Effect of Added Benzoic Acid on the Phase-Transfer Catalysed Permanganate Oxidation of Organosulfur Compounds

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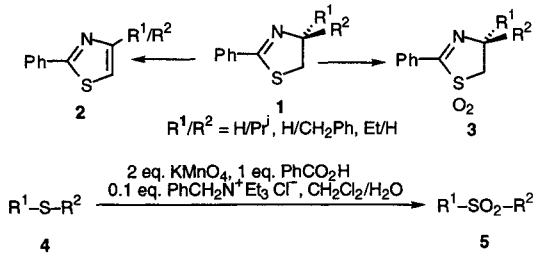
The addition of benzoic acid in the oxidation of a range of sulfides and thiazolidinethiones using $KMnO_4$ under phase-transfer conditions provides a convenient and high yielding procedure for formation of the corresponding sulfones, thiazolidinones and thiazolidinone *S,S*-dioxides.

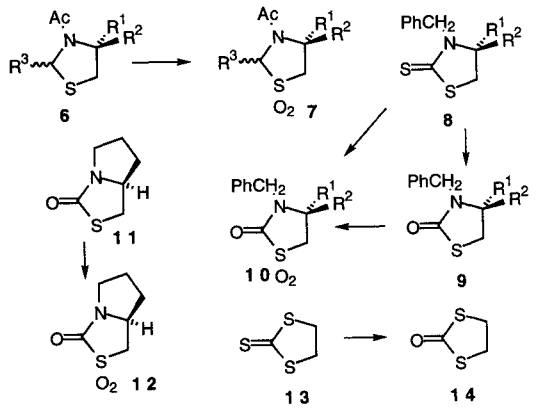
Among the many oxidants commonly used for oxidation of sulfides to sulfoxides and sulfones, potassium permanganate is well established both in homogeneous media, particularly acetic acid, and under phase-transfer catalysis (PTC) conditions.[1] Despite this, the precise mechanism involved in these reactions is still the subject of some controversy.[2] In the course of a detailed study of the behaviour of chiral 2-thiazolines **1** towards a variety of oxidising agents,[3] we made the surprising observation that, while reaction of **1** with $KMnO_4$ under PTC conditions gave the corresponding thiazoles **2**, addition of 1 equivalent of benzoic acid resulted in a complete change in favour of *S*-oxidation to give the thiazoline *S,S*-dioxides **3** in 85–93% yield. This is indicative that the nature of the oxidising species has changed. The obvious explanation, that peroxybenzoic acid is being formed *in situ*, seems unlikely since treatment of **1** with $PhCO_3H$ in $CHCl_3$ gave some **2** in addition to **3** and its hydrolysis products. While the precise nature of the oxidising species remains unknown, we report here that this method allows convenient oxidation of a variety of sulfides **4** to the corresponding sulfones **5** in high yield (Scheme 1).



Scheme 1

The oxidation was carried out by vigorously stirring a solution of sulfide and benzoic acid (1 equiv) in dichloromethane with an aqueous solution of $KMnO_4$ (2 equiv) and benzyltriethylammonium chloride (0.1 equiv) at room temperature. After addition of metabisulfite to dissolve the MnO_2, the mixture is simply filtered and the organic layer separated and evaporated to afford the analytically pure sulfone. As shown in the Table this procedure is suitable for a variety of simple sulfides **4**, for dibenzyl sulfoxide, and for the thiazolidines **6**. In these cases one mole of $KMnO_4$ is sufficient to oxidise 0.75 mole of sulfide to sulfone so the 2 equivalents used is 50% excess. The amount of benzoic acid was found to be optimal at 1 mole per mole of sulfide: use of 2 moles gave no advantage while use of < 1 mole resulted in incomplete reaction. The benzoic acid ends up as potassium benzoate in the aqueous layer and indeed its action in neutralising the KOH which would otherwise be formed in the oxidation may partly explain the high yields obtained for products such as **3** which are susceptible to hydrolysis.

As we have recently noted in a brief report,[4] this reagent system also gave excellent results in converting the exocyclic C=S of thiazolidine-2-thiones **8** into C=O and in this case, although sulfur was precipitated, three equivalents of $KMnO_4$ were required for optimum yields. The resulting thiazolidin-2-ones **9** could then be further oxidised to their *S,S*-dioxides as before or, alternatively, treatment of **8** with 5 equivalents of $KMnO_4$ gave the sulfones **10** directly. The bicyclic thiazolidinone **11** and the dithiolanethione **13** also gave good results (Scheme 2).



Scheme 2

As expected other carboxylic acids can be used to give similar results. Replacement of benzoic acid by 1 equivalent of acetic acid in the oxidation of **1a** gave just as good a result, but the method described here is clearly superior to use of $KMnO_4$ in aqueous acetic acid which with **8a** gave only 10% oxidation to a mixture of **9a** and **10a**. For all three compounds **1**, oxidation with peracetic acid in acetic acid gave $\leq 5\%$ of **3** while with **9** yields of **10** were only $\approx 30\%$. As already noted, omission of the benzoic acid under PTC conditions gave the thiazoles **2** from **1**, while with **8** oxidation only proceeded as far as the thiazolidinones **9** in poor yield and these could not be oxidised further even with a large excess of $KMnO_4$. For the simple sulfides **4** omission of the benzoic acid led to much reduced yields of the sulfones **5**. A further attraction of the present procedure is the convenient workup in which all the byproducts and excess

