Pummerer and Related Rearrangements in 2-Acyl-1,3-Dithiane 1-Oxides

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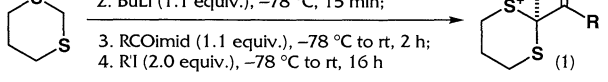
syn- and *anti*-2-Acyl-2-alkyl-1,3-dithiane 1-oxides, when treated with trifluoroacetic anhydride, undergo either an unexpected Pummerer rearrangement or equilibration in near quantitative yield, depending upon the reaction conditions; 2-acyl-1,3-dithiane 1-oxides readily undergo a related rearrangement upon treatment with Lewis acid or exposure to silica gel.

We have developed the uses of 1,3-dithiane 1-oxide (DiTOX) derivatives as combined chiral auxiliaries and asymmetric building blocks for the stereocontrol of a range of carbonyl group reactions.[1-6] In addition we have extended the scope of our alkylation chemistry to the highly stereocontrolled synthesis of substituted seven- and eight-membered carbocyclic rings by diastereoselective one-pot cyclization.[7] We are able to prepare 1,3-dithiane 1-oxide and derivatives in enantiomerically pure form.[8]

Recently we found that the use of *N*-acylimidazoles as electrophiles allows the efficient acylation of non-racemic 1,3-dithiane 1-oxide anion in the presence of excess base, allowing, for the first time, efficient preparation of acylated dithiane oxides with high ee on a reasonable scale, an achievement central to our research effort in this area.[9]

Treatment of the anion derived from 1,3-dithiane 1-oxide with *N*-acylimidazoles under mixed base conditions, as described above, followed by in situ tandem reaction with alkyl iodides is an efficient one-pot method of preparation of 2-acyl-2-alkyl-1,3-dithiane 1-oxides **1** and **2**, with high levels of diastereoselectivity in favour of the *syn* isomers **1** (Scheme 1).[7] This procedure is complementary to our earlier route involving sulfur oxidation as the final stage, which provides predominantly *anti* material.[1] The procedure also circumvents problems of rearrangements, described below, as 2-acyl-1,3-dithiane 1-oxide, which contains a very acidic proton at the C-2 position, is never formed in the reaction.

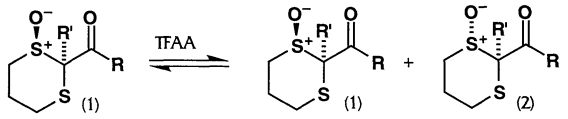


Scheme 1

We were intrigued to discover that treatment of these *syn*-2-acyl-2-alkyl-1,3-dithiane 1-oxides with TFAA (1.1 equiv.) at −78 °C, followed by quenching with water at low temperature, furnishes predominantly the *anti* isomers **2** in high yields (Table 1). A proportion of *syn* isomer remains in each case, however, suggesting that this is an equilibration process and that the *anti* isomers are the more thermodynamically stable.

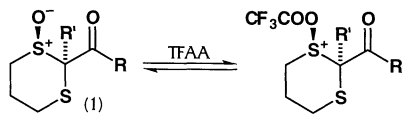
Several mechanisms for such an equilibration in a thioacetal sulfoxide, each involving initial sulfoxide acylation, may be envisaged (Scheme 2). These include participation of the other sulfur atom in a process akin to

Table 1. Epimerization of 2-Acyl-2-Alkyl-1,3-Dithiane 1-Oxides



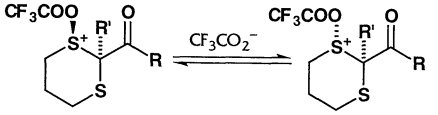
Entry	R'	R	Ratio (1) : (2)	Yield/%
a	Me	Me	1 : 2.1	92
b	Me	Et	1 : 3.3	89
c	Et	Et	1 : 1.1	77

thioacetal hydrolysis (Eq. 1),[10] simple S_N2-like loss of trifluoroacetate with readdition, a known mechanism of sulfoxide racemization (Eq. 2),[11] reversible loss of trifluoroacetic acid as in the first step of a Pummerer rearrangement, a process which could be assisted by an intramolecular proton transfer, (Eq. 3),[12] and sulfenic ester elimination/readdition (Eq. 4).[13]

