Synthesis and pyrolytic behaviour of thiazolidin-2-one 1,1-dioxides

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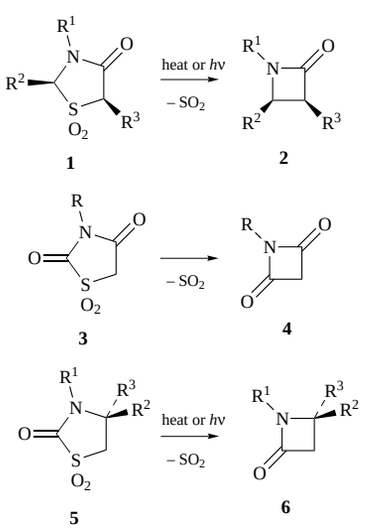
Four examples of the chiral thiazolidin-2-one 1,1-dioxides 5 have been prepared by reaction of the appropriate amino alcohols 11 with CS_2 in aqueous sodium hydroxide to give the thiazolidine-2-thiones 12, followed by oxidation with $KMnO_4$ under phase-transfer conditions in the presence of benzoic acid, either directly or *via* the thiazolidin-2-ones 13. Upon flash vacuum pyrolysis (FVP) at 650 °C, 5a–c decompose mainly by loss of SO_2 to give an alkene and benzyl isocyanate together with other products from fragmentation of the *N*-benzyl group. A significant minor pathway involves net loss of CO_2 and water to give the 2-phenyl-4,5-dihydrothiazoles 21 together with their aromatisation products 22 and 23. A mechanism for this new heterocyclic transformation is proposed involving initial expansion to a cyclic carbamic–sulfinic anhydride (2,1,4-oxathiazin-3-one 1-oxide). The fully assigned ^{13}C NMR spectra are presented for 5, 12 and 13 and the ^{33}S NMR spectrum has been obtained for 5c.

Thermal and photochemical extrusion of SO_2 from suitable ring systems has recently been used to achieve a wide variety of synthetic transformations.[1] Among the most interesting targets have been β-lactams and these have been obtained in several cases by SO_2 extrusion from appropriate thiazolidin-4-one 1,1-dioxides **1**.[2] In one case stereoselectivity was achieved with the *cis* compound **1** giving mainly the *cis* product **2** photochemically but mainly the *trans* isomer on pyrolysis (Scheme 1).[3]



1 **2** **3** **4** **5** **6**

Scheme 1

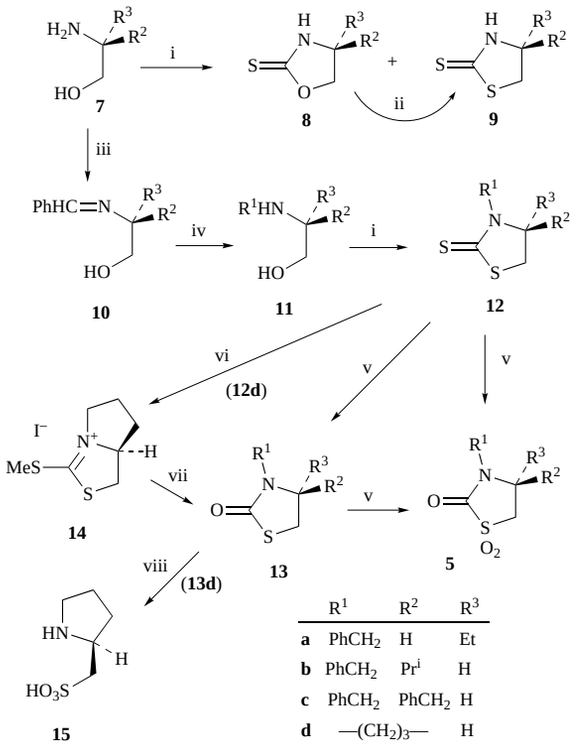
The corresponding reaction of the thiazolidine-2,4-dione 1,1-dioxides **3** to give malonic acid imides **4** has also been reported.[4] We were interested to examine the isomers of **1**, the thiazolidin-2-one 1,1-dioxides **5** as possible precursors of the β-lactams **6**. These have the advantage of being readily accessible in enantiomerically pure form from amino acid-derived amino alcohols, and if the extrusion were possible, it would be of interest to examine the reaction of their 5-anions with electrophiles in which the expected diastereoselectivity might lead to an efficient overall asymmetric synthesis of β-lactams. In this paper we describe the synthesis of representative thiazolidin-2-one 1,1-dioxides **5** in enantiomerically pure form and the first study of their pyrolytic behaviour.[5]

Results and discussion

The target thiazolidin-2-one 1,1-dioxides are a very little known class of compounds and the only previous examples were obtained by Gaul and Fremuth in 1961 by oxidation of the corresponding thiazolidine-2-thiones using peracetic acid.[6] The synthesis of the latter by reaction of β-amino alcohols with CS_2 in aqueous sodium hydroxide is well known but, as recently examined in detail by Delaunay *et al.*,[7] it may also lead to the corresponding oxazolidine-2-thiones or to mixtures of both, depending on the conditions used. We first subjected (*S*)-phenylalaninol **7c** to reaction with CS_2 in aqueous sodium hydroxide using the conditions reported by Roth and Schlump.[8] The product consisted of a mixture of the oxazolidine-2-thione **8c** and the thiazolidine-2-thione **9c** but the former could be converted entirely into the latter by treatment with P_2S_5 (Scheme 2). Although this was obtained in low yield, it had properties, including the ^{13}C NMR data (Table 1), in good agreement with those reported.[7] When **9c** was subjected to oxidation using a wide variety of oxidants and conditions, complex mixtures of intractable products were obtained, most likely owing to oxidative dimerisation through the 2-mercaptothiazoline tautomeric form, a reaction previously reported for these compounds,[9] followed by ring-opening and further degradation.

Attention was therefore turned to *N*-substituted examples since it was these that were used in the successful oxidation method of Gaul and Fremuth;[6] to facilitate later deprotection, we chose the *N*-benzyl compounds. The required *N*-benzylamino alcohols **11a–c** were readily obtained by condensation of **7a–c** with benzaldehyde to give **10**, followed by catalytic hydrogenation. When these were subjected to reaction with CS_2 in aqueous sodium hydroxide under the same conditions as before, the desired thiazolidinethiones **12a–c** were obtained in moderate to good yield and no oxazolidinethiones were formed. This is in agreement with the work of Delaunay *et al.*[7] where *N*-methylamino alcohols also gave exclusively the thiazolidinethiones. The colourless crystalline compounds **12a–c** gave analytical and spectroscopic data in good agreement with expectations and the fully assigned ^{13}C NMR spectra presented in Table 1 formed a highly consistent pattern.

