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# Green Iodine Mediated Thiolation of Indole Derivatives: A Review

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Abstract: Indole derivatives represent a pivotal class of heterocyclic compounds with broad applications in pharmaceuticals, agrochemicals, and materials science. The development of efficient, selective, and environmentally benign synthetic methodologies for their functionalization remains a central focus in organic chemistry. Iodine-based reagents, particularly molecular iodine and hypervalent iodine (III) species, have emerged as versatile and sustainable tools in this domain. This review highlights recent advances in the synthesis and functionalization of indole scaffolds using iodine reagents, emphasizing their role in C–H activation, oxidative coupling, halogenation, and cyclization reactions. The mild reaction conditions, high regioselectivity, and eco-friendly nature of iodine-mediated protocols underscore their growing significance in modern synthetic strategies. In this review paper, we want to draw attention to the important developments in molecular iodine-catalyzed/promoted reactions of indole for C-S bond formation i.e. thiolation of indole that have occurred since 2014 for chemistry researchers.

Keywords: Indole, Iodine catalysis, Thiolation, Green

#### 1. Introduction

Indole nucleus is the most important constituent of various heterocycles that can smoothly undergo various substitution reactions. This provides the opportunity to researchers to synthesize various derivatives of indoles. These derivatives of indoles comprise the core of many natural products, drug and medicines [1]. Thus researchers are always interested in searching the routes to synthesize various derivatives of indoles. Among the various indole derivatives 3sulfenylindole or 3-thioindole skeleton has been explored for their valuable therapeutic values as antitumor, antiviral and antibacterial [2]. Literature study reveals that numerous methodologies are well documented for the synthesis of various 3-sulfenylindole derivatives. These methods either involve electrophilic cyclization of the starting material or electrophilic thiolation/ sulfenylation of indole skeleton [1]. The electrophilic sulfenylation of indole nucleus with various sulfenylating agents gained too much attention of the researchers rather than cyclization. The electrophilic thiolation of indole skeleton most commonly is carried out by reaction of indoles with thiols. The thiolation here may be catalyzed by various catalyst such as AlCl<sub>3</sub>, vanadium etc [3]. In addition, other thiolating regents reported in literature are arylsulfonyl hydrazides, disulfides, sulfinates, sulfonium salts, arylsulfonyl chloride, sulfenyl halides, quinine mono O, S-acetals and sulfinic acid [4,5]. These thiolating reagents no doubt work well as source of sulfur electrophile for accomplishing the thiolation in good yield but are with some disadvantages also. Many of these reagents foul smell and are very expensive. They require heavy transition metal as catalyst. This leads to the mingling of the products with metal residue in reaction mixture and difficult to separate. Some other reagents are difficult to prepare and unstable to air and moisture. Most of the reaction involve harsh condition and require excessive additives. These reactions are with poor substrate scope and often end up with environmentally no friendly byproduct. Thus, there is always a demand for the alternatives which fulfill the requirements green chemistry principles up to the optimum level.

Zeni and co-worker reported metal catalyzed indole core construction utilizing alkynes and nitrogen in the cyclization reactions [6]. Zou and He group showed the reports of the iodine-DMSO catalysis to construct C-C and C-Heteroatom bonds including examples of indoles from the year 2015 to 2022 [7]. In a review reported by Das showed the work to prepare indole core by many transition metal free methods from 2019 to mid-2023 [8]. In 2021, Terent'ev group also reported a review on the sulfenylation of indoles carried out by iodine and its derivatives showing examples from middle of the 20th century to 2021, in which many examples were shown of iodine compounds catalysis [9]. However, our review is mainly based on the reactions catalyzed generally by iodine at C-2 or C-3 position of indoles in the presence of an oxidant/or not showing the reports mainly from last decade. The main objective of the mini-review of thiolation of indoles is to highlight only iodine mediated protocols because the synthesis of iodine reagents in the laboratory may involve non green pathway, moreover, iodine is cheap, non-toxic, readily available and can be easily removed from the reaction mixture in comparison to heavy transition metals. We have been working in the field of heterocyclic compounds synthesis and funtionalization since 2009 and we have reported the iodine mediated approach for chlorination of quinolones and review articles on heterocyclic compounds [10-13]. The review of iodine mediated thiolation of indoles will definitely help and motivate the researchers to unfold other green alternatives of thiolation with high atom economy and broad substrate scope.

