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Selective Sulfenylation

Regioselective Mono- and Bis-Sulfenylation of Active Methylene Compounds

Namita Devi,[a] Rajjakfur Rahaman,[a] Kuladip Sarma,[a] and Pranjit Barman*[a]

Abstract: Selective mono- and bis-sulfenylation of active methylene groups with a variety of disulfides at an ambient temperature is reported. Sulfenylation is promoted by iodine as a catalyst and sulfenyl iodides as intermediates, under metal-free conditions. The method is greener in terms of solvent selection and the use of less hazardous DMSO as an oxidant. The procedure is highly efficient with readily available starting materials, giving good to excellent yields.

Introduction

C–S bond formation has received considerable interest over the past few decades, due to the presence of these bonds in compounds of pharmacological and therapeutic value.[1] Diaryl thioethers display a large spectrum of biological activities. Sulfur-substituted heterocycles such as indole, imidazole, thiazole, purine and deazapurine[2] have potential applications in the fields of HIV,[3] breast cancer,[4] diabetes, tubulin polymerization,[5] inflammatory effects, tumors[6] and vascular and respiratory diseases.[7] Sulfur functionalities are important intermediates in many synthetically important reactions. α-Sulfenylated carbonyl compounds promote numerous organic transformations.[8] The antitumor activity of Myleran is due to the presence of a sulfonate group. Therefore, the introduction of a sulfonate and a thiosulfonate group in the active methylene moiety is highly desirable.[9] All these applications make sulfenylation an interesting topic in synthetic chemistry that continues to draw the attention of researchers.[10]

Most sulfur-transfer agents – such as sulfenamides, *N*-(phenylthio)succinimide, sulfenyl halides,[11] sulfonyl hydrazides[12] and *N*-phenylthiocaprolactam[13] – are electrophilic in nature. At present, disulfides have become alternate sulfenylating agents to thiols[14] in metal-catalysed[15] and metal-free[7a,16] reactions. This is because of their stability, cost efficiency, easy preparation and commercial availability.[17] Metal-mediated and metal-free sulfenylation of indole[18] and imidazole[19] derivatives with different sulfenylating agents has often been reported, but only a few works to date have discussed the sulfenylation of active methylene compounds such as acetylacetone, ethyl acetoacetate and malononitrile. Traditionally, sulfenamides,[20] thiosulfonates,[9] sulfuryl chloride[21] and disulfides[22] have been used as thio sources for the preparation of mono- and bis-sulfenyl products from active methylene compounds. However, the reactions were often temperature-sensitive, which led to side reactions and poor yields. Moreover, the claimed[20b] sulfenylation with sulfenamides has also been contradicted.[23] The method of sulfenylation reported by Fujisawa and co-worker[22a] was a simple one in which a deprotonated anion attacks a disulfide. Nevertheless, the method was limited due to the formation of thiols as major byproducts. However, bis-sulfenylation was possible only for malononitrile and not applicable to other cases.

A few reports of particular interest on mono-sulfenylation deal with the sulfenylation and dehydrosulfenylation of amides,[24] the sulfenylation of esters and ketones,[25] rhodium-catalysed thiolation of 1-nitroalkanes[26] and the synthesis of thioethers by use of carbon tetrachloride as a mild oxidant.[27] The asymmetric sulfenylation of β-keto esters[28] would be expected to provide versatile building templates and synthons for biologically active molecules,[29] which is also in the purview of mono-sulfenylation. Tan et al. reported carbon-tetrabromide-mediated sulfenylation of active methylenes, via sulfenyl bromides as intermediates.[30] Sulfenylation with sulfenyl halides has been reported in the cases of indole and imidazole,[16b,18j,31] and a few reactions of importance with active methylene compounds[32] have been carried out. Recently, Chennapuram et al. have established I_2/DMSO/PTSA-promoted oxidative cross-coupling of imidazopyridines and methyl ketones.[33] During our research into active methylene compounds and tetrabutylammonium tribromide (TBATB) we found that mono-sulfenyl derivatives were synthesized within short reaction times with high yields. However, the same could not be achieved in the synthesis of disulfenylated products.[34]