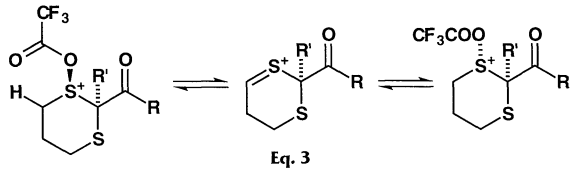


Scheme 2

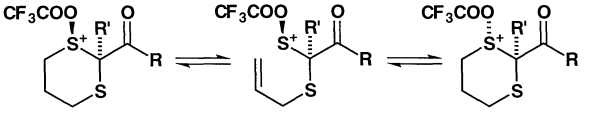
Eq. 1



Eq. 2



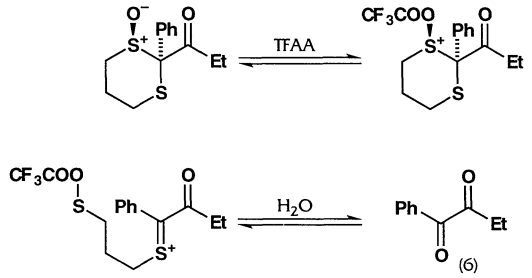
Eq. 3



Eq. 4

The first alternative, which we initally believed to be the most likely, would result in racemization. This proposition was tested by preparation of **1** and **2** (R = Et, R′ = Me) with 89% ee;[8] equilibration and isolation of the isomeric products in each case allowed us to prove that no loss of stereochemical integrity had occurred and that isomerization had taken place at the sulfoxide sulfur atom.

Curiously, use of *syn*-2-phenyl-2-propanoyl-1,3-dithiane 1-oxide **(1)** (R = Et, R′ = Ph) as substrate did not result in isomerization, but in exclusive formation of diketone **6** in 54% yield, suggesting a possible change in reaction pathway to thioacetal hydrolysis (Scheme 3).

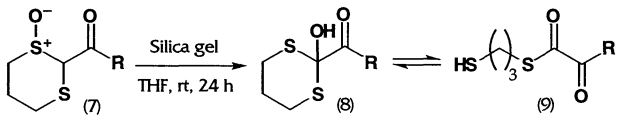


Scheme 3

Evidence that the postulated Pummerer mechanism (Eq. 3) is feasible was provided when the reaction mixtures containing TFAA were allowed to reach room temperature before treatment with water. Pummerer rearrangement was then observed, producing separable mixtures each composed of a stable hemioxathioacetal **3**,[14] together with a vinyl sulfide **4** perhaps resulting from elimination of trifluoroacetate from **5** (Table 2).[15]

During our studies of dithiane acylation we had occasionally observed unwanted transformation of acylated dithiane oxide derivatives containing a proton at C-2 into stable, non-polar materials with an unpleasant odour upon exposure to silica gel for a short period of time (ca. < 2 hours). The same transformation is induced by treatment with zinc(II) chloride. Routine spectroscopic data indicated that the product mixtures contain thiol esters. This led us to reason that acyl dithiane oxides **7** undergo an alternative, unusually facile Pummerer rearrangement under these conditions to produce 2-acyl-2-hydroxy-1,3-dithianes **8**, which undergo isomerization with ring cleavage to form an equilibrium mixture with the thiol esters **9** under the reaction conditions. Accordingly, we exposed solutions of a number of acyl derivatives in THF to silica gel (Merck 9385) for 24 hours, and routinely observed formation of thiol ester containing product mixtures in excellent yields (Table 3). Reactions involving aromatic acyl dithiane oxides were sluggish, requiring treatment with stoichiometric quantities of zinc(II) chloride to liberate the desired thiol ester efficiently. In all cases the products appear to exist as a mixture of the two isomeric forms.

Table 3. Thiolesters from Pummerer Rearrangement of 2-Acyl-1,3-Dithiane 1-Oxides



Substrate	Products	R	Additive	Yield (%)
7a	8/9a	CH_3	—	92
7b	8/9b	CH_3CH_2	—	94
7c	8/9c	$CH_3(CH_2)_5$	—	95
7d	8/9d	$PhCH_2$	$ZnCl_2$	90
7e	8/9e	*t*-BuC_6H_4	$ZnCl_2$	92
7f	8/9f	4-CF_3-C_6H_4	$ZnCl_2$	92

Commercially available reagents were used as supplied unless otherwise stated. Butyllithium was purchased from Aldrich in 100 mL bottles as 1.0 M solutions in hexane, and sodium hexamethyldisilazide (NHMDS) was purchased in 100 mL bottles as 1.0 M solutions in THF. *N*-Acylimidazoles were prepared from the corresponding acid chlorides by treatment with two equivalents of imidazole in THF at 0°C.

