Oxidative removal of 1,3-dithiane protecting groups by 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ)

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A number of 1,3-dithianes have been efficiently converted into the parent carbonyl compounds in good yields by treatment with 1.5 equiv. of 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) in MeCN–H_2O (9:1). The reactions of 2-aryl-substituted 1,3-dithianes bearing electron-donating groups on the benzene ring with DDQ afforded thioesters along with aldehydes. 1,3-Dithiolanes derived from aromatic aldehydes were transformed to thioesters, whereas 1,3-dithiolanes derived from aliphatic and aromatic ketones were stable under these reaction conditions. Diphenyl dithioacetals were stable except for 4-methoxy- and 3,4-dimethoxy-benzaldehyde diphenyl dithioacetals which gave the corresponding aldehydes. Selective cleavage reactions of 1,3-dithiane in the presence of 1,3-dithiolane or diphenyl dithioacetal have been investigated.

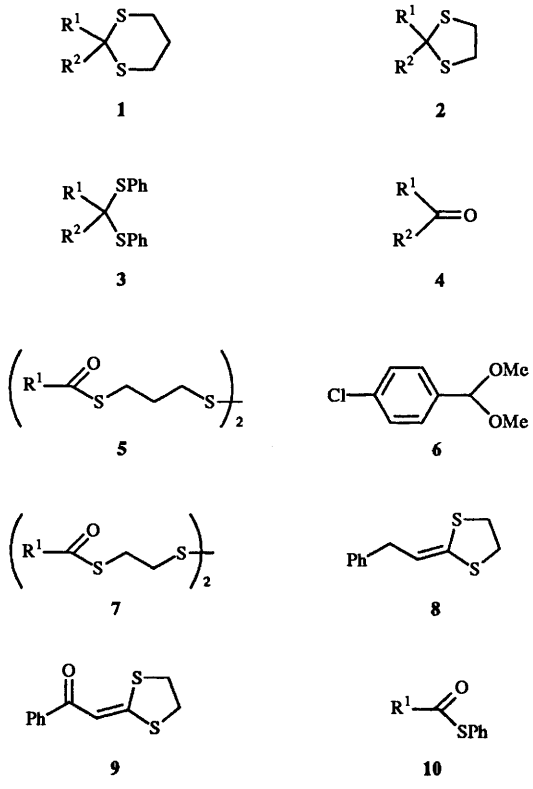
Deprotection of dithioacetals to the corresponding carbonyl compounds is one of the most important reactions in synthetic organic chemistry.[1] For this transformation, many procedures such as mercury(II) salts-induced, alkylative, halogenative and oxidative[2] hydrolysis are known. However, it is necessary to develop a mild and efficient method because mercury salts are highly toxic and some oxidative methods require drastic conditions or inconvenient procedures.

In the course of our continuing study using DDQ for useful synthetic transformations,[3] it was found that 1,3-dithianes were deprotected to give the corresponding carbonyl compounds in good yields by DDQ in aqueous MeCN.[4] As an extension of the work, this paper describes full details of the reactions of dithioacetals **1**–**3** with DDQ in aqueous MeCN.

First, 2-(4-chlorophenyl)-1,3-dithiane **1a** (R^1 = 4-ClC_6H_4, R^2 = H) was treated with various amounts of DDQ in MeCN–H_2O (9:1) at room temperature under nitrogen. When a catalytic amount of DDQ was used, only a small amount of 4-chlorobenzaldehyde **4a** was obtained (Table 1, entries 1 and 2). When 1.5 equiv. of DDQ was employed, the best results were obtained (entry 5). Decrease of the water ratio (MeCN–H_2O = 97:3) somewhat lowered the yields (entries 8 and 9). In the absence of water, most of dithiane **1a** was recovered (entry 10).