Attempted oxidation of **12** using peracetic acid under a variety of conditions did give the desired sulfones **5** but in disap-



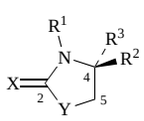
	R^1	R^2	R^3
a	$PhCH_2$	H	Et
b	$PhCH_2$	Pr^i	H
c	$PhCH_2$	$PhCH_2$	H
d	—$(CH_2)_3$—		H

Scheme 2 *Reagents*: i, CS_2, aq. NaOH; ii, P_2S_5; iii, PhCHO, cat. TsOH; iv, H_2, Pd/C; v, $KMnO_4$, $PhCO_2H$, phase transfer catalyst, CH_2Cl_2–H_2O; vi, MeI, acetone; vii, NaOMe, MeOH; viii, AcOOH

pointing yield and always accompanied by some of the thiazolidinones **13**. The reagent of choice was found to be $KMnO_4$ in a mixed phase system of CH_2Cl_2–water with both 0.1 equiv. benzyltriethylammonium chloride and 1 equiv. of benzoic acid as additives, a system which has also recently proved valuable for the oxidation of 4,5-dihydrothiazoles to their 1,1-dioxides.[10] Using this system the oxidation could be completely controlled with 3 equiv. of $KMnO_4$ converting **12** cleanly into **13** and either **12** or **13** being converted into **5** using 5 and 2 equiv. $KMnO_4$ respectively, the yields in all reactions exceeding 60%. In view of problems later encountered in the pyrolysis (*vide infra*), it was desirable to have an example of **5** in which R^1 was linked to either R^2 or R^3 and **5d** was therefore prepared by starting from (*S*)-prolinol **11d** which reacted with CS_2 in aqueous sodium hydroxide under the standard conditions to give **12d**. In this case it was found to be preferable to obtain **5** *via* oxidation of **13** rather than directly from **12**; **13d** was obtained in good overall yield by reaction of **12d** with methyl iodide to give **14**, followed by treatment with sodium methoxide to give **13d**. This unusual method for converting a thiazolidinethione to a thiazolidinone is based on a recently reported method for the thiazolinethione to thiazolinone transformation.[11] Attempted oxidation of **13d** using peracetic acid did give **5d** but in low yield and this was accompanied by a new product which proved to be the sulfonic acid **15** resulting from hydrolytic ring-opening of **5**, decarboxylation and further oxidation. Again the permanganate–benzoic acid method provided the method of choice for conversion of **13d** into **5d**.

Although the compounds **5a–d** were perfectly stable under dry conditions and gave good analytical and spectroscopic data, some hydrolysis, as hinted at by the formation of **15**, could be observed on prolonged storage. This is not surprising since α-oxo sulfones are notoriously elusive and in cases where they have been obtained they are readily hydrolysed.[12] Acyclic carboxamido sulfones have been obtained before and are somewhat more resistant to hydrolysis.[13] As shown in Table 1, the ^{13}C NMR data for **12a–d**, **13a–d** and **5a–d** form a consistent pattern and the trends on going from **12** to **13** to **5** are somewhat surprising. The fall of *ca.* 25 ppm in the value for C-2 on going from **12** to **13** is as expected, but the reason for the further fall of *ca.* 12 ppm for C-2 on going from **13** to **5** is not clear, particularly when at the same time the values for C-5 increase by 17–20 ppm upon *S*-oxidation. The signals for the remaining ring carbon, C-4, are also affected to a surprising degree by oxidation, with falls of *ca.* 8 ppm associated with each oxidation step. Further confirmation of the five-membered ring structure of the compounds **5** as opposed to the isomeric six-membered cyclic carbamic–sulfinic anhydride structure **19** was obtained by ^{33}S NMR spectroscopy. The use of this technique to clarify a similar structural ambiguity has been described by Farrar *et al.*,[14] and relies on the fact that the line widths in ^{33}S NMR spectra are highly dependant on the degree of symmetry around the sulfur atom. Thus **5** would be expected to give a

Table 1 ^{13}C NMR spectra of heterocycles **9**, **12**, **13** and **5**



	R^1	R^2	R^3	X	Y	δ_C C-2[a]	C-4	C-5	R^1 signals	R^2 and R^3 signals
9c	H	CH_2Ph	H	S	S	200.5	65.1	39.7	—	135.7 (4^{ry}), 129.1 (2C), 129.0 (2C), 127.3, 37.9
12a	CH_2Ph	H	Et	S	S	197.0	67.7	31.7	135.2 (4^{ry}), 128.8 (2C), 127.9, 127.7 (2C), 50.1	24.1, 9.2
12b	CH_2Ph	Pr^i	H	S	S	197.4	71.0	26.9	135.1 (4^{ry}), 128.7 (2C), 127.8 (3C), 50.0	28.9, 18.6, 14.7
12c	CH_2Ph	CH_2Ph	H	S	S	196.7	67.5	32.2	135.4 (4^{ry}), 128.9 (2C), 128.2, 128.0 (2C), 50.7	135.9 (4^{ry}), 129.1 (2C), 129.0 (2C), 127.2, 36.3
12d	–$(CH_2)_3$–		H	S	S	191.1	71.9	35.8	46.3, 31.4, 28.8	—
13a	CH_2Ph	H	Et	O	S	172.0	59.1	29.9	136.2 (4^{ry}), 128.6 (2C), 127.7 (2C), 127.6, 46.3	24.3, 8.6
13b	CH_2Ph	Pr^i	H	O	S	172.9	62.0	24.9	135.9 (4^{ry}), 128.7 (2C), 128.0 (2C), 127.7, 46.6	28.1, 18.2, 14.5
13c	CH_2Ph	CH_2Ph	H	O	S	171.8	59.5	30.4	136.3 (4^{ry}), 128.6 (2C), 128.0 (2C), 127.9, 46.7	136.4 (4^{ry}), 129.2 (2C), 128.7 (2C), 127.1, 37.3
13d	–$(CH_2)_3$–		H	O	S	169.8	63.0	33.2	43.3, 30.8, 27.2	—
5a	CH_2Ph	H	Et	O	SO_2	159.8	51.3	47.2	133.4 (4^{ry}), 129.3 (2C), 128.8, 128.2 (2C), 47.2	24.6, 8.7
5b	CH_2Ph	Pr^i	H	O	SO_2	160.6	54.5	42.7	133.4 (4^{ry}), 129.2 (2C), 128.7, 128.2 (2C), 47.1	27.4, 18.2, 13.9
5c	CH_2Ph	CH_2Ph	H	O	SO_2	159.5	51.7	47.9	133.2 (4^{ry}), 129.2 (2C), 129.0, 128.5 (2C), 47.4	134.7 (4^{ry}), 129.4 (2C), 129.3 (2C), 127.8, 38.1
5d	–$(CH_2)_3$–		H	O	SO_2	157.7	52.6	53.8	43.7, 32.4, 23.4	—

