

# DDQ-mediated synthesis of functionalized unsymmetrical disulfanes

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**We developed a simple and efficient method for the synthesis of functionalized unsymmetrical disulfanes under mild conditions in good yields. The designed method is based on the reaction of bis(5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinan-2-yl)disulfane with thiols in the presence of 2,3-dichloro-5,6-dicyanobenzoquinone (DDQ). The developed method allows the preparation of unsymmetrical disulfanes bearing additional hydroxy, carboxy, or amino functionalities.**

Compounds with the structure R-S-S-R, where the R group can be alkyl, vinyl or aryl are termed symmetrical disulfides when the R groups are the same. The wide range of unsymmetrical disulfides in which the R groups are different is also well known. These compounds are often termed organic disulfides in the literature; however, the IUPAC recommended nomenclature is disulfanes.<sup>1</sup> The name disulfide should only be applied to ionic compounds, such as sodium disulfide (Na<sub>2</sub>S<sub>2</sub>). Moreover, the term disulfane is more widely applicable than disulfide because it facilitates naming, even when the R groups are acyl and/or phosphoryl.

The synthesis of unsymmetrical disulfanes is an important transformation in organic synthesis and medicinal chemistry.<sup>2-5</sup> Recent developments in disulfide bond formation have been reviewed.<sup>6-9</sup> Although many different methods exist for the preparation of unsymmetrical disulfanes, the most prevalent approach involves substitution of a sulfonyl derivative with a thiol or its derivative. To date, the most commonly utilized sulfonyl derivatives are the following: sulfonyl chlorides,<sup>10-12</sup> S-alkyl thiosulfates and S-aryl thiosulfates (Bunte salts),<sup>13-14</sup> S-alkylsulfanyl-isothioureas,<sup>15</sup> benzothiazol-2-yl disulfanes,<sup>16-17</sup> benzotriazolyl-sulfanes,<sup>18</sup> dithioperoxyesters,<sup>19</sup> (alkylsulfanyl)dialkylsulfonium salts,<sup>20</sup> 2-pyridyl disulfanes and derivatives,<sup>21-22</sup> N-alkyltetrazolyl disulfanes,<sup>23</sup> sulfenamides,<sup>24</sup> sulfonyldimesylamines,<sup>25</sup> sulfonylthiocyanates,<sup>26</sup> 4-nitroarenesulfenylidines,<sup>27</sup> thiolsulfonates and thiol sulfonates,<sup>28-31</sup> sulfanyl-sulfenylidines,<sup>32</sup> thionitrites,<sup>33</sup> sulfonylthiocarbonates,<sup>34</sup> thioimides,<sup>35-37</sup> and thiophosphonium salts.<sup>38</sup> Other practical procedures involve the reaction of a thiol with a sulfonylbenzimidazole,<sup>39</sup> the rhodium-catalyzed disulfide exchange,<sup>40-42</sup> an electrochemical method,<sup>42</sup> ring opening of aziridines using tetrathiomolybdate in the presence of symmetrical disulfanes,<sup>43-44</sup> and the use of diethyl azodicarboxylate (DEAD)<sup>45</sup> or a solid support<sup>46</sup> in a sequential coupling of two different thiol groups. Recently, the oxidation of a mixture of two different thiols by 2,3-dichloro-5,6-

dicyanobenzoquinone (DDQ) to produce an unsymmetrical disulfane has also been reported.<sup>47-48</sup>

Disulfanes have been used for the preparation of self-assembled monolayers (SAMs)<sup>49-50</sup> and monolayer-protected clusters (MPCs) with a number of versatile properties.<sup>51-52</sup> Compounds containing the disulfide linkage have also been used for the preparation of dynamic combinatorial libraries,<sup>53</sup> catenanes,<sup>54-55</sup> macrocycles,<sup>56,5</sup> carceplexes,<sup>57</sup> dendrimers,<sup>58</sup> rotaxanes, micelles,<sup>59-60</sup> and a wide range of chemosensors and pro-drugs.<sup>61</sup> These species illustrate the wide applications of disulfanes and show that the synthesis of the disulfide bond is a critical transformation in organic chemistry.<sup>6-9</sup>

We have previously demonstrated the preparation of functionalized unsymmetrical molecules, such as dialkyl disulfanes,<sup>62</sup> alkyl-aryl disulfanes,<sup>63</sup> 'bioresistant' disulfanes,<sup>64</sup> the unsymmetrical disulfanes of L-cysteine and L-cystine,<sup>65</sup> and diaryl disulfanes,<sup>66</sup> based on the readily available 5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinan-2-disulfanyl derivatives **1**. These disulfanyl derivatives **1** of phosphorodithioic acid were also convenient for the preparation of  $\alpha$ -sulfonylated carbonyl compounds,<sup>67</sup> functionalized phosphorothioates,<sup>68</sup> as well as symmetrical<sup>69-70</sup> and unsymmetrical<sup>71-72</sup> trisulfanes (Figure 1).