The solvent effect on product yields was examined using 1.5 equiv. of DDQ. In polar solvents such as MeCN–H_2O (9:1) or MeOH–H_2O (9:1), dithiane **1a** was hydrolysed to give aldehyde **4a** (entries 5 and 11). In less polar solvents such as C_6H_6–H_2O (9:1) or CH_2Cl_2–H_2O (9:1), thioester **5a** (R^1 = 4-ClC_6H_4) was produced exclusively (entries 14 and 15). In MeOH, an exchange reaction was observed, leading to dimethyl acetal **6** (entry 18).[5]

The hydrolysis of various dithianes **1** was examined. The results are summarized in Table 2. In most cases, the reaction proceeds smoothly to give the corresponding aldehydes or ketones in good yields. Dithianes **1b** and **1c**, possessing an electron-withdrawing group such as nitro and cyano groups on the benzene ring, require longer reaction times (entries 1 and 2). Dithianes **1g–i** bearing electron-donating groups on the benzene ring afforded thioesters **5g–i** together with aldehydes **4g–i** (entries 7–9). Recently, Sankararaman *et al.*[6] have reported the photochemical and thermal (reflux conditions) methods for deprotection of dithioacetals using DDQ in MeCN. Although they explained that the mixtures of dithioacetals and DDQ were stable in MeCN at room temperature when protected from room light, deprotection of 1,3-dithianes proceeded at almost the same rate in the dark under our aqueous conditions.



Next, the reactions of 1,3-dithiolanes **2** with DDQ were examined. The results are summarized in Table 3. In these cases, conversion of 1,3-dithiolanes **2** into the corresponding carbonyl compounds was much slower than that of dithianes **1**. In the cases of 1,3-dithiolanes **2**, derived from aromatic aldehydes, thioesters **7** were obtained as major products (entries 1–3). 2-(2-Phenylethyl)-1,3-dithiolane **2j** reacted with DDQ to give **8** (3%) and **9** (20%) in addition to a small amount of the deprotected **4j**

Table 1 The reaction of dithiane **1a** with DDQ

Entry	Solvent	DDQ (mmol)	*t*/h	Conv. (%)	Yield (%)[a] **4a**	**5a**
1	MeCN–H_2O (9:1)	0.1	6	7	3	0
2	MeCN–H_2O (9:1)	0.2	6	16	8	0
3	MeCN–H_2O (9:1)	1.0	3	79	64	0
4	MeCN–H_2O (9:1)	1.2	3	87	69	0
5	MeCN–H_2O (9:1)	1.5	2	100	87	0
6	MeCN–H_2O (9:1)	1.8	2	100	79	0
7	MeCN–H_2O (9:1)	2.0	2	100	60	0
8	MeCN–H_2O (97:3)	1.2	3	95	77	0
9	MeCN–H_2O (97:3)	1.5	3	99	77	0
10	MeCN	1.5	2	19	7	0
11	MeOH–H_2O (9:1)	1.5	6	61	32	0
12	THF–H_2O (9:1)	1.5	2	27	9	0
13	Et_2O–H_2O (9:1)	1.5	3	56	31	22
14	C_6H_6–H_2O (9:1)	1.5	4	62	0	39
15	CH_2Cl_2–H_2O (9:1)[b]	1.5	5	100	0	93
16	$CHCl_3$–H_2O (9:1)[c]	1.5	4	53	0	47
17	CCl_4–H_2O (9:1)[c]	1.5	5	35	0	20
18	MeOH	1.5	4	100	0[d]	0

[a] Isolated yields. [b] 14 cm^3 of the solvent was used. [c] 10 cm^3 of the solvent was used. [d] Acetal **6** was obtained in 82% yield.

Table 2 The reaction of the dithianes **1** with DDQ in aqueous MeCN

Entry	Substrate	R^1	R^2	*t*/h	Conv. (%)	Yield (%)[a] **4**	**5**
1	**1b**	4-$O_2NC_6H_4$	H	6	66	30	0
2	**1c**	4-NCC_6H_4	H	6	76	61	0
3	**1d**	4-$MeOCOC_6H_4$	H	3	100	97	0
4	**1a**	4-ClC_6H_4	H	2	100	87	0
5	**1e**	4-PhC_6H_4	H	2	100	92	0
6	**1f**	Ph	H	1	100	70[b]	0
7	**1g**	4-MeC_6H_4	H	3	100	88	8
8	**1h**	4-$MeOC_6H_4$	H	2	100	43	41
9	**1i**	3,4-$(MeO)_2C_6H_3$	H	1	100	23	74
10	**1j**	$PhCH_2CH_2$	H	2	91	70	0
11	**1k**	$C_{11}H_{23}$	H	1	95	71	0
12	**1l**	Ph	Me	0.5	100	75	—
13	**1m**	Ph	Ph	2	87	82	—
14	**1n**	$-(CH_2)_2CH(Bu^t)(CH_2)_2-$		1.5	97	81	—
15	**1o**	C_9H_{19}	Me	1	100	87	—

[a] Isolated yields. [b] Determined by ^1H NMR spectroscopy.