Table. Oxidation of Organosulfur Compounds

Starting Material[a]	R^1	R^2	R^3	$KMnO_4$ (equiv)	Product	Yield[b] (%)
4a	Ph	$PhCH_2$	–	2	**5a**	82
4b	Et	$PhCH_2$	–	2	**5b**	66
4c	*i*-Pr	$PhCH_2$	–	2	**5c**	61
4d	$PhCH_2$	$PhCH_2$	–	2	**5d**	78
4d*	$PhCH_2$	$PhCH_2$	–	1	**5d***	75
4e	$4\text{-}ClC_6H_4$	$PhCH_2$	–	2	**5e**	63
4f	$4\text{-}NO_2C_6H_4CH_2$	Ph	–	2	**5f**	71
4g	CH_2CO_2Me	Et	–	2	**5g**	79
4h	CH_2CO_2Et	Et	–	2	**5h**	60
4i	CH_2CO_2Me	Ph	–	2	**5i**	66
4j	CH_2CO_2Et	Ph	–	2	**5j**	52
6a	CO_2Me	H	H	2	**7a**	50
6b	CO_2Me	H	Et	2	**7b**	90
6c	CO_2Me	H	*i*-Pr	2	**7c**	95
6d	CO_2Me	H	Ph	2	**7d**	93
6e	H	$PhCH_2$	*t*-Bu	2	**7e**	90
8a	H	$PhCH_2$	–	3	**9a**	75
8b	H	*i*-Pr	–	3	**9b**	65
8c	Et	H	–	3	**9c**	76
8a	H	$PhCH_2$	–	5	**10a**	67
8b	H	*i*-Pr	–	5	**10b**	33
9c	Et	H	–	2	**10c**	72
8c	Et	H	–	5	**10c**	70
11	–	–	–	2	**12**	70
13	–	–	–	3	**14**	70

[a] **4d*** = Dibenzyl sulfoxide.
[b] Yield of isolated product.

reagents are removed by simple separation of the aqueous layer to give the products directly in pure form.

Melting points were determined on a Reichert hot-stage microscope and are uncorrected. IR spectra were recorded for solids as Nujol mulls and for liquids as thin films on a Perkin Elmer 1420 spectrophotometer. NMR spectra were recorded for ^1H at 300 MHz and for ^{13}C at 75 MHz on a Bruker AM300 instrument in $CDCl_3$ unless otherwise indicated, with TMS as internal reference. Chemical shifts are reported in ppm to high frequency of the reference and coupling constants J are given in Hz. The abbreviation quat in ^{13}C NMR data refers to quaternary carbons. Mass spectra were obtained on an A.E.I. MS902 instrument using electron impact at 70 eV unless otherwise indicated. Chemical ionisation spectra were obtained on a VG Autospec using ammonia as the ionising gas. Optical rotations were measured on an Optical Activity AA1000 polarimeter and are given in units of 10^{-1} deg cm^2 g^{-1}.

The sulfides **4a**,[5] **4b**,[6] **4c**,[7] **4d**,[8] **4e**,[9] **4f**,[10] **4g**,[11] **4h**,[12] **4i**[13] and **4j**[12] and dibenzyl sulfoxide (**4d***), all known compounds, were either commercially available or were prepared by treating the appropriate thiol in EtOH with NaOEt followed by the appropriate alkyl halide and had properties in good agreement with the literature data as shown.

The thiazolidines **6a–d** were prepared following a literature procedure[14] involving treatment of (*R*)-cysteine in H_2O with the appropriate aldehyde in EtOH, followed by esterification with MeOH in the presence of $SOCl_2$ and acetylation with Ac_2O.

(R)-3-Acetyl-4-methoxycarbonylthiazolidine (**6a**):

Colourless oil, bp (oven temp.) 160 °C/0.2 Torr (Lit.[15] bp 152 °C/0.5 Torr).

(R)-3-Acetyl-2-ethyl-4-methoxycarbonylthiazolidine (**6b**):

Colourless oil (as a 63:37 mixture of diastereomers), bp 180 °C/0.8 Torr.

HRMS: *m/z* calcd for $C_9H_{15}NO_3S$ 217.0773; found 217.0783.

IR: ν = 1750 (CO), 1650 (CO) cm^{-1}.

major diastereomer:

^1H NMR: δ = 1.05 (t, 3 H, J = 7), 1.80 (m, 1 H), 2.00 (m, 1 H), 2.20 (s, 3 H), 3.3–3.5 (m, 2 H), 3.75 (s, 3 H), 4.8–5.0 (m, 2 H).

^{13}C NMR: δ = 11.4 (CH_3), 22.0 (CH_3), 30.7 (CH_2), 31.6 (CH_2), 52.5 (OCH_3), 62.1 (CH), 67.3 (CH), 168.1 (CO), 171.1 (CO).

minor diastereomer:

^1H NMR: δ = 0.9 (t, 3 H, J = 7), 1.55 (m, 1 H), 2.10 (s, 3 H), 2.15 (m, 1 H), 3.3–3.5 (m, 2 H), 3.85 (s, 3 H), 4.8 (m, 1 H), 5.3 (dd, 1 H, J = 11, 4).

^{13}C NMR: δ = 11.2 (CH_3), 23.0 (CH_3), 29.2 (CH_2), 33.2 (CH_2), 52.9 (CH_3), 63.1 (CH), 66.1 (CH), 168.6 (CO), 170.9 (CO).

MS: *m/z* (%) = 217 (M^+, 55), 188 (60), 158 (40), 146 (95), 131 (75), 116 (75), 98 (45), 86 (80), 68 (50), 59 (85), 43 (100).

(R)-3-Acetyl-2-isopropyl-4-methoxycarbonylthiazolidine (**6c**):

Colourless oil (as a 64:36 mixture of diastereomers), bp 193 °C/0.4 Torr.

