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Iodine-Catalyzed Sulfenylation of Pyrazolones Using Dimethyl Sulfoxide as an Oxidant

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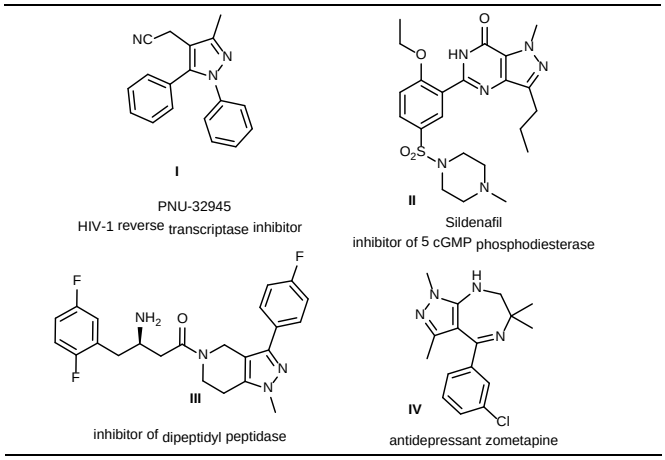
An iodine catalyzed sulfenylation of pyrazalones with a diverse range of heterocyclic thiols, heterocyclic thiones and disulfides has been described using dimethyl sulfoxide as an oxidant, which is an inexpensive, readily available and green oxidant. The present methodology exhibits a wide range of substrate scope and targeted products were obtained in good to excellent yields under metal-free conditions in short duration. This methodology provides a simple process for the formation of C–S bonds through the thioetherification of pyrazalones.

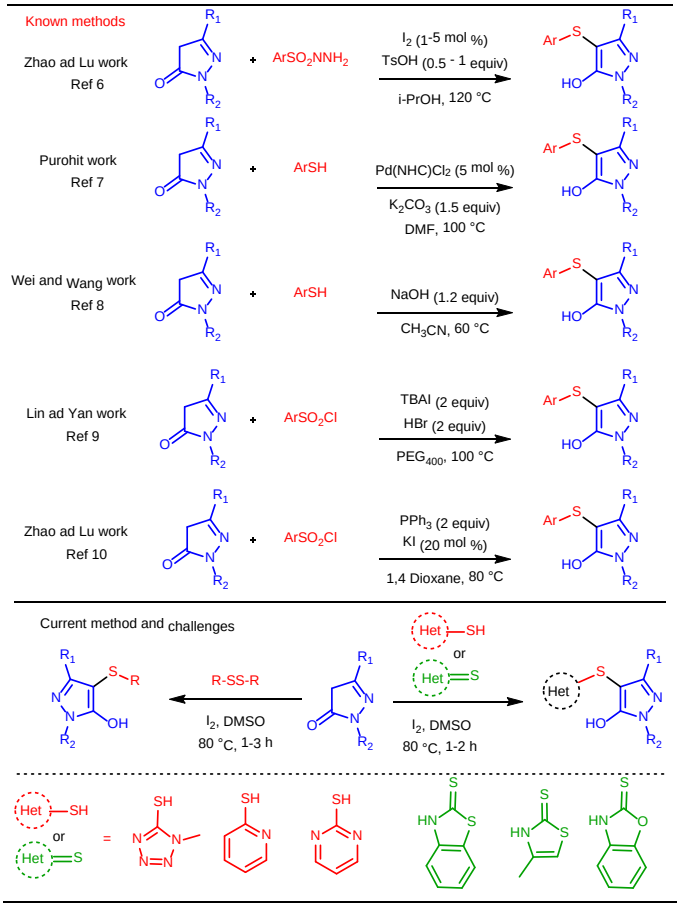
Introduction

Pyrazoles are an important class of heterocyclic moieties that can be found in a wide range of compounds including natural products and medicinally active compounds (Fig 1).[1] In light of their applications in the medicinal field, a considerable effort has been directed towards the construction of pyrazole derivatives.[2] In recent years, synthesis of pyrazole thioether derivatives is gaining much attention owing to their application as antioxidants[3] and herbicidal agents.[4] As a result, the development of mild and efficient methods for the formation of C-S bonds has gained significant attention. In this direction, the traditional methods of C-S bond forming reactions require prefunctionalized precursors employing (i) nucleophilic substitution reaction of sodium thiolate with bromopyrazolones,[3,5] (ii) the cyclization reaction of methyl 3-oxo-2-(phenylthio)butanoate with phenylhydrazine,[3,5] and (iii)