Table 3 The reaction of the dithiolanes **2** with DDQ in aqueous MeCN

Entry	Substrate	R^1	R^2	*t*/h	Conv. (%)	Yield (%)[a] **4**	**7**
1	**2a**	4-ClC_6H_4	H	0.5	84	11	70
2	**2g**	4-MeC_6H_4	H	1	100	2	75
3	**2h**	4-$MeOC_6H_4$	H	1	100	15	69
4	**2j**	$PhCH_2CH_2$	H	1	62	7	0[b]
5	**2k**	$C_{11}H_{23}$	H	1	58	21	0
6	**2l**	Ph	Me	2	21	2	—
7	**2m**	Ph	Ph	2	19	1	—
8	**2n**	$-(CH_2)_2CH(Bu^t)(CH_2)_2-$		1	14	1	—
9	**2o**	C_9H_{19}	Me	2	12	6	—

[a] Isolated yields. [b] Compounds **8** and **9** were obtained in 3 and 20% yields, respectively.

(7%) (entry 4). In the case of **2k**, however, many unidentified products were obtained together with a small amount of the parent aldehyde **4k** (21%) (entry 5). 1,3-Dithiolanes **2**, derived from aliphatic and aromatic ketones, were stable under these reaction conditions (entries 6–9).

Most of diphenyl dithioacetals **3** were inert under the conditions employed (Table 4). Only compounds **3h** and **3i**, possessing electron-donating substituents on the benzene ring, were converted into the corresponding aldehydes **4h** and **4i** in good yields, respectively (entries 2 and 3). In these cases, a large amount of diphenyl disulfide was isolated. Thioesters **10** were not detected by TLC or ^1H NMR spectroscopy.

Taking into account the difference in reactivity of these dithioacetals **1**–**3**, we investigated the competitive cleavage reactions of 1,3-dithiane **1** in the presence of 1,3-dithiolane **2** or diphenyl dithioacetal **3**. Indeed, the treatment of dithianes **1**

Table 4 The reaction of diphenyl dithioacetals **3** with DDQ in aqueous MeCN

Entry	Substrate	R^1	R^2	*t*/h	Conv. (%)	Yield of **4** (%)[a]
1	**3a**	4-ClC_6H_4	H	3	16	0
2	**3h**	4-$MeOC_6H_4$	H	1	100	78
3	**3i**	3,4-$(MeO)_2C_6H_3$	H	1	100	78
4	**3j**	$PhCH_2CH_2$	H	5	20	0
5	**3k**	$C_{11}H_{23}$	H	5	20	0
6	**3l**	Ph	Me	5	18	0
7	**3n**	$-(CH_2)_2CH(Bu^t)(CH_2)_2-$		5	13	0
8	**3o**	C_9H_{19}	Me	5	26	0

[a] Isolated yields.

Table 5 Competitive cleavage reaction of dithianes **1** in the presence of dithiolanes **2** or diphenyl dithioacetals **3** with DDQ

Entry	R^1	R^2	Compounds	*t*/h	Products (Yield/%[a])
1	$-(CH_2)_2CH(Bu^t)(CH_2)_2-$		**1n** + **2n**	3	**1n** (11%) **2n** (97%) **4n** (86%)
2			**1n** + **3n**	3	**1n** (8%) **3n** (95%) **4n** (86%)
3	C_9H_{19}	Me	**1o** + **2o**	2	**1o** (10%) **2o** (95%) **4o** (89%)
4			**1o** + **3o**	2	**1o** (10%) **3o** (91%) **4o** (90%)
5	4-ClC_6H_4	H	**1a** + **2a**	3	**1a** (12%) **2a** (90%) **4a** (80%)
6			**1a** + **3a**	3	**1a** (10%) **3a** (93%) **4a** (83%)

[a] Isolated yields.