As part of our continued interest in the preparation of functionalized unsymmetrical disulfanes, in this study, we report an efficient and convenient synthesis of unsymmetrical disulfanes **1** directly from phosphorodithioic acid disulfane **2a** and functionalized thiols **3**.

Wang and co-workers have developed a new method for the synthesis of unsymmetrical disulfanes from simple aliphatic and aromatic thiols

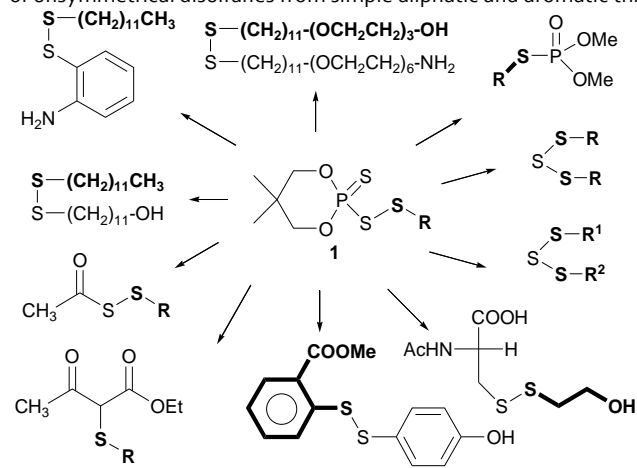


Figure 1 Synthetic applications of unsymmetrical disulfanes 1.

using DDQ as the oxidant.<sup>47</sup> This method is particularly interesting due to its apparent selectivity for the exclusive formation of unsymmetrical disulfanes, despite the presence of two different thiols in the reaction mixture in a 1:1 ratio before the addition of DDQ. We expected that this method might also be applicable to the synthesis of unsymmetrical disulfanes **1**. As a test reaction, 5,5-dimethyl-2-sulfanyl-2-thioxo-1,3,2-dioxaphosphorinane and dodecane-1-thiol **3a** (1:1 ratio) were mixed and then treated with DDQ (0.5 equivalent) following Wang's procedure.<sup>47</sup> Unfortunately, the yield of unsymmetrical disulfane **1a** after separation was moderate, and the observed ratio of products (**1a**:**2a**:**4**) was typical for the oxidation of most thiol mixtures<sup>8</sup> (Figure 2).

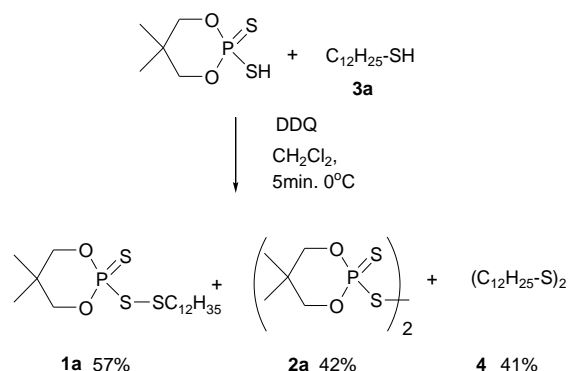


Figure 2 Oxidation of phosphorodithioic acid and thiol **3a** mixture by DDQ.

Although Wang and co-workers did not discuss the mechanism of the formation of the unsymmetrical disulfanes, it can be speculated that DDQ converts the more easily oxidized thiol to the symmetrical disulfane and the second thiol to the alkylthio radical (thiyl radical RS) which then reacts with symmetrical disulfane to produce the unsymmetrical product. To verify this hypothesis, we performed a reaction of bis-(5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinane-2-yl) disulfane **2a** (variable amount) and dodecane-1-thiol **3a** (1 equivalent) in the presence of DDQ (0.5 equivalent) (Table 1).