Figure 1. Pharmaceutically active pyrazoline derivatives



Scheme 1. Approach for Sulfenylation of Pyrazolones



the reaction of pyrazolones with unstable sulphenyl chlorides.[5] Recently, a variety of reports have appeared in the literature on sulfenylation of pyrazolones using sulfonyl hydrazide, aromatic thiols, and aryl sulfonyl chloride.[6-10] The Zhao and Lu group reported sulfenylation of pyrazalones using sulphonyl hydrazide, which are odourless and stable solids.[6] Whereas,

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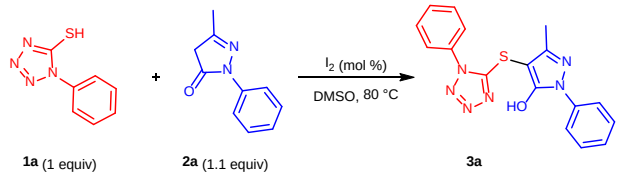
the groups of Purohit , Wei and Wang independently reported sulfenylations of pyrazolones using cross dehydrogenative coupling (CDC) strategy (Scheme 1).[7,8] Purohit and coworker reported a palladium N-heterocyclic carbene catalysed CDC reaction of thiophenol derivatives with various pyrazalones,[7] whereas Wei and Wang developed an efficient CDC method for a similar transformation using NaOH under metal-free conditions.8 Lin and Yan group reported a method for sulfenylation using aryl sulfonyl chlorides employing PEG_{400} as a green solvent.[9] Zhao and Lu reported another method for sulfenylation using arylsulfonyl chlorides.[10] Even though sulfenylation of pyrazalones have been studied extensively, sulfenylation of heterocyclic thiols, thiones and aliphatic thiols using C–H functionalization strategy have drawn lesser attention and remain as an unaddressed problem.[6-10] Heterocyclic thiols and thiones serve as precursors for a variety of biologically active compounds. Development of efficient C–H functionalization strategies using heterocyclic thiols and thiones are well sought after as they have high potential of providing results that are useful in academia and industry.[11] Unlike thiophenol derivatives, most of the heterocyclic thiols and thiones are not smelling and are stable compounds. Therefore, heterocyclic thiols and thiones can be directly used for CDC reactions.[12] In recent years, iodine promoted C–H functionalization reactions are emerging as one of the hot areas due to the low toxicity and easy availability of iodine, and the environmental benign reaction conditions enabled by iodine.13 Similarly, reactions involving DMSO as an oxidant have attracted organic chemists as DMSO is less toxic and green oxidant.14 In this context, research on sulfenylation of pyrazalone through C–H functionalization strategy using iodine and DMSO combinations provides an efficient, useful, and green strategy. In continuation of our effort on metal-free reactions,[14f]-h′ 15 herein we report a convenient and efficient approach for the sulfenylation of pyrazolone using heterocyclic thiols, thiones and disulfides.

Results and Discussion

The exploration for the optimization of the reaction conditions began with 1-phenyl-1*H*-tetrazole-5-thiol (**1a**) and 5-methyl-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one (**2a**) as model substrates and performing the reaction with 20 mol % of iodine and 3 equiv of DMSO as oxidant. To our delight, in this reaction the sulfenylated product **3a** was obtained in 83% yield (entry 1, Table 1). The solvent screening studies revealed that solvents such as acetonitrile, ethyl acetate and toluene with DMSO (3 equiv) as an oxidant resulted in the formation of product **3a** in 48, 82, and 81%, respectively (entries 2-4, Table 1, also see the ESI Table 1 for more details). Use of DMSO as a solvent (1 mL) furnished **3a** in excellent yield (90%, entry 5, Table 1). Further screening was performed using DMSO as a solvent (entries 6-14, Table 1). Using aq. HI (55% in water, 20 mol %) instead of iodine, the desired product **3a** was obtained in 77% (entry 6), whereas aq. HBr (55% in water, 20 mol %) did not afford the expected product (entry 7, Table 1). Increasing or decreasing the equivalent of **1a**, or **2a** or iodine, was not helpful in enhancing the yield of **3a** (entries 8-11, Table 1). The reaction also proceeded well either under an argon or oxygen balloon (entries 12 and 13, Table 1). However, the reaction did not proceed in the absence of iodine or DMSO (entries 14 and 15, Table 1). With these screening studies, further investigation was continued using **1a** (1 equiv), **2a** (1.1 equiv) and iodine 20 mol % in DMSO (1 mL) at 80 °C (entry 5, Table 1).