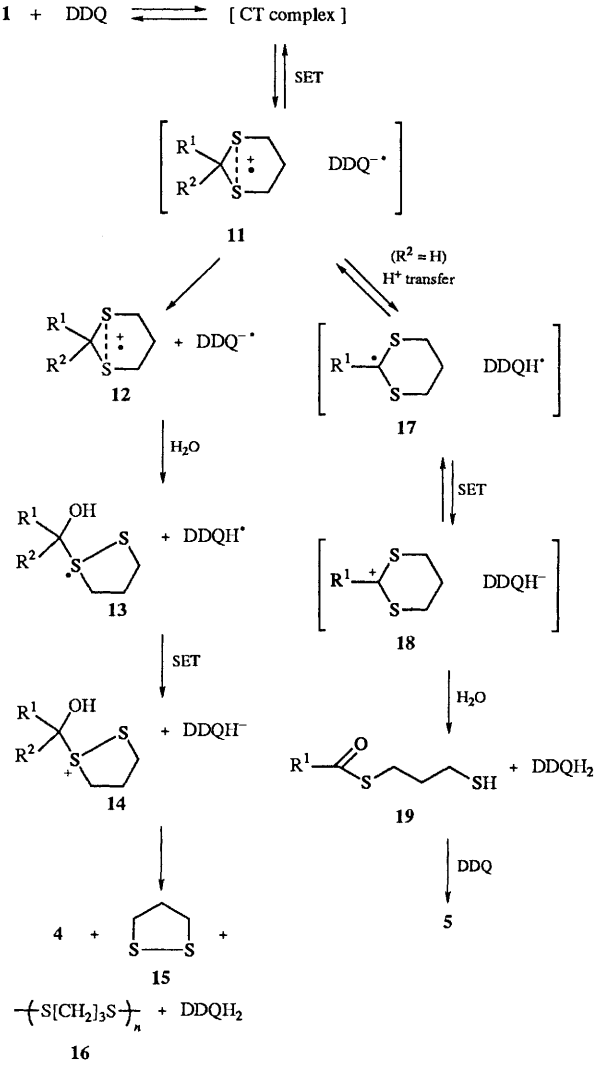
with 1.2 equiv. of DDQ in MeCN–H_2O (97:3), in the presence of dithiolanes **2** or diphenyl dithioacetals **3**, caused hydrolysis of **1** without appreciable changes of **2** or **3** (Table 5). Even for a mixture of **1a** and **2a**, dithiane **1a** was effectively transformed to aldehyde **4a** without conversion of **2a** into thioester **7a** (entry 5).

As shown in Scheme 1, the formation of aldehyde **4** and thioester **5** could be explained by a single electron transfer (SET) mechanism, although the exact path is not clear at this moment.[7] The first step is a SET process from dithiane **1** to DDQ *via* a charge-transfer (CT) complex to give a geminate radical ion pair. The resulting cation radical **11** is stabilized by a transannular interaction with the adjacent sulfur atom.[8] Subsequent reactions of the radical ion pair, which involve diffusion to cation radical **12** and DDQ anion radical, attack by water and a second SET process, would lead to aldehyde **4**.

The reaction pathways are supported by the following facts. During the reaction, a dark red coloration due to the formation of a CT complex was observed. CT absorption maxima were 544 and 584 nm for **1a**. 1,2-Dithiolane **15** (2%),[9] polymeric organosulfur compound **16** (42%)[9] and $DDQH_2$ (1.0 equiv.) were isolated from the reaction of **1a** with DDQ. 1,2-Dithiolane **15** was unstable at ambient temperature and underwent facile polymerization to the polymeric **16**. Addition of 1,2,4,5-tetramethoxybenzene (TMB) (1.5 equiv.), which is a SET quencher, suppressed the formation of **4l** (2%), while 1,4-dimethoxybenzene (DMB) did not [E_{ox} (**1l**) = 1.13 V,[7a] E_{ox} (TMB) = 0.77 V,[2c] E_{ox} (DMB) = 1.28 V[2c] (*vs.* SCE in MeCN)]. These results suggest that SET processes are involved in the reaction. An acid-catalysed mechanism was ruled out since acidic materials[10] generated from complete decomposition of DDQ in aqueous MeCN did not cause deprotection of **1a**. Interestingly, the yield of **4** was not reduced in the presence of oxygen, which was in contrast to other SET reactions of dithioacetals.[2b,7b]

