in pharmaceutical, clinical, together with their wide range of industrial applications [2]. Because of the widespread application of thiosulfates, considerable effort has been made in the development of synthetic methods for such compounds. The frequently employed methods involve the oxidation of symmetrical and unsymmetrical disulfides. There are numerous approaches for the synthesis of thiosulfonates including selective reduction of sulfonyl chlorides [3], reaction of thiosulfonates with diaryliodonium salts [4], reaction of thiols with sulfonic acid using cyanuric chloride [5], iodine/bromine oxidative sulfenylation of sulfonates with disulfides [6], and oxidation of disulfides or thiosulfinates [7]. From disulfides or thiols [8]. In general, the traditional preparation involves the sulfone–sulphur bond formation, which mainly based on the sulfenylation of sodium sulfinates with disulfides in the presence of AgNO3, or halogen-based oxidants [9]. Notably, the coupling of thiols with sulfonyl chlorides has been less studied due to the rapid formation of disulfides via the nucleophilic substitution of

thiosulfonates by thiols [10] Currently, the copper- or iron mediated oxidative coupling of thiols with sodium sulfinates has also been developed [11]. Therefore, the development of a convenient and practical protocol for the synthesis of thiosulfonates is still a significant issue. In the past few years, sulfonyl hydrazides have been widely used as convenient sulphur electrophiles or nucleophiles in the presence of (TBHP) tert-butyl hydroperoxide and molecular iodine, copper and iron salts, which have been considered to be ideal and useful sulfonylation or sulfenylation agents. [12]. Recently, the cross-coupling reaction of sulfonyl hydrazides with thiols (or sodium sulfinates with disulfides) has been developed for the preparation of thiosulfonates with the help of transitional metal catalysts [13], Sodium sulfinates [14] and sulfoxides [15] are also important organosulfur compounds. Alternatively, thiosulfonates can be obtained by thiosulfonate exchange reactions of sulfenamides, by the reaction of potassium thiosulfonates with diaryliodonium salts [16]. Most of the existing methods involve the use of a stoichiometric number of oxidants, such as diazenecarboxamides [17], clay-supported ferric nitrate [18], silica sulfuric acid/sodium nitrite [19], and peroxynitrite [20]. Many of these methods suffer from long reaction times, laborious isolation procedures, difficult preparation, or, drastic reaction conditions, costly reagents, unsatisfactory yields, tedious workup procedures, and co-occurrence of several side reactions. In short, for the synthesis of thiosulfonates in the reported methods, some special additives as catalyst (oxidants or reductants), toxic reagents (e.g., RSH), or harsh conditions are still demanded for these transformations. The safety of the environment and consciousness about the reduction in global warming inspires the use of renewable energy resources and minimization of waste products. In the past several years, the development of a sustainable, eco efficient energy source for the construction of biologically important organic compounds has become an important

research area in the field of synthesis. Visible light induced synthesis has evoked the interest of chemists and researchers due to the easy availability of visible radiation. In addition, cost effective radiation is useful and harmless to human beings [21]. Light is a perfect reagent for the environmentally benign, green organic synthesis of scaffolds because it activates organic molecules, facilitating a smooth completion of the chemical reaction [22]. In recent years, visible light catalysis has emerged as a powerful tool for realizing novel organic transformations under mild reaction conditions. Therefore, in this article we carried out the visible light-induced catalysed transformations of N-Hydroxysulphonamides to symmetrical thiosulfonates derivatives as bioactive molecules in of ethanol which is observed as a green medium for synthesis.