$C_{10}H_{17}NO_3S$	calc.	C 51.92	H 7.41	N 6.05
(231.3)	found	52.14	7.44	6.10

HRMS: *m/z* calcd for $C_{10}H_{17}NO_3S$ 231.0929; found 231.0934.

IR: ν = 1750 (CO), 1650 (CO) cm^{-1}.

major diastereomer:

^1H NMR: δ = 1.10 (d, 6 H, J = 7), 2.05 (m, 1 H), 2.20 (s, 3 H), 3.30 (m, 2 H), 3.75 (s, 3 H), 4.75 (d, 1 H, J = 8), 5.00 (t, 1 H, J = 8).

^{13}C NMR: δ = 19.1 (CH_3), 20.2 (CH_3), 22.5 (CH_3), 31.9 (CH_2), 35.2 (CH), 52.4 (CH_3), 62.2 (CH), 72.1 (CH), 169.2 (CO), 171.6 (CO).

minor diastereomer:

^1H NMR: δ = 1.00 (d, 6 H, J = 7), 2.05 (m, 1 H), 2.10 (s, 3 H), 3.40 (m, 2 H), 3.80 (s, 3 H), 4.80 (t, 1 H, J = 8), 5.30 (d, 1 H, J = 8).

^{13}C NMR: δ = 19.1 (CH_3), 19.9 (CH_3), 22.8 (CH_3), 33.3 (CH_2), 34.2 (CH), 52.8 (CH_3), 63.3 (CH), 70.4 (CH), 169.6 (CO), 171.1 (CO).

MS: *m/z* (%) = 231 (M^+, 20), 188 (75), 172 (15), 146 (100), 130 (40), 86 (80), 59 (60), 43 (100).

(R)-3-Acetyl-4-methoxycarbonyl-2-phenylthiazolidine (**6d**):

Colourless crystals (as a 88:12 mixture of diastereomers); mp 120–122 °C.

$C_{13}H_{15}NO_3S$	calc.	C 58.85	H 5.70	N 5.28
(265.3)	found	58.53	5.78	5.29

IR: ν = 1750 (CO), 1640 (CO) cm^{-1}.

major diastereomer:

^1H NMR: δ = 1.90 (s, 3 H), 3.25 (m, 2 H), 3.80 (s, 3 H), 4.95 (t, 1 H), 6.05 (s, 1 H), 7.35 (m, 3 H), 7.65 (m, 2 H).

^{13}C NMR: δ = 22.7 (CH_3), 32.0 (CH_2), 52.6 (CH_3), 64.4 (CH), 66.6 (CH), 126.3 (2 CH), 128.3 (CH), 128.8 (2 CH), 140.6 (quat), 170.0 (CO), 170.5 (CO).

MS: *m/z* (%) = 265 (M^+, 3), 222 (35), 179 (50), 164 (45), 146 (20), 43 (100).

The thiazolidine **6e** was prepared from (*S*)-4-benzyl-2-*tert*-butyl-2-thiazoline[3] by reduction with aluminum amalgam[16] followed by acetylation with Ac_2O.

(S)-3-Acetyl-4-benzyl-2-tert-butylthiazolidine (**6e**):

Colourless solid (as a 96.5:3.5 mixture of diastereomers); mp 75–92 °C.

$C_{16}H_{23}NOS$	calc.	C 69.27	H 8.36	N 5.05
(277.4)	found	69.17	8.49	5.02

IR: ν = 1735 (CO), 1650 (CO) cm^{-1}.

^1H NMR (50 °C): δ = 1.10 (s, 9 H), 2.25 (s, 3 H), 2.80 (br s, 1 H), 2.90 (m, 2 H), 3.40 (br s, 1 H), 4.50 (br s, 1 H), 5.2–5.4 (br s, 1 H), 7.25 (m, 5 H).

^{13}C NMR (50 °C): δ = 23.7 (CH_3), 27.9 (3 CH_3), 36.2 (CH_2), 39.0 (quat), 42.3 (CH_2), 65.6 (CH), 74.1 (CH), 126.9 (CH), 128.8 (2 CH), 129.0 (2 CH), 138.3 (quat), 171.7 (CO).

MS: *m/z* (%) = 277 (M^+, 1), 233 (70), 220 (80), 178 (70), 142 (100), 117 (65), 92 (30).

The thiazolidin-2-thiones **8a–c** were prepared[4] by reaction of the appropriate *N*-benzylamino alcohol with CS_2 in aq NaOH solution.

(S)-3,4-Dibenzylthiazolidine-2-thione (**8a**):

Colourless needles; mp 137–139 °C; $[\alpha]_D^{25}$ – 25.8 (*c* = 1.6, CH_2Cl_2).

$C_{17}H_{17}NS_2$	calc.	C 68.18	H 5.73	N 4.68
(299.5)	found	68.42	5.57	4.66

IR: *v* = 1490, 1450, 1420, 1350, 1300, 1220, 1170, 1080, 1030, 920 cm^{-1}.

^1H NMR: δ = 2.85 (half AB pattern of d, 1 H, *J* = 14, 10), 2.88 (half AB pattern of d, 1 H, *J* = 12, 10), 3.15 (half AB pattern of d, 1 H, *J* = 14, 5), 3.20 (half AB pattern of d, 1 H, *J* = 12, 8), 4.15–4.30 (m, 1 H), 4.20 and 5.85 (AB pattern, 2 H, *J* = 16), 7.10 (m, 2 H), 7.2–7.5 (m, 8 H).