On the other hand, proton transfer from the cation radical **11** to the DDQ anion radical, followed by a second SET process, would lead to a geminate ion pair.[11] Cation **18** is hydrolysed to give thiol **19**, which is further oxidized to **5** by DDQ. Under the reaction conditions employed, thiols such as dodecane-1-thiol were oxidized to disulfides rapidly by DDQ. Oxidation of *p*-methoxybenzylidene acetals to the corresponding esters by DDQ is known and explained by a similar mechanism.[12]

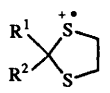
In polar solvents such as aqueous MeCN, which encourage the radical ion pair to escape from the solvent cage, deprotection occurred predominantly.[13] In less polar solvents,



Scheme 1

proton transfer within the solvent cage is favoured to lead to thioester **5**. The effect of substituents on the benzene ring is consistent with the proposed mechanism. For dithianes bearing electron-withdrawing groups on the benzene ring, longer reaction times were required because the first SET process proceeds with much more difficulty and deprotection proceeded exclusively since the benzylic cation **18** is destabilized. In contrast, electron-donating groups promote the formation of thioester **5** markedly.

In the case of dithiolane **2**, cation radical **20** is less stable than dithiane cation radical **11** because of the absence of a



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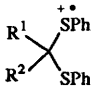

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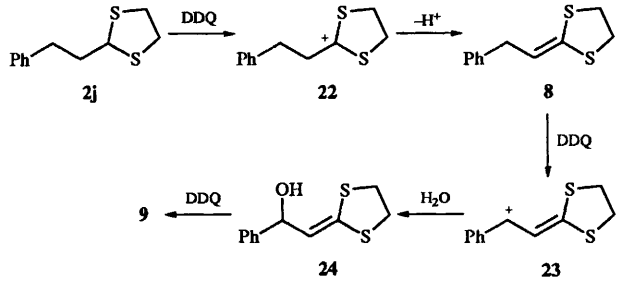
transannular interaction.[8] Therefore, **20** is transformed to thioester **7** or returns to the starting **2** before escape from the solvent cage. From the reaction of compound **2j** with DDQ, compounds **8** and **9** were obtained. The mechanism is shown in Scheme 2. Hydride transfer from dithiolane **2j** to DDQ affords



Scheme 2

cation **22**, which is deprotonated to give compound **8**. Product **9** would be produced by benzylic oxidation of **8** with DDQ.

Cation radical **21** generated from diphenyl dithioacetal **3** would be cleaved to a carbocation and stable phenylsulfanyl radical. The resulting cation is hydrolysed to give carbonyl compound **4**.

In conclusion, the present method constitutes a useful methodology for deprotection of 1,3-dithianes. The remarkable advantages of this method are mild and convenient procedures and selective cleavage of 1,3-dithianes in the presence of 1,3-dithiolanes and diphenyl dithioacetals.

Experimental

Mps are uncorrected. IR spectra were recorded on a Hitachi Model 270-30 spectrophotometer. ^1H and ^{13}C NMR spectra were measured on a JEOL JNM-FX 90Q spectrometer at 90 MHz and 22.5 MHz using Me_4Si as an internal standard. UV spectra were recorded on a Hitachi Model 320 spectrophotometer. Column chromatography was performed on Wakogel C-200. DDQ was recrystallized from benzene–hexane. Dithioacetals **1**–**3** were prepared by the reported methods.[14,15]

General procedure for the reaction of dithioacetals 1–3 with DDQ in MeCN–H_2O (9:1)

To a solution of dithiane **1a** (231 mg, 1.0 mmol) in MeCN (4.8 cm^3) and H_2O (0.7 cm^3) was added a solution of DDQ (341 mg, 1.5 mmol) in MeCN (1.5 cm^3) under nitrogen. After stirring at room temperature for 2 h, the mixture was quenched with saturated aqueous $NaHCO_3$ (50 cm^3) and extracted with ether. The extracts were washed with water, dried and evaporated and the residue was chromatographed (benzene) on silica gel to give 4-chlorobenzaldehyde **4a** (122 mg, 87%).