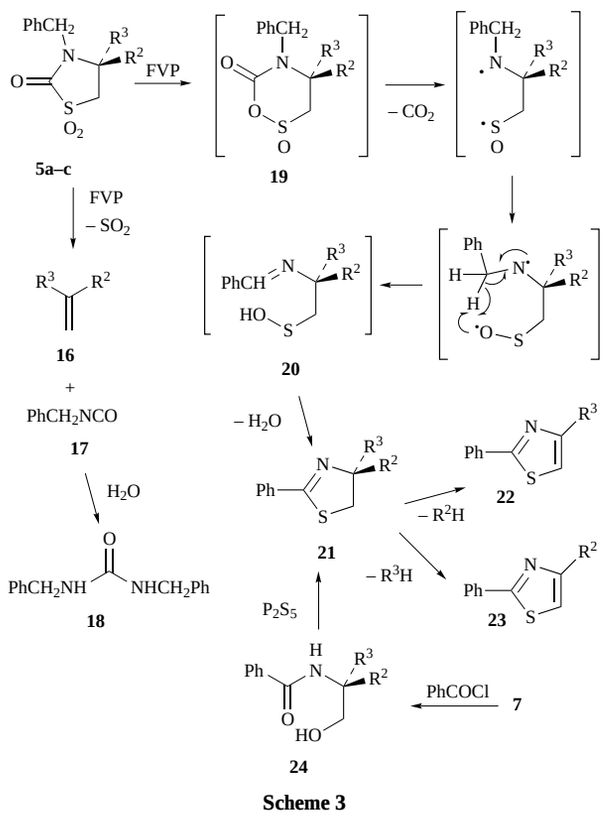
[a] δ_C Values are given with reference to Me_4Si as the internal standard.

Table 2 Products from FVP of thiazolidin-2-one 1,1-dioxides **5** at 650 °C (%)

Product	Starting material		
	5a	**5b**	**5c**
16	13	12	18
17	2	—	—
18	24	10	15
21	5	4	3
22	—	4	8
23	3	4	2
PhC≡N	19	16	7
$PhCH_2CH_2Ph$	10	6	12
$PhCH{=}NCH_2Ph$	5	7	—
PhCHO	2	2	4
PhMe	4	1	5
Pr^iCHO	—	5	—
EtCHO	2	—	—

relatively sharp signal while **19** would give a signal too broad to be observed. In the event, the spectrum of **5c** was readily obtained at natural abundance and consisted of a single signal of $w_{1/2}$ 130 Hz. The chemical shift of δ_S −6.5 with respect to aqueous Na_2SO_4 is in the expected range for cyclic sulfones,[15] although no α-oxo sulfone has previously been observed.

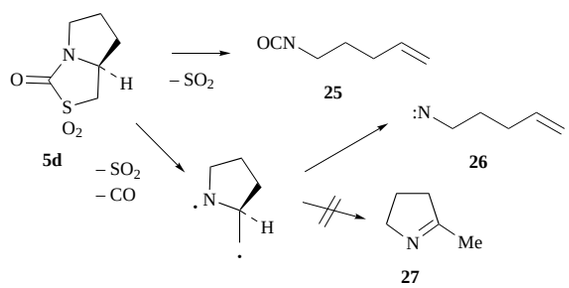
The sulfones **5a**–**c** were subjected to flash vacuum pyrolysis (FVP) using a conventional flow system with a horizontal furnace tube, operating at 10^{-3} Torr and involving contact times of ≈1–10 ms. Under these conditions all three compounds underwent complete reaction at the relatively mild temperature of 650 °C to give rather complex mixtures of products as shown in Table 2. It is disappointing to note that the desired extrusion of SO_2 does occur, but is accompanied by complete fragmentation to give the alkene **16** together with benzyl isocyanate **17**, obtained largely in the form of its hydrolysis product **18** (Scheme 3). Pyrolysis of an authentic sample of **17** under the same conditions confirmed both that it does not undergo any further thermal reactions and that, using our normal techniques, it underwent substantial hydrolysis owing to adventitious moisture in the cold trap to give **18**. It appears that the extrusion from **5a**–**c** requires more forcing conditions as compared to **1** such that the β-lactam cannot survive intact. The formation of benzonitrile, bibenzyl, toluene, *N*-benzylidenebenzylamine and benzaldehyde in all cases is probably associated with fragmentation of the *N*-benzyl group. The origin of the aliphatic aldehydes corresponding to R^2/R^3CHO is unclear. Most interesting however is the formation of small but significant quantities of the 2-phenyl-4,5-dihydrothiazoles **21** and their aromatization products **22** and **23**. The identity of these unexpected products was demonstrated by comparison with authentic samples prepared by reaction of **7a**–**c** with benzoyl chloride to give **24** followed by cyclisation with P_4S_{10}.[10] Heating **21b**,**c** with sulfur at 200–210 °C afforded samples of **23b**,**c** while 2-phenylthiazole **23a** (=**22b**,**c**) was prepared by a literature method[16] and these were identical with the pyrolysis products.



Scheme 3

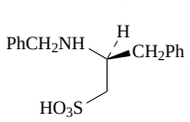
The mechanism of this unprecedented heterocyclic transformation is believed to involve the sequence of steps shown in Scheme 3, resulting in the required net loss of CO_2 and H_2O. Ring expansion to the cyclic sulfinic–carbamic anhydride **19**, a process well known in the pyrolysis of cyclic sulfones,[1] allows ready loss of CO_2. Rearrangement of the resulting diradical and intramolecular abstraction of the benzylic CH gives the imino sulfenic acid **20** which can then lose water to afford **21**. Overall the process is somewhat reminiscent of the pyrolysis of benzothiophene 1,1-dioxide to give benzothiete,[17] which also involves loss of CO_2 and initial ring expansion.

In an attempt to prevent the fragmentation to alkene and isocyanate we then examined the pyrolysis of **5d** in which the routes leading to **21**–**23** are also impossible. This underwent complete reaction at the lower temperature of 600 °C but the product consisted of a complex mixture of products which could not be identified. The presence of alkene signals in the NMR spectra pointed to ring-opening and this might be expected, as shown in Scheme 4, since the diradical resulting from loss of SO_2 can readily open to give the pentenyl isocyanate **25** while additional loss of CO can lead to pentenylnitrene **26**. Synthesis of an authentic sample of **27**, an alternative possible product from the diradical shown, confirmed that it was not present. Both **25** and **26** are expected to be highly reactive and can undergo a variety of secondary reactions either in the furnace or in the cold trap so the complex mixture produced is not surprising.