N-Hydroxy sulphonamides

1(a-r)

Symmetrical sulfonothioate

3(a-r)

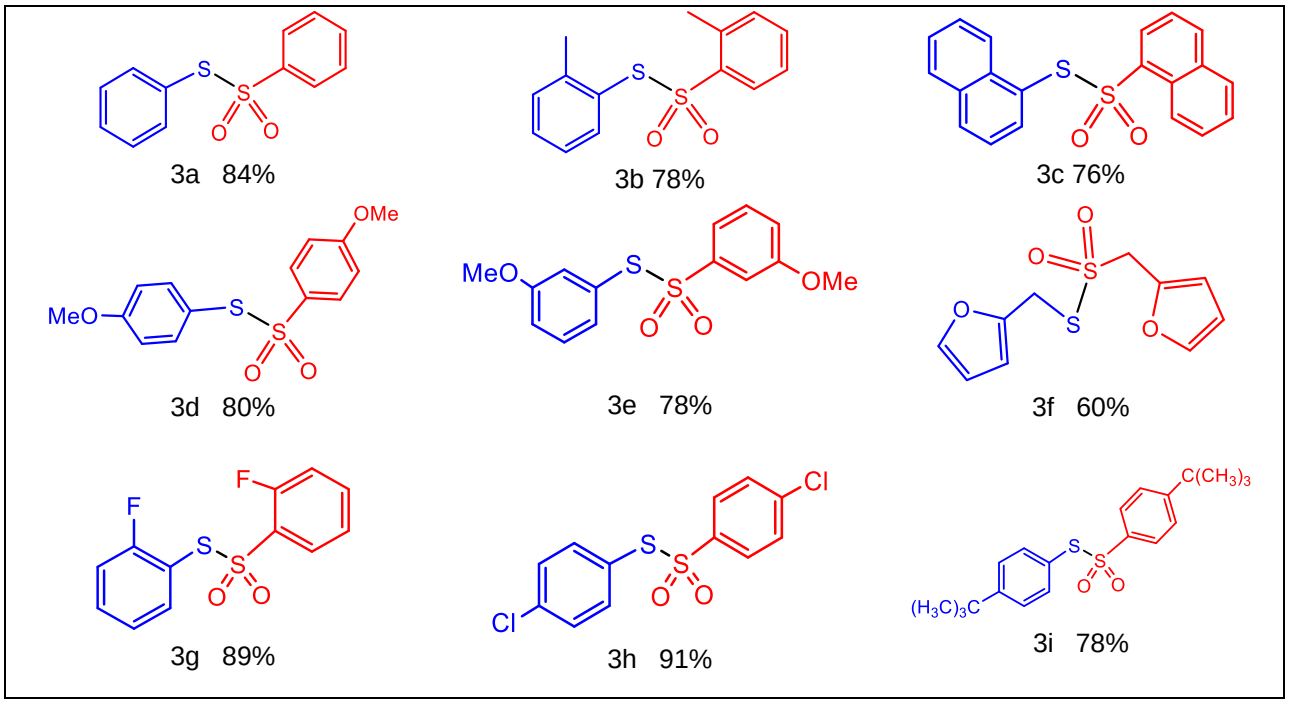
Table 1: Synthesis of thiosulfonates derivatives from N-Hydroxy sulphonamides using blue light[a]