In this work we focus on an improved regioselective method for the synthesis of mono and bis derivatives by use of sulfenyl iodides, with variable reaction conditions. These reactions are in compliance with green chemistry principles in terms of solvent selection, a less hazardous oxidant (DMSO) and use of iodine as a catalyst. The use of I_2 as a catalyst is an attractive alternative to corrosive and hazardous chlorine, sulfuryl chloride etc. The use of disulfides instead of thiols offers atom economy and

[a] *Department of Chemistry, National Institute of Technology Silchar, Silchar 788010, India*
E-mail: barmanpranjit@yahoo.co.in
http://www.nits.ac.in/departments/chem/chem.php

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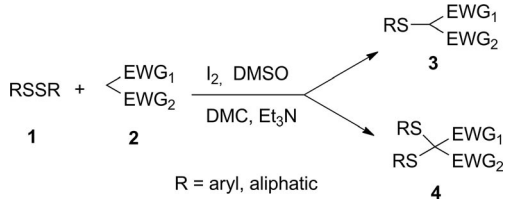
limits the wastage associated with thiols. The reactions were conducted at ambient temperature, leading to high yields. Interestingly, the oxidation of the disulfides to sulfoxides or sulfones was restricted.

Results and Discussion

Our initial studies were focused on the synthesis of the mono derivatives **3** in a regioselective manner. However, it was found that at different concentrations of base, oxidant and disulfide, **3** and **4** are both obtained as exclusive products, selectively with high yields (Scheme 1).

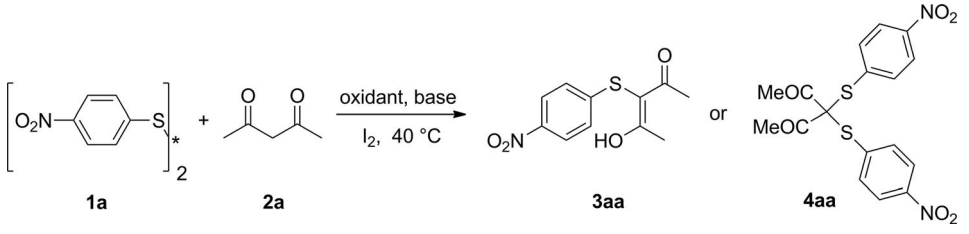


Scheme 1. Mono- and bis-sulfenylation.

A model reaction between bis(*p*-nitrophenyl) disulfide (**1a**) and acetylacetone (**2a**) in the presence of iodine was first examined under various conditions (Table 1).

The solvent screening showed that use of nonpolar solvents such as THF and cyclohexane gives mono derivative **3aa**, whereas use of toluene gives **4aa** selectively with lower yields. Use of polar solvents was effective for the reaction, and in this study dimethyl carbonate (DMC, Entries 8 and 21) was found to be the optimal solvent. The reactions were carried out at ambient temperature. After the optimization process, a mixture of **1a** (0.5 equiv.), **2a** (1.2 equiv.), DMSO (3.0 equiv.), Et_3N (1.2 equiv.), and I_2 (0.06 equiv., 5 mol-%) was allowed to react for 2.5 h, to give the mono derivative, C–S coupling product **3aa**, in almost 88 % yield (≈ 95 % purity). The identity of product **3aa** was confirmed by its spectral and analytical characterization (Figure S3**aa** in the Supporting Information). Here, iodine is used as a catalyst for the complete utilization of –SR groups from disulfide, and so an improved yield relative to others was obtained. Increasing the amounts of oxidant, base and disulfide gives the bisulfenylated product as the major component in the presence of Br_2 or I_2 as catalyst. However, with the higher concentration of disulfide and base (Entry 3), Br_2 gives both mono- and bis-sulfenylated products, but in the presence of I_2, under optimized reaction conditions, only mono-sulfenylation occurs. Thus, the regioselectivity of the product is dependent on the amounts of disulfide, base and oxidant. Moreover,

Table 1. Optimization of coupling between bis(*p*-nitrophenyl) disulfide (**1a**) and acetylacetone (**2a**) under different conditions.