Table 1 Reaction of disulfane **2a** with thiol **3a** and DDQ<sup>a</sup>

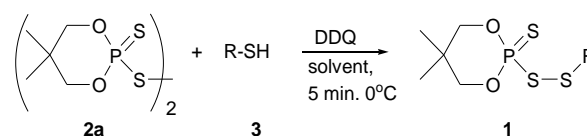
Entry	<b>2a</b> (equiv.)	Yield <sup>b</sup> (%)	
		CH <sub>2</sub> Cl <sub>2</sub>	CH <sub>3</sub> CN
1	6 <sup>c</sup>	100	100
2	2	100	99
3	1.5	100	98
4	1	99	96
5	0.6	81	78
6	0.5	72	69

<sup>a</sup> Conditions: disulfane **2a** (0.5-6.0 mmol), thiol **3a** (1 mmol), DDQ (0.5 mmol), 4.0 mL of solvent. <sup>b</sup> Isolated yields. <sup>c</sup> 10 mL of solvent was used.

As the data in Table 1 demonstrate, the excess symmetrical disulfane **2a** improved the yield of unsymmetrical product **1a**. The reactions using 1 equivalent of disulfane **2a** in CH<sub>2</sub>Cl<sub>2</sub> and CH<sub>3</sub>CN produced unsymmetrical product **1a** in a 99% and 96% yield, respectively (entry 4). Further studies were performed with 1 equivalent of disulfane **2a** because the yield of product **1a** was high when the excess amount of **2a** was acceptable.

Under the optimized conditions, the scope and limitations of this new unsymmetrical disulfane formation reaction were investigated, and the results are summarized in Table 2.

Table 2 Synthesis of unsymmetrical disulfanes **1** from functionalized thiols **3**<sup>a</sup>.



Entry	RSH	Product	Yield <sup>b</sup> (%)	
			CH <sub>2</sub> Cl <sub>2</sub>	CH <sub>3</sub> CN
1	HS-(CH <sub>2</sub> ) <sub>11</sub> CH <sub>3</sub> <b>3a</b>	<b>1a</b>	99	96
2	HS-(CH <sub>2</sub> ) <sub>11</sub> OH <b>3b</b>	<b>1b</b>	88	89
3	HS-(CH <sub>2</sub> ) <sub>10</sub> CO <sub>2</sub> H <b>3c</b>	<b>1c</b>	77	82
4	HS-(CH <sub>2</sub> ) <sub>11</sub> N <sub>3</sub> <b>3d</b>	<b>1d</b>	93	96
5	HS-(CH <sub>2</sub> ) <sub>10</sub> CONHS <b>3e</b>	<b>1e</b>	88	89
6	HS-(CH <sub>2</sub> ) <sub>10</sub> CO-Ferrocene <b>3f</b>	<b>1f</b>	82	85
7	HS-Ph <b>3g</b>	<b>1g</b>	99	98
8	HS-C <sub>6</sub> H <sub>4</sub> -4-CH <sub>3</sub> <b>3h</b>	<b>1h</b>	98	97
9	HS-C <sub>6</sub> H <sub>4</sub> -2-CO <sub>2</sub> H <b>3i</b>	<b>1i</b>	96	95
10	HS-(CH <sub>2</sub> ) <sub>9</sub> -CH=CH <sub>2</sub> <b>3j</b>	<b>1j</b>	87	92
11	Ac-Cys-OH <b>3k</b>	<b>1k</b>	-	89
12	HS-(CH <sub>2</sub> ) <sub>11</sub> NH <sub>2</sub> ·HCl <b>3l</b>	<b>1l</b>	0	0

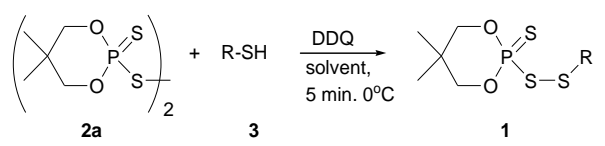
<sup>a</sup> Conditions: disulfane **2a** (1 mmol), thiol **3** (1 mmol), DDQ (0.5 mmol), 4.0 mL of solvent. <sup>b</sup> Isolated yields