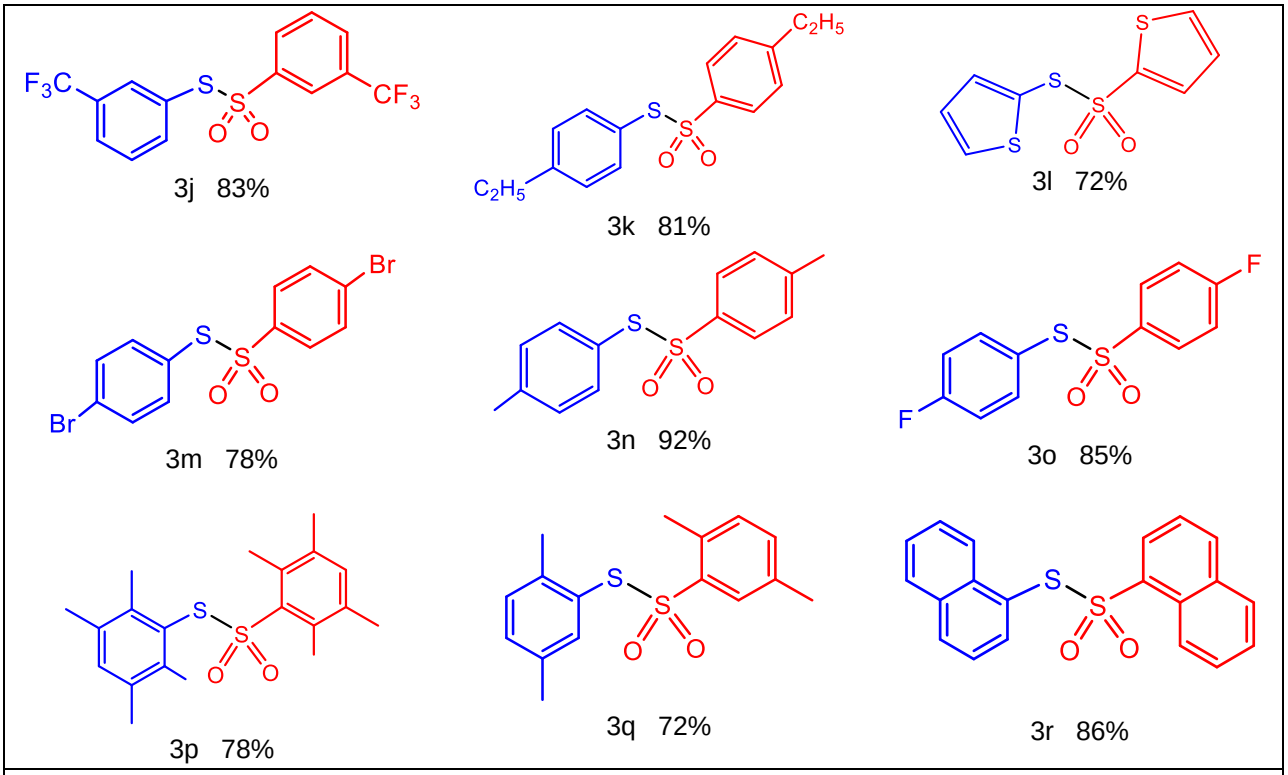
Entry	Solvent	Catalyst	Led Light	Temp. (°C)	Time (h)	Yield[b] (%)
1	EtOH	Eosin Y (0.5 mol%)	Blue Led	Rt	3	nr
2	EtOH	Rhodamine B (5 mol%)	Blue Led	Rt	3	nr
3	EtOH	Rose Bengal (5 mol%)	Blue Led	Rt	3	nr
4	EtOH	Fluorescein (5 mol%)	Blue Led	Rt	3	Trace
5	EtOH	Fluorescein (50 mol%)	Blue Led	Rt	3	Trace
6	EtOH	Fluorescein (1 eqiv.)	Blue Led	Rt	3	Trace

7	MeOH	I_2 (0.5 eqiv.)	Blue Led	rt	3	63
8	EtOH	--	Blue Led	rt	3	nr[c]
9	EtOH	I_2 (0.5 eqiv.)	Blue Led	rt	3	68
10	EtOH	I_2 (1 eqiv.)	Blue Led	rt	3	94
11	EtOH	I_2 (1.5 eqiv.)	Blue Led	rt	3	70
12	EtOH	I_2 (2 eqiv.)	Blue Led	rt	3	67
13	EtOH	I_2 (2.5 eqiv.)	Blue Led	rt	3	65
14	EtOH	I_2 (3 eqiv.)	Blue Led	rt	3	64
15	EtOH	I_2 (1 eqiv.)	Blue Led	rt	6	71

[a]Reaction conditions: 1a-r (1 mmol), I_2 (1 mmol), in EtOH (3 mL), 3 h. [b]Isolated yield based on 1a, [c]nr = no reaction.