Entry	**1a**/**2a**/oxidant/base	Oxidant	Base	Solvent[c]	Catalyst	Yield [%][d] **3aa**	Yield [%][d] **4aa**
1	0.5:1.2:3.0:1.2	H_2O_2	KO*t*Bu	ethanol	I_2	40	–
2	0.5:1.2:3.0:1.0	H_2O_2	EtONa	ethanol	*n*-TBAB	38	–
3	1.0:1.2:2.0:2.0	H_2O_2	Et_3N	DMC	Br_2	10	50
4	0.5:1.2:3.0:2.0	H_2O_2	Et_3N	DMF	I_2	15	62
5	0.5:1.2:1.0:1.2	DMSO	Et_3N	DCM	I_2	48	25
6	0.5:1.2:3.0:1.2	DMSO	Et_3N	DCM	I_2	63	12
7	0.5:1.2:3.0:1.2	DMSO	Et_3N	dioxane	I_2	59	15
8[a]	**0.5:1.2:3.0:1.2**	**DMSO**	Et_3N	**DMC**	I_2	88	–
9	0.5:1.2:3.0:1.2	DMSO	–	DMC	I_2	49	–
10	0.5:1.2:3.0:1.2	DMSO	K*t*OBu	DMC	I_2	55	–
11	0.5:1.2:3.0:1.2	DMSO	EtONa	DMC	I_2	42	–
12	1.0:1.2:3.0:2.5	DMSO	Et_3N	DMC	I_2	–	68
13	0.5:1.2:3.0:1.2	$(NH_4)_2S_2O_8$	Et_3N	DMC	I_2	48	24
14	0.5:1.2:6.0:1.2	$(NH_4)_2S_2O_8$	Et_3N	DMC	I_2	10	65
15	0.5:1.2:3.0:1.0	DMSO	KOH	DMC	I_2	23	–
16	0.5:1.2:6.0:1.0	DMSO	Et_3N	DMC	Br_2	30	45
17	0.5:1.2:3.0:1.0	DMSO	Et_3N	DMC	NCS	10	15
18	0.5:1.2:3.0:1.0	DMSO	KOH	DMF	I_2	20	–
19	0.5:1.2:3.0:1.2	DMSO	Et_3N	toluene	I_2	–	45
20	0.5:1.2:3.0:1.2	DMSO	Et_3N	THF	I_2	38	–
21[b]	**1.0:1.2:6.0:2.5**	**DMSO**	Et_3N	**DMC**	I_2	–	**90**
22	1.0:1.2:6.0:1.2	DMSO	Et_3N	DMC	I_2	–	64
23	0.5:1.2:3.0:1.0	DMSO	Et_3N	cyclohexane	I_2	24	–
24	0.5:1.2:3.0:1.0	DMSO	KOH	DMC	I_2	10	–

[a] Disulfide (0.5 equiv.), I_2 (0.06 equiv., 5 mol-%), DMSO (3 equiv.), acetylacetone (1.2 equiv.), Et_3N (1.2 equiv.), DMC (2–5 mL). [b] Disulfide (1.0 equiv.), I_2 (0.06 equiv., 5 mol-%), DMSO (6 equiv.), acetylacetone (1.2 equiv.), Et_3N (2.5 equiv.), DMC (10 mL). [c] DMC: dimethyl carbonate, DCM: dichloromethane, DMF: dimethylformamide. [d] Isolated yields.

when Br_2 was used in place of I_2 under optimized reaction conditions (Entry 8), the procedure lost its regioselective nature, affording a mixture of products.

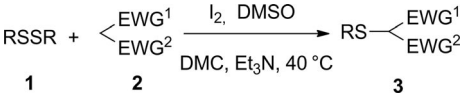
When iodine-containing catalysts such as I_2O_5 and TBAI were screened, no products were formed. The absence of iodine in the reaction under basic conditions resulted in a 20–25 % yield of **3aa** with *p*-nitrothiophenol as major byproduct, but in the absence of both base and catalytic iodine no product was formed. The reaction in the presence of various oxidants and bases was further examined. The solvents DMSO and Et_3N were found to be more efficient than the others. If strong oxidants are used, a disulfide will be converted into a benzenesulfonothioate, thus lowering the formation of the desired product. The use of NaOEt and KO*t*Bu (Entries 1 and 2) resulted in only 30–55 % conversion of the disulfide into **3aa** and the unreacted disulfide precipitated when the solution was kept for 24 h. When KOH (Entry 24) was used, *o*-nitrobenzenethiol became the major product, together with a small amount of **3aa**. However, the reaction was feasible even in the absence of any base (Entry 9, 49 %), giving **3aa** but with a comparatively longer reaction time (≈ 48 h).