A broad range of thiols reacted smoothly under the optimized reaction conditions. The reaction was tolerant of various functional groups, including the hydroxy, carboxy, azide, ferrocene, active ester and carbon-carbon double bond groups. Aromatic thiols (**3g-i**) underwent disulfide bond formation to furnish the desired products (**1g-i**) with excellent yields (95-99%, entries 7-9, Table 2). Steric hindrance does not appear to affect the progress of the reaction (entry 9, Table 2). The aliphatic thiols also provided unsymmetrical disulfanes **1** in high yields (77-99%, entries 1-6, Table 2). Note that the aliphatic thiol **3j** underwent the reaction in the presence of a carbon-carbon double bond (entry 10, Table 2), and the hydroxy and carboxy groups did not require protection (entries 2-3, Table 2). In the case of *N*-acetyl-L-cysteine **3k**, the reaction did not occur in CH<sub>2</sub>Cl<sub>2</sub> due to the low solubility of the starting material in the solvent. However, using acetonitrile as the solvent allowed the preparation of the corresponding unsymmetrical disulfane **1k** in high yield (89%, entry 11, Table 2).

Unfortunately, an unprotected amino group was not tolerated under the developed conditions. Although thiol **3l** was consumed during the reaction, the unsymmetrical disulfane was not produced (entry 12, Table 2). DDQ most likely reacted with an amino group to produce a

complex reaction mixture without the formation of unsymmetrical disulfane **1**. Similar unsuccessful results have also been observed by Wang and co-workers in the case of amine-substituted thiols.<sup>47</sup> To overcome that limitation, we decided to use protected amino-thiols under the developed conditions (Table 3).

Table 3. Reaction of disulfane **2a** with amino-thiol and DDQ<sup>a</sup>



Entry	RSH	Product	Yield <sup>b</sup> (%)	
			CH <sub>2</sub> Cl <sub>2</sub>	CH <sub>3</sub> CN
1	HS-(CH <sub>2</sub> ) <sub>11</sub> NH <sub>2</sub> ·HCl <b>3l</b>	<b>1l</b>	0	0
2	HS-(CH <sub>2</sub> ) <sub>11</sub> NHBoc <b>3m</b>	<b>1m</b>	53	56
3	HS-(CH <sub>2</sub> ) <sub>11</sub> NBoc <sub>2</sub> <b>3n</b>	<b>1n</b>	94	96

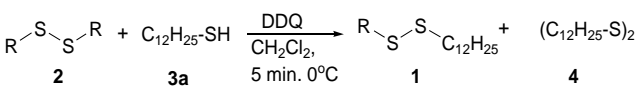
<sup>a</sup> Conditions: disulfane **2a** (1 mmol), thiol **3** (1 mmol), DDQ (0.5 mmol), 4.0 mL of solvent. <sup>b</sup> Isolated yields.

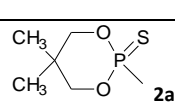
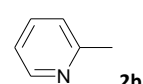
Our data show that the protection of the amino group plays a vital role in the yield of the unsymmetrical disulfanes **1m** and **1n**. When the amino group is protected by a single Boc group, the corresponding unsymmetrical disulfane **1m** is produced in moderate yield (53-56%, entry 2, Table 3). However, using thiol **3n** with a double-protected amino group provided unsymmetrical product **1n** in high yields (94-96%, entry 3, Table 2). The appropriate protection of the amino group appears to facilitate the preparation of unsymmetrical disulfanes **1m** and **1n** under the developed reaction conditions.

We were curious to continue our investigation with other symmetrical disulfanes, such as 2,2'-dipyridyl disulfane **2b** and diphenyldisulfane **2c** (Table 4).

As demonstrated, the formation of unsymmetrical disulfanes **1** strongly depends on the structure of the starting material **2**. In the case of disulfane **2a** and **2b**, the unsymmetrical product **1** was obtained in 99% and 23% yield, respectively. However, the reaction of diphenyldisulfane **2c** with dodecane-1-thiol **3a** in the presence of DDQ did not produce an unsymmetrical product, and exclusive formation of

Table 4 Reaction of symmetrical disulfane **2** with thiol **3a** and DDQ<sup>a</sup>



Entry	R	Yield <sup>b</sup> (%)	
		<b>1</b>	<b>4</b>
1		99	0
2		23	70
3	Ph- <b>2c</b>	0	99

<sup>a</sup> Conditions: disulfane **2** (1 mmol), thiol **3a** (1 mmol), DDQ (0.5 mmol), 4.0 mL of CH<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup> Isolated yields.

didodecyldisulfane **4** was observed. The determination of the scope of disulfanes **2** capable of producing unsymmetrical disulfanes under the developed conditions is under investigation.