Table 1. Optimization studies[a]



1a (1 equiv) **2a** (1.1 equiv) **3a**

entry	catalyst or additive (mol %)	oxidant (equiv)	solvent	time (h)	isolated yield (%) [b]
1	I_2 (20)	DMSO (3)	none	1.5	83
2	I_2 (20)	DMSO (3)	ACN	12	48
3	I_2 (20)	DMSO (3)	EtOAc	2	82
4	I_2 (20)	DMSO (3)	toluene	2	81
5	**I_2 (20)**	**none**	**DMSO**	**1.5**	**90**
6	55% aq. HI (20)	none	DMSO	2	77
7	55% aq. HBr (20)	none	DMSO	12	nd
8	I_2 (20)	none	DMSO	1.5	90 [c]
9	I_2 (20)	none	DMSO	1.5	82 [d]
10	I_2 (10)	none	DMSO	2.5	82
11	I_2 (30)	none	DMSO	1	90
12	I_2 (20)	none	DMSO	2	88 [e]
13	I_2 (20)	none	DMSO	1	89 [f]
14	none	none	DMSO	12	nd
15	I_2 (20)	none	none	12	nd

[a]Reaction conditions: **1a** (0.6 mmol), **2a** (0.66 mmol), catalyst (0.12 mmol) in 1 mL of solvent at 80 °C. [b]Isolated yield. [c]1 Equiv of **1a** and 1.5 equiv of **2a**. [d]1.5 Equiv of **1a** and 1 equiv of **2a**. [e]Reaction under argon atmosphere. [f]Reaction under oxygen atmosphere. nd = not detected.

Under the optimized reaction conditions, the sulfenylation of a variety of pyrazolone derivatives were explored (Scheme 2). In general, the reactions were clean and furnished the sulfenylated products in excellent yields (Scheme 2). The reactions of pyrazolones **2b**-**e** proceeded smoothly affording the products **3b**-**e** in 81-97% yield. The influence of *tert*-butyl and amine functional groups at C-5 position of pyrazolone was examined. From these reactions, it was found that reactivity was unaffected with sterically hindered *tert*-butyl group or amino functional groups, and the reactions yielded the corresponding sulfenylated products **3f** and **3g** in 94 and 78% yields, respectively. Furthermore, it was interesting to note that in the reaction of 5-amino-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one, the basic amine functional group survived under highly acidic reaction conditions and the corresponding sulfenylated product was obtained in good yield (Scheme 2). Further, 2-methyl-5-propyl-2,4-dihydro-3*H*-pyrazol-3-one and 5-methyl-2,4-dihydro-3*H*-pyrazol-3-one failed to undergo the sulfenylation reaction under the standard conditions (**3h** and **3i**, Scheme 2). Our attempts for isolation of nitrile and nitro substituted pyrazolone derivatives such as 4-(3-methyl-5-oxo-4, 5-dihydro-1*H*-pyrazol-1-yl)benzonitrile and 5-methyl-2-(4-