#### 2. Thiolation at C-3 Position of indole

crucial heterocyclic scaffold found in pharmaceuticals, natural products, and physiologically active substances is indole. Because of its capacity to interact with a wide range of biological targets, the indole nucleus demonstrates enormous biological promise. The wide range of biological and pharmacological characteristics of 3-sulfenylindoles, make them particularly appealing among indole derivatives. 3-sulfanylindoles find valuable application in medicinal and pharmacological field and have a variety of important biological activities, including as antiinflammatory, anti-cancer, antibacterial, and antioxidant properties. They are a promising class of molecules in medicinal chemistry because of their biological importance and structural plasticity [14,15]. Therefore a mild, efficient environment friendly, with broad substrate scope protocol was always desirable to organic chemist.

In 2014, Xiao et al. utilized a metal free method to form arylsulfonyl indoles at C-2 position with sodium sulfinates using catalytic amount of molecular iodine, TBHP oxidant in acetic acid under air in good to high yields (Scheme 1a) [16]. The required product was formed in the presence of potassium iodide, N-iodosuccinimide, and TBAI but excellent yield was obtained with iodine. Electron withdrawing or releasing groups on indoles or sodium sulfinates were well tolerated. The aliphatic sodium methane sulfinate also produced the desired product in excellent yield. If there was a substituent present at C-2 position of indole, the C-3 product was obtained in very low yield. The N-substituted indole gave comparatively less yield of product than that of unsubstituted indole. In the mechanism proposed, initially, sulfinate is oxidized with TBHP to produce an oxygen-centered radical which is in resonance with a sulphonyl radical. An intermediate radical is produced when the sulphonyl radical is added to indole. This radical can then react with molecular iodine to produce an iodide radical and another intermediate which on elimination produced the desired product along with HI, which TBHP may then reoxidize into an iodide radical. The monosulfenylation at C-3 position of indole was done Rahaman and Barman (2017). The mono- and 2,3-bissulfenyl indoles were synthesized using a eco-friendly process with noteworthy characteristics like quick reaction time, ease of use, moderate reaction circumstances, and well functional group tolerance with high to outstanding yields [17]. A variety of indoles can react with alkyl or aryl sodium sulfinates catalyzed by iodine using hydrogen peroxide as an oxidizing agent in PEG400 under microwave conditions (Scheme 1b). The plausible mechanism and effect of various substituents on indoles as well as on sodium arylsulfinates were also discussed. It was found that C-3 sulfenylated products were generally obtained; however, when a methyl group is present at C-3 position of indole, the reaction took place at C-2 position to give C-2 sulfenylated product. Moreover, on increasing the amount of iodine from 10 mol% to 20 mol% and peroxide from 1.2 to 2.2 eq, the disubstituted product, 2,3-bis-sulfenylindoles produced.

Scheme 1a: I2-catalyzed reaction of indoles by sodium sulfinates

$$R^{1}$$
 +  $R^{3}SO_{2}Na$   $\frac{I_{2}$ ,  $H_{2}O_{2}$ , diethyl phosphite  $R^{1}$   $R^{2}$   $R^{3}$   $R^{3}$   $R^{3}$   $R^{2}$   $R^{3}$   $R^{3}$   $R^{3}$   $R^{3}$   $R^{3}$   $R^{3}$   $R^{4}$   $R^{3}SO_{2}Na$   $R^{2}$   $R^{4}$   $R^{3}SO_{2}Na$   $R^{2}$   $R^{3}$   $R^{3}$   $R^{4}$   $R^{4}$   $R^{4}$   $R^{4}$   $R^{5}$   $R^{5}$ 

**Scheme 1b:** I<sub>2</sub>-catalyzed reaction of indoles with sodium sulfinates

Qi et al (2016) synthesized various 3-thioindoles by treating indoles with odourless Bunte salts, non-metallic iodine and DMSO at 80 °C (Scheme 2a) [1]. DMSO served the purpose of both solvent as well as oxidant and worked well in comparison to water and ethanol. Both aryl and alkyl Bunte salts gave the product but alkyl Bunte salts gave the product faster than aryl salts. The method found to be environmentally benign and extended to have better yield of Methyl 5-methoxy-3-(3,4,5-trimethoxyphenylthio)-1H- indole-2-carboxylate with remarkable antitumor activity. In the same way, Singh and coworkers also successfully used Bunte salts of Baylis-Hillman bromides under metal free conditions i.e. with catalysis of molecular iodine (20 mol%) in DMSO at room temperature for the thioallylation of indoles at C-3 position (Scheme 2b) [5]. Further, a plausible mechanism of the reaction through the intermediacy of dimeric sulfides depicting the role of iodine was also discussed. The mechanism also highlighted the decrease in