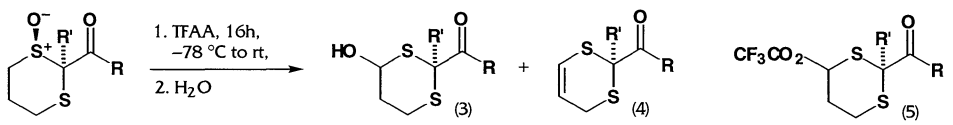
EtOAc and petroleum ether were distilled prior to use. THF was freshly distilled under Ar from the Na/benzophenone ketyl radical before use. Flash column chromatography was carried out using Merck 9385 Kieselgel 60 (230–400 mesh), using an air line to apply pressure to the column. Infrared spectra were recorded in the range 4000–600 cm^{-1} using a Perkin–Elmer 298 spectrophotometer, and were calibrated against the 1602 cm^{-1} absorption of polystyrene ^1HNMR spectra were recorded using Bruker WM250, Bruker ACE200, or Bruker AMX400 instruments using $CDCl_3$ solutions and TMS as internal reference. Mass spectra were obtained on VG Micromass 7070E or AEI MS 902 mass spectrometers. Microanalyses were performed using a Carlo Erba elemental analyser at the University of Liverpool, Department of Chemistry microanalytical laboratory.

Preparation of 2-Acyl-2-alkyl-1,3-dithiane 1-Oxides

syn- and anti-2-Ethanoyl-2-methyl-1,3-dithiane 1-oxide (Table 1, entries **1a and 2a**):

To a solution of *syn*-2-ethanoyl-2-methyl-1,3-dithiane 1-oxide (0.15 g, 0.78 mmol) in THF (20 mL) at −78°C was added trifluoroacetic anhydride (0.12 mL, 0.85 mmol). After 2 h distilled H_2O

Table 2. Pummerer Rearrangement of 2-Acyl-2-alkyl-1,3-dithiane 1-Oxides



Entry	R′	R	Yield (3)/%	Yield (4)/%	Ratio (3) : (4)
a	Me	Me	50	26	1.7 : 1
b	Me	Et	60	27	2.2 : 1
c	Et	Et	40	29	1.4 : 1

(5 mL) was added and the solution was allowed to reach r.t. The crude product was extracted with CH_2Cl_2 and dried ($MgSO_4$). Removal of solvent under reduced pressure gave a yellow oil which was purified by flash column chromatography, eluting with light petroleum/EtOAc (1:1) to give **1a** (0.045 g, 30%) and **2a** (0.093 g, 62%).

For **1a**: mp 63–65 °C

IR (film): $\nu = 1699, 1050\ cm^{-1}$.

^1H NMR ($CDCl_3$, 200 MHz): $\delta = 3.27–2.96$ (3 H, m), 2.48–2.14 (3 H, m), 2.32 (3 H, s), 1.82 (3 H, s).

HRMS (*m/z*) obs: 192.02791 (M^+). Calc. for $C_7H_{12}O_2S_2$: 192.02787.

For **2a**: mp 50–52 °C.

IR (film): $\nu = 1690, 1049\ cm^{-1}$.

^1H NMR ($CDCl_3$, 200 MHz): $\delta = 3.21–2.87$ (2 H, m), 2.37 (3 H, s), 2.63–2.22 (3 H, m), 1.84–1.69 (1 H, m), 1.61 (3 H, s).

HRMS (*m/z*) obs: 192.02791 (M^+). Calc. for $C_7H_{12}O_2S_2$: 192.02787.

syn- and anti-2-Methyl-2-propanoyl-1,3-dithiane 1-Oxide (Table 1, entries **1b and 2b**):

To a solution of *syn*-2-methyl-2-propanoyl-1,3-dithiane 1-oxide (0.10 g, 0.49 mmol) in THF (20 mL) at −78 °C was added trifluoroacetic anhydride (0.075 mL, 0.53 mmol). After 2 h distilled H_2O (5 mL) was added and the solution was allowed to reach r.t. The crude product was extracted with CH_2Cl_2 and dried ($MgSO_4$). Removal of solvent under reduced pressure gave a yellow oil which was purified by flash column chromatography, eluting with light petroleum/EtOAc (1:1) to give **1b** (0.021 g, 21%) and **2b** (0.068 g, 68%).