^{13}C NMR: δ = 32.2 (CH_2), 36.3 (CH_2), 50.7 (CH_2), 67.5 (CH), 127.2 (CH), 128.0 (2 CH), 128.2 (CH), 128.9 (2 CH), 129.0 (2 CH), 129.1 (2 CH), 135.4 (quat), 135.9 (quat), 196.7 (CS).

MS: *m/z* (%) = 299 (M^+, 42), 277 (20), 238 (10), 208 (100), 148 (92), 117 (31).

(S)-3-Benyzl-4-isopropylthiazolidine-2-thione (**8b**):

Colourless crystals; mp 77–78 °C; $[\alpha]_D^{25}$ – 143.1 (*c* = 0.5, $CHCl_3$).

$C_{13}H_{17}NS_2$	calc.	C 62.10	H 6.82	N 5.57
(251.4)	found	62.23	6.92	5.59

IR: *v* = 1460, 1450, 1330, 1240, 1220, 1200, 1180, 1130, 1040, 990, 960 cm^{-1}.

^1H NMR: δ = 0.90 (d, 3 H, *J* = 7), 0.95 (d, 3 H, *J* = 7), 2.30 (d of septets, 1 H, *J* = 7, 4), 3.05 (half AB pattern of d, 1 H, *J* = 11, 6), 3.20 (half AB pattern of d, 1 H, *J* = 11, 9), 4.05 (d of t, 1 H, *J* = 6, 4), 4.20 and 6.00 (AB pattern, 2 H, *J* = 16), 7.40 (s, 5 H).

^{13}C NMR: δ = 14.7 (CH_3), 18.6 (CH_3), 26.9 (CH_2), 28.9 (CH), 50.0 (CH_2), 71.0 (CH), 127.8 (3 CH), 128.7 (2 CH), 135.1 (quat), 197.4 (CS).

MS: *m/z* (%) = 251 (M^+, 100), 208 (15), 187 (24), 148 (82), 144 (24), 91 (35).

(R)-3-Benzyl-4-ethylthiazolidine-2-thione (**8c**):

Colourless crystals; mp 61–62 °C; $[\alpha]_D^{20}$ + 91.3 (*c* = 1.0, CH_2Cl_2).

$C_{12}H_{15}NS_2$	calc.	C 60.71	H 6.37	N 5.90
(237.4)	found	60.74	6.07	5.90

IR: *v* = 1475–1425, 1225, 1175, 1025, 760, 700 cm^{-1}.

^1H NMR: δ = 0.90 (t, 3 H, *J* = 7), 1.65 (m, 2 H), 2.95 (half AB pattern of d, 1 H, *J* = 10, 5), 3.35 (half AB pattern of d, 1 H, *J* = 10, 8), 4.00 (m, 1 H), 4.25 and 5.75 (AB pattern, 2 H, *J* = 17), 7.30 (m, 5 H).

^{13}C NMR: δ = 9.2 (CH_3), 24.1 (CH_2), 31.7 (CH_2), 50.1 (CH_2), 67.7 (CH), 127.7 (2 CH), 127.9 (CH), 128.8 (2 CH), 135.2 (quat), 197.0 (CS).

MS: *m/z* (%) = 237 (M^+, 15), 148 (100), 132 (5), 121 (10), 104 (5), 91 (70), 65 (25).

The same procedure using (*S*)-prolinol gave (*S*)-3-thia-1-azabicyclo[3.3.0]octane-2-thione which was treated with MeI in acetone and then NaOMe in MeOH to obtain **11**.

(S)-3-Thia-1-azabicyclo[3.3.0]octan-2-one (**11**):

Colourless crystals; mp 70–71 °C; $[\alpha]_D^{20}$ – 35.4 (*c* = 1.0, CH_2Cl_2).

C_6H_9NOS	calc.	C 50.32	H 6.34	N 9.78
(143.2)	found	50.07	6.30	9.59

IR: *v* = 1700 (CO), 1385, 930, 890 cm^{-1}.

^1H NMR: δ = 1.60 (m, 1 H), 2.0–2.3 (m, 3 H), 3.20 (m, 1 H), 3.25 (half AB pattern of d, 1 H, *J* = 12, 10), 3.40 (half AB pattern of d, 1 H, *J* = 12, 9), 3.55 (m, 1 H), 4.25 (m, 1 H).

^{13}C NMR: δ = 27.2 (CH_2), 30.8 (CH_2), 33.2 (CH_2), 43.3 (CH_2), 63.0 (CH), 169.8 (CO).

MS: *m/z* (%) = 143 (M^+, 30), 114 (5), 85 (5), 80 (5), 74 (20), 70 (30), 55 (100).

1,3-Dithiolane-2-thione (**13**) was prepared by the literature method.[17]

Phase-Transfer Catalysed Permanganate Oxidation of Organosulfur Compounds 4, 6, 8, 9, 11 and 13; General Procedure:

A solution of the organosulfur substrate (5 mmol), benzoic acid (0.62 g, 5 mmol) and benzyltriethylammonium chloride (0.11 g, 0.5 mmol) in CH_2Cl_2 (50 mL) was stirred vigorously with the required amount of $KMnO_4$ (5, 10, 15 or 25 mmol, see Table) in H_2O (100 mL) for 3 h. Sufficient solid $Na_2S_2O_5$ was added to decolourise the mixture which was then filtered through Celite, the organic layer separated and the aqueous layer washed with CH_2Cl_2 (3 × 50 mL). The combined organic extracts were washed with aq 1 M $H_2NNH_2 \cdot 2HCl$ solution,[18] followed by aq Na_2CO_3 solution, dried ($MgSO_4$) and evaporated to give the product.

Benzyl Phenyl Sulfone (**5a**): from **4a** as colourless crystals; mp 149–150 °C (Lit.[19] mp 148 °C).