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the yield of the product under nitrogen atmosphere. Liu and co-workers in 2022 used fluoroalkyl and aryl sulfonic anhydrides and successfully prepared trifluoromethyl, perfluoroalkyl and aryl derivatives of indoles by sulfenylation at C-3 position of indole by iodine catalysis

using triphenylphospine as reducing agent with broad substrate scope [18]. Both N-substituted (Me, Et, Ts) and unsubstituted indoles gave the desired product in good yields except N-Boc indole (Scheme 3).

Zhang et al. (2015) performed iodine mediated thiolation of indoles by thiophenols to form mono- and bisarylthioindoles. On increasing the concentration of the oxidant, TBHP from 1.05 equivelants to 2.1 equivelants, 2,3-bis-sulfenyl indoles were obtained (Scheme 4a) [19]. The reaction condition was mild and with broad sub substrate scope. Both electron withdrawing and donation functional groups containing indoles shown adequate tolerance to the procedure and produced required products with acceptable to outstanding yields. Thiolation of indoles with green approach such as O2 or air is always desired. Using this approach, in the study by Sinha and co-workers, the coupled bio-chemocatalyst i.e. bovine serum albumin and iodine was used to thiolate various indoles in the presence of air and aqueous condition by aryl and heteroaryl thiols to produce 3-sulfenyl indoles without using any oxidant (Scheme 4b) [20]. The highly efficient green protocol developed was also extended to thiolate various hydroxyaryls, while the apliphatic thiol did undergo the reaction. Liu et al (2016) reported the direct thiolation of indoles with iodine and readily available, environmentally benign air as oxidant to prepare 3-thioindoles [21]. The method was shown to be mild, green and afforded various 3sulfanyl derivatives of indoles in good to excellent yield and is well tolerated to functional groups and is also suitable for both alkyl and aryl thiols (Scheme 4c). The mechanism follows an electrophilic substitution of a species (formed by reaction of molecular iodine with thiol) on indoles followed by loss of hydrogen iodide to give the required product. Li et al (2020) coupled indoles with thiols under manganese dioxide and iodine catalysis in anisole under oxygen atmosphere to provide 3-sulfenyl indoles via C-3 thiolation [22]. The EWG and EDG containing thiophenols gave the products in outstanding yields; the heteroaryl thiols provided the products in poor to very good yields (Scheme 4d). The EWG and EDGs on indoles were also well tolerated.

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R = H, Me, OMe,  $CO_2Me$ , F, Br

R<sup>1</sup> = H, Me, OMe, OH, heteroaryl, alkyl, F, Br

26 examples (64-94%)

Scheme 4a: I2-catalyzed reaction of indoles using TBHP

R=H, Me
R<sup>1</sup>= H, Me
R<sup>1</sup>= H, Me
R<sup>1</sup>= alkyl, aryl, benzyl
Scheme 4c: 
$$I_2$$
-catalyzed reaction of indoles under air

R=H, Me
R=H, Me
R<sup>2</sup>= alkyl, aryl, benzyl
Scheme 4c:  $I_2$ -catalyzed reaction of indoles under air

R=H, Et
R<sup>1</sup>= H, Me, Et, OMe, Cl, Br, CO<sub>2</sub>Me, CN,
R<sup>2</sup>= H, Me, CO<sub>2</sub>Et,
R<sup>3</sup>= aryl, heteroaryl, alkyl

Scheme 4d: Reaction of indoles under MnO<sub>2</sub> and iodine catalysis in anisole under O<sub>2</sub>