The suggested mechanism to explain this transformation involves the initial formation of the thiyl radical (RS<sup>•</sup>) through the oxidation of thiol RSH **3** by DDQ. The resulting thiyl radical reacts with the symmetrical disulfane **2a** to yield the unsymmetrical product **1** and the phosphorodithioic acid radical, which undergoes recombination to produce symmetrical disulfane **2a** (Figure 3).

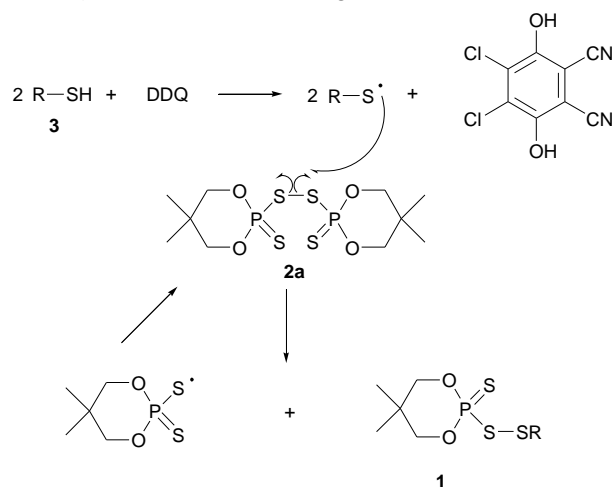


Figure 3 Plausible reaction mechanism The phosphorodithioic acid radical cannot extract hydrogen from the starting thiol because in this case, the catalytic amount of DDQ would be sufficient to produce unsymmetrical disulfane **1** in high yield. When a smaller amount of DDQ was used, a lower yield of product was obtained. In addition, we did not observe the formation of phosphorothioic acid in the reaction mixture. Moreover, the suggested mechanism explains why the excess of disulfane **2** improved the yield of the reaction. The initially formed thiyl radical (RS<sup>•</sup>) can undergo either recombination or reaction with product **1** to produce symmetrical disulfane RSSR. These side reactions can be avoided when an excess of disulfane **2** is present in the reaction mixture. The reactivity of symmetrical disulfane **2** with the thiyl radical appears to play a vital role in the formation of unsymmetrical disulfane **1**. Most likely, 2,2'-dipyridyl disulfane **2b** and diphenyldisulfane **2c** are less reactive toward thiyl radicals than the produced unsymmetrical disulfanes **1**, which resulted in the formation of symmetrical disulfane **4** (entries 2-3, Table 4).

## Conclusions

In summary, we developed an efficient and convenient method for the preparation of unsymmetrical disulfanes **1** directly from the disulfane of phosphorodithioic acid **2a** and functionalized thiols **3** in the presence of DDQ. A wide range of functional groups is tolerated, including the hydroxy, carboxy, azido, ferrocene, protected amino, and carbon-carbon double bond groups. Reactions of **2a** with a variety of functionalized thiols **3** in the presence of DDQ in CH<sub>2</sub>Cl<sub>2</sub> or CH<sub>3</sub>CN

at 0°C were generally complete within 5 minutes and gave unsymmetrical disulfanes **1** exclusively in good or very good yield after isolation. The simplicity and good yields render this method one of the most attractive approaches to the preparation of functionalized unsymmetrical disulfanes, especially derivatives of phosphorodithioic acid with versatile synthetic applications.

### General procedure for the preparation of disulfanyl derivatives **1** and representative analytical data

A thiol **3** (1.0 mmol) and bis-(5,5-dimethyl-2-thioxo-1,3,2-dioxaphosphorinan-2-yl) disulfane **2a** 394 mg (1.0 mmol) were dissolved in solvent (2.0 mL, dichloromethane or acetonitrile) and cooled to 0 °C in the ice bath. Then a solution of DDQ 114 mg (0.5mmol) in solvent (2.0 mL, dichloromethane or acetonitrile) was added slowly to the reaction mixture and stirred for 5 min at 0 °C. The reaction was monitored by TLC analysis. Solvent was removed under reduced pressure and the residue was directly purified by column chromatography (SiO<sub>2</sub>) to afford the desired products (**1a–1n**).

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### Notes and references

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†Electronic Supplementary Information (ESI) available: [experimental details and spectroscopic data for all new compounds **1**]. See DOI: 10.1039/c000000x/

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