Acid-Induced Rearrangement Reactions of α-Hydroxy-1,3-dithianes

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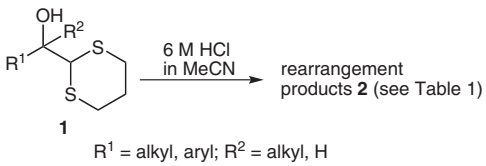
Abstract: Secondary benzylic or aliphatic α-hydroxydithianes **1a–c** rearrange to α-thioketones when treated with acid. Related tertiary alcohols **1d–g** eliminate to dithioketene ketals (e.g., **2d**), which are ring-opened to thiols in some cases (**1e**, **1f**). Allylic α-hydroxydithianes **1h** and **1i** form the thioesters **2h** and **2i** (homologation), and the tertiary alcohols **1j** and **1k** undergo deoxygenation to **2j** and **2k**.

Key words: 1,3-dithianes, dithioacetals, 1,3-dithian-1-oxides, rearrangement, deoxygenation, homologation

Dithioacetals are useful protecting groups for carbonyl compounds due to their ease of formation and their stability under acidic and basic conditions.[1] In addition, they are also umpolung reagents that play an increasing role in natural product synthesis.[2] Recently, we have systematically reinvestigated[3] the scope and limitation of the Kuhn method for cleaving 1,3-dithianes to their parent carbonyl compounds.[4] In this procedure, the monosulfoxides of the respective 1,3-dithianes are cleaved to the carbonyl compounds by treatment with acids. It turned out that the 2-alkyl-1,3-dithianemonosulfoxides are cleaved in essentially quantitative yield under much milder conditions (20–40 °C) than originally proposed by Kuhn, irrespective of steric and electronic factors in the substrates.

However, α-hydroxydithianes, formed by addition of lithio-1,3-dithianes to aldehydes and ketones, are the most important intermediates in umpolung chemistry, and their cleavage under mild acidic conditions would be of great interest. It is known that α-hydroxydithianes are labile under acidic conditions and can undergo several rearrangement reactions,[5] for instance to 1,4-dithiepanes.[5b]

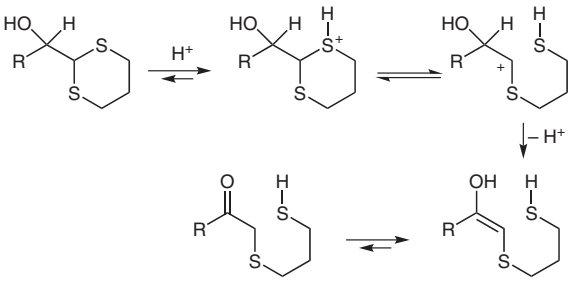
In the course of our ongoing work on the deprotection of 1,3-dithianes, we have now investigated the reaction of some α-hydroxydithianes **1** with the discovery of a number of surprising new and mechanistically interesting rearrangement reactions of α-hydroxydithianes (Scheme 1).



Scheme 1 Rearrangement of α-hydroxydithianes

All substrates **1a–k** were synthesized using a modified version of the Corey and Seebach procedure.[6] The substrates and the resulting products after treatment with acid are compiled in Table 1. All reactions, carried out in acetonitrile solution under reflux with addition of aqueous 6 N HCl, were carefully monitored by TLC. The acid-catalyzed reactions of **1a–c** afforded not the expected α-hydroxy carbonyl compounds, but the rearranged α-keto thiols **2a–c**. To the best of our knowledge, this type of rearrangement of α-hydroxydithianes with oxidation of the hydroxy group and reduction of the dithiane is without precedent.

A possible mechanism for the formation of the keto thiols is shown in Scheme 2. Thus, protonation of a sulfur atom, elimination of the β-atom from the stabilized open chain carbocation, enol formation, and tautomerization would lead to the keto thiols.[7]



Scheme 2 Formation of keto thiols from α-hydroxydithianes

Compounds **1d** and **1g** both gave elimination products. Reaction of **1d** resulted in the formation of the ketene acetal **2d** and cyclohexene **2g** was obtained from **1g**. Interestingly, the endocyclic double bond is more stable than the dithiane conjugated double bond. The formation of **2g** is probably due to acid-induced isomerization of the corresponding ketene acetal, which is formed initially. Reactions of **1e** and **1f** surprisingly gave the olefins **2e** and **2f**, instead of the expected ketene acetals (or ring-expansion products) in 64 and 71% yield, respectively. This unusual reaction can possibly be induced photochemically[8] or by participation of the reductive 1,3-dithiane.[9] The reactions of **1h**,**i** resulted in the formation of thiol esters **2h**,**i**. The putative mechanism for this conversion via the intermediate dithioketene acetals is shown in Scheme 3.[10]