3-sulfanylindoles find valuable application in medicinal field. Therefore, a mild, efficient environment friendly, with broad substrate scope protocol was always desirable to organic chemist. One such methodology i.e. oxidative thiolation was explored by Huang group (Scheme 4e) [14]. They synthesized 3-sulfanyl indoles by treating indoles with various aryl/heteroaryl thiols in aqueous medium at 80 °C with 30%  $\rm H_2O_2$  as cheap and environmentally benign oxidant. The iodine was found to be essential as the reaction did not occur without it. The developed protocol is highly selective affording C3-functionalised indoles in high yield. Moreover, the method was also found to be insensitive to

steric and electronic effects. The method was shown to be green as the study claimed the use of water as solvent in this reaction. In 2016, Shen et al (2016) synthesized C-3 derivatives of indoles by regioselective thiolation with a variety of thiols (Scheme 4f) [23]. The effect of electron withdrawing or donating group or of steric hindrance from C-2 moiety was not much observed. The reaction proceeds with iodine and DMSO in DCE at 60 °C. The developed protocol has been found effective event with aliphatic thiol or with *N*-methylindole. This is important to mention here that these substrates did not undergo thiolation with earlier reported protocol [24].

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$$R^{1} \stackrel{\text{$\stackrel{\frown}{\text{$\parallel$}}}}{\longrightarrow} NR + R^{2}SH \qquad \frac{I_{2}, H_{2}O_{2}}{H_{2}O, 80 \ ^{\circ}C} \qquad R^{1} \stackrel{\text{$\stackrel{\frown}{\text{$\parallel$}}}}{\longrightarrow} NR$$

R = H. Me

R<sup>1</sup> = H, Me, OMe, OPh, F, Cl,

Br, CHO, COOH, CO<sub>2</sub>Me, NO<sub>2</sub>

 $R^2$  = aryl, heteroaryl

Scheme 4e: I<sub>2</sub>-catalyzed reaction of indoles using H<sub>2</sub>O<sub>2</sub>

$$R^{1}$$
 $R^{2}$ 
 $R^{2}$ 
 $R^{2}$ 
 $R^{3}$ 
 $R^{2}$ 
 $R^{2}$ 
 $R^{3}$ 
 $R^{2}$ 
 $R^{3}$ 
 $R^{2}$ 
 $R^{3}$ 
 $R^{2}$ 
 $R^{3}$ 
 $R^{2}$ 
 $R^{3}$ 
 $R^{2}$ 
 $R^{3}$ 
 $R^{3}$ 
 $R^{3}$ 
 $R^{2}$ 

R = H, Me

R<sup>1</sup> = H. Br. OMe. CN

R<sup>2</sup> = H, Me, Ph, COOEt

 $R^3$  = alkyl, aryl, benzyl

Scheme 4f: I<sub>2</sub>-catalyzed reaction of indoles using DMSO-DCE

3-Thioindoles have been found to be associated with therapeutic values in the treatment of various diseases. Another class of thiolating agents i.e. dichalcogenides were used by Chen et al (2016) for iodine-catalyzed thiolation of indoles to form 3-selanyl- and 3-sulfenyl indoles in ethanol under air (Scheme 5a) [25]. Both electron-donati/ng and electron withdrawing groups were acceptable in good to outstanding yields. The mechanism involves electrophilic addition of an intermediate (formed by reaction of dichalcogenides with iodine) to indoles to produce another intermediate and by deprotonating it the desired product was obtained. Pudukulatha and co-workers (2018) used diaryldisuphides and developed an efficient, mild, iodine mediated method for carrying the thiolation of indoles at third position [26]. Although the conversion of indoles to sulfenyl indoles using diaryldisuphides through iodine (10 mol%) was occurred in both DCM and DMSO at room temperature, but the reaction led to product formation in excellent yield in DMSO at 70 °C (Scheme 5b). It is worthwhile to mention here that iodine is essential for the conversion as the reaction did not take place in its absence. It is worthwhile to mention here that iodine is essential for the conversion as the reaction did not take place in its absence. Moreover the developed protocol has been found to be well tolerant with respect to substituents both on indole and disulphide. Liu et al (2019) also used with diorgano (aryl/heteroarl) disulfides and performed efficient C-3 thiolation of 7-azindole N-oxides using iodine-PEG catalytic system [27]. The EWG on aryls were reported to give higher yield as compared to that with EDGs and benzyl and alkyl disulfides gave good yield of products (Scheme 5c). The developed protocol has been found green with broad substrate scope and has depicted tuneable regioselectivity as per the reaction condition.