Benzyl Ethyl Sulfone (**5b**): from **4b** as colourless crystals; mp 83 °C (Lit.[6] mp 84 °C).

Benzyl Isopropyl Sulfone (**5c**): from **4c** as colourless crystals; mp 65–67 °C (Lit.[7] mp 65 °C).

Dibenzyl Sulfone (**5d**): from **4d** or **4d*** as colourless crystals; mp 150 °C (Lit.[20] mp 150 °C).

Benzyl 4-Chlorophenyl Sulfone (**5e**): from **4e** as colourless crystals; mp 157–158 °C (Lit.[21] mp 157–158 °C).

4-Nitrobenzyl Phenyl Sulfone (**5f**): from **4f** as yellow crystals; mp 212–214 °C (Lit.[22] mp 209.5–210.5 °C).

Methyl Ethylsulfonylacetate (**5g**): from **4g** as colourless crystals; mp 40 °C (Lit.[23] mp 42–44 °C).

Ethyl Ethylsulfonylacetate (**5h**): from **4h** as a colourless liquid; bp (oven temp.) 160 °C/0.7 Torr (Lit.[24] bp 110 °C/0.3 Torr).

Methyl Phenylsulfonylacetate (**5i**): from **4i** as a colourless liquid; bp (oven temp.) 160 °C/0.3 Torr (Lit.[25] bp 145 °C/0.01 Torr).

Ethyl Phenylsulfonylacetate (**5j**): from **4e** as a colourless liquid; bp (oven temp.) 155 °C/0.3 Torr (Lit.[26] bp 134–135 °C/0.01 Torr).

(R)-3-Acetyl-4-methoxycarbonylthiazolidine 1,1-Dioxide (**7a**): from **6a** as a colourless oil which crystallised on standing; bp (oven temp.) 160 °C/0.1 Torr, mp 75–76 °C (Lit.[15] bp 170 °C/0.5 Torr).

(R)-3-Acetyl-2-ethyl-4-methoxycarbonylthiazolidine 1,1-Dioxide (**7b**): From **6b** as colourless crystals (66:34 mixture of diastereomers); mp 72–103 °C.

$C_9H_{15}NO_5S$	calc.	C 43.36	H 6.07	N 5.62
(249.3)	found	43.40	5.94	5.56

IR: *v* = 1745 (CO), 1660 (CO), 1320–1170, 1110, 1005, 940, 875, 820 cm^{-1}.

major diastereomer:

^1H NMR: δ = 1.20 (t, 3 H, *J* = 7), 1.80 (m, 2 H), 2.20 (s, 3 H), 3.40 (half AB pattern of d, 1 H, *J* = 13, 8), 3.6 (half AB pattern of d, 1 H, *J* = 13, 11), 3.75 (s, 3 H), 4.55 (t, 1 H, *J* = 7), 5.30 (t, 1 H, *J* = 8).

^{13}C NMR: δ = 10.1 (CH_3), 22.1 (CH_3), 25.5 (CH_2), 47.7 (CH_2), 52.8 (CH_3), 53.2 (CH), 74.5 (CH), 169.4 (CO), 170.0 (CO).

minor diastereomer:

^1H NMR: δ = 1.10 (t, 3 H, *J* = 7), 1.95–2.1 (m, 2 H), 2.20 (s, 3 H), 3.5–3.7 (m, 2 H), 3.85 (s, 3 H), 4.9–5.1 (m, 2 H).

^{13}C NMR: δ = 9.9 (CH_3), 21.2 (CH_3), 23.9 (CH_2), 49.4 (CH_2), 53.7 (CH_3), 55.2 (CH), 72.0 (CH), 170.3 (CO), 171.1 (CO).

MS: *m/z* (%) = 185 ($M^+ - SO_2$, 10), 143 (75), 84 (95), 55 (40), 43 (100).

(R)-3-Acetyl-2-isopropyl-4-methoxycarbonyl Thiazolidine 1,1-Dioxide (**7c**): from **6c** as colourless crystals (59:41 mixture of diastereomers); mp 76–79 °C.

$C_{10}H_{17}NO_5S$	calc.	C 45.61	H 6.51	N 5.32
(263.3)	found	45.43	6.35	5.19

IR: *v* = 1750 (CO), 1660 (CO), 1380, 1310, 1150, 1120, 890, 810 cm^{-1}.

major diastereomer:

^{1}H NMR: δ = 1.20 (d, 3H, J = 8), 1.30 (d, 3H, J = 8), 2.10 (m, 1H), 2.25 (s, 3H), 3.4–3.7 (m, 2H), 3.80 (s, 3H), 4.35 (d, 1H, J = 9), 5.3 (t, 1H, J = 9).

^{13}C NMR: δ = 19.1 (CH_3), 19.2 (CH_3), 22.4 (CH_3), 31.1 (CH), 47.4 (CH_2), 52.7 (CH_3), 53.1 (CH), 78.7 (CH), 169.2 (CO), 170.8 (CO).

minor diastereomer:

^{1}H NMR: δ = 1.00 (d, 3H, J = 8), 1.20 (d, 3H, J = 8), 2.10 (m, 1H), 2.25 (s, 3H), 3.4–3.7 (m, 2H), 3.85 (s, 3H), 4.90 (d, 1H, J = 8), 5.05 (t, 1H, J = 8).

^{13}C NMR: δ = 18.8 (CH_3), 19.2 (CH_3), 21.2 (CH_3), 30.4 (CH), 48.9 (CH_2), 53.6 (CH_3), 55.1 (CH), 75.4 (CH), 169.2 (CO), 171.1 (CO).