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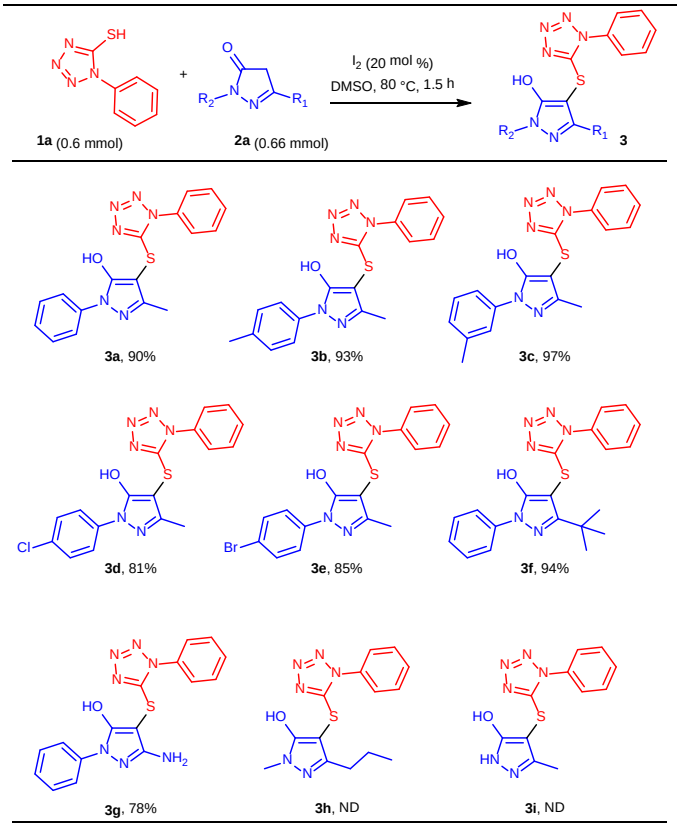
nitrophenyl)-2,4-dihydro-3*H*-pyrazol-3-one with **1a** afforded insoluble compounds in DMSO (for structures see ESI Table 11).

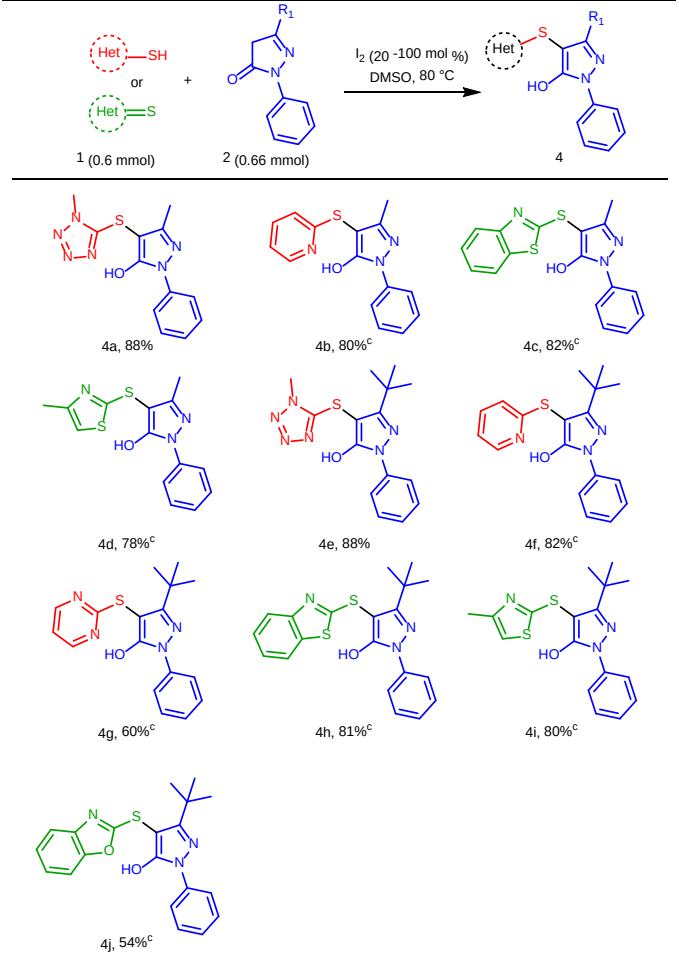
Scheme 2. Substrate Scope for the reaction of heterocyclic thiols with pyrazoles[a,b]



[a]Reaction conditions: **1a** (0.6 mmol), **2a** (0.66 mmol), catalyst (0.12 mmol), DMSO (1 mL) at 80 °C, 1.5 h. [b] Isolated yield. ND= Not detected