The reaction showed a significant effect of Et_3N and DMSO, depending on their molar proportions. It was observed that when Et_3N and DMSO were used individually (at twice the amounts listed in Entry 8), instead of giving mono derivative **3aa**, the reaction produced the bis-sulfenylated product **4aa** in 68 % or 64 % yield (Entries 12 and 22, respectively). Optimization showed that use of a mixture of **1a** (1.0 equiv.), **2a** (1.2 equiv.), DMSO (6 equiv.), Et_3N (2.5 equiv.) and I_2 (0.06 equiv., 5 mol-%) improved the yield of **4aa** to almost 90 % within 4 h. The product was characterized spectroscopically. When only a catalytic amount of Et_3N (5 mol-%) was used the yield of mono derivative (52 %) was lowered significantly, and so a stoichiometric quantity of Et_3N was used. There was always a small amount of **2a** left unreacted. For completion of the reaction, acetylacetone was added in slight excess to the disulfide. The presence of a phenylthio group (adjacent to a diketone) enhances the reactivity of the remaining methylenic proton,[35] which results in the substitution of the proton by another phenylthio group. In this reaction scenario, steric effects are also an important factor that needs to be considered. The reactivity or thermodynamic acidity of that proton during the synthesis of compound **4** dominates over the steric effect, but the reaction time is increased. The formation of the mono derivative is confirmed by the presence of a –CH peak, observed at around 4 ppm (or at δ = 14 ppm in the case of an enol derivative), which is absent in the case of the bis-sulfenylated product.

Monitoring of temperature effects showed that at room temperature no conversion occurred. When the temperature was maintained at 40–50 °C, high yields of products were obtained. With increasing temperature above 60 °C the reaction gave mixtures of products **3aa** and **4aa** with very low yields. This may be due to the low reactivity of acetylacetone at high temperature. Therefore, the optimized reaction temperature was set at 40–50 °C for all the reactions.

The substrate scope was then examined, under the set of optimized conditions (as above) for mono derivatives (Table 1, Entry 8). The obtained results (Table 2) revealed that the mono-sulfenylation reaction has tolerance to changes of functional groups both of active methylene compounds and of disulfides.

Table 2. Substrate scope of disulfides **1** and active methylenes **2**.[a]



1 2 3

Entry	Disulfide 1	2	EWG^1	EWG^2	Product 3	Yield [%][b]
1	**1a**	**2a**	MeCO	MeCO	**3aa**	88
2	**1a**	**2b**	MeCO	EtOCO	**3ab**	91
3	**1a**	**2c**	EtOCO	EtOCO	**3ac**	81
4	**1a**	**2d**	CN	CN	**3ad**	74
5	**1a**	**2e**	MeCO	MeOCO	**3ae**	83
6	**1b**	**2a**	MeCO	MeCO	**3ba**	92
7	**1b**	**2b**	MeCO	EtOCO	**3bb**	96
8	**1b**	**2c**	EtOCO	EtOCO	**3bc**	87
9	**1b**	**2d**	CN	CN	**3bd**	83
10	**1c**	**2a**	MeCO	MeCO	**3ca**	79
11	**1c**	**2b**	MeCO	EtOCO	**3cb**	82
12	**1c**	**2c**	EtOCO	EtOCO	**3cc**	68
13	**1c**	**2e**	MeCO	MeOCO	**3ce**	70
14	**1d**	**2a**	MeCO	MeCO	**3da**	65
15	**1d**	**2b**	MeCO	EtOCO	**3db**	71
16	**1d**	**2c**	EtOCO	EtOCO	**3dc**	65
17	**1d**	**2d**	CN	CN	**3dd**	64
18	**1e**	**2a**	MeCO	MeCO	**3ea**	48
19	**1e**	**2d**	CN	CN	**3ed**	46
20	**1f**	**2a**	MeCO	MeCO	**3fa**	58

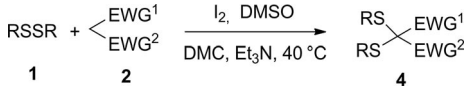
[a] Disulfide (0.5 equiv.), I_2 (0.06 equiv., 5 mol-%), DMSO (3 equiv.), active methylene compounds (1.2 equiv.), base (1.2 equiv.), DMC (2–5 mL). [b] Isolated yields.