MS: m/z (%) = 263 (M^+, 0.5), 199 (15), 184 (30), 157 (70), 98 (85), 87 (60), 55 (80), 43 (100).

(R)-3-Acetyl-4-methoxycarbonyl-2-phenylthiazolidine 1,1-Dioxide (**7d**): from **6d** as colourless crystals (85:15 mixture of diastereomers); mp 211–215°C (subl.).

$C_{13}H_{15}NO_5S$	calc.	C 52.51	H 5.09	N 4.71
(297.3)	found	52.39	5.04	4.64

IR: ν = 1760 (CO), 1660 (CO), 1380, 1350, 1210, 1145, 1005, 700 cm^{-1}.

major diastereomer:

^{1}H NMR: δ = 2.00 (s, 3H), 3.35 (half AB pattern of d, 1H, J = 11, 9), 3.60 (half AB pattern of d, 1H, J = 11, 8), 3.90 (s, 3H), 4.95 (dd, 1H, J = 9, 7), 5.50 (s, 1H), 7.50 (m, 3H), 7.75 (m, 2H).

^{13}C NMR (DMSO-d_6): δ = 22.2 (CH_3), 47.9 (CH_2), 52.7 (CH_3), 54.1 (CH), 75.3 (CH), 128.0 (2CH), 128.7 (2CH), 129.4 (CH), 132.1 (quat), 168.9 (CO), 170.5 (CO).

MS: m/z (%) = 297 (M^+, 5), 233 (60), 190 (100), 174 (70), 132 (100), 130 (100), 104 (100), 89 (90), 77 (85), 43 (100).

(S)-3-Acetyl-4-benzyl-2-tert-butylthiazolidine 1,1-Dioxide (**7e**): from **6e** as colourless crystals; mp 140–145°C.

$C_{16}H_{23}NO_3S$	calc.	C 62.10	H 7.50	N 4.53
(309.4)	found	61.85	7.65	4.52

IR: ν = 1735 (CO), 1665 (CO), 1375, 1315, 1265, 1150, 1110, 750, 700 cm^{-1}.

^{1}H NMR (50°C): δ = 1.30 (9H, s), 2.25 (3H, s), 2.80 (1H, m), 3.05 (2H, m), 3.50 (1H, m), 4.65 (1H, br s), 4.80 (1H, br s), 7.2–7.35 (5H, m).

^{13}C NMR (50°C): δ = 22.5 (CH_3), 27.3 (3CH_3), 35.8 (quat), 42.4 (CH_2), 52.4 (CH_2), 56.5 (CH), 80.8 (CH), 127.5 (CH), 128.8 (2CH), 129.2 (2CH), 136.0 (quat), 172.9 (CO).

MS: m/z (%) = 309 (M^+, 5), 245 (30), 218 (70), 128 (100), 118 (85), 112 (95), 86 (25), 43 (50).

(S)-3,4-Dibenzylthiazolidin-2-one (**9a**): from **8a** as colourless prisms; mp 70–71°C; $[\alpha]_D^{25}$ + 11.8 (c = 0.9, $CHCl_3$).

$C_{17}H_{17}NOS$	calc.	C 72.05	H 6.05	N 4.94
(283.4)	found	72.19	6.29	4.78

IR: ν = 1650 (CO), 1490, 1450, 1440, 1400, 1350, 1200, 1080, 1030, 970, 930 cm^{-1}.

^{1}H NMR: δ = 2.80 (half AB pattern of d, 1H, J = 12, 8), 2.95 (half AB pattern of d, 1H, J = 12, 4), 3.05–3.20 (m, 2H), 3.80 (m, 1H), 4.00 and 5.10 (AB pattern, 2H, J = 16), 7.10 (m, 2H), 7.2–7.4 (m, 8H).

^{13}C NMR: δ = 30.4 (CH_2), 37.3 (CH_2), 46.7 (CH_2), 59.5 (CH), 127.1 (CH), 127.9 (CH), 128.0 (2CH), 128.6 (2CH), 128.7 (2CH), 129.2 (2CH), 136.3 (quat), 136.4 (quat), 171.8 (CO).

MS (CI): m/z (%) = 284 ($M+H^+$, 100), 192 (46), 108 (7), 91 (65), 65 (7).

(S)-3-Benzyl-4-isopropylthiazolidin-2-one (**9b**): from **8b** as a pale yellow solid; mp 33–35°C; bp 185°C/0.7 Torr; $[\alpha]_D^{20}$ + 34.0 (c = 1.02, CH_2Cl_2).

$C_{13}H_{17}NOS$	calc.	C 66.34	H 7.29	N 5.95
(235.4)	found	66.50	7.67	6.06

HRMS: m/z calcd for $C_{13}H_{17}NOS$ 235.1030; found 235.1026.

IR: ν = 1664 (CO), 1455, 1435, 1260, 1215, 705 cm^{-1}.

^{1}H NMR: δ = 0.85 (d, 3H, J = 9), 0.90 (d, 3H, J = 9), 2.20 (m, 1H), 3.00 (half AB pattern of d, 1H, J = 13, 7), 3.10 (half AB pattern of d, 1H, J = 13, 9), 3.55 (m, 1H), 3.90 and 5.10 (AB pattern, 2H, J = 17), 7.25 (m, 5H).

^{13}C NMR: δ = 14.5 (CH_3), 18.2 (CH_3), 24.9 (CH_2), 28.1 (CH), 46.6 (CH_2), 62.0 (CH), 127.7 (CH), 128.0 (2CH), 128.7 (2CH), 135.9 (quat), 172.9 (CO).

MS: m/z (%) = 235 (M^+, 15), 192 (45), 176 (5), 133 (10), 105 (5), 91 (100).