Scheme 4

In a final attempt to obtain a β-lactam, **5a**–**c** were subjected to photolysis in a variety of solvents. In contrast to the isomeric compounds **1**,[3] they were found to be photochemically inert and the only new product, obtained in low yield from **5c**, was the amino sulfonic acid **28** resulting from hydrolysis by adventitious moisture, decarboxylation and oxidation. In conclusion, it is clear that the thiazolidin-2-one 1,1-dioxides **5** are not suitable precursors for the thermal or photochemical generation of



β-lactams, in contrast to the isomeric thiazolidin-4-one 1,1-dioxides **1**. Due to subtle differences between the two ring systems, the more severe conditions required to achieve SO_2 extrusion in the former case lead to complete fragmentation to an alkene and isocyanate. The unexpected formation of **21**–**23** is however of some mechanistic interest.

Experimental

Melting points were determined on a Reichert hot-stage microscope and are uncorrected. Infrared 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 ^{1}H at 80 MHz on a Bruker WP80 instrument or at 300 MHz on a Bruker AM300 instrument, for ^{13}C at 20 MHz on a Varian CFT 20 or at 75 MHz on a Bruker AM300 instrument, and for ^{33}S at 38 MHz on a Bruker MSL500 spectrometer. Spectra were obtained for solutions in $CDCl_3$ unless otherwise indicated with Me_4Si as internal reference for ^{1}H and ^{13}C and aqueous Na_2SO_4 as external reference for ^{33}S. Chemical shifts are reported in ppm relative to the reference and coupling constants *J* are given in Hz. In the assignments for the ^{13}C NMR data 4^{ry} refers to quaternary carbon. Mass spectra were obtained on an A.E.I. MS902 instrument using electron impact at 70 eV. GC–MS was performed with a Hewlett Packard 5890A chromatograph coupled to a Finnigan Incos 50 mass spectrometer. Optical rotations were measured on an Optical Activity AA1000 polarimeter and are given in units of 10^{-1} deg cm^2 g^{-1}. The amino alcohols **7a**–**c** and **11d** were prepared by reduction of the corresponding amino acids, or were commercially available.

Preparation of 2-benzylideneamino alcohols 10

Benzaldehyde (24.4 g, 230 mmol) was added to a stirred solution of the appropriate amino alcohol **7** (220 mmol) in toluene (250 cm^3) and the mixture heated under reflux for 1 h using a Dean–Stark separator. Evaporation yielded the product which was recrystallised from hexane. Using this method, the following compounds were prepared.

(2*R*)-2-Benzylideneaminobutan-1-ol 10a. (2*R*)-2-Aminobutan-1-ol **7a** gave **10a** as colourless needles (77%), mp 57–58 °C (Found: C, 74.6; H, 8.8; N, 7.9. $C_{11}H_{15}NO$ requires C, 74.5; H, 8.5; N, 7.9%); $[\alpha]_D^{20}$ +37.8 (*c* 1.0 in CH_2Cl_2); ν_{max}/cm^{-1} 3280 (OH), 1645 (CN) 1060, 1000, 780 and 705; δ_H 8.20 (1 H, s), 7.65 (2 H, m), 7.35 (3 H, m), 3.78 (1 H, half AB pattern of d, *J* 12, 10), 3.72 (1 H, half AB pattern of d, *J* 12, 4), 3.18 (1 H, m), 2.86 (1 H, br s), 1.60 (2 H, m) and 0.85 (3 H, t, *J* 7); δ_C 162.0 (CH), 135.8 (4^{ry}), 130.7 (CH), 128.5 (2 CH), 128.3 (2 CH), 74.7 (CH), 66.0 (CH_2), 25.0 (CH_2) and 10.7 (CH_3); *m*/*z* 177 (M^+, 15%), 176 (50), 146 (100), 132 (25), 118 (30), 104 (50), 91 (85), 77 (35) and 41 (60).

(2*S*)-2-Benzylideneamino-3-methylbutan-1-ol 10b. (2*S*)-2-Amino-3-methylbutan-1-ol **7b** gave **10b** as colourless crystals (77%), mp 70–71 °C (Found: C, 75.2; H, 9.0; N, 7.3. $C_{12}H_{17}NO$ requires C, 75.3; H, 9.0; N, 7.3%); $[\alpha]_D^{25}$ −83.3 (*c* 0.3 in $CHCl_3$); ν_{max}/cm^{-1} 3700–2400 (br, OH), 1640, 1470, 1450, 1380, 1260, 1220, 1060 and 1020; δ_H 8.29 (1 H, s), 7.85–7.6 (2 H, m), 7.6–7.3 (3 H, m), 3.80 (2 H, m), 3.2–2.8 (1 H, m), 1.90 (1 H, octet, *J* 7), 0.95 (3 H, d, *J* 7) and 0.90 (3 H, d, *J* 7); δ_C 161.7 (C=N), 136.0 (4^{ry}), 130.4 (CH), 128.4 (4 CH), 79.2 (CH), 64.1 (CH_2), 30.0 (CH), 19.7 (CH_3) and 19.2 (CH_3); *m*/*z* 190 (M − H^+, 5%), 189 (2), 160 (100), 148 (70), 130 (25) and 118 (35).

(2*S*)-2-Benzylideneamino-3-phenylpropan-1-ol 10c. (2*S*)-2-Amino-3-phenylpropan-1-ol **7c** gave **10c** as colourless prisms (64%), mp 78–80 °C (Found: C, 80.1; H, 7.2; N, 5.8. $C_{16}H_{17}NO$ requires C, 80.0; H, 7.1; N, 5.8%); $[\alpha]_D^{25}$ −215.6 (*c* 2.0 in $CHCl_3$); ν_{max}/cm^{-1} 3600–2700 (br, OH), 1640, 1490, 1450, 1380, 1220, 1030 and 700; δ_H 7.98 (1 H, s), 7.7–7.55 (2 H, m), 7.45–7.3 (3 H, m), 7.25–7.1 (5 H, m), 3.85 (1 H, half of AB pattern of d, *J* 10, 6), 3.70 (1 H, half of AB pattern of d, *J* 10, 4), 3.7–3.4 (1 H, m), 3.00 (1 H, half of AB pattern of d, *J* 14, 5), 2.80 (1 H, half of AB pattern of d, *J* 14, 8) and 2.26 (1 H, br s); δ_C 162.4 (C=N), 138.6 (4^{ry}), 135.6 (4^{ry}), 130.6 (CH), 129.6 (2 CH), 128.4 (2 CH), 128.2 (4 CH), 126.0 (CH), 74.4 (CH), 65.6 (CH_2) and 38.9 (CH_2); *m*/*z* 208 (M^+ − CH_2OH, 8%), 148 (M^+ − CH_2Ph, 50), 130 (12), 128 (32), 127 (35) and 91 (100).