Bis[3-(4-chlorobenzoylsulfanyl)propyl] disulfide 5a. Colourless oil (Found: C, 49.2; H, 4.35. $C_{20}H_{20}Cl_2O_2S_4$ requires C, 48.9; H, 4.1%); ν_{max}(neat) 1670 cm^{-1} (C=O); δ_H($CDCl_3$) 2.12 (4 H, tt, *J* 7.0 and 7.0, CH_2), 2.80 (4 H, t, *J* 7.0, CH_2), 3.18 (4 H, t, *J* 7.0, CH_2), 7.38 (4 H, d, *J* 8.3, ArH) and 7.87 (4 H, d, *J* 8.3, ArH); δ_C($CDCl_3$) 27.7 (t), 29.0 (t), 37.6 (t), 128.5 (d), 128.9 (d), 135.3 (s), 139.7 (s) and 190.1 (s).

Bis[3-(4-methylbenzoylsulfanyl)propyl] disulfide 5g. Colourless oil (Found: C, 58.8; H, 5.9. $C_{22}H_{26}O_2S_4$ requires C, 58.6; H, 5.8%); ν_{max}(neat) 1665 cm^{-1} (C=O); δ_H($CDCl_3$) 2.11 (4 H, tt, *J* 7.0 and 7.0, CH_2), 2.40 (6 H, s, Me), 2.80 (4 H, t, *J* 7.0, CH_2), 3.16 (4 H, t, *J* 7.0, CH_2), 7.22 (4 H, d, *J* 8.4, ArH) and 7.86 (4 H, d, *J* 8.4, ArH); δ_C($CDCl_3$) 21.4 (q), 28.4 (t), 29.7 (t), 37.9 (t), 127.6 (d), 129.1 (d), 134.7 (s), 143.9 (s) and 190.2 (s).

Bis[3-(4-methoxybenzoylsulfanyl)propyl] disulfide 5h. Colourless oil (Found: C, 54.4; H, 5.6. $C_{22}H_{26}O_4S_4$ requires C, 54.7; H, 5.4%); ν_{max}(neat) 1660 cm^{-1} (C=O); δ_H($CDCl_3$) 2.10 (4 H, tt, *J* 7.0 and 7.0, CH_2), 2.79 (4 H, t, *J* 7.0, CH_2), 3.15 (4 H, t, *J* 7.0, CH_2), 3.85 (6 H, s, MeO), 6.91 (4 H, d, *J* 8.9, ArH) and 7.93 (4 H, d, *J* 8.9, ArH); δ_C($CDCl_3$) 28.1 (t), 37.4 (t), 37.9 (t), 55.2 (q), 113.5 (d), 129.1 (d), 129.3 (s), 163.6 (s) and 189.0 (s).

Bis[3-(3,4-dimethoxybenzoylsulfanyl)propyl] disulfide 5i. Colourless oil (Found: C, 53.0; H, 5.8. $C_{24}H_{30}O_6S_4$ requires C, 53.1; H, 5.6%); ν_{max}(neat) 1660 cm^{-1} (C=O); δ_H($CDCl_3$) 2.03 (4 H, tt, *J* 7.0 and 7.0, CH_2), 2.80 (4 H, t, *J* 7.0, CH_2), 3.17 (4 H, t, *J* 7.0, CH_2), 3.93 (12 H, s, MeO), 6.87 (2 H, d, *J* 8.5, ArH) and 7.32–7.71 (4 H, m, ArH); δ_C($CDCl_3$) 27.5 (t), 29.1 (t), 37.5 (t), 56.0 (q), 56.1 (q), 109.4 (d), 110.2 (d), 121.7 (d), 129.9 (s), 148.9 (s), 153.4 (s) and 190.1 (s).