After exploring the reactivity of various pyrazolone derivatives with 1-phenyl-1*H*-tetrazole-5-thiol (**1a**), further exploration has been continued using a variety of heterocyclic thiols and thiones (Scheme 3). These reactions led to smooth sulfenylation. The reaction of **2a** with heterocyclic thiol such as 1-methyl-1*H*-tetrazole-5-thiol furnished the corresponding sulfenylated product **4a** in good yield (88%). Similarly, pyridine-2-thiol underwent sulfenylation with **2a** to form **4b** in good yield (80%). However, this reaction required stoichiometric amount of iodine (see ESI Table 6 for more details). The scope of the sulfenylation reaction was further extended to the heterocyclic thiones such as benzo[*d*]thiazole-2(3*H*)-thione derivatives. Thus, the reaction of benzo[*d*]thiazole-2(3*H*)-thione under optimal reaction conditions afforded the expected sulfenylated product **4c** in low yield (28 %) (see the ESI Table 7 for more details). However, the yield of **4c** has increased to 82% by using iodine in stoichiometric amount. Similarly, benzo[*d*]thiazole-2(3*H*)-thione derivatives such as 4-methylthiazole-2(3*H*)-thione afforded the product **4d** in good yield (78% Scheme 3). The scope of the reaction was further extended for the sulfenylation of sterically hindered pyrazolone such as 5-(*tert*-butyl)-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one with various heterocyclic thiols and heterocyclic thiones. Thus, 5-(*tert*-butyl)-2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one was successfully coupled with heterocyclic thiols such as 1-methyl-1*H*-tetrazole-5-thiol, pyridine-2-thiol and pyrimidine-2-thiol and the corresponding sulfenylated products **4e**-**4g** were obtained in good to excellent yields. It was noticed that addition of pyridine as an additive (100 mol %) results in lowering the yield of **3a** to 36% from 90% (see ESI Table 5 for more details). As pyridine thiol and pyramidine thiols contains basic nitrogen group, we believe that the strong acid HI (which is formed in the reaction) was quenched by pyridine or pyramidine. As a result, stoichiometric amount of iodine is necessary for these reactions. Similarly, heterocyclic thiones such as benzo[*d*]thiazole-2(3*H*)-thione and 4-methylthiazole-2(3*H*)-thione successfully participated in CDC reaction affording **4h** and **4i**, respectively, in good yields (81 and 80%, respectively). Benzo[*d*]oxazole-2(3*H*)-thione found to be less reactive under the reaction conditions and afforded **4j** in moderate yield (54%, Scheme 3).

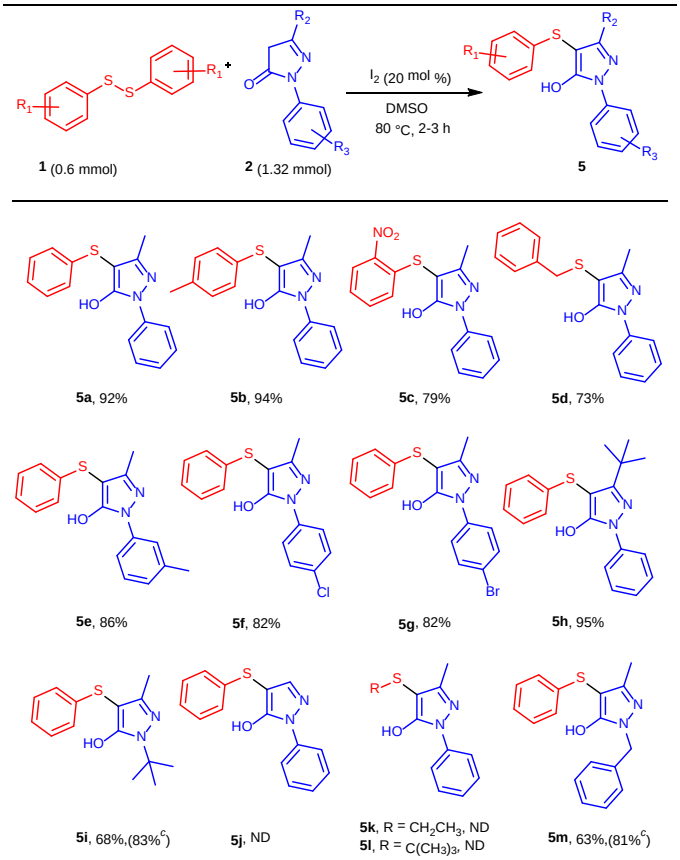
Scheme 3. Substrate Scope for the reaction of heterocyclic thiols and thiones with pyrazoles[a,b]