With the optimized reaction conditions in hand, a series of N-hydroxy sulphonamide were applied in the reaction to establish the scope and generality of this protocol (Table 1). The results indicated that a wide range of substituted groups, such as methyl, ethyl, tertbutyl, halogens, trifluoro methyl, methoxy, furan, thiofuran were well tolerated under the present conditions and afforded the corresponding thiosulfonates 3(a−r) in good yields.





Symmetrical sulfonothioate derivatives (3a-r) with yield

General Experimental

All the reactions were carried out in 15 mL Ace-pressure tube with constant stirring using a Teflon-coated magnetic stirring bar. Flash chromatography was performed using Merck silica gel (230-400 mesh). Thin-layer chromatography (TLC) was performed using Merck GF254 plates (thickness 0.25 mm). Visualization of spots on TLC plate was accomplished with UV. The chromatographic solvents are mentioned as v/v ratios. All the synthesized compounds were fully characterized by ^{1}H, ^{13}C NMR, and further confirmed through ESI-MS and HRMS analyses. NMR spectra were recorded with Bruker 500 MHz spectrometers for ^{1}H NMR, 125 MHz for ^{13}C NMR respectively. Chemical shifts are reported in δ (ppm) relative to TMS (^{1}H), $CDCl_3$ and DMSO-d6 (^{13}C) as internal standards. Integrals are in accordance with assignments;

coupling constants are given in Hz. Product yields refer to isolated yields after flash chromatography.

Reagents

All the chemicals including iodine, hydroxylamine hydrochloride, potassium carbonate, sulfonyl chloride derivatives and other chemicals were procured from Sigma Aldrich and Alfa Aesar and were used as received.

General procedure: Preparation of symmetrical Thiosulfonates

A mixture of N-hydroxy sulphonamide (prepared by the reported procedure [1] (1 mmol), iodine (1 mmol) in EtOH (3mL) placed in a 15-mL Ace-pressure tube, was stirred at room temperature for the time 3 h. After completion of the reaction (monitored by TLC), the solvent was removed under reduced pressure. The residue was quenched by the addition of a saturated sodium thiosulfate solution. The resulting mixture was extracted with ethyl acetate (3 ×20 mL) and the combined organic layer was washed with water, dried over anhydrous sodium sulphate, and filtered. The filtrate was concentrated under reduced pressure, and the residue was purified by flash chromatography.

Spectral analysis of Synthesised Compounds

S-phenyl benzenesulfonothioate (3a)- A colourless Oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.28-7.38 (m, 7H, ArH), 7.55-7.60 (m, 3H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 127.60, 127.90, 128.80, 129.55, 131.48, 133.66, 136.68, and 143.00;

S-(o-tolyl) 2-methylbenzenesulfonothioate (3b) - White solid m.p.48-50 ºC , ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 2.30 (s, 3H, Ar-Me), 2.34 (s, 3H, Ar-Me), 7.15-7.18 (m, 2H, ArH), 7.16-7.25 (m,1H, ArH) 7.24-7.33 (m,2H, ArH), 7.34-7.41 (m,3H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 21.00, 21.15, 124.80, 127.72, 128.05, 128.64, 129.18, 132.20, 133.65, 134.30, 137.28, 139.05, 139.48, 142.80.

S-(naphthalen-2-yl) naphthalene-2-sulfonothioate (3c)- White solid m.p. 100-102 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.34-7.40 (d,J= 8.0 Hz, 1H, ArH), 7.45-7.59 (m, 3H, ArH), 7.62-7.68 (m,4H, ArH), 7.73-7.75 (d,J= 8.0 Hz, 1H, ArH), 7.80-7.86 (m, 2H, ArH), 7.82-7.88 (m, 2H, ArH), 7.88-7.95 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 122.40, 125.22, 126.98, 127.65, 127.77, 127.95, 128.22, 128.46, 129.10, 129.25, 129.30, 129.45, 129.50, 131.64, 131.80, 133.27, 134.17, 135.10, 137.70, 139.75.