Preparation of 2-benzylamino alcohols 11

A solution of the appropriate benzylideneamino alcohol **10** (0.52 mol) and 5% palladium/charcoal catalyst (3.0 g) in ethyl acetate (500 cm^3) was stirred vigorously in the presence of hydrogen gas (12 dm^3, 0.54 mol) at room temp. for 24 h. The solution was then filtered through Celite and evaporated to afford the product. Using this method, the following compounds were prepared.

(2*R*)-2-Benzylaminobutan-1-ol 11a. (2*R*)-2-Benzylideneaminobutan-1-ol **10a** gave **11a**, following recrystallisation from hexane, as a colourless solid (77%), mp 74–75 °C (Found: C, 73.4; H, 9.6; N, 7.7. $C_{11}H_{17}NO$ requires C, 73.7; H, 9.6; N, 7.8%); $[\alpha]_D^{20}$ −28.5 (*c* 1.0 in CH_2Cl_2); ν_{max}/cm^{-1} 3400–3000 (OH), 3280 (NH), 1060, 865, 745 and 700; δ_H 7.30 (5 H, m), 3.80 and 3.72 (2 H, AB pattern, *J* 14), 3.62 (1 H, half of AB pattern of d, *J* 10, 4), 3.35 (1 H, half AB pattern of d, *J* 10, 6), 2.62 (1 H, m), 2.40 (2 H, br s), 1.6–1.4 (2 H, m) and 0.90 (3 H, t, *J* 7); δ_C 140.3 (4^{ry}), 128.5 (2 CH), 128.1 (2 CH), 127.1 (CH), 62.6 (CH_2), 59.8 (CH), 51.0 (CH_2), 24.2 (CH_2) and 10.4 (CH_3); *m*/*z* 179 (M^+, 1%), 148 (100), 106 (55), 91 (100), 77 (50), 65 (75) and 56 (70).

(2*S*)-2-Benzylamino-3-methylbutan-1-ol 11b. (2*S*)-2-Benzylideneamino-3-methylbutan-1-ol **10b** gave **11b**, following Kugelrohr distillation, as a colourless oil (80%), bp (oven temp.) 106–108 °C at 0.4 Torr (lit.,[18] 103–107 °C at 0.2 Torr).

(2*S*)-2-Benzylamino-3-phenylpropan-1-ol 11c. (2*S*)-2-Benzylideneamino-3-phenylpropan-1-ol **10c** gave **11c**, following recrystallisation from hexane–ethyl acetate (5:1), as colourless prisms (71%), mp 124–126 °C (Found: C, 79.6; H, 8.0; N, 5.7. $C_{16}H_{19}NO$ requires C, 79.6; H, 7.9; N, 5.8%); $[\alpha]_D^{25}$ −49.8 (*c* 2.0 in $CHCl_3$); ν_{max}/cm^{-1} 3700–2400 (br, OH), 1640, 1490, 1450, 1400, 1220, 1110, 1030, 910 and 700; δ_H 7.25 (11 H, m), 3.9–3.6 (1 H, m), 3.80 (2 H, s), 3.60 (1 H, half AB pattern of d, *J* 10, 4), 3.40 (1 H, half AB pattern of d, *J* 10, 5), 2.90 and 2.70 (2 H, AB pattern of d, *J* 8, 4) and 2.80 (1 H, br s); δ_C 139.9 (4^{ry}), 138.8 (4^{ry}), 129.2 (2 CH), 128.4 (4 CH), 128.0 (2 CH), 126.9 (CH), 126.2 (CH), 62.6 (CH_2), 59.7 (CH), 51.1 (CH_2) and 37.8 (CH_2); *m*/*z* 242 (M + H^+, 1.2%), 241 (M^+, 1), 210 (8), 150 (20) and 91 (100).

Preparation of thiazolidine-2-thiones 9 and 12

A mixture of the appropriate amino alcohol (45 mmol), 2 M sodium hydroxide (150 cm^3) and carbon disulfide (9.8 cm^3, 12.4 g, 163 mmol) was stirred at room temp. for 20 h. A further portion of carbon disulfide (5.0 cm^3, 6.3 g, 83 mmol) was added and the solution stirred for an additional 4 h. The mixture was extracted with CH_2Cl_2 and the organic layer washed with water, dried and evaporated to afford the product. Using this method, the following compounds were prepared.

(4*S*)-4-Benzylthiazolidine-2-thione 9c. (2*S*)-2-Amino-3-phenylpropan-1-ol **7c** (8.0 g, 52 mmol) gave a mixture of the desired product **9c** and the corresponding oxazolidine-2-thione **8c**. This was dissolved in toluene (200 cm^3) and heated under reflux with P_2S_5 (20 g, 90 mmol) for 48 h. Filtration and evaporation followed by column chromatography [SiO_2, diethyl ether–petroleum (bp 40–60 °C) 1:1] gave a red solid which was recrystallised from hexane–ethyl acetate (5:1) to give the product as red needles (18%), mp 79–80 °C (lit.,[7] 84–85 °C) (Found: C, 57.4; H, 5.3; N, 6.6. $C_{10}H_{11}NS_2$ requires C, 57.4; H, 5.3; N, 6.7%); $[\alpha]_D^{25}$ −112.2 (*c* 1.7 in $CHCl_3$); ν_{max}/cm^{-1} 3480, 1470, 1290, 1250, 1220, 1140, 1040, 1010, 960 and 700; δ_H 8.40 (1 H, br s), 7.4–7.2 (3 H, m), 7.2–7.1 (2 H, m), 4.46 (1 H, quintet, *J* 10), 3.50 and 3.26 (2 H, AB pattern of d, *J* 14, 10), 3.05 and 2.93 (2 H, AB pattern of d, *J* 12, 10); δ_C see Table 1; *m*/*z* 209 (M^+, 40%), 182 (12), 167 (15), 146 (93), 132 (12), 118 (27), 117 (20) and 91 (100).