[a]Reaction conditions: **1a** (0.6 mmol), **2a** (0.66 mmol), catalyst (0.12 mmol) in 1 mL of DMSO at 80 °C, 1.5 h. [b]Isolated yield. [c]1 equiv of iodine used, 80 °C for 1 h

Next to demonstrate the generality of this methodology, the sulfenylation reaction with thiophenol was investigated. However, this reaction furnished the sulfenylated product **5a** in poor yield (26%) (see the ESI Table 10 for more details). This problem was circumvented by using disulfides instead of thiols (Scheme 4). Thus the disulfides with either electron-donating or electron withdrawing groups on phenyl ring reacted well furnishing the corresponding sulfenylated products **5a, 5b** and **5c** in 92, 94, and 79% yields, respectively. The reaction proceeded well with dibenzyl disulfide to form **5d** in good yield (73%) showing the robustness of this methodology. It is noteworthy that it is difficult to achieve the sulfenylation using dibenzyl disulfide under previous reported methods.[6-10] Further, a variety of pyrazalone derivatives underwent sulfenylation with diphenyl sulfide affording the corresponding sulfenylated products **5e**-**5h** in excellent yields (82-95%, respectively)**.** Alkyl-substituted pyrazolone such as 2-(*tert*-butyl)-2,4-dihydro-3*H*-pyrazol-3-one afforded **5i** in 83% yield. The pyrazolones without a substituent at C5 position such as 2-phenyl-2,4-dihydro-3*H*-pyrazol-3-one failed to undergoes sulfenylation. Our attempts for sulfenylation of 1,2-diethyldisulfane and 1,2-di-*tert*-butyldisulfane with pyrazalone were unsuccessful (Scheme 4). To achieve the synthesis of 1-alkyl-3-methyl-1H-pyrazol-5(4H)-one, the benylated pyrazolone derivative was synthesized, which was susuccessfully sulfenylated under optimal reaction conditions to obtain the product **5m** in 81% yield. Our attempts to deprotect the benzylic group from **5m** were unsuccessful.

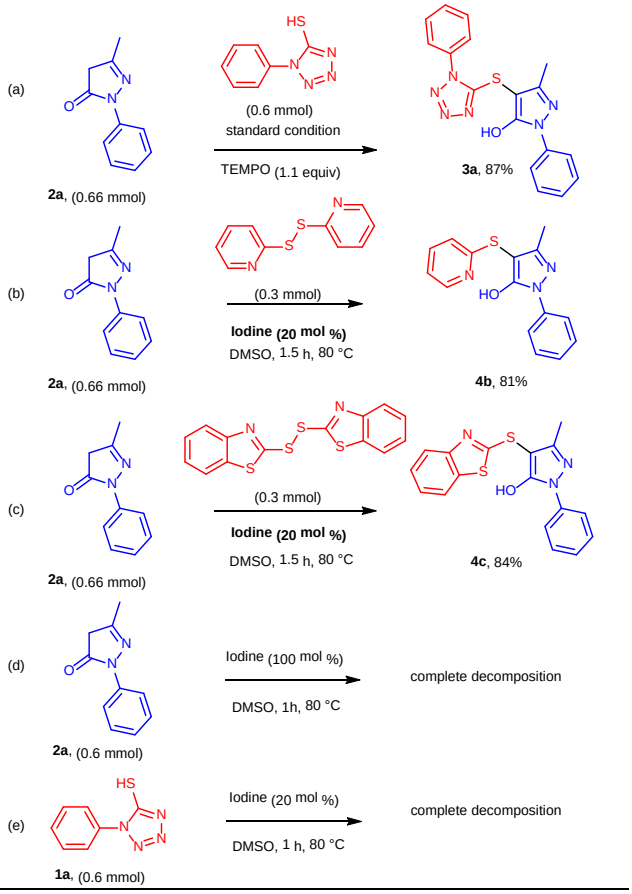
Scheme 4. Substrate Scope for the reaction of disulfides with pyrazoles[a,b]



[a]Reaction conditions: **1a** (0.6 mmol), **2a** (1.31 mmol), catalyst (0.12 mmol) in 1 mL of DMSO at 80 °C, 2-3 h. [b]Isolated yield. [c]50 mol % of iodine used. ND= Not detected