Elimination leads to the ketene acetal, which is then hydrolyzed stepwise via two intermediates, the carbocation **D** and the orthothioester **E**, to give the thiol ester. The mechanism was confirmed by conversion of isolated pure

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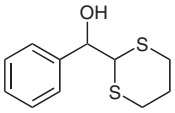
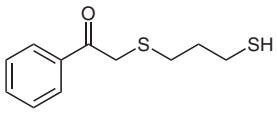
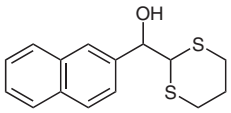
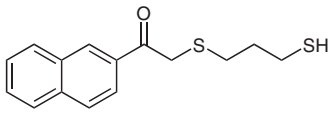
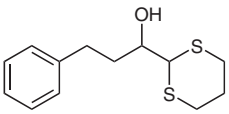
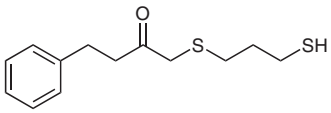
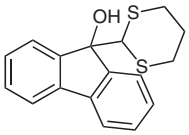
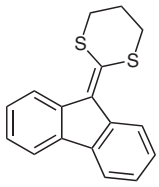
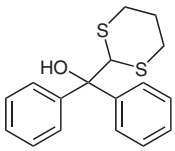
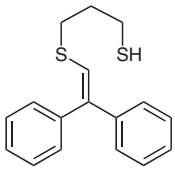
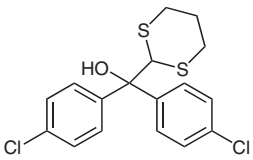
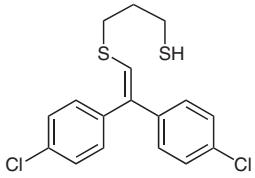
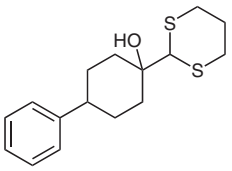
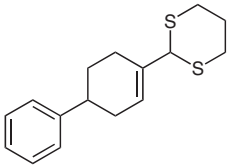
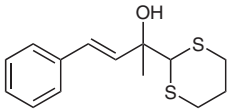
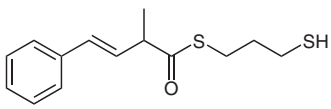
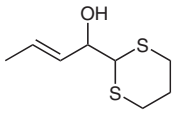
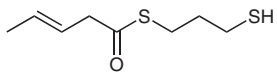
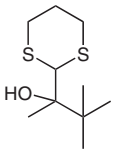
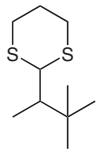
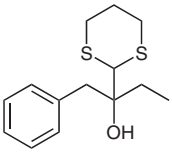
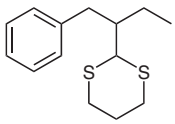
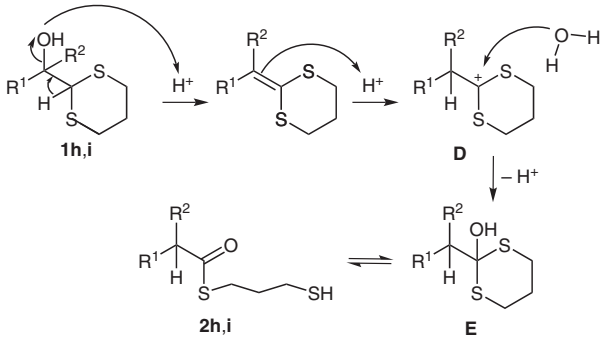
Table 1 Results of Rearrangement Reactions

Entry	Dithiane	Time (h)	Product	Yield (%)
1a		3.5	**2a** 	48
1b		3	**2b** 	53
1c		35	**2c** 	45
1d		1.5	**2d** 	88
1e		2	**2e** 	64
1f		16	**2f** 	71
1g		24	**2g** 	53
1h		1	**2h** 	80
1i		20 min	**2i** 	50
1j		3	**2j** 	79
1k		24	**2k** 	49