Bis[2-(4-chlorobenzoylsulfanyl)ethyl] disulfide 7a. Colourless oil (Found: C, 46.4; H, 3.4. $C_{18}H_{16}Cl_2O_2S_4$ requires C, 46.65; H, 3.5%); ν_{max}(neat) 1660 cm^{-1} (C=O); δ_H($CDCl_3$) 2.84–3.10 (4 H, m, CH_2), 3.30–3.52 (4 H, m, CH_2), 7.41 (4 H, d, *J* 8.5, ArH) and 7.89 (4 H, d, *J* 8.5, ArH); δ_C($CDCl_3$) 28.6 (t), 37.9 (t), 128.6 (d), 128.9 (d), 135.0 (s), 139.9 (s) and 190.0 (s).

Bis[2-(4-methylbenzoylsulfanyl)ethyl] disulfide 7g. Colourless oil (Found: C, 56.5; H, 5.5. $C_{20}H_{22}O_2S_4$ requires C, 56.8; H, 5.25%); ν_{max}(neat) 1660 cm^{-1} (C=O); δ_H($CDCl_3$) 2.40 (6 H, s, Me), 2.90–3.08 (4 H, m, CH_2), 3.35–3.46 (4 H, m, CH_2), 7.24 (4 H, d, *J* 8.2, ArH) and 7.86 (4 H, d, *J* 8.2, ArH); δ_C($CDCl_3$) 21.7 (q), 28.4 (t), 38.1 (t), 127.4 (d), 129.3 (d), 134.3 (s), 144.4 (s) and 189.2 (s).

Bis[2-(4-methoxybenzoylsulfanyl)ethyl] disulfide 7h. Colourless oil (Found: C, 52.6; H, 4.9. $C_{20}H_{22}O_4S_4$ requires C, 52.8; H, 4.9%); ν_{max}(neat) 1660 cm^{-1} (C=O); δ_H($CDCl_3$) 2.86–3.07 (4 H, m, CH_2), 3.31–3.50 (4 H, m, CH_2), 3.84 (6 H, s, MeO), 6.90 (4 H, d, *J* 8.8, ArH) and 7.92 (4 H, d, *J* 8.8, ArH); δ_C($CDCl_3$) 28.1 (t), 37.9 (t), 55.1 (q), 113.9 (d), 129.3 (d), 131.5 (s), 163.5 (s) and 189.0 (s).

2-(2-Phenylethylidene)-1,3-dithiolane 8. Colourless oil (Found: C, 63.7; H, 5.9. $C_{11}H_{12}S_2$ requires C, 63.4; H, 5.8%); δ_H($CDCl_3$) 2.69–3.25 (6 H, m, CH_2) and 7.01–7.36 (6 H, m, ArH and C=CH).

2-Benzoylmethylidene-1,3-dithiolane 9. Pale yellow prisms, mp 79–80 °C (from benzene–hexane) (Found: C, 59.5; H, 4.7. $C_{11}H_{10}OS_2$ requires C, 59.4; H, 4.5%); ν_{max}(KBr) 1610 cm^{-1} (C=O); δ_H($CDCl_3$) 3.36–3.49 (4 H, m, CH_2), 7.24–7.54 (4 H, m, ArH and C=CH) and 7.89–7.99 (2 H, m, ArH); δ_C($CDCl_3$) 35.4 (t), 38.9 (t), 108.1 (d), 127.7 (d), 128.5 (d), 131.9 (d), 138.3 (s), 168.3 (s) and 185.6 (s).

Quenching experiments

To the mixture of the dithiane **1l** (210 mg, 1.0 mmol) and tetramethoxybenzene (297 mg, 1.5 mmol) in MeCN (4.8 cm^3) and H_2O (0.7 cm^3) was added a solution of DDQ (341 mg, 1.5 mmol) in MeCN (1.5 cm^3) under nitrogen. After stirring at room temperature for 0.5 h, the mixture was worked up as described above to give the dithiane **1l** (191 mg, 91%) and aldehyde **4l** (2 mg, 2%).

Competing experiments between dithiane 1a and dithiolane 2a

To the mixture of **1a** (231 mg, 1.0 mmol) and **2a** (217 mg, 1.0 mmol) in MeCN (5.29 cm^3) and H_2O (0.21 cm^3) was added a solution of DDQ (272 mg, 1.2 mmol) in MeCN (1.5 cm^3) under nitrogen. After stirring at room temperature for 3 h, the mixture was worked up as described above to give **1a** (27 mg, 12%), **2a** (195 mg, 90%) and **4a** (113 mg, 80%).

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