(4*R*)-3-Benzyl-4-ethylthiazolidine-2-thione 12a. (2*R*)-2-Benzylaminobutan-1-ol **11a** gave **12a**, following recrystallisation from hexane–ethyl acetate (2:1), as colourless crystals (72%), mp 61–62 °C (Found: C, 60.7; H, 6.1; N, 5.9. $C_{12}H_{15}NS_2$ requires C, 60.7; H, 6.4; N, 5.9%); $[\alpha]_D^{20}$ +91.3 (*c* 1.0 in CH_2Cl_2); ν_{max}/cm^{-1} 3060, 3040, 1475–1425, 1225, 1175, 1025 (CS), 760 and 700; δ_H 7.30 (5 H, m), 5.75 and 4.25 (2 H, AB pattern, *J* 17), 4.00 (1 H, m), 3.35 (1 H, half AB pattern of d, *J* 10, 8), 2.96 (1 H, half AB pattern of d, *J* 10, 5), 1.77 (2 H, m) and 0.92 (3 H, t, *J* 7); δ_C see Table 1; *m*/*z* 237 (M^+, 15%), 148 (100), 132 (5), 121 (10), 104 (5), 91 (70) and 65 (25).

(4*S*)-3-Benzyl-4-isopropylthiazolidine-2-thione 12b. (2*S*)-Benzylamino-3-methylbutan-1-ol **11b** gave **12b**, following recrystallisation from hexane–ethyl acetate (5:1) with cooling (−20 °C), as colourless crystals (36%), mp 77–78 °C (Found: C, 62.2; H, 6.9; N, 5.6. $C_{13}H_{17}NS_2$ requires C, 62.1; H, 6.8; N, 5.6%); $[\alpha]_D^{25}$ −143.1 (*c* 0.5 in $CHCl_3$); ν_{max}/cm^{-1} 1460, 1450, 1330, 1240, 1220, 1200, 1180, 1130, 1040, 990 and 960; δ_H 7.40 (5 H, s), 6.00 and 4.14 (2 H, AB pattern, *J* 16), 4.05 (1 H, m), 3.20 (1 H, half AB pattern of d, *J* 11, 9), 3.05 (1 H, half AB pattern of d, *J* 11, 6), 2.34 (1 H, septet of d, *J* 7, 4), 0.95 (3 H, d, *J* 7) and 0.90 (3 H, d, *J* 7); δ_C see Table 1; *m*/*z* 251 (M^+, 100%), 208 (15), 187 (24), 148 (82), 144 (24) and 91 (35).

(4*S*)-3,4-Dibenzylthiazolidine-2-thione 12c. (2*S*)-2-Benzylamino-3-phenylpropan-1-ol **11c** gave **12c**, following recrystallisation from hexane–ethyl acetate (3:1), as colourless needles (53%), mp 137–139 °C (Found: C, 68.4; H, 5.55; N, 4.65. $C_{17}H_{17}NS_2$ requires C, 68.2; H, 5.7; N, 4.7%); $[\alpha]_D^{25}$ −25.8 (*c* 1.6 in CH_2Cl_2); ν_{max}/cm^{-1} 1490, 1450, 1420, 1350, 1300, 1220, 1170, 1080, 1030, 920 and 700; δ_H 7.4–7.2 (8 H, m), 7.1–7.0 (2 H, m), 5.82 and 4.20 (2 H, AB pattern, *J* 16), 4.30–4.15 (1 H, m), 3.20 (1 H, half AB pattern of d, *J* 12, 8), 3.15 (1 H, half AB pattern of d, *J* 14, 5), 2.86 (1 H, half AB pattern of d, *J* 12, 10) and 2.83 (1 H, half AB pattern of d, *J* 14, 10); δ_C see Table 1; *m*/*z* 299 (M^+, 42%), 277 (20), 238 (10), 208 (100), 148 (92) and 117 (31).

(5*S*)-3-Thia-1-azabicyclo[3.3.0]octane-2-thione 12d. (2*S*)-2-Hydroxymethylpyrrolidine **11d** gave **12d**, following recrystallisation from ethanol, as colourless crystals (49%), mp 130–131 °C (lit.,[19] 132–133 °C) (Found: C, 45.1; H, 5.5; N, 8.78. $C_6H_9NS_2$ requires C, 45.2; H, 5.7; N, 8.8%); $[\alpha]_D^{20}$ −159.8 (*c* 1.0 in CH_2Cl_2); ν_{max}/cm^{-1} 1360, 1340, 1245, 1210, 1180, 1055, 1030 (CS), 940 and 850; δ_H 4.63 (1 H, m), 3.60 (1 H, m), 3.48 (1 H, m), 3.32 (2 H, dd, *J* 7, 2), 2.5–2.3 (2 H, m), 2.20 (1 H, m) and 1.80 (1 H, m); δ_C see Table 1; *m*/*z* 159 (M^+, 70%), 126 (5), 118 (10), 85 (30), 72 (25), 67 (50), 45 (35) and 41 (100).

Preparation of thiazolidin-2-ones 13a–c

A solution of the appropriate thiazolidinethione **12** (5 mmol), benzoic acid (0.62 g, 5 mmol) and benzyltriethylammonium chloride (0.11 g, 0.5 mmol) in dichloromethane (50 cm^3) was stirred vigorously with a solution of potassium permanganate (2.37 g, 15 mmol) in water (100 cm^3) for 3 h. Sufficient solid sodium metabisulfite was added to decolourise the mixture which was then filtered through Celite, the organic layer was separated and the aqueous layer washed with dichloromethane (3 × 50 cm^3). The combined organic extracts were washed with 1 M hydrazine dihydrochloride, followed by aqueous sodium carbonate, dried with anhydrous magnesium sulfate and evaporated to give the product. Using this method, the following compounds were prepared.

(4*R*)-3-Benzyl-4-ethylthiazolidin-2-one 13a. (4*R*)-3-Benzyl-4-ethylthiazolidine-2-thione **12a** gave **13a**, following Kugelrohr distillation, as a pale green oil (76%), bp (oven temp.) 215 °C at 0.7 Torr (Found: C, 65.6; H, 7.0; N, 6.6%; M, 221.0859. $C_{12}H_{15}NOS$ requires C, 65.1; H, 6.8; N, 6.3%; *M*, 221.0874); $[\alpha]_D^{20}$ −26.1 (*c* 1.07 in CH_2Cl_2); ν_{max}/cm^{-1} 2970–2940, 1670 (CO), 1460, 1410, 1230 and 710; δ_H 7.35–7.2 (5 H, m), 4.96 and 4.00 (2 H, AB, *J* 15), 3.55 (1 H, m), 3.26 (1 H, half AB pattern of d, *J* 11, 8), 2.93 (1 H, half AB pattern of d, *J* 11, 6), 1.75–1.5 (2 H, m) and 0.86 (3 H, t, *J* 7); δ_C see Table 1; *m*/*z* 221 (M^+, 90%), 192 (85), 165 (20), 122 (25), 104 (70), 91 (100) and 65 (80).