Scheme 3 Formation of thiol esters **2h**,**i**[6]

ketene acetals into the thioesters. Overall, α-hydroxy aldehydes are transformed into the saturated esters, again with transfer of the oxidation state, but this time with oxidation and not reduction of the dithiane. Taken together, this transformation is the homologation of a ketone to the corresponding thioester.[11]

Another surprising result was the conversion of **1j** and **1k** into the dithianes **2j** and **2k**, which proceeded in good yields; the mechanism of this reduction is not clear but it must involve a reduction step, perhaps by the presence of excess dithiane.[9]

In summary, we found a new rearrangement reaction of secondary benzylic and aliphatic α-hydroxydithianes **1a–c** to α-thioketones, while related allylic α-hydroxydithianes **1h** and **1i** gave thioesters under the same reaction conditions. The open chain stabilized olefinic thiols **2e** and **2f** were generated from diphenylic α-hydroxydithianes **1e** and **1f**, while the reaction of the related fluorene-derived dithiane **1d** resulted in the formation of the dithioketene acetal **2d**. Remarkably, the deoxygenated products **2j** and **2k** were formed in the reaction of the aliphatic tertiary α-hydroxydithianes **1j** and **1k**.

Column chromatography was performed on silica gel 60 (particle size 0.040–0.063 mm). Melting points were measured on a Büchi SMP-20 melting point apparatus using one-side-open capillary tubes and are not corrected. NMR spectra were recorded on a Bruker ARX 200 or ARX 500 instrument at r.t. Chemical shifts are given in ppm relative to TMS. IR spectra were measured on a Nicolet 510P FT-IR Spectrometer. Solvents were purified, if necessary, by standard methods. Petroleum ether (PE) used refers to the fraction boiling in the range 30–50 °C.

α-Hydroxy-1,3-dithianes 1; General Procedure

A solution of 1,3-dithiane (10 mmol) in anhyd THF (50 mL) was cooled to –20 °C under N_2. *n*-BuLi (11 mmol) was added dropwise and the mixture was stirred for 1.5–2 h. The respective aldehyde/ketone (10 mmol) in THF (10 mL) was then added at –78 °C and the mixture was stirred for 4–5 h at this temperature. The reaction was quenched by the addition of aq NH_4Cl (30 mL) and extracted with CH_2Cl_2 (2 × 50 mL). The combined organic layers were dried (Na_2SO_4), the solvent was evaporated at reduced pressure, and the residue purified by silica gel column chromatography using gradients of PE and EtOAc as the eluents.

(1,3-Dithian-2-yl)(phenyl)methanol (1a)

Yield: 81%.

IR (KBr): 3452, 2904, 1504, 1452, 1272 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.87–2.19 (m, 2 H), 2.64–3.04 (m, 4 H), 4.12 (d, *J* = 8 Hz, 1 H), 4.94 (d, *J* = 8 Hz, 1 H), 7.28–7.52 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.8, 28.1, 28.7, 53.2, 75.1, 127.2, 127.5, 128.6, 128.8, 140.6.

(1,3-Dithian-2-yl)(naphthalen-2-yl)methanol (1b)

Yield: 82%.

IR (KBr): 3417, 2888, 1600, 1417, 1274 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.73–1.97 (m, 2 H), 2.58–2.66 (m, 2 H), 2.77–2.86 (m, 2 H), 4.21 (d, *J* = 7 Hz, 1 H), 5.03 (d, *J* = 7 Hz, 1 H), 7.46–7.87 (m, 7 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.4, 27.9, 28.5, 53.0, 75.1, 124.3, 125.3, 126.1, 127.7, 127.8, 127.9, 128.0, 128.3, 133.4, 137.9.

1-(1,3-Dithian-2-yl)-3-phenylpropan-1-ol (1c)

Yield: 78%.

IR (KBr): 3434, 2904, 1602, 1454, 1276 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.81–2.34 (m, 4 H), 2.65–3.04 (m, 6 H), 3.85–3.97 (m, 2 H), 7.17–7.39 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 26.1, 28.2, 28.7, 32.8, 36.1, 52.7, 71.8, 126.3, 128.8, 12.9, 142.1.