S-(4-methoxyphenyl) 4-methoxybenzenesulfonothioate (3d)-White solid m.p. 74-76.2ºC, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 3.84 (s, 3H, ArCH3), 3.88 (s, 3H, ArCH3), 6.88 (d,J= 8.0 Hz, 2H, ArH), 6.82 (d,J= 8.0 Hz, 2H, ArH), 7.28 (d,J= 8.0 Hz, 2H, ArH), 7.55 (d,J= 8.0 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 55.55, 55.77, 113.80, 114.95, 118.90, 129.96, 134.93, 138.30, 162.23, 163.58.

S-m-Tolyl 3-methylbenzenesulfonothioate (3e)- Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): 2.28-3.00 (s, 3H), 2.30-2.35 (s, 3H), 7.12–7.25 (m, 2H, ArH), 7.25–7.35 (m, 6H, ArH). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm): 21.02, 21.08, 124.60, 127.45, 127.98, 128.54, 129.10, 132.15, 133.25, 134.35, 137.20, 138.90, 139.33, and 142.50.

S-Furan-2-ylmethyl furan-2-ylmethanesulfonothioate (3f)- Oil. ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm): = 4.25 (s, 2H, CH2), 4.46 (s, 2H, CH2), 6.38–6.45 (m, 4H, ArH), 7.40–7.48 (m, 2H, ArH). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): = 33.22, 61.60, 109.80, 111.10, 111.30, 113.422, 142.50, 143.13, 144.24, 148.20.

S-(3-fluorophenyl) 3-fluorobenzenesulfonothioate (3g)- Colourless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.10 (d,J= 8.0 Hz, 1H, ArH), 7.15-7.25 (m, 2H, ArH), 7.28-7.38 (m, 4H, ArH), 7.44-7.48 (m, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 114.82 (d,J= 25 Hz), 119.10 (d,J= 20 Hz), 121.22 (d,J= 21 Hz), 123.12 (d,J= 22 Hz), 123.33 (d,J= 4 Hz), 129.10 (d,J= 8 Hz), 130.27 (d,J= 8 Hz), 130.08 (d,J= 8 Hz), 132.02 (d,J= 4 Hz), 144.32 (d,J= 7 Hz), 162.0 (d,J= 252 Hz), 162.33 (d,J= 250 Hz).

S-(4-chlorophenyl) 4-chlorobenzenesulfonothioate (3h)- White solid m.p. 135-136. ºC , ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.32 (d,J= 8.0 Hz, 2H, ArH), 7.35 (d,J= 8.0 Hz, 2H, ArH), 7.42 (d,J= 8.0 Hz, 2H, ArH), 7.52 (d,J= 8.0 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$):, δ (ppm): 126.10, 128.94, 129.35, 129.93, 137.77, 138.50, 140.52, 141.30.

S-(4-(tert-butyl) phenyl) 4-(tert-butyl) benzenesulfonothioate (3i)- A white solid, m.p. 150-151ºC, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 1.30 (s, 9H, CH3), 1.35 (s, 9H, CH3), 7.26 (d,J= 8.0 Hz, 2H, ArH), 7.30 (d,J= 8.0 Hz, 2H, ArH) 7.44 (d,J= 8.0 Hz, 2H, ArH), 7.48 (d,J= 8.0 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$):, δ (ppm): 31.15, 31.24, 34.80, 35.30, 124.70, 125.64, 126.50, 127.62, 136.38, 140.52, 1551.10, 157.60.

S-(4-(trifluoromethyl) phenyl) 4-(trifluoromethyl) benzenesulfonothioate (3j)- White solid m.p. 108-110ºC, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.50-7.54 (m, 2H, ArH), 7.60-7.65 (d,J= 8.0 Hz, 2H, ArH) 7.64-7.74 (m,4H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$):, δ (ppm): 122.90 (q,J= 272 Hz), 123.32 (q,J= 272 Hz), 126.33 (q,J= 4 Hz), 126.45 (q,J= 4 Hz), 127.19, 131.62, 133.64, (q,J= 33 Hz), 135.15 (q,J= 33 Hz), 136.37, 146.15;

