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FULL PAPER

Versatile Method for the Preparation of Unsymmetrical Disulfides from Thioacetates and Thiosulfonates

Lorenzo Delarue Bizzini,[a] Patrick Zwick,[a] and Marcel Mayor*[a,b,c]

Abstract: A method for the transformation of organic thioacetates, a widely used functionality for the preparation of self-assembled monolayers on gold surfaces, into unsymmetrical disulfides is reported. Disulfides are readily immobilized on gold in contrast to thioacetates, which usually require a deprotection step prior to bonding to the metal surface. The potential of the method for the controlled preparation of unsymmetrical disulfides has been demonstrated with model compounds comprising several thioacetates, which were readily converted into the corresponding unsymmetrical disulfides.

Introduction

The thiol (sulfhydryl) group is one of the most prominent anchor groups for the immobilization of organic molecules on noble metal surfaces, mainly due to the balanced features of the resulting metal sulfur bond. For example, the sulfur-gold bond is strong enough to retain a molecule on the surface even under ultra-high vacuum conditions, but weak enough to provide the mobility required to enable self-assembly behaviors. The anchor group is thus not only frequently used for the preparation of self-assembled monolayers (SAMs),[1–4] but also for the immobilization of functional structures in single molecule junctions.[5–7] In the latter case, the molecule of interest bridges the gap between two metal electrodes and thus exposes a thiolate anchor group at both ends. The tendency of free thiols to form disulfides in the presence of an oxidizing agent like oxygen makes their handling challenging. While this is a minor issue in the case of molecules with a single anchor group forming SAMs, it becomes a serious handicap for structures exposing several thiol groups due to the formation of insoluble polymers upon disulfide formation. The strategies addressing this issue are either to make disulfides on purpose, or to mask the thiol group e.g. by an acetyl group, which is hydrolyzed prior to bond formation with the noble metal surface.[2]

The disulfide approach is particular advantageous for SAM precursors, as the disulfide bond is cleaved electrochemically by the reduction potential of the noble metal surface. Consequently, a SAM formed from the corresponding homo-disulfide contains exclusively the molecule of interest.[8]

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For molecules exposing several thiol anchor groups, like e.g. functional rods bridging the electrodes of a single molecule junction[9–12] or tripodal platforms controlling the spatial arrangement of molecular architectures on surfaces,[13,14] the disulfide strategy is still appealing, as the cleavage of the disulfide bond on the noble metal sample renders the presence of additional deprotection chemicals unnecessary. The approach however requires the ability of forming unsymmetrical disulfides. Ideally, the thiol anchor groups of the molecule of interest should be engaged in the disulfide formation with a small alkylthiol, guaranteeing the differentiation of both immobilized thiolates in the experiment.

Guided by this thought, we became interested in a general method for the synthesis of unsymmetrical disulfides, which would allow the preparation of discrete molecular species bearing disulfides as sulfur anchor groups. Numerous functional model compounds for single molecule junctions are available as acetyl protected derivatives, but the required additional deprotection reagents might interfere with the transport experiments. Thus making those derivatives available as unsymmetrical disulfides releasing the experiment form the presence of additional reagents would increase its trustworthiness. Consequently, we focused our efforts towards methods enabling the transformation of an acetyl-protected thiophenol into an unsymmetrical 1-alkyl-2-aryl-disulfane.

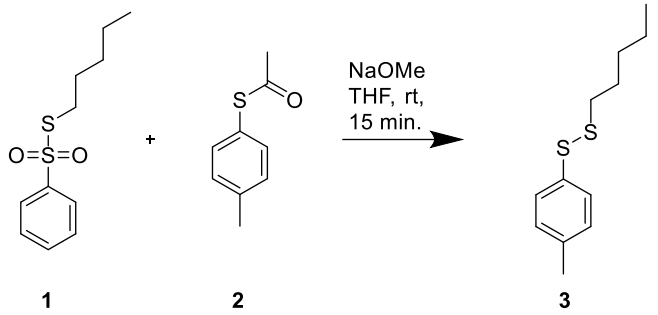
The synthesis of unsymmetrical disulfides has been extensively investigated[15] whereby two general concepts have been employed. (i) Generation of an electrophilic sulfenyl derivative followed by reaction with a thiol or one of its derivatives[16–24] or (ii) oxidative heterocoupling.[25–27] The concept of an electrophilic reagent is appealing since it allows for a more controlled reactivity without the inherent distribution of products usually observed in oxidative heterocoupling, which relies on the electronic difference between the thiols.