To get insight into the reaction mechanism, a few control experiments were performed (Scheme 5). The reaction of **1a** with **2a** under the optimal conditions, in the presence of TEMPO proceeded well suggesting the absence of a radical intermediacy in the reaction (Scheme 5a). Further to find whether disulfide is an intermediate, a reaction of 1,2-di(pyridin-2-yl)disulfane and 1,2-bis(benzo[*d*]thiazol-2-yl)disulfane with **1a** was performed. This reaction proceeded well with catalytic amount of iodine furnishing the sulfenylated product **4b** and **4c** in 81 and 84%, respectively (Scheme 5b and 5c), whereas the same reaction with pyridine thiol or benzo[*d*]thiazole-2(3*H*)-thione required stoichiometric amount of iodine for sulfenylation (**4b** and **4c**, Scheme 3). This experiment clearly supports that the reaction is proceeding through disulfide intermediate. ^{1}H NMR experiment for trapping disulfide intermediate in the reaction of 1-methyl-1*H*-tetrazole-5-thiol and **2a** was (see the ESI Table 13 and NMR studies for more details). To confirm the role of DMSO as an oxidant, a reaction of **1a** and **2a** was performed

Scheme 5. Control experiments for mechanistic studies



using 3 equiv of DMSO in solvents such as ethyl acetate and toluene. Interestingly, these reactions proceeded well furnishing the product **3a** in 82 and 81% yield, respectively, and the same reaction failed to form **3a** in the absence of DMSO (entry 3 and 4, Table 1, also see ESI Table 1 for more details). In the absence of any oxidants, the reaction of **1a** with **2a**, proceeded well under an argon atmosphere (entry 12, Table 1). These experiments clearly confirm the role of DMSO as an oxidant. However, the reaction of thiol **1a** or pyrazolone **2a** under the reaction conditions led to the complete decomposition of starting materials (Scheme 5d and 5e).

On the basis of these experimental studies (Schme 5) and the literature precedence,[14] a tentative mechanism has been proposed in Scheme 6. 1-Phenyl-1*H*-tetrazole-5-thiol (**1a**) in the presence of iodine forms intermediate 1,2-bis(1-phenyl-1*H*-tetrazol-5-yl)disulfane (**II**) and HI as a byproduct. 1,2-*bis*(1-Phenyl-1*H*-tetrazol-5-yl)disulfane (**II**) reacts with DMS:I_2 or I_2 to form intermediate that contains S-I bond (**III**). Further nucleophillic displacement of the iodo group by pyrazalone led to the formation of the product **3a** and byproduct HI. Further, iodine is regenerated by the reaction of HI with DMSO and cycle continues (Scheme 6).

Scheme 6. A tentative mechanism

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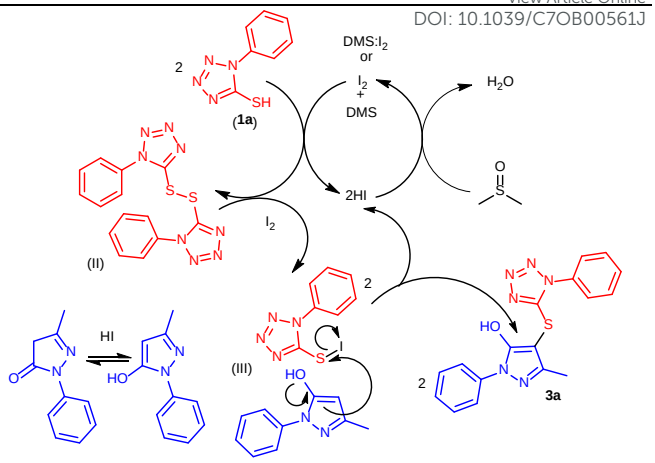

Conclusion

In conclusion, we have developed a sustainable and efficient strategy for the sulfenylation of pyrazalones under metal-free reaction conditions using DMSO as an oxidant and iodine as a catalyst. This strategy is highly practical as most of the compounds can be isolated in pure form without column purification. To the best of our knowledge, this is the first report on sulfenylation of diverse range of heterocyclic thiols and heterocyclic thiones to pyrazalones derivatives using CDC reactions.

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