32 examples

(90-98%)

26 examples

71-92%

27 examples

(67-96%)

$$R^{1}$$
  $R^{2}$   $R^{2}$   $R^{3}$   $R^{3}$   $R^{2}$   $R^{3}$   $R^{3$ 

 $R^1$  = H, Me, OMe, F, Cl, Br, NO<sub>2</sub>,

 $R^2$  = H, Me, CO<sub>2</sub>Me

R<sup>3</sup> = aryl, benzyl, heteroaryl, cycloalkyl

Scheme 5a: I<sub>2</sub>-catalyzed reaction of indoles with dichalcogenides

$$R \longrightarrow R^{1} + R^{2} \longrightarrow S \longrightarrow R^{2} \longrightarrow R^{2} \longrightarrow R^{1}$$

$$R \longrightarrow R^{1} \longrightarrow R^{2} \longrightarrow R^{2} \longrightarrow R^{1}$$

$$R \longrightarrow R^{1} \longrightarrow R^{1}$$

$$R \longrightarrow R^{1}$$

R = H, OMe, OH, Br

 $R^1$  = H, CO<sub>2</sub>Et, CO<sub>2</sub>Me, COOH, CONH<sub>2</sub>, Me  $R^2$  = H, F, Cl, Br, OMe

**Scheme 5b:** I<sub>2</sub>-catalyzed reaction of indoles with diaryldisuphides

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$$R^{1}$$
  $R^{2}$   $R^{2}$   $R^{3}$   $R^{2}$   $R^{2$ 

Scheme 5c: Reaction of indoles using iodine-PEG catalytic system with diorgano disulfides

A highly efficient, flavin-iodine coupled green approach was reported by Ohkado et al. (2018) to synthesize 3-sulfenyl indoles by flavin and iodine catalysis to couple indole and aryl/alkyl thiols in the presence of molecular oxygen as well as to oxidise iodide ion generated in situ to iodine [28]. The thiols having electron donating or electron attracted moieties on the phenyl ring of thiols were well tolerated (Scheme 6a). Flavin I and iodine coupled organocatalyst was also reported by Jiang et al (2020) to oxidise indolines with different thiols for their C-3 thiolation to give 3-sulfenylindoles under aerobic conditions in a moderate environment with exceptional atom economy and outstanding functional group tolerance [29]. This method provided modearte to exceleint yield of products with varous EDG and EWGs bearing

thiophenols, however, heteroaryl and alkyl thiols gave moderate yield of desired products (Scheme 6b). Flaviniodine catalysts were utilized by Tanimoto *et al.* (2021). They treated indoles with pyrazole under molecular oxygen in acetonitrile at 50 °C to provide 2-azolylindoles. The addition of thiols in the same reaction mixture produced azolylthioindoles via thiolation [30]. The method showed that there was no azolation following thiolation and the thiolation reaction was faster than the azolation process therefore the group conducted the consecutive azolation and thiolation reactions in one pot (Scheme 6c). Literature study reveals that most of the reagents known for carrying out thiolation are with foul smell, expensive and leads to the formation of various by-products.

$$R^{1} \stackrel{\text{II}}{\text{II}} \qquad R^{2} + R^{3}SH \xrightarrow{\text{8.TfO, I}_{2}, O_{2}} \qquad R^{1} \stackrel{\text{II}}{\text{II}} \qquad R$$

$$R = H, Me$$

$$R^{1} = H, OMe, Br$$

$$R^{2} = H, Me$$

$$R^{3} = \text{aryl, Bn, octyl}$$

$$R^{1} \stackrel{\text{II}}{\text{R}} \qquad R^{1} \stackrel{\text{II}}{\text{R}} \qquad R^{2} \qquad$$

Scheme 6a: Flavin and  $I_2$ -catalyzed reaction of indoles using  $O_2$ 

$$R^{1} \stackrel{\text{II}}{ \downarrow \downarrow} \qquad R^{2} + R^{3}SH \xrightarrow{\text{flavin, I}_{2}, O_{2}} R^{1} \stackrel{\text{II}}{ \downarrow \downarrow} \qquad R^{1} \stackrel{\text{II}}{ \downarrow \downarrow} \qquad R^{2} \stackrel{\text{flavin, I}_{2}, O_{2}}{\text{DMSO, 60 °C, 24 h}} \\ R = H, Et \\ R^{1} = H, Br, OMe, Cl, NO_{2} \\ R^{2} = H, Me \\ R^{3} = \text{aryl, heteroaryl, alkyl}$$