(4*S*)-3-Benzyl-4-isopropylthiazolidin-2-one 13b. (4*S*)-3-Benzyl-4-isopropylthiazolidine-2-thione **12b** gave **13b**, following Kugelrohr distillation, as a pale yellow solid (43%), mp 33–35 °C, bp (oven temp.) 185 °C at 0.7 Torr (Found: C, 66.5; H, 7.7; N, 6.1%; M, 235.1026. $C_{13}H_{17}NOS$ requires C, 66.3; H, 7.3; N, 6.0%; *M*, 235.1031); $[\alpha]_D^{20}$ +34.0 (*c* 1.02 in CH_2Cl_2); ν_{max}/cm^{-1} 3025, 2964, 1723, 1664 (CO), 1455, 1435, 1260, 1215 and 705; δ_H 7.35–7.2 (5 H, m), 5.10 and 3.90 (2 H, AB pattern, *J* 17), 3.57 (1 H, m), 3.10 (1 H, half AB pattern of d, *J* 13, 9), 3.03 (1 H, half of AB pattern of d, *J* 13, 7), 2.20 (1 H, m), 0.87 (3 H, d, *J* 9) and 0.85 (3 H, d, *J* 9); δ_C see Table 1; *m*/*z* 235 (M^+, 15%), 192 (45), 176 (5), 133 (10), 105 (5), 91 (100) and 77 (5).

(4*S*)-3,4-Dibenzylthiazolidin-2-one 13c. (4*S*)-3,4-Dibenzylthiazolidine-2-thione **12c** gave **13c**, following Kugelrohr distillation, as a colourless oil which formed colourless prisms with time (45%), bp (oven temp.) 225 °C at 0.3 Torr; mp 70–71 °C (Found: C, 72.2; H, 6.3; N, 4.8. $C_{17}H_{17}NOS$ requires C, 72.0; H, 6.1; N, 4.9%); $[\alpha]_D^{25}$ +11.8 (*c* 0.9 in $CHCl_3$); ν_{max}/cm^{-1} 1650, 1490, 1450, 1440, 1400, 1350, 1200, 1080, 1030, 970 and 930; δ_H 7.4–7.2 (8 H, m), 7.08 (2 H, m), 5.08 and 4.00 (2 H, AB pattern, *J* 16), 3.80 (1 H, m), 3.15–3.05 (2 H, m), 2.92 (1 H, half AB pattern of d, *J* 12, 4) and 2.77 (1 H, half AB pattern of d, *J* 12, 8); δ_C see Table 1; *m*/*z* (CI) 284 (M + H^+, 100%), 192 (46), 108 (7), 91 (65) and 65 (7).

(5*S*)-2-Methylthio-3-thia-1-azabicyclo[3.3.0]oct-1-en-1-ium iodide 14

A solution of (5*S*)-3-thia-1-azabicyclo[3.3.0]octane-2-thione **12d** (4.0 g, 25 mmol) and methyl iodide (15.6 cm^3, 35.5 g, 250 mmol) in acetone (110 cm^3) was stirred for 16 h at room temp. The resulting precipitate was filtered off and washed with diethyl ether. The filtrate was concentrated and a second crop of the product filtered off and washed with diethyl ether. The solids were combined to yield the product (6.74 g, 90%) as a pale yellow powder, mp 111–112 °C (Found: C, 27.8; H, 3.9; N, 4.6. $C_7H_{12}INS_2$ requires C, 27.9; H, 4.0; N, 4.7%); $[\alpha]_D^{20}$ −256.5 (*c* 1.66 in CH_2Cl_2); ν_{max}/cm^{-1} 1555, 1300, 1200, 1170 and 950; δ_H 5.20 (1 H, m), 3.87 (2 H, m), 3.68 (1 H, m), 3.58 (1 H, m), 2.77 (3 H, s), 2.46 (2 H, m) and 2.25–2.10 (2 H, m); δ_C 186.7 (4^{ry}), 77.5 (CH), 49.3 (CH_2), 38.5 (CH_2), 29.5 (CH_2), 29.4 (CH_2) and 19.8 (CH_3); *m*/*z* 159 (M^+ − MeI, 30%), 126 (5), 118 (10), 85 (30), 82 (10) and 67 (50).

(5*S*)-3-Thia-1-azabicyclo[3.3.0]octan-2-one 13d

(5*S*)-2-Methylthio-3-thia-1-azabicyclo[3.3.0]oct-1-en-1-ium iodide **14** (22.58 g, 75 mmol) was added to a solution of sodium methoxide (75 mmol) in methanol (200 cm^3) and the mixture stirred for 16 h at room temp. Water (400 cm^3) was added and the mixture extracted with CH_2Cl_2. The combined organic layers were washed with water, dried and evaporated to yield a yellow solid. Recrystallisation of this from diethyl ether–ethyl acetate with cooling (−20 °C), afforded the product (8.37 g, 78%) as colourless crystals, mp 70–71 °C (Found: C, 50.1; H, 6.3; N, 9.6. C_6H_9NOS requires C, 50.3; H, 6.3; N, 9.8%); $[\alpha]_D^{20}$ −35.4 (*c* 1.0 in CH_2Cl_2); ν_{max}/cm^{-1} 3320, 1700 (CO), 1385, 930 and 890; δ_H 4.22 (1 H, m), 3.55 (1 H, m), 3.38 (1 H, half AB pattern of d, *J* 12, 9), 3.22 (1 H, half AB pattern of d, *J* 12, 10), 3.17 (1 H, m), 2.3–2.0 (3 H, m) and 1.62 (1 H, m); δ_C see Table 1; *m*/*z* 143 (M^+, 30%), 114 (5), 85 (5), 80 (5), 74 (20), 70 (30) and 55 (100).

Preparation of thiazolidin-2-one 1,1-dioxides 5

Exactly the same method was used as described for the thiazolidin-2-ones above, except that the quantity of potassium permanganate was increased to 3.95 g (25 mmol) and the products were recrystallised from diethyl ether–CH_2Cl_2 (1:1). Using this method, the following compounds were prepared.