(R)-3-Benzyl-4-ethylthiazolidin-2-one (**9c**): from **8c** as pale green oil, bp 215°C/0.7 Torr; $[\alpha]_D^{20}$ − 26.1 (c = 1.07, CH_2Cl_2).

$C_{12}H_{15}NOS$	calc.	C 65.12	H 6.84	N 6.33
(221.3)	found	65.61	6.98	6.60

HRMS: m/z calcd for $C_{12}H_{15}NOS$ 221.0874; found 221.0859.

IR: ν = 1670 (CO), 1460, 1410, 1230, and 710 cm^{-1}.

^{1}H NMR: δ = 0.87 (t, 3H, J = 7), 1.5–1.75 (m, 2H), 2.90 (half AB pattern of d, 1H, J = 11, 6), 3.25 (half AB pattern of d, 1H, J = 11, 8), 3.55 (m, 1H), 4.00 and 4.90 (AB pattern, 2H, J = 15), 7.30 (m, 5H).

^{13}C NMR: δ = 8.6 (CH_3), 24.4 (CH_2), 29.9 (CH_2), 46.3 (CH_2), 59.1 (CH), 127.5 (CH), 127.7 (2CH), 128.6 (2CH), 136.3 (quat), 171.9 (CO).

MS: m/z (%) = 221 (M^+, 90), 192 (85), 165 (20), 122 (25), 104 (70), 91 (100).

(S)-3,4-Dibenzylthiazolidin-2-one 1,1-Dioxide (**10a**): from **8a** as colourless needles; mp 143–144°C; $[\alpha]_D^{25}$ − 22.6 (c = 0.7, $CHCl_3$).

$C_{17}H_{17}NO_3S$	calc.	C 64.74	H 5.44	N 4.44
(315.4)	found	64.66	5.34	4.37

IR: ν = 1730 (CO), 1490, 1450, 1420, 1330, 1220, 1140, 770 cm^{-1}.

^{1}H NMR: δ = 2.85 (half AB pattern of d, 1H, J = 16, 10), 3.05 (half AB pattern of d, 1H, J = 12, 8), 3.20 (half AB pattern of d, 1H, J = 12, 4), 3.30 (half AB pattern of d, 1H, J = 16, 6), 3.90 (m, 1H), 4.20 and 5.15 (AB pattern, 2H, J = 16), 7.10 (m, 2H), 7.3–7.5 (m, 8H).

^{13}C NMR: δ = 38.1 (CH_2), 47.4 (CH_2), 47.9 (CH_2), 51.7 (CH), 127.8 (CH), 128.5 (2CH), 129.0 (CH), 129.2 (2CH), 129.3 (2CH), 129.4 (2CH), 133.2 (quat), 134.7 (quat), 159.5 (CO).

MS: m/z (%) = 316 ($M+H^+$, 1), 251 (M^+-SO_2, 7), 192 (8), 176 (19), 160 (28), 134 (12), 118 (38), 91 (100).

(S)-3-Benzyl-4-isopropylthiazolidin-2-one 1,1-Dioxide (**10b**): from **8b** as pale yellow needles; mp 114–115°C; $[\alpha]_D^{20}$ − 39.6 (c = 1.02, CH_2Cl_2).

$C_{13}H_{17}NO_3S$	calc.	C 58.40	H 6.41	N 5.24
(267.4)	found	58.38	6.40	5.20

IR: ν = 1720 (CO), 1325, 1135, 760, 740, 700 cm^{-1}.

^{1}H NMR: δ = 0.85 (d, 3H, J = 7), 0.89 (d, 3H, J = 7), 2.40 (m, 1H), 3.1 (half AB pattern of d, 1H), J = 14, 6), 3.25 (half AB pattern of d, 1H, J = 14, 8), 3.75 (m, 1H), 4.2 and 5.1 (AB pattern, 2H, J = 15), 7.2–7.3 (m, 5H).

^{13}C NMR: δ = 13.9 (CH_3), 18.2 (CH_3), 27.4 (CH), 42.7 (CH_2), 47.1 (CH_2), 54.5 (CH), 128.2 (2CH), 128.7 (CH), 129.2 (2CH), 133.4 (quat), 160.7 (CO).

MS: m/z (%) = 203 (M^+-SO_2, 15), 160 (10), 133 (90), 105 (30), 91 (100).

(R)-3-Benzyl-4-ethylthiazolidin-2-one 1,1-Dioxide (**10c**): from **8c** or **9c** as colourless crystals; mp 102–103°C; $[\alpha]_D^{20}$ + 47.0 (c = 0.1, CH_2Cl_2).

$C_{12}H_{15}NO_3S$	calc.	C 56.90	H 5.97	N 5.53
(253.3)	found	56.75	5.98	5.50

IR: ν = 1710 (CO), 1320, 1140, 940, 850, 755, 700 cm^{-1}.

^{1}H NMR: δ = 0.90 (t, 3H, J = 8), 1.85 (m, 1H), 1.95 (m, 1H), 3.15 (half AB pattern of d, 1H, J = 14, 4), 3.35 (half AB pattern of d, 1H, J = 14, 8), 3.70 (m, 1H), 4.20 and 5.10 (AB pattern, 2H, J = 15), 7.25 (m, 1H), 7.40 (m, 4H).

^{13}C NMR: δ = 8.7 (CH_3), 24.6 (CH_2), 47.2 (2 CH_2), 51.3 (CH), 128.2 (2 CH), 128.8 (CH), 129.3 (2 CH), 133.4 (quat), 159.8 (CO).