MS (EI): *m*/*z* (%) = 254 (40, $[M]^+$), 119 (100), 91 (35), 77 (20), 41 (10).

HRMS: *m*/*z* calcd for $C_{13}H_{18}OS_2$: 254.08001; found: 254.10492.

9-(1,3-Dithian-2-yl)-9*H*-fluoren-9-ol (1d)

Yield: 85%; mp 154 °C.

IR (KBr): 3534, 2923, 1654, 1446, 1274 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.64–2.13 (m, 2 H), 2.67–2.88 (m, 4 H), 3.03 (s, 1 H), 7.28–7.82 (m, 8 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 26.1, 30.8, 30.9, 27.8, 83.7, 120.3, 124.6, 128.3, 130.2, 140.6, 146.5.

MS (EI): *m*/*z* (%) = 300 (20, $[M]^+$), 181 (25), 165 (30), 152 (45), 119 (100), 72 (10), 45 (5).

HRMS: *m*/*z* calcd for $C_{17}H_{16}OS_2$: 300.06426; found: 300.09541.

(1,3-Dithian-2-yl)diphenylmethanol (1e)

Yield: 85%.

IR (KBr): 3534, 2923, 1654, 1450, 1270 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.81–1.90 (m, 1 H), 2.04–2.11 (m, 1 H), 2.83–2.94 (m, 4 H), 3.29 (s, 1 H), 7.22–7.59 (m, 10 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.2, 30.5, 30.8, 58.6, 80.2, 126.3, 126.7, 127.4, 128.0, 128.3, 143.5.

MS (EI): *m*/*z* (%) = 302 (5, $[M]^+$), 183 (100), 119 (65), 105 (60), 77 (25).

HRMS: *m*/*z* calcd for $C_{17}H_{18}OS_2$: 302.08023; found: 302.13077.

Bis(4-chlorophenyl)(1,3-dithian-2-yl)methanol (1f)

Yield: 83%; mp 116 °C.

IR (KBr): 3521, 2896, 1654, 1450, 1272 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.74–2.24 (m, 2 H), 2.78–3.09 (m, 4 H), 3.53 (s, 1 H), 7.27–7.72 (m, 8 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.4, 30.8, 31.0, 58.8, 80.1, 128.3, 128.4, 128.7, 128.8, 133.9, 142.2.

MS (EI): *m*/*z* (%) = 370 (5, $[M]^+$), 280 (20), 240 (30), 165 (35), 139 (50), 119 (100).

HRMS: *m*/*z* calcd for $C_{17}H_{16}Cl_2OS_2$: 370.00196; found: 370.01052.

1-(1,3-Dithian-2-yl)-4-phenylcyclohexanol (1g)
Yield: 81%.

IR (KBr): 3463, 2931, 1654, 1446, 1209 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.59–1.68 (m, 4 H), 1.83–2.14 (m, 4 H), 2.33–2.39 (m, 2 H), 2.61–2.69 (m, 1 H), 2.88–3.02 (m, 4 H), 4.62 (s, 1 H), 7.18–7.33 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.6, 30.2, 30.3, 35.7, 42.4, 54.7, 73.9, 126.1, 126.8, 128.3, 145.7.

MS (EI): *m*/*z* (%) = 294 (10, $[M]^+$), 276 (20), 175 (75), 157 (85), 119 (90), 104 (65), 91 (100), 77 (20), 41 (50).

HRMS: *m*/*z* calcd for $C_{16}H_{22}OS_2$: 294.11147; found: 294.14925.

***trans*-2-(1,3-Dithian-2-yl)-4-phenylbut-3-en-2-ol (1h)**
Yield: 71%.

IR (KBr): 3444, 2900, 1706, 1446, 1272 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.55 (s, 3 H), 1.87–1.90 (m, 1 H), 2.04–2.09 (m, 1 H), 2.79–2.93 (m, 4 H), 4.22 (s, 1 H), 6.41 (d, *J* = 15.2 Hz, 1 H), 6.75 (d, *J* = 15.2 Hz, 1 H), 7.21–7.43 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.5, 26.2, 29.9, 30.3, 59.2, 75.4, 126.6, 126.9, 127.6, 128.5, 128.9, 133.1, 136.1, 146.5.