For **1b**: mp 42–44 °C.

IR (film): $\nu = 1706, 1040\ cm^{-1}$.

^1H NMR ($CDCl_3$, 200 MHz): $\delta = 3.28–2.96$ (3 H, m), 2.78–2.50 (2 H, m), 2.44–2.21 (3 H, m), 1.82 (3 H, s), 1.03 (3 H, t, $J = 7.14$ Hz).

HRMS (*m/z*) obs: 206.04355 (M^+). Calc. for $C_8H_{14}O_2S_2$: 206.04352.

For **2b**: mp 55–57 °C.

IR (film): $\nu = 1689, 1043\ cm^{-1}$.

^1H NMR ($CDCl_3$, 200 MHz): $\delta = 3.23–3.09$ (1 H, m), 3.01–2.81 (2 H, m) 2.71–2.55 (4 H, m), 1.84–1.68 (1 H, m), 1.61 (3 H, s), 1.05 (3 H, t, $J = 7.15$ Hz).

HRMS (*m/z*) obs. 206.04355 (M^+). Calc. for $C_8H_{14}O_2S_2$: 206.04352.

syn- and anti-2-Ethyl-2-propanoyl-1,3-dithiane 1-Oxide (Table 1, entries **1c and 2c**):

To a solution of *syn*-2-ethyl-2-propanoyl-1,3-dithiane 1-oxide (0.42 g, 1.91 mmol) in THF (50 mL) at −78 °C was added trifluoroacetic anhydride (0.30 mL, 2.12 mmol). After 2 h distilled H_2O (10 mL) was added and the solution was allowed to reach r.t. The crude product was extracted with CH_2Cl_2 and dried ($MgSO_4$). Removal of solvent under reduced pressure gave a yellow oil which was purified by flash column chromatography, eluting with light petroleum/EtOAc (1:1) to give **1c** (0.154 g, 37%) and **2c** (0.171 g, 40%).

For **1c**: mp 69–71 °C.

IR (film): $\nu = 1708, 1046\ cm^{-1}$.

^1H NMR ($CDCl_3$, 200 MHz): $\delta = 3.28–2.01$ (10 H, m), 1.11 (3 H, t, $J = 14$ Hz), 1.06 (3 H, t, $J = 7.42$ Hz).

HRMS (*m/z*) obs: 220.05953 (M^+).

Calc. for $C_9H_{16}O_2S_2$: 220.05917.

For **2c**: mp 63–65 °C.

IR (film): $\nu_{max} = 1688, 1054\ cm^{-1}$.

^1H NMR ($CDCl_3$, 200 MHz): $\delta = 3.14–2.94$ (2 H, m), 2.73–2.35 (3 H, m), 2.29–2.10 (2 H, m), 1.92–1.73 (3 H, m), 1.14 (3 H, t, $J = 7.42$ Hz), 1.02 (3 H, t, $J = 7.42$ Hz).

HRMS (*m/z*) obs: 220.05953 (M^+). Calc. for $C_9H_{16}O_2S_2$: 220.05917.

Rearrangement of 2-Acyl-2-allyl-1,3-dithiane Oxides

2-Ethanoyl-4-hydroxy-2-methyl-1,3-dithiane (Table 2, entry **3a**) *and 2-Acetyl-2-methyl-1,3-dithi-4-in* (Table 2, entry **4a**):

To a solution of *syn*-2-ethanoyl-2-methyl-1,3-dithiane 1-oxide (0.20 g, 1.04 mmol) in THF (50 mL) at −78 °C was added trifluoroacetic anhydride (0.16 mL, 1.13 mmol). The solution was stirred at −78 °C for 2 h, was allowed to reach r.t. over 17 h and was then treated with distilled H_2O (10 mL). The crude product was extracted with CH_2Cl_2 and dried ($MgSO_4$). Removal of solvent under reduced pressure gave a yellow oil which was purified by flash column chromatography, eluting with light petroleum/EtOAc (95:5) to furnish **3a** (0.10 g, 50%) and **4a** (0.05 g, 26%) as yellow oils.

For **3a**:

IR (film): $\nu = 3376, 1685\ cm^{-1}$.