In order to convert thioacetates into unsymmetrical disulfides, we investigated the suitability of thiosulfonates as a sulfenylating agent, with the aim of applying this method to compounds bearing multiple disulfide functionalities. Formation of unsymmetrical disulfides from thioacetate and thiosulfonates was already reported for the synthesis of 1,6-disulfide-bridged D-hexo-pyranoses[28] and ajoene analogues[29–31] containing unsymmetrical alkyl vinyl disulfides. However, these reported synthetic methods require methanol as a solvent which limits its application for larger polyaromatic structures of interest.

In comparison to other electrophilic agents used to prepare unsymmetrical disulfides such as *N*-sulfenamides,[21] sufenyl chlorides[22] or dialkoxythioxaphosphorane disulfides,[23,24] thio-sulfonates[32] are both, easily prepared in one step and highly reactive towards thiolates. This is necessary in order to prevent thiolysis of the formed product and therefore giving rise to symmetrical disulfides as a side reaction.

Results and Discussion

From literature precedence[28,29] we expected that the electrophile *S*-pentyl benzenethiosulfonate **1** (prepared from pentylthiol and sodium benzene sulfinate using a modified literature procedure[32]) and thioacetate **2** should form the unsymmetrical disulfide **3** upon *in situ* formation of the thiolate of **2** (Scheme 1). To our delight, addition of sodium methoxide (NaOMe, 5.4 M in methanol) to a solution of thiosulfonate **1** and thioacetate **2** in either THF or DMF at room temperature led to fast and clean conversion to the desired unsymmetrical disulfide **3** whereby no symmetric disulfide was monitored by GC-MS.

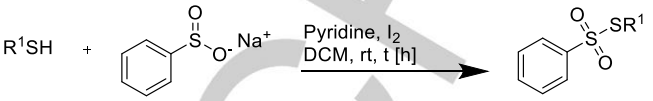


Scheme 1. Proof-of-concept reaction using **1** (1.10 eq.), **2** (1.00 eq.) and sodium methoxide (1.20 eq.) in THF at room temperature.

To investigate the scope of the method a series of thiosulfonates were prepared from their corresponding thiols, following the modified literature protocol.[32] Using pyridine as a base allows thiosulfonates to be prepared in one-pot fashion together with sodium benzene sulfonate and iodine in dichloromethane (DCM) (Table 1). Different alkyl- and aryl- benzene thiosulfonates were prepared in good yields, but the limitations of the protocol became obvious as soon as bulky thiols were considered.

1-Adamanethiol (entry 1) showed low reactivity as after 3 hours, the desired *S*-adamantyl benzene thiosulfonate could be isolated in only 6% yield after column chromatography. Conducting the reaction in DCM at reflux for 3 hours yielded only 1-adamantyl iodide as a side product together with unreacted intermediary symmetric disulfide. Further, *S*-pentyl-, *S*-4-methoxyphenyl-, and *S*-1*H*,1*H*,2*H,2*H-perfluorodecyl benzenethiosulfonate (entries 2, 4 and 5) could be prepared in excellent yield. Electronic effects appears to have a minor role in the formation of thiosulfonates as both electron withdrawing (entries 7 and 8) and donating substituents (entry 2) could be isolated in excellent yield. However, *S*-triphenylmethyl benzenethiosulfonate (entry 6) could not be obtained using this method, as the only isolatable product from this reaction was triphenylmethan-1-ol. The transformation of 2-(2-ethoxyethoxy) ethane-1-thiol[33] to the benzenethiosulfonate derivative (entry 3) provided only a moderate isolated yield of 36% after purification by column chromatography. Similarly, methyl thiosalicylate and 4-amino thiophenol (entries 8 and 10) could be transformed to the corresponding thiosulfonates in moderate yield. In the case of methyl thiosalicylate (entry 8) the moderate reactivity appears to arise due to steric reasons, since after 3 h the corresponding disulfide was still present in the reaction mixture. This stands in contrast to the reaction of 4-aminothiophenol where complete conversion of the disulfide was observed after 1 h, yet accompanied by oxidative side reactions resulting in a lower yield of the thiosulfonate of 40%.