Then, reactions between various active methylene compounds and other disulfides were also carried out. Under identical conditions, reactions of bis(2,4-dinitrophenyl) disulfide (**1b**), bis(*o*-nitrophenyl) disulfide (**1c**), 1,2-diphenyldisulfide (**1d**), diethyl disulfide (**1e**), and bis(*p*-methoxyphenyl) disulfide (**1f**) were performed. All the reactions proceeded smoothly, giving the desired products **3aa**–**3fa**. The order of substituent effect in relation to yields is: electron-withdrawing groups > unsubstituted disulfides > electron-donating groups > aliphatic disulfides (**1b** > **1a** > **1c** > **1d** > **1f** > **1e**). In the case of diphenyl disulfide, a minimal amount of thiophenol was produced along with the desired mono- and bis-sulfenylated products.

After the efficient synthesis of mono derivatives **3aa**–**3fa**, we carried out reactions between acetylacetone (**2a**) and different disulfides **1a**–**1d** with the goal of bis-sulfenylation. Under optimized conditions (Table 1, Entry 21), the bis-sulfenylated derivatives **4aa**–**4ca** (11 examples) were prepared efficiently (Table 3).

To determine a plausible mechanism, exploration of the catalytic cycle was essential, and this was attempted by using HI and DMSO. When HI and DMSO were used directly, the reaction produced a higher yield of mono-sulfenylated derivative (Table 4, Entry 1). On treatment with KI in the absence either of HCl (Table 4, Entry 2) or of DMSO (Table 4, Entry 3), no conversion into sulfenylated product was observed. However, with a suitable HCl concentration and DMSO, generation of HI was followed by the successful synthesis of sulfenyl derivatives.

Table 3. Substrate scope of bis-sulfenylated derivatives **4**.[a]



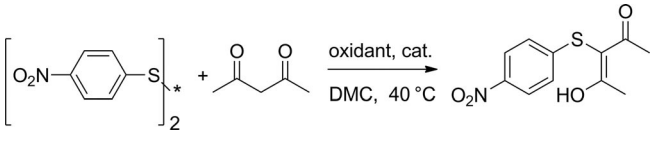
1 2 4

Entry	Disulfide 1	2	EWG[1]	EWG [2]	Product 4	Yield [%][b]
1	**1a**	**2a**	MeCO	MeCO	**4aa**	90
2	**1a**	**2b**	MeCO	EtOCO	**4ab**	92
3	**1a**	**2d**	CN	CN	**4ad**	94
4	**1a**	**2e**	MeCO	MeOCO	**4ae**	86
5	**1b**	**2a**	MeCO	MeCO	**4ba**	93
6	**1c**	**2a**	MeCO	MeCO	**4ca**	82
7	**1c**	**1b**	MeCO	EtOCO	**4cb**	84
8	**1c**	**2d**	CN	CN	**4cd**	88
9	**1d**	**2a**	MeCO	MeCO	**4da**	68
10	**1e**	**2d**	CN	CN	**4ed**	51
11	**1f**	**1a**	MeCO	MeCO	**4fa**	46

[a] Disulfide (1.0 equiv.), I_2 (0.06 equiv., 5 mol-%), DMSO (6 equiv.), active methylene compounds (1.2 equiv.), base (2.5 equiv.), DMC (10 mL). [b] Isolated yields.

Thus, the prominent reactivity of HI and DMSO for the C–S coupling is optimized.