^1H NMR ($CDCl_3$, 200 MHz): $\delta = 5.97$ (1 H, d, $J = 8.8$ Hz), 4.89 (1 H, dt, $J = 8.8$ Hz), 2.94–2.79 (1 H, m), 2.50–2.39 (1 H, m), 2.31 (3 H, s), 2.19–2.06 (1 H, m), 1.99–1.72 (1 H, m), 1.66 (3 H, s).

^{13}C NMR ($CDCl_3$, 200 MHz): $\delta = 21.4, 23.6, 25.4, 32.5, 55.8, 70.3, 203.4$.

HRMS (*m/z*) obs: 192.02859 (M^+). Calc. for $C_7H_{12}O_2S_2$: 192.02787.

For **4a**:

IR (film): $\nu = 1709\ cm^{-1}$.

^1H NMR ($CDCl_3$, 200 MHz): $\delta = 6.38–6.33$ (1 H, m), 6.02–5.93 (1 H, m), 3.45–3.14 (2 H, m), 2.35 (3 H, s), 1.83 (3 H, s).

HRMS (*m/z*) obs: 174.01691 (M^+). Calc. for $C_7H_{10}OS_2$: 174.01731.

4-Hydroxy-2-methyl-2-propanoyl-1,3-dithiane (Table 2, entry **3b**) *and 2-Methyl-2-propanoyl-1,3-dithi-4-in* (entry **4b**):

To a solution of *syn*-2-methyl-2-propanoyl-1,3-dithiane 1-oxide (0.20 g, 0.97 mmol) in THF (40 mL) at −78 °C was added trifluoroacetic anhydride (0.15 mL, 1.06 mmol). The solution was stirred at −78 °C for 2 h, was allowed to reach r.t. over 17 h and was then treated with distilled water (10 mL). The crude product was extracted with CH_2Cl_2 and dried ($MgSO_4$). Removal of solvent under reduced pressure gave a yellow oil which was purified by flash column chromatography, eluting with light petroleum/EtOAc (95:5) to furnish **3b** (0.12 g, 60%) and **4b** (0.05 g, 27%) as yellow oils.

For **3b**:

IR (film): $\nu = 3375, 1685\ cm^{-1}$.

^1H NMR ($CDCl_3$, 200 MHz): $\delta = 6.19$ (1 H, m), 4.98–4.93 (1 H, m), 2.77–3.13 (2 H, m), 2.55–1.90 (4 H, m), 1.74 (3 H, s), 1.14 (3 H, t, $J = 7.14$ Hz).

^{13}C NMR ($CDCl_3$, 200 MHz): $\delta = 8.81, 21.4, 24.9, 28.5, 32.6, 55.7, 70.4, 206.2$.

HRMS (*m/z*) obs: 206.04390 (M^+). Calc. for $C_8H_{14}O_2S_2$: 206.04352.

For **4b**: IR (film): $\nu = 1712\ cm^{-1}$.

^1H NMR ($CDCl_3$, 200 MHz): $\delta = 6.22–6.17$ (1 H, m), 6.02–5.92 (1 H, m), 3.43–3.13 (2 H, m), 2.96–2.49 (2 H, m), 1.83 (3 H, s), 1.10 (3 H, t, $J = 7.15$ Hz).

HRMS (*m/z*) obs: 188.03345 (M^+). Calc. for $C_8H_{12}OS_2$: 188.03296.

2-Ethyl-4-hydroxy-2-propanoyl-1,3-dithiane (Table 2, entry **3c**) *and 2-Ethyl-2-propanoyl-1,3-dithi-4-in* (entry **4c**):

To a solution of *syn*-2-ethyl-2-propanoyl-1,3-dithiane 1-oxide (0.075 g, 0.34 mmol) in THF (30 mL) at −78 °C was added trifluoroacetic anhydride (0.05 mL, 0.35 mmol). The solution was stirred at −78 °C for 2 h, was allowed to reach r.t. over 17 h and was then treated with distilled H_2O (10 mL). The crude product was extracted with CH_2Cl_2 and dried ($MgSO_4$). Removal of solvent under reduced pressure gave a yellow oil which was purified by flash column chromatography, eluting with light petroleum/EtOAc (95:5) to furnish **3c** (0.03 g, 40%) and **4c** (0.02 g, 29%) as yellow oils.

For **3c**:

IR (film): $\nu = 3386, 1681\ cm^{-1}$.