Table 1. One-pot sulfonylation of thiols.[a]



Entry	R_1SH	t [h]	Yield [%][b]
1	1-AdamantylSH	3	6
2	4-MeOC_6H_4SH	0.5	97
3	$CH_3CH_2(OCH_2CH_2)_2SH$	2	36
4	$CF_3(CF_2)_7CH_2CH_2SH$	3[c]	87
5	PentylSH	0.5	95
6	$(C_6H_5)_3CSH$	3	-
7	$4\text{-NO}_2C_6H_4SH$	1	81
8	2-COOMeC_6H_4SH	3	40
9	$3,5\text{-F}_2C_6H_3SH$	0.5	88
10	$4\text{-NH}_2C_6H_4SH$	1	52

[a] Reaction conditions: mixture of thiol (1.00 eq.), pyridine (1.05 eq.), iodine (2.00 eq.) in dichloromethane with added sodium benzene sulfinate (1.7 eq.) under ambient conditions. [b] Yield of isolated product after column chromatography. [c] Reaction at 40°C.

With these thiosulfonates derivatives in hands, the previously evaluated reaction conditions were used to synthesize unsymmetrical disulfides using *S*-4-methylphenyl thioacetate as model substrate (Table 2, entries 1-5). With the exception of *S*-(2-(2-ethoxyethoxy)ethyl thiosulfonate (entry 3), all thiosulfonates of this first series behaved as anticipated and the corresponding unsymmetrical disulfides could be isolated in excellent yield (84-89%) after purification by column chromatography. In the case of *S*-(2-(2-ethoxyethoxy)ethyl thiosulfonate only the symmetrical tolyldisulfide was obtained. To explore the scope of the reaction sequence, hexyl thioacetate as an unactivated thioacetate (Table 2, entries 6-9) was exposed. And indeed, the reaction with electron deficient 4-nitrophenyl benzenethiosulfonate (entry 6) at room temperature provided the unsymmetrical disulfide in low yield (33% isolated) and favored the formation of symmetrical disulfides upon work up. Upon inverting the reacting groups however (entry 10), the unsymmetrical product was isolated in 75% yield. It appears that 4-nitrophenyl benzenethiosulfonate undergoes methanolysis competing with the unactivated hexyl thioacetate leading to low formation of the unsymmetrical product. Therefore the reaction (entry 6) was repeated at 0 °C and the selectivity towards the unsymmetrical product increased considerably with 67% isolated yield.

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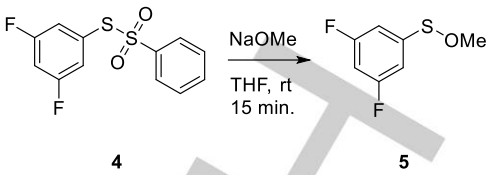
To further investigate the functional group tolerance of the method 4-aminophenyl benzenethiosulfonate and hexyl thioacetate (entry 7) were reacted yielding the unsymmetrical product in moderate yield of 57%. Another challenging issue of the method was spotted upon reacting the methyl ester substituted phenyl benzenethiosulfonate and hexyl thioacetate (entry 9). In this case the symmetrical disulfides were formed as major product and the unsymmetrical target compound could be isolated in only 15% yield.

The methanolysis of thiosulfonates seems to be the major competing side reaction decomposing the starting material. To investigate this hypothesis, 3,5 difluoro phenyl benzene thiosulfonate was treated with 1 equivalent of sodium methoxide in THF at room temperature without any thioacetate present (Scheme 2). And indeed, the quantitative formation of methyl 3,5-difluoro sulfenate after 15 minutes was observed. Sulfenates are known to hydrolyze under basic or neutral conditions giving rise to symmetric disulfides.[34] This competing reaction path is more pronounced with thiosulfonates bearing electron withdrawing groups and thus rationalizes the observed lower yields in the formation of unsymmetrical disulfides in entries 6 and 9.



4 **5**

Scheme 2. Formation of methyl sulfonate by methanolysis of thiosulfonates.

As shown in entries 5, 10 and 11, the reported method shows only low dependency on electronic effects of the substituents on the thioacetate in the reaction with pentyl benzenethiolsulfonate.