MS (EI): *m*/*z* (%) = 266 (10, $[M]^+$), 248 (25), 147 (80), 119 (100), 91 (30), 43 (65).

HRMS: *m*/*z* calcd for $C_{14}H_{18}OS_2$: 266.07983; found: 266.08016.

1-(1,3-Dithian-2-yl)but-2-en-1-ol (1i)
Yield: 66%.

IR (KBr): 3426, 2896, 1671, 1421, 1276 cm^{-1}.

^1H NMR (500 MHz, $CDCl_3$): δ = 1.67 (d, *J* = 6.5 Hz, 3 H), 1.78–2.17 (m, 2 H), 2.67–2.96 (m, 4 H), 3.93 (d, *J* = 6.5 Hz, 1 H), 4.21 (t, *J* = 6.4 Hz, 1 H), 5.51 (dd, *J* = 15.3, 6.4 Hz, 1 H), 5.73 (m, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 18.1, 26.0, 28.8, 29.1, 52.9, 74.0, 130.0, 130.2.

MS (EI): *m*/*z* (%) = 190 (15, $[M]^+$), 119 (100), 106 (15), 91 (30), 75 (65), 41 (80).

HRMS: *m*/*z* calcd for $C_8H_{14}OS_2$: 190.04857; found: 190.05057.

2-(1,3-Dithian-2-yl)-3,3-dimethylbutan-2-ol (1j)
Yield: 70%.

IR (KBr): 3505, 2956, 1689, 1421, 1276 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.05 (s, 9 H), 1.30 (s, 3 H), 1.71–2.14 (m, 2 H), 2.78–3.04 (m, 4 H), 4.37 (s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 20.8, 26.2, 26.7, 32.0, 32.1, 39.3, 60.0, 78.2.

MS (EI): *m*/*z* (%) = 220 (20, $[M]^+$), 163 (40), 120 (100), 101 (55), 83 (40).

HRMS: *m*/*z* calcd for $C_{10}H_{20}OS_2$: 220.09568; found: 220.13583.

2-(1,3-Dithian-2-yl)-1-phenylbutan-2-ol (1k)
Yield: 75%.

IR (KBr): 3463, 2931, 1654, 1446, 1209 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.01 (t, *J* = 7.2 Hz, 3 H), 1.59 (q, *J* = 7.3 Hz, 2 H), 1.97–2.13 (m, 2 H), 2.77–2.96 (m, 4 H), 2.91 (d, *J* = 14.1 Hz, 1 H), 3.07 (d, *J* = 14.1 Hz, 1 H), 4.13 (s, 1 H), 7.19–7.36 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 7.4, 25.9, 29.7, 31.1, 31.2, 41.8, 58.4, 76.4, 126.5, 128.1, 130.8, 136.7.

MS (EI): *m*/*z* (%) = 268 (5, $[M]^+$), 176 (10), 148 (30), 119 (100), 91 (55), 57 (75).

HRMS: *m*/*z* calcd for $C_{14}H_{20}OS_2$: 268.09578; found: 268.05951.

Rearrangement Reactions of α-Hydroxy 1,3-Dithianes 1a–k; General Procedure
A solution of α-hydroxy 1,3-dithianes **1a–k** (1 mmol) in MeCN (10 mL) was treated with aq 6 N HCl (0.5 mL) and the mixture was refluxed until the starting material was consumed (TLC monitoring). The solution was then poured into H_2O (20 mL) and extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were washed with brine (20 mL) and dried (Na_2SO_4). The solvent was evaporated at reduced pressure and the residue purified by silica gel column chromatography using gradients of PE and EtOAc as the eluents.

1-Phenyl-2-[(3-sulfanylpropyl)sulfanyl]ethan-1-one (2a)
Yield: 48%.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.94–2.01 (m, 2 H), 2.64–2.75 (m, 4 H), 3.79 (s, 2 H), 7.44–7.59 (m, 3 H), 7.94–7.98 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 28.1, 30.8, 37.0, 37.1, 128.6, 128.7, 133.3, 135.2, 194.4

MS (EI): *m*/*z* (%) = 226 (10, $[M]^+$), 119 (30), 105 (100), 77 (70), 57 (35), 41 (50).

HRMS: *m*/*z* calcd for $C_{11}H_{14}OS_2$: 226.04851; found: 226.10547.