MS: *m/z* (%) = 189 ($M^+ - SO_2$, 2), 161 (2), 133 (50), 105 (30), 91 (100).

(S)-3-Thia-1-azabicyclo[3.3.0]octan-2-one 3,3-Dioxide (**12**): from **11** as colourless crystals; mp 175–176°C; $[\alpha]_D^{20}$ +30.7 (*c* = 0.104, Me_2SO).

$C_6H_9NO_3S$	calc.	C 41.13	H 5.18	N 7.99
(175.2)	found	41.10	5.21	7.95

IR: ν = 1740 (CO), 1320, 1160, 1130 cm^{-1}.

^{1}H NMR (CD_2Cl_2): δ = 1.55 (qd, 1 H, *J* = 12, 8), 2.02 (m, 1 H), 2.20 (m, 1 H), 2.39 (m, 1 H), 3.10 (dd, 1 H, *J* = 13, 9), 3.55 (m, 2 H), 3.80 (dd, 1 H, *J* = 13, 6), 3.95 (m, 1 H).

^{13}C NMR (CD_2Cl_2): δ = 23.4 (CH_2), 32.3 (CH_2), 43.8 (CH_2), 52.6 (CH), 53.7 (CH_2), 157.7 (CO).

MS: *m/z* (%) = 111 ($M^+ - SO_2$, 25), 82 (10), 68 (80), 67 (100), 55 (70), 53 (55).

1,3-Dithiolan-2-one (**14**):
From **13** as a pale yellow oil which crystallised on standing; bp (oven temp.) 95°C/1 Torr; mp 32–33°C (Lit.[27] bp 90–92°C/4 Torr; mp 35°C).

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(1) Stewart, R. In *Oxidation in Organic Chemistry*; Wiberg, K.B., Ed.; Academic Press: New York, 1965; Chapter 1, p 1.
Lee, D.G. In *Oxidation in Organic Chemistry*; Trahanovsky, W.S., Ed.; Academic Press: New York, 1982; Chapter 2, p 147.
Arndt, D. In *Methoden der Organischen Chemie (Houben-Weyl)*, 4th Ed.; Müller, E., Ed.; Thieme: Stuttgart, 1975; Vol. E 4/1b, p 647.
(2) Fatiadi, A.J. *Synthesis* **1987**, 85.
Lee, D.G.; Chen, T. *J. Org. Chem.* **1991**, 56, 5346.
(3) Aitken, R.A.; Armstrong, D.P.; Galt, R.H.B.; Mesher, S.T.E. *J. Chem. Soc., Perkin Trans 1* **1997**, 935.
(4) Aitken, R.A.; Armstrong, D.P.; Mesher, S.T.E.; Galt, R.H.B. *Tetrahedron Lett.* **1994**, *35*, 6143.
(5) Pummerer, R. *Ber. Dtsch. Chem. Ges.* **1910**, *43*, 1406.
(6) Böhme, H. *Ber. Dtsch. Chem. Ges.* **1936**, *69*, 1610.
(7) Buchi, J.; Prost, H.; Eichenberger, H.; Lieberherr, R. *Helv. Chim. Acta* **1952**, *35*, 1527.
(8) Fromm, E. *Liebigs Ann. Chem.* **1913**, *396*, 97.
(9) Taboury, F. *Ann. Chim. (Paris)* **1903**, *15*, 5; *Chem. Abstr.* **1908**, *2*, 3330.
(10) Waldron, W.R.; Emmet Reid, E. *J. Am. Chem. Soc.* **1923**, *45*, 2408.
(11) Langler, R.F.; Marini, Z.; Spalding, E.S. *Can. J. Chem.* **1979**, *57*, 3193.
(12) Uyeda, Y. *J. Chem. Soc. Jpn.* **1931**, *52*, 410.
(13) Purvis, J.E.; Jones, H.O.; Tasker, H.S. *J. Chem. Soc.* **1910**, *97*, 2287.
(14) Ratner, S.; Clarke, H.T. *J. Am. Chem. Soc.* **1937**, *59*, 200.
(15) Farmaceutici Italia, Brit. Patent 811816, 1959; *Chem. Abstr.* **1960**, *54*, 576.
(16) Meyers, A.I.; Durandetta, J.L. *J. Org. Chem.* **1975**, *40*, 2021.
(17) Culvenor, C.C.J.; Davies, W.; Pausacker, K.H. *J. Chem. Soc.* **1946**, 1050.
(18) If this step was omitted the products were found to give very broad NMR signals due to contamination with traces of paramagnetic manganese salts.
(19) Knoevenagel, E. *Ber. Dtsch. Chem. Ges.* **1888**, *21*, 1344.
(20) Otto, R.; Lüders, O. *Ber. Dtsch. Chem. Ges.* **1880**, *13*, 1284.
(21) Purgotti A. *Ann. r. scuola superiore d'agr. in Portia* **1915**, *13*, 8; *Chem. Abstr.* **1915**, *9*, 70.
(22) Jarvis, B.D.; Saukaitis, J.C. *J. Am. Chem. Soc.* **1973**, *95*, 7708.
(23) Tolstikov, G.A.; Rosentvet, O.A.; Kunakova, R.B.; Novitskaya, N.N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1983**, 589; *Chem. Abstr.* **1983**, *99*, 53057.
(24) Rothstein, E. *J. Am. Chem. Soc.* **1937**, *55*, 309.
(25) Beck, G.; Günther, D. *Chem. Ber.* **1973**, *106*, 2761.
(26) Huppatz, J.L. *Aust. J. Chem.* **1971**, *24*, 653.
(27) Jones, F.N.; Andreades, S. *J. Org. Chem.* **1969**, *34*, 3011.