While most of the isolated unsymmetrical disulfides were stable under ambient conditions, an interesting intrinsic structural lability of *p*-methoxyphenyl *p*-methylphenyl disulfide (Table 2, entryl 2) was observed. The unsymmetric disulfide disproportionated slowly to the symmetric disulfides not only dissolved, but also in substance. The disproportionation reaction was followed by ^{1}H-NMR (CD_2Cl_2, 298 K, Figure 1) over the course of 280 h and is in well agreement with previously measured first order dependencies of unsymmetrical diaryl disulfides[35] The only further example of an unstable unsymmetrical disulfide observed in the series was *p*-methoxyphenyl pentyl disulfide (Table 2, entry 11) which equilibrates to an approximate 1:1 mixture of the unsymmetrical and symmetrical disulfides after 4 h at room temperature (see SI). We thus hypothesize that the electron rich anisole-type aryl is responsible for the degradation of the corresponding unsymmetrical disulfides.

Table 2. Sulfenylation reactions.[a]

Entry	R^1	R^2	Yield [%][b]
1	1-Adamantyl	4-MeC_6H_4	88
2	4-$MeOC_6H_4$	4-MeC_6H_4	89
3	$CH_3CH_2(OCH_2CH_2)_2$	4-MeC_6H_4	-
4	$CF_3(CF_2)_7CH_2CH_2$	4-MeC_6H_4	88
5	Pentyl	4-MeC_6H_4	84
6	4-NO_2Ph	Hexyl	33 (67)[c]
7	4-NH_2Ph	Hexyl	57
8	3,5-$F_2C_6H_3$	Hexyl	81
9	2-$COOMeC_6H_4$	Hexyl	15
10	Pentyl	4-NO_2Ph	75
11	Pentyl	4-$MeOC_6H_4$	85

[a] Reaction conditions: Mixture of thioacetate (1.00 eq.), thiosulfonate (1.10 eq.), sodium methoxide (1.20 eq.) in tetrahydrofuran under argon at room temperature. [b] Yield of isolated product after column chromatography. [c] Isolated yield after reaction at 0°C.

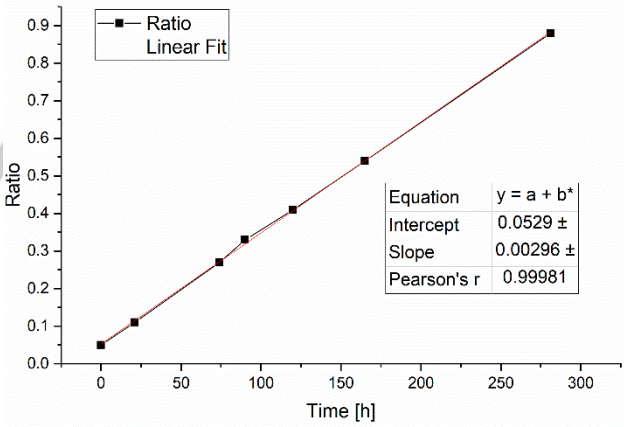
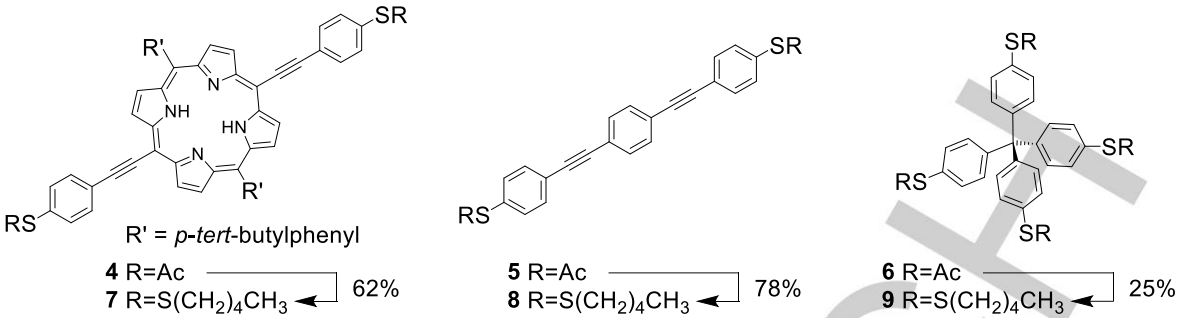


Figure 1. Ratio of unsymmetrical *p*-methoxyphenyl *p*-methylpheny disulfide to symmetrical *p*-methoxyphenyl disulfide.