1-(2-Naphthyl)-2-[(3-sulfanylpropyl)sulfanyl]ethan-1-one (2b)
Yield: 53%.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.97–2.05 (m, 2 H), 2.67–2.76 (m, 4 H), 3.91 (s, 2 H), 7.52–7.61 (m, 2 H), 7.85–7.91 (m, 3 H), 8.00 (d, *J* = 8.0 Hz, 1 H), 8.49 (s, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 28.1, 30.8, 37.1, 37.2, 124.3, 126.8, 127.7, 128.5, 128.6, 1287.7, 129.6, 130.5, 132.5, 135.7.

MS (EI): *m*/*z* (%) = 276 (5, $[M]^+$), 170 (30), 155 (100), 127 (85), 106 (25), 77 (10), 41 (10).

HRMS: *m*/*z* calcd for $C_{15}H_{16}OS_2$: 276.06426; found: 276.06534.

4-Phenyl-1-[(3-sulfanylpropyl)sulfanyl]butan-2-one (2c)
Yield: 45%.

IR (KBr): 2925, 2360, 1704, 1454 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 1.78–1.84 (m, 2 H), 2.49–2.60 (m, 4 H), 2.92–2.96 (m, 4 H), 3.16 (s, 2 H), 7.17–7.31 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 23.2, 29.9, 30.3, 32.6, 41.0, 41.6, 126.1, 128.3, 128.4, 140.7, 204.7.

MS (EI): *m*/*z* (%) = 254 (60, $[M]^+$), 236 (10), 133 (20), 106 (100), 91 (90).

HRMS: *m*/*z* calcd for $C_{13}H_{18}OS_2$: 254.08001; found: 254.08721.

2-(9*H*-Fluoren-9-ylidene)-1,3-dithiane (2d)
Yield: 88%.

IR (KBr): 2923, 1685, 1560, 1448 cm^{-1}.

^1H NMR (200 MHz, $CDCl_3$): δ = 2.15–2.22 (m, 2 H), 2.18–3.12 (m, 4 H), 7.26–7.79 (m, 8 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 29.5, 34.4, 36.4, 119.7 125.2, 126.8, 126.9, 127.1, 127.4, 128.4, 130.3, 132.3, 137.0, 138.2, 140.0, 141.1.

MS (EI): *m*/*z* (%) = 282 (10, $[M]^+$), 181 (90), 152 (100), 118 (20), 105 (20), 76 (60), 57 (15), 41 (25).

HRMS: *m*/*z* calcd for $C_{17}H_{14}S_2$: 282.05393; found: 282.05439.

3-[(2,2-Diphenylvinyl)sulfanyl]propane-1-thiol (2e)
Yield: 64%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.03–2.13 (m, 2 H), 2.74–2.91 (m, 4 H), 6.56 (s, 1 H), 7.17–7.44 (m, 10 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 29.3, 32.2, 36.8, 125.4, 126.9, 127.5, 128.3, 129.9, 139.5, 141.8.

MS (EI): *m*/*z* (%) = 286 (10, $[M]^+$), 178 (30), 165 (60), 149 (75), 118 (100), 105 (80), 77 (45), 57 (30), 41 (25).

HRMS: *m*/*z* calcd for $C_{17}H_{18}S_2$: 286.08514; found: 286.08598.

3-{[2,2-Bis(4-chlorophenyl)vinyl]sulfanyl}propane-1-thiol (2f)
Yield: 71%.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.02–2.09 (m, 2 H), 2.74–2.09 (m, 4 H), 6.55 (s, 1 H), 7.07–7.37 (m, 8 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 29.2, 33.1, 36.6, 126.7, 128.1, 128.2, 128.5, 131.0, 133.0, 133.5, 136.8, 137.4, 139.8.

MS (EI): *m*/*z* (%) = 354 (30, $[M]^+$), 280 (20), 244 (30), 165 (25), 119 (85), 106 (100).

HRMS: *m*/*z* calcd for $C_{17}H_{16}Cl_2S_2$: 354.00696; found: 354.00882.

2-(4-Phenylcyclohex-1-en-1-yl)-1,3-dithiane (2g)
Yield: 53%.