^1H NMR ($CDCl_3$, 200 MHz): $\delta = 5.94–5.98$ (1 H, d), 4.95–5.03 (1 H, m), 3.12–3.21 (1 H, m), 1.82–2.92 (7 H, m), 1.17 (3 H, t, $J = 7.7$ Hz), 1.06 (3 H, t, $J = 7.42$ Hz).

HRMS (m/z) obs: 220.05909 (M^+). Calc. for $C_9H_{16}O_2S_2$: 220.05917.

For **4c**:

IR (film): $\nu = 1710\ cm^{-1}$.

^1H NMR ($CDCl_3$, 200 MHz): $\delta = 6.30–6.36$ (1 H, m), 5.88–5.98 (1 H, m), 3.10–3.36 (2 H, m), 2.78–2.97 (1 H, m), 2.48–2.68 (1 H, m), 2.15–2.27 (2 H, m), 1.11 (3 H, t, $J = 7.42$ Hz), 1.05 (3 H, t, $J = 7.14$ Hz).

HRMS (m/z) obs: 202.04849 (M^+). Calc. for $C_9H_{14}OS_2$: 202.04861.

1-Phenylbutane-1,2-dione **(6):**

To a solution of *syn*-2-phenyl-2-propanoyl-1,3-dithiane 1-oxide (0.160 g, 0.60 mmol) in THF (20 mL) at −78 °C was added trifluoroacetic anhydride (0.09 mL, 0.64 mmol). The solution was stirred at −78 °C for 2 h, was allowed to reach r.t. over 17 h and was then treated with distilled H_2O (10 mL). The crude product was extracted with $CHCl_2$ and dried ($MgSO_4$). Removal of solvent under reduced pressure gave a yellow oil which was purified by flash column chromatography, eluting with light petroleum/EtOAc (95:5) to furnish 6 (0.052 g, 54%) as a bright yellow oil.

IR (film): $\nu = 1715, 1674\ cm^{-1}$.

^1H NMR ($CDCl_3$, 200 MHz): $\delta = 7.96–8.01$ (2 H, m), 7.61–7.69 (1 H, m), 7.46–7.54 (2 H, m), 2.92 (2 H, q, $J = 7.43$ Hz), 1.20 (3 H, t, $J = 7.43$ Hz).

HRMS (m/z) obs: 162.06752 (M^+). Calc. for $C_{10}H_{10}O_2$: 162.06808.

Preparation of 2-Acyl-1,3-dithiane 1-Oxides:

To a solution of 1,3-dithiane 1-oxide (DiTOX) in THF was added sodium hexamethyldisilazide (NHMDS, 1.1 equiv. of a 1.0 mol dm^{-3} solution in THF) at −78 °C under a N_2 atmosphere. The solution was stirred for 10 min and was then treated with BuLi (1.1 equiv. of a 1.6 mol dm^{-3} solution in hexanes). After a further 10 min at −78 °C, *N*-acylimidazole (1.1 equiv) was added; the resulting yellow precipitate was stirred for 2 h and was allowed to warm to r.t. The reaction mixture was quenched with sat. NH_4Cl, and the crude product was extracted into CH_2Cl_2 (3 × 100 mL). The organic extracts were washed with sat. $NaHCO_3$ (100 mL) and were dried ($MgSO_4$). The solvent was removed by evaporation under reduced pressure to liberate the crude material which was purified by flash column chromatography on silica gel, eluting with EtOAc, to furnish the product as a pale yellow oil, which was dried in vacuo.

2-Ethanoyl-1,3-dithiane 1-Oxide (Table 3, entry **7a**):

1,3-Dithiane 1-oxide (1 g, 7.35 mmol) was treated with NHMDS (8.1 mL, 8.08 mmol), BuLi (5.1 mL, 8.08 mmol) and *N*-acetylimidazole (0.89 g, 8.08 mmol) as described above to furnish **7a** (1.07 g, 81%) after normal workup, extraction, and purification.

IR (film): $\nu = 1700, 1048\ cm^{-1}$.

^1H NMR ($CDCl_3$, 200 MHz): $\delta = 4.7$ and 4.4 (1 H, s), 4.0–3.5 (1 H, m), 3.4–3.2 (1 H, m), 3.0–2.3 (6 H, m), 2.2–1.9 (1 H, m).