Scheme 6b: Flavin and I<sub>2</sub>-catalyzed reaction of indolines using O<sub>2</sub>

R<sup>1</sup> 
$$\stackrel{\text{ii}}{=}$$
  $\stackrel{\text{ii}}{=}$   $\stackrel{\text{ii}}{$ 

Scheme 6c: Flavin and I2 catalyzed reaction of indoles with pyrazole under O2

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Pandey et al (2020) used the combination of 1-aryltriazines and carbon disulfide and accomplished 3-thiolation of various indoles were successfully in excellent yield and in highly regioselective manner mediated through molecular iodine [31]. The indoles substituted at C-2 position gave the product in good yields but substitution at C-3 position (methyl) could not provide the product (Scheme 7a). The reaction is well tolerated to EW and ED groups in 71-95% yields; however heteroaromatic 1-aryltriazene could not give the desired product. The plausible free radical mechanism for sulfenylation was also discussed. Recently, Sutar and group (2025) used a green approach with different 1-aryltriazenes and CS2 in ionic liquids by ultrasonication and thiolated indoles under iodine catalysis to form 3-sulphenylindoles, the ionic liquid was used to unmask the aryltriazenes [2]. The EDG and EWGs bearing indoles gave the desired

products in good to high yields (Scheme 7b). The recyclability and reuse of ionic liquids is another beauty of this reaction in addition to mild reaction conditions. Ghosh and group in 2022 carried out C-3 thiolation of indole by 1,3,4-oxadiazole-2-thiols successfully environmentally benign molecular iodine catalysis in DMSO acting as co-oxidant to form C-3 sulfenyl indoles [32]. The method explored in the study is with mild conditions enabling the hybridization of indole oxadiazole moieties through mercapto group of 1,3,4-oxadiazoles (Scheme 8). The hybrid molecules so formed were also screened for their antiproliferative activities against human breast cancer cell and were found very potent. Further, the notable finding of the study is that the thiolation by oxadiazole-2-thiol is highly regioselective with respect to the third position of indole.

$$R = H, \text{ Br, Me, OMe, CN, Ph}$$

$$R^{1} = H, \text{ Me, Ph}$$

$$R^{3} = H, \text{ Me, OMe, F, Cl, Br, I, CF}_{3}, \text{ NO}_{2}, \text{ heteroaryl}$$

$$Scheme 7a: I_{2}-catalyzed reaction of indoles using 1-aryltriazines and CS}_{2}$$

$$R^{1} = H, \text{ Me}$$

$$R^{2} = H, \text{ Me}$$

$$R^{3} = H, \text{ Me}$$

$$R^{4} = H, \text{ Me}$$

$$R^{1} = H, \text{ Br, OMe}$$

$$R^{1} = H, \text{ Br, OMe}$$

$$R^{1} = H, \text{ Br, OMe}$$

Scheme 7b: I<sub>2</sub>-catalyzed reaction of indoles with 1-aryltriazenes and CS<sub>2</sub> in ionic liquids

$$R^{1}$$
  $R^{2}$  +  $R^{2}$  +  $R^{3}$   $R^{2}$   $R^{3}$   $R^{2}$   $R^{3}$   $R^{2}$   $R^{2}$   $R^{2}$   $R^{2}$   $R^{2}$   $R^{3}$   $R^{2}$   $R^{2}$ 

**Scheme 8:** I<sub>2</sub>-catalyzed reaction of indoles with 1,3,4-oxadiazole-2-thiols

### 3. Conclusion

Sulfenylindole derivatives being associated with valuable therapeutic values in antimicrobial, antiviral and antibacterial activities always attracted the attention of research community. The mini review presented here includes only iodine catalyzed protocols for regioselective mono-thiolation of indoles particularly at the third position with a green approach. A few cases of bis thiolation are also

 $R^2$  = H, Me, Ph

 $R^3$  = H, Me, OMe, Cl, Br, NO<sub>2</sub>,

highlighted. The exploration of many more methods of bis thiolation is desirable. The review will definitely motivate and help researchers to explore other more efficient protocols with green approach not only for mono-thiolation but for bis-thiolation of heterocyles.

17 examples

(74-93%)

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