S-(4-ethylphenyl) 4-ethylbenzenesulfonothioate (3k)- Colourless oil, ^{1}H NMR (400 MHz, $CDCl_3$): , δ (ppm): 1.22-1.26 (m, 6H, ArCH3), 2.60-2.74 (m, 4H, CH2), 7.10-7.20 (d,J= 8.0 Hz, 2H, ArH), 7.22-7.28 (d,J= 8.0 Hz, 2H, ArH) 7.24-7.30 (d,J= 8.0 Hz, 2H, ArH), 7.42-7.48 (d,J= 8.0 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 15.15, 15.25, 28.72, 28.94, 124.88, 127.74, 128.25, 129.10, 136.26, 140.60, 148.2, 150.75;

S-(thiophen-2-yl) thiophene-2-sulfonothioate (3l) -White solid m.p.58-61 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.05-7.08 (m, 1H, ArH), 7.05-7.19 (m, 1H, ArH), 7.20-7.28 (d,J= 4.0 Hz, 1H, ArH), 7.34-7.38 (d,J= 4.0 Hz, 1H, ArH), 7.62-7.60 (d,J= 4.0 Hz, 1H, ArH), 7.63-7.70 (d,J= 4.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm):: 125.11, 127.30, 128.15, 134.50, 134.6, 135.62, 139.26, 142.44.

S-(4-bromophenyl) 4-bromobenzenesulfonothioate (3m) - White solid, m.p. 147.0-148.4 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.24 (d,J= 8.0 Hz, 2H, ArH), 7.48 (d,J= 8.0 Hz, 2H, ArH), 7.54 (d,J= 8.0 Hz, 2H, ArH), 7.56 (d,J= 8.0 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 126.60, 127.10, 128.90, 129.28, 132.33, 132.94, 137.88, 141.80.

S-(p-tolyl) 4-methylbenzenesulfonothioate (3n)- White solid m.p. 74.5-76 ºC, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 2.34 (s, 3H, ArCH3), 2.40 (s, 3H, ArCH3), 7.18 (d,J= 8.0 Hz, 2H, ArH), 7.22 (d,J= 8.0 Hz, 2H, ArH) 7.20 (d,J= 8.0 Hz, 2H, ArH), 7.46 (d,J= 8.0 Hz, 2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$):, δ (ppm): 21.54, 21.71, 124.52, 127.65, 129.45, 130.24, 136.50, 140.44, 142.00, 1440.6.

S-(4-fluorophenyl) 4-fluorobenzenesulfonothioate (3o) - White solid m.p. (66-67ºC, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.04-7.08 (m, 2H, ArH), 7.08-7.18 (m, 2H, ArH), 7.31-7.38 (m,2H, ArH), 7.53-7.60 (m,2H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 116.20, 116.92, 123.22, 130.40, 138.28, 138.94, 164.90, 165.60.

S-(2, 5-dimethylphenyl) 2, 5-dimethylbenzenesulfonothioate (3p) - Colourless oil, ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 2.14 (s, 3H, ArCH3), 2.18 (s, 3H, ArCH3), 2.22 (s, 3H, ArCH3), 2.63 (s, 3H, ArCH3), 6.94 (s, 1H, ArH), 7.08-7.16 (m, 2H, ArH), 7.15-7.25 (m,2H, ArH), 7.20-7.30 (s, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 19.92,

20.10, 20.44, 20.52, 126.80, 130.15, 130.37, 132.14, 132.60, 134.33, 134.60, 135.17, 136.40, 138.72, 140.60, 141.00.

S-(2, 3, 5, 6-tetramethylphenyl) 2, 3, 5, 6-tetramethylbenzenesulfonothioate (3q)- White solid, m.p. 135-137ºC; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 2.13 (s, 6H, ArCH3), 2.16 (s, 6H, ArCH3), 2.16 (s, 12H, ArCH3), 7.05 (s, 1H, ArCH3), 7.15 (s, 1H, ArCH3); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 17.5, 18.5, 20.7, 20.9, 127.1, 134.7, 134.8, 135.8, 136.0, 136.4, 141.4, and 143.2.