HRMS (m/z) obs. 178.01248 (M^+). Calc. for $C_6H_{10}O_2S_2$: 178.01222.

2-Propanoyl-1,3-dithiane 1-Oxide (Table 3, entry **7b**):

1,3-Dithiane 1-oxide (1.14 g, 8.42 mmol) was treated with NHMDS (9.3 mL, 9.26 mmol), BuLi (5.8 mL, 9.26 mmol) and *N*-propionylimidazole (1.15 g, 9.26 mmol) as described above to furnish **7b** (1.3 g, 79%) after normal workup, extraction, and purification.

IR (film): $\nu = 1710, 1052\ cm^{-1}$.

^1H NMR ($CDCl_3$, 400 MHz): $\delta = 4.6$ and 4.1 (1 H, s), 3.4 (1 H, m), 2.9–2.4 (7 H, m), 1.05–1.0 (3 H, t, $J = 7$ Hz).

HRMS (m/z) obs: 192.02787 (M^+). Calc. for $C_7H_{12}O_2S_2$: 192.02787.

2-Heptanoyl-1,3-dithiane 1-Oxide (Table 3, entry **7c**):

1,3-Dithiane 1-oxide (0.24 g, 1.76 mmol) was treated with NHMDS (1.9 mL, 1.9 mmol), BuLi (1.2 mL, 1.9 mmol) and *N*-heptanoylimidazole (0.47 g, 1.9 mmol) as described above to furnish **7c** (0.30 g, 94%) after normal workup, extraction, and purification.

IR (film): $\nu = 1710, 1040\ cm^{-1}$.

^1H NMR ($CDCl_3$, 200 MHz): $\delta = 4.8$ and 4.4 (1 H, s), 3.5 (1 H, m), 2.9–2.0 (5 H, m), 2.0–1.7 (3 H, m), 1.2 (3 H, m), 1.0–0.9 (3 H, t, $J = 7$ Hz).

MS (EI) $m/z = 248$ (M^+).

2-(Phenylethanoyl)-1,3-dithiane 1-Oxide (Table 3, entry **7d**):

1,3-Dithiane 1-oxide (0.24 g, 1.76 mmol) was treated with NHMDS (1.9 mL, 1.9 mmol), BuLi (1.2 mL, 1.9 mmol) and *N*-(phenylethanoyl)imidazole (0.49 g, 2.64 mmol) as described above to furnish **7d** (0.41 g, 92%) after normal workup, extraction, and purification.

IR (film): $\nu = 701, 1038\ cm^{-1}$.

^1H NMR ($CDCl_3$, 200 MHz): $\delta = 7.4–7.2$ (5 H, m), 4.8 and 4.5 (1 H, s), 3.7–3.5 (2 H, m), 3.5–2.0 (6 H, m).

HRMS (m/z) obs: 254.04366 (M^+). Calc. for $C_{12}H_{14}O_2S_2$: 254.04352.

2-(4-tert-Butylphenyl)-1,3-dithiane 1-Oxide (Table 3, entry **7e**):

1,3-Dithiane 1-oxide (0.31 g; 2.27 mmol) was treated with NHMDS (2.5 mL, 2.5 mmol), BuLi (1.5 mL, 2.5 mmol) and *N*-(4-*tert*-butylphenyl)imidazole (0.77 g, 3.42 mmol) as described above to furnish **7e** (0.62 g, 92%) after normal workup, extraction, and purification.

IR (film): $\nu = 1679, 1043\ cm^{-1}$.

^1H NMR ($CDCl_3$, 200 MHz): $\delta = 8.0–7.8$ (2 H, m), 7.7–7.2 (2 H, m), 5.6 and 5.4 (1 H, s), 3.2–2.9 (3 H, m), 2.9–2.2 (3 H, m), 1.5 (9 H, s).

HRMS (m/z) obs: 296.09037 (M^+). Calc. for $C_{15}H_{20}O_2S_2$: 296.090047.

2-(4-trifluorobenzoyl)-1,3-dithiane 1-Oxide (Table 3, entry **7f**):

1,3-Dithiane 1-oxide (0.21 g, 1.69 mmol) was treated with NHMDS (1.7 mL, 1.69 mmol), BuLi (1.1 mL, 1.69 mmol) and *N*-(*p*-trifluoro)benzoylimidazole (0.55 g, 2.5 mmol) as described above to furnish **7f** (0.48 g, 92%) after normal workup, extraction, and purification.