IR (KBr): 2921, 1688, 1446, 1272 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.78–3.03 (m, 13 H), 4.61 (s, 1 H), 6.04 (m, 1 H), 7.17–7.32 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 25.7, 27.7, 29.8, 30.6, 31.6, 33.9, 39.6, 53.3, 126.1, 126.8, 128.4, 135.8, 146.5.

MS (EI): *m*/*z* (%) = 276 (90, $[M]^+$), 202 (30), 169 (70), 119 (100), 91 (85), 77 (20), 41 (25).

HRMS: *m*/*z* calcd for $C_{16}H_{20}S_2$: 276.10092; found: 276.10143.

***S*-(3-Sulfanylpropyl) (*E*)-2-Methyl-4-phenylbut-3-enethioate (2h)**
Yield: 80%.

IR (KBr): 2980, 2254, 1687, 1421, 1265 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.39 (d, *J* = 7.6 Hz, 3 H), 1.85–2.01 (m, 2 H), 2.58–2.69 (m, 2 H), 2.94–3.05 (m, 2 H), 3.41–3.52 (m, 1 H), 6.22 (dd, *J* = 14.9, 7.6 Hz, 1 H), 6.53 (d, *J* = 14.9 Hz, 1 H), 7.29–7.42 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.1, 23.4, 27.5, 29.7, 52.2, 126.4, 127.8, 128.4, 128.6, 132.5, 136.7, 200.8.

MS (EI): *m*/*z* (%) = 266 (5, $[M]^+$), 176 (20), 159 (20), 131 (100), 107 (80), 91 (75), 77 (60), 57 (70), 41 (75).

HRMS: *m*/*z* calcd for $C_{14}H_{18}OS_2$: 266.07983; found: 266.08591.

***S*-(3-Sulfanylpropyl) (*E*)-Pent-3-enethioate (2i)**
Yield: 43%.

IR (KBr): 2923, 2360, 1681, 1427 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.75 (d, *J* = 6.4 Hz, 3 H), 2.04–2.11 (m, 2 H), 2.64–2.85 (m, 6 H), 5.37–5.75 (m, 2 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 17.6, 25.4, 29.0, 31.0, 47.1, 128.5, 129.2, 207.3.

MS (EI): *m*/*z* (%) = 190 (30, $[M]^+$), 132 (100), 106 (25), 83 (20), 55 (15).

HRMS: *m*/*z* calcd for $C_8H_{14}OS_2$: 190.04857; found: 190.09946.

2-(3,3-Dimethylbutan-2-yl)-1,3-dithiane (2j)
Yield: 85%.

IR (KBr): 2921, 2360, 1694, 1444 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.99 (s, 9 H), 1.12 (d, *J* = 7.9 Hz, 3 H), 1.62 (m, 1 H), 1.75–1.85 (m, 1 H), 2.03–2.11 (m, 1 H), 2.75–3.09 (m, 4 H), 4.42 (d, *J* = 2.1 Hz, 1 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 11.5, 26.0, 28.3, 30.7, 32.2, 48.9, 52.3.

MS (EI): *m*/*z* (%) = 204 (20, $[M]^+$), 167 (60), 149 (90), 119 (50), 85 (50), 57 (100).

HRMS: *m*/*z* calcd for $C_{14}H_{18}OS_2$: 204.10076; found: 204.10549.

2-(1-Phenylbutan-2-yl)-1,3-dithiane (2k)
Yield: 76%.

IR (KBr): 2929, 2358, 1600, 1454, 1274 cm^{-1}.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 0.95 (t, *J* = 7.5 Hz, 3 H), 1.36–1.46 (m, 1 H), 1.64–1.74 (m, 1 H), 1.80–1.97 (m, 2 H), 2.06–2.13 (m, 1 H), 2.63–2.95 (m, 6 H), 4.15 (d, *J* = 3.6 Hz, 1 H), 7.18–7.31 (m, 5 H).

^{13}C NMR (50 MHz, $CDCl_3$): δ = 12.0, 23.5, 26.4, 31.0, 31.2, 37.0, 47.7, 52.9, 125.9, 128.3, 129.2, 140.6.

MS (EI): *m*/*z* (%) = 252 (30, $[M]^+$), 240 (20), 156 (35), 141 (45), 119 (100), 91 (65), 57 (50), 41 (25).

HRMS: *m*/*z* calcd for $C_{14}H_{20}S_2$: 252.10056; found: 251.99349.

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