S-(naphthalen-1-yl) naphthalene-1-sulfonothioate (3r) - White solid, m.p. 113-115ºC , ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 7.02-7.08 (m,2H, ArH), 7.32-7.36 (m,2H, ArH), 7.40-7.50 (d,J= 8.0 Hz, 1H, ArH), 7.50-7.60 (d,J= 8.0 Hz, 1H, ArH), 7.60-7.72 (m,4H, ArH), 7.80-7.90 (d,J= 8.0 Hz, 3H, ArH), 8.85-8.90 (d,J= 8.0 Hz, 1H, ArH); ^{13}C NMR (100 MHz, $CDCl_3$):δ (ppm): 123.42, 124.16, 125.20, 125.14, 125.64, 126.40, 127.10, 127.21, 127.39, 128.22, 128.16, 128.28, 130.6, 132.27, 133.88, 134.34, 134.42, 135.23, 137.20, 137.80.

Result and Discussion

To investigating our model reaction and to find the optimal reaction condition, N-hydroxyphenylsulfonamide was stirred at room temperature in ethanol using blue LED as visible light source. Initially, reactant was stirred in the absence of any catalyst and no product was observed even after 3 hour of stirring (table 1 entry 8). Knowing the ability of photocatalysts to promote organic reactions in visible light, we subsequently used eosin Y as a photocatalyst for our reaction. We observed that no product formation was occurring in the presence of eosin Y after 12 hours (table 1 entry 1). Next, we took rhodamine and rosebengal as the photocatalysts but no progress of reaction was observed in the 12 hour stirring time (table 1, entries 2 & 3). Based on the recent development of iodine mediated reactions in the presence of blue led light, we initiated our investigation with the reaction of N-hydroxysulfonamide 3(a-r) was investigated in detail by varying different parameters such as catalyst, solvent and time duration to develop the favourable conditions (Table 1). At the outset, different photo catalyst like Eosin Y, Rhodamine B, Rose Bengal, Fluorescein and Iodine with varying

mole ratio were screened to determine their catalytic efficacy (Table 1, entries 1-7). We were astonished to see that only I_2 (Iodine) could bring the desired conversion (Table 1, entry 10), and other catalytic conditions provided the desired product with low reaction yield or no reaction (Table 1, entries 1–6). Encouraged by these findings, our studies were directed to look at the prospective different molar ratio of iodine and Cs_2Co_3 (cesium carbonate) with ethanol as a solvent (Table 1, entry 11-14), but none of these could match the efficacy of model condition which provided thiosulfonate product 3(a-r) in good yield at room temperature in the presence of blue led light (Table 1, entry 10). To screen the effect of time, the model reaction was undertaken under the prevailing conditions in pressure tube using I_2 as a catalyst at varying time duration. (Table 1, entry 15), no remarkable change was observed in the product yield. To see the solvent effect, we tried different solvents, (Table 1, entry 7). No reaction was observed in the absence of iodine (Table 1, entry 8). The optimum conversion was achieved under condition I_2 (1 equiv.) in EtOH at room temperature in blue light for 3 h (Table 1, entry 10).

Conclusion

In summary, we have developed a simple, yet highly efficient, visible light activated, 'real' green synthetic strategy to symmetrical thiosulfonate derivatives by N-Hydroxysulphonamides. A visible light assisted, metal free and easy workup procedure are some of the prime advantages of our reaction. To the best of our knowledge, the reported conditions are the first ever reported visible light mediated, synthesis of symmetrical thiosulfonate derivatives. Due to the mild reaction conditions, a wide range of substrates can be tolerated. The visible light as catalyst, short reaction

times, operational simplicity, easy workup procedures, and high yields are the other important aspects of this methodology.

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Conflict of interest

Authors declare no competing financial interest.

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