(4*R*)-3-Benzyl-4-ethylthiazolidin-2-one 1,1-dioxide 5a. (4*R*)-3-Benzyl-4-ethylthiazolidine-2-thione **12a** gave **5a** as colourless

crystals (72%), mp 102–103 °C (Found: C, 56.8; H, 6.0; N, 5.5. $C_{12}H_{15}NO_3S$ requires C, 56.9; H, 6.0; N, 5.5%); $[a]_D^{20}$ +47.0 (*c* 0.1 in CH_2Cl_2); ν_{max}/cm^{-1} 3420, 1710 (CO), 1320, 1140, 940, 850, 755 and 700; δ_H 7.4–7.3 (3 H, m), 7.25–7.2 (2 H, m), 5.10 and 4.22 (2 H, AB pattern, *J* 15), 3.70 (1 H, m), 3.35 (1 H, half AB pattern of d, *J* 14, 8), 3.15 (1 H, half AB pattern of d, *J* 14, 4), 1.95 (1 H, m), 1.76 (1 H, m) and 0.94 (3 H, t, *J* 8); δ_C see Table 1; *m*/*z* 189 ($M^+ - SO_2$, 2%), 161 (2), 133 (50), 105 (30), 91 (100) and 77 (10).

This product could alternatively be prepared from (4*R*)-3-benzyl-4-ethylthiazolidin-2-one **13a** using 2 equiv. of $KMnO_4$.

(4*S*)-3-Benzyl-4-isopropylthiazolidin-2-one 1,1-dioxide 5b. (4*S*)-3-Benzyl-4-isopropylthiazolidine-2-thione **12b** gave **5b** as pale yellow needles (33%), mp 114–115 °C (Found: C, 58.4; H, 6.4; N, 5.2. $C_{13}H_{17}NO_3S$ requires C, 58.4; H, 6.4; N, 5.2%); $[a]_D^{20}$ −39.6 (*c* 1.02 in CH_2Cl_2); ν_{max}/cm^{-1} 3420, 1720 (CO), 1325 and 1135 (SO_2), 760, 740 and 700; δ_H 7.4–7.3 (3 H, m), 7.3–7.2 (2 H, m), 5.10 and 4.18 (2 H, AB pattern, *J* 15), 3.77 (1 H, m), 3.26 (1 H, half AB pattern of d, *J* 14, 8), 3.12 (1 H, half AB pattern of d, *J* 14, 6), 2.38 (1 H, m), 0.89 (3 H, d, *J* 7) and 0.85 (3 H, d, *J* 7); δ_C see Table 1; *m*/*z* 203 ($M^+ - SO_2$, 15%), 160 (10), 133 (90), 105 (30), 91 (100) and 77 (5).

(4*S*)-3,4-Dibenzylthiazolidin-2-one 1,1-dioxide 5c. (4*S*)-3,4-Dibenzylthiazolidine-2-thione **12c** gave **5c** as colourless needles (67%), mp 143–144 °C (Found: C, 65.0; H, 5.4; N, 4.4. $C_{17}H_{17}NO_3S$ requires C, 64.7; H, 5.4; N, 4.4%); $[a]_D^{25}$ −22.6 (*c* 0.7 in $CHCl_3$); ν_{max}/cm^{-1} 1730 (CO), 1490, 1450, 1420, 1330, 1220, 1140 and 770; δ_H 7.45–7.35 (3 H, m), 7.3–7.2 (5 H, m), 7.07 (2 H, m), 5.16 and 4.20 (2 H, AB pattern, *J* 16), 3.90 (1 H, m), 3.34 (1 H, half AB pattern of d, *J* 16, 6), 3.20 (1 H, half AB pattern of d, *J* 12, 4), 3.03 (1 H, half AB pattern of d, *J* 12, 8) and 2.88 (1 H, half AB pattern of d, *J* 16, 10); δ_C see Table 1; δ_S −6.5 ($w_{1/2}$ 130 Hz); *m*/*z* 316 ($M + H^+$, 1%), 251 ($M^+ - SO_2$, 7), 192 (8), 176 (19), 160 (28), 134 (12), 118 (38) and 91 (100).

(5*S*)-3-Thia-1-azabicyclo[3.3.0]octan-2-one 3,3-dioxide 5d. (5*S*)-3-Thia-1-azabicyclo[3.3.0]octan-2-one **13d** gave **5d** as colourless crystals (70%), mp 175–176 °C (Found: C, 41.1; H, 5.2; N, 7.95. $C_6H_9NO_3S$ requires C, 41.1; H, 5.2; N, 8.0%); $[a]_D^{20}$ +30.7 (*c* 0.104, Me_2SO); ν_{max}/cm^{-1} 3440, 1740 (CO), 1320 and 1130 (SO_2) and 1160; $\delta_H(CD_2Cl_2)$ 3.95 (1 H, m), 3.80 (1 H, dd, *J* 13, 6), 3.55 (2 H, m), 3.02 (1 H, dd, *J* 13, 9), 2.39 (1 H, m), 2.20 (1 H, m), 2.02 (1 H, m) and 1.56 (1 H, qd, *J* 12, 8); δ_C see Table 1; *m*/*z* 111 ($M^+ - SO_2$, 25%), 82 (10), 68 (80), 67 (100), 55 (70) and 53 (55).

An attempt to prepare **5d** by oxidation of **13d** using 32% peroxyacetic acid in acetic acid,[6] gave the desired product in 37% yield, but this was now accompanied by (2S)-*pyrrolidine*-2-*methanesulfonic acid* **15** (24%) as a colourless powder, mp 260 °C (decomp.) (Found: C, 36.0; H, 6.6; N, 8.2. $C_5H_{11}NO_3S$ requires C, 36.4; H, 6.7; N, 8.5%); $[a]_D^{20}$ +31.2 (*c* 1.0 in H_2O); ν_{max}/cm^{-1} 2900–2400, 1377, 1172 and 1045; $\delta_H(CD_3SOCD_3)$ 8.90 (1 H, br s), 8.40 (1 H, br s), 3.75 (1 H, m), 3.15 (2 H, m), 2.90 (1 H, m), 2.87 (1 H, d, *J* 2), 2.10 (1 H, m), 1.90 (1 H, m), 1.80 (1 H, m) and 1.60 (1 H, m); $\delta_C(CD_3SOCD_3)$ 56.4 (CH), 51.8 (CH_2), 44.8 (CH_2), 29.9 (CH_2) and 22.7 (CH_2); *m*/*z* 165 (M^+, 5%), 157 (5), 122 (5), 111 (10), 97 (10), 84 (55) and 44 (90).

FVP of thiazolidin-2-one 1,1-dioxides 5

The apparatus used is similar to one which has been illustrated and described recently.[20] The sample was volatilised from a tube in a Büchi Kugelrohr oven through a 30 × 2.5 cm horizontal fused quartz tube. This was heated externally by a Carbolite Eurotherm tube furnace MTF-12/38