Table 4. Reaction between bis(*p*-nitrophenyl) disulfide and acetylacetone.[a]

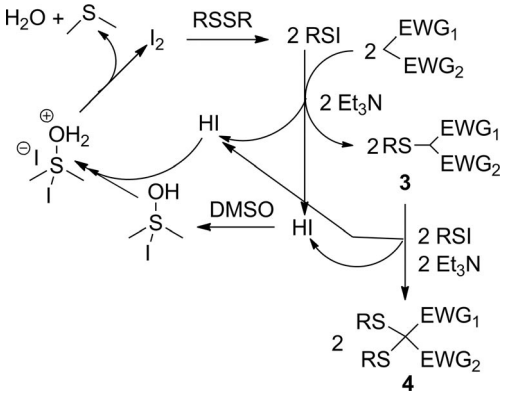


Entry	Catalyst	Oxidant	Acid	Yield [%][b]
1	–	DMSO	HI	75
2	KI	DMSO	–	0
3	KI	–	HCl	0
4	KI	DMSO	HCl	70

[a] Reaction conditions: KI (10 mol-%), HCl (10 mol-%), DMSO (3 equiv.). [b] Isolated yields after column separation.

From the above experimental observations, the promotion of the reaction through intermediary reaction steps through the following plausible mechanism can be assumed. Scheme 2 shows two catalytic cycles. In the first cycle, the active methylene group (in the presence of Et_3N) easily losses active H and binds to the sulfenyl iodide to form a product **3** and the catalyst I_2 is regenerated. However, if the amounts of the intermediate (RSI), Et_3N and DMSO are sufficiently large, the reaction selectively affords a product **4** at high yield. Quenching of acid by base does not occur because the addition of base promotes the reaction by abstracting the active proton, whereas its absence leads to a very slow process with lower levels of conversion. The formation of RSI species from iodine and disulfides at 40 °C has already been reported.[16b]

In order to confirm that the hypothetical reaction pathway (Scheme 2) proceeds through the RSI intermediate, we performed a reaction between diphenyl disulfide and styrene to trap the intermediate RSI. Under optimized conditions, the reaction afforded [1-phenyl-2-(phenylthio)ethylthio]benzene (**5a**) instead of any trapped product. The formation of the disubstituted thioether **5a** was confirmed by ^1H NMR (see the Supporting Information). Trapping of the sulfenyl iodide (RSI) by olefin is not possible, because sulfenyl iodides are not stable at room temperature. The instability is probably due to the very easy disproportionation reaction of the RSI to the more stable disulfide (2RSI → RSSR + I_2).[36]



Scheme 2. Plausible reaction pathway.

It can be clarified that the reaction is tolerant to a wide range of substituents, such as various disulfides and active methylene compounds. The only limitation is that diethyl malonate (DEM) cannot be transformed into bis-sulfenyl derivatives. This may be related to the acidity constant, which is lower in DEM ($\approx 10^{-14}$) than in other active methylene compounds. The steric effect due to the presence of two bulkier –COOEt groups in DEM may be another reason for the lower reactivity towards bis-sulfenylation. However, mono derivatives are successfully prepared, and this is a limitation of other methods.[29]

Conclusions

We have shown an improved procedure to sulfenylate active methylene compounds in a straightforward and regioselective manner, with high yields and short reaction times. In comparison with reported procedures, the present work is more regioselective with regard either to mono or to bis derivatives. The reaction has wide substrate scope and is "greener" in terms of substrate, solvent, oxidant and base. Under mild reaction conditions, the method regioselectively gives a wide range of products with minimal quantities of byproducts.

Experimental Section

Experimental Procedures: All reagents were purchased from commercial suppliers and used without further purification. The solvents and reagents were dried wherever necessary and the reactions were carried out with predried glassware. DMSO was distilled from CaH_2. Yields corresponding to isolated compounds were almost quantitative. For TLC, silica gel-GF was used, with monitoring with a UV fluorescence analysis cabinet (Ikon instruments) to visualize developed chromatograms. Separations were carried out on Merck silica mesh (60–120 mm). FT-NMR spectra were recorded with Bruker 500 MHz, 400 MHz and 300 MHz instruments. Chemical shifts are reported in δ (ppm) with reference to the residual peak of $CDCl_3$ for both ^1H and ^{13}C NMR; multiplicity is denoted as s = singlet, d = doublet, t = triplet, dd = doublet of doublets, dt = doublet of trip-

lets, and m = multiplet. The elemental analyses were performed with a Flash 2000 Thermo Scientific instrument. The preparation and characterization of all the reported mono- and bis-sulfenylated derivatives are available as Supporting Information.

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Keywords: Regioselectivity · Green chemistry · Sulfenylation

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