IR (film): $\nu = 1734, 1044\ cm^{-1}$.

^1H NMR ($CDCl_3$, 200 MHz): $\delta = 8.4–8.1$ (2 H, m), 8.0–7.8 (1 H, m), 7.7–7.5 (1 H, m), 5.4 and 5.1 (1 H, s), 3.9–3.2 (1 H, m), 3.4–2.2 (5 H, m).

HRMS (m/z) obs: 308.01534 (M^+). Calc. for $C_{12}F_3H_{11}O_2S_2$: 308.01526.

Pummerer Rearrangement of 2-Acyl-1,3-dithiane 1-Oxides:

A solution of 2-acyl-1,3-dithiane 1-oxide in THF under a N_2 atmosphere was treated with a small quantity of silica gel (Merck 9385) and was stirred for 24 h at r.t.. In the case of aromatic derivatives, zinc(II) chloride (1.0 equiv of a 1.0 mol dm^{-3} solution in Et_2O) was added. A colour change from pale yellow to deep amber was observed, indicating the formation of thiol ester containing product. The crude material was purified by column chromatography on silica gel, eluting with light petroleum/EtOAc (98:2), to furnish the product mixture in near quantitative yield.

Pummerer Rearrangement of **7a** (Table 3, entry **8/9a**):

A solution of **7a** (0.12 g, 0.67 mmol) in THF (50 mL) was treated with silica gel and purified as described above to furnish **8/9a** (0.11 g, 92%).

IR (film): $\nu = 3117, 2911, 1722\ cm^{-1}$.
MS (EI): m/z 119, 106, 93, 71, and 43.

Pummerer Rearrangement of **7b** (Table 3, entry **8/9b**):

A solution of **7b** (0.70 g, 3.65 mmol) in THF (80 mL) was treated with silica gel and purified as described above to furnish **8/9b** (0.66 g, 94%).

IR (film): $\nu = 3459, 2937, 1668\ cm^{-1}$.

^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.3–3.1 (1 H, m), 3.0 (3 H, m), 2.8 (3 H, m), 2.6 (2 H, m), 2.0 (3 H, m), 1.8 (1 H, s), 1.2 (3 H, t, J = 7 Hz).

^{13}C NMR ($CDCl_3$, 250 MHz): δ = 201.853, 196.330, 191.798, 33.334, 30.705, 29.673, 29.374, 29.114, 28.2567, 28.074, 27.871, 25.298, 7.617.

MS (EI): m/z = 191, 123, 119, 106, 85, 71, 57 and 43.

Pummerer Rearrangement of **7c** (Table 3, entry **8/9c**):

A solution of **7c** (0.10 g, 0.4 mmol) in THF (50 mL) was treated with silica gel and purified as described above to furnish **8/9c** (0.095 g, 95%).

IR (film): ν = 3421, 2929, 1719, 1675 cm^{-1}.

MS (EI) m/z = 21, 119, 85, 71, 57, 43.

Pummerer Rearrangement of **7d** (Table 3, entry **8/9d**):

A solution of **7d** (0.10 g, 0.39 mmol) in THF (50 mL) was treated with silica gel and $ZnCl_2$ (0.35 mL, 0.35 mmol) and was purified as described above to furnish **8/9d** (0.09 g, 90%).

IR (film): ν = 3195, 2975, 1669, 1495 cm^{-1}.

MS (EI): m/z = 19, 45.

Pummerer Rearrangement of **7e** (Table 3, entry **8/9e**):

A solution of **7e** (0.13 g, 0.43 mmol) in THF (50 mL) was treated with silica gel and $ZnCl_2$ (0.43 mL, 0.43 mmol) and was purified as described above to furnish **8/9e** (0.12 g, 92%).

IR (film): ν = 3421, 2927, 1719, 1675 cm^{-1}.

MS (EI): m/z = 91, 119, 106, and 41.

Pummerer Rearrangement of **7f** (Table 3, entry **8/9f**):

A solution of **7f** (0.10 g, 0.324 mmol) in THF (50 mL) was treated with silica gel and $ZnCl_2$ (0.35 mL, 0.35 mmol) and was purified as described above to furnish **8/9f** (0.095 g, 92%).

IR (film): ν = 3199, 2969, 1685, 1611 cm^{-1}.

MS (EI): m/z = 297, 174, 125, 106, 85, 57, and 41.

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