To investigate the potential of the method to decorate the periphery of more complex molecules with unsymmetrical disulfides, the protocol was applied to the three model compounds **4**-**6** (Scheme 3) exposing several thioacetates. These structures were already investigated in the past either by mechanically controlled break junction experiments analyzing their transport behavior (compounds **4**[36] and **5**[7,37]), or in scanning tunneling microscopy studies as self-assembled monolayer (compound **6**[38]).



Scheme 3. Example of relevant molecules bearing multiple asymmetric disulfides synthesized from the corresponding thioacetates and *S*-pentyl benzene thiosulfonate using the here reported one-pot method. The displayed yields are the isolated amounts after column chromatography.

Indeed, the unsymmetrical disulfides of all the three compounds could be isolated with yields varying from 25% in case of the four-fold disulfide formation (compound **9** in Scheme 3), 62% and 78% for the two-fold reaction (compounds **7** and **8**, respectively).

Conclusions

In conclusion, we report a versatile and robust method to synthesize unsymmetrical disulfides. The *in situ* deprotection of thioacetates in presence of a variety of thiosulfonates gave after 15 to 30 minutes at room temperature unsymmetrical disulfides in good yields, thus enabling the synthesis of compounds bearing multiple unsymmetrical disulfide moieties. The preferential formation of unsymmetrical disulfides and the polarity difference of the starting material and the product facilitates the purification by column chromatography, as the desired product is the first eluting substance.

With this versatile and convenient synthetic access to unsymmetrical disulfides we are currently investigating their potential as anchor groups on noble metal substrates.

Experimental Section

General procedure for the preparation of thiosulfonates:
To a solution of thiol (1.00 eq.) and pyridine (1.05 eq.) in DCM (1 M in respect to the thiol) iodine (2.00 eq.) was added slowly. After 5 minutes sodium benzene sulfinate (1.7 eq.) was added to the reaction mixture under stirring (time and temperatures are given in Table 1). After all the disulfide intermediate was consumed (as monitored by TLC SiO_2, cyclohexane/EtOAc 10:1, UV_{254nm}) the reaction was quenched by addition of water and diluted with EtOAc. The organic phase was separated, washed with water (2x), sat. aq. $Na_2S_2O_3$ (2x), dried over anhydrous Na_2SO_4, filtered and the solvent was removed und reduced pressure. The crude product was further purified by column chromatography (SiO_2, cyclohexane/EtOAc 5:1) yielding the thiosulfonate.

General procedure for the preparation of asymmetric disulfides:
To a solution of thioacetate (1.00 eq.) and thiosulfonate (1.10 eq.) in degassed THF (0.15 M) at room temperature was added sodium methanolate (1.2 eq., 5.4 M in methanol). Directly after addition a white precipitate formed. After 15 to 30 minutes the thiosulfonate is usually consumed (as monitored by TLC SiO_2, cyclohexane/EtOAc 5:1, UV_{254nm}) and the reaction is quenched by addition of water and diluted with *n*-heptane. The organic phase was separated and the aqueous phase was extracted with *n*-heptane (3x). The combined organic phase was dried over anhydrous Na_2SO_4, filtered and the solvent was removed under reduced pressure affording the crude product. The mixture was further purified by column chromatography (SiO_2, pentane/DCM 10:1 or pure pentane) affording the asymmetric disulfide.

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Keywords: unsymmetrical disulfides • gold anchor group • thiosulfonate • SAM • MCBJ

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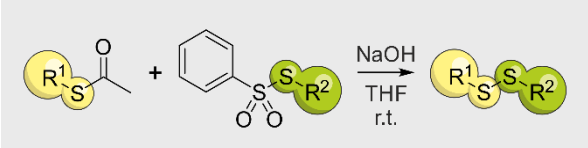

A versatile method for the preparation of unsymmetrical disulfides from thiosulfonates and thioacetates is described, together with a one-pot method for the preparation of the required thiosulfonates. The strategy is compatible with a variety of thiosulfonate-reagents (R^2) and substrates (R^1), including multifunctional ones.

Unsymmetrical disulfides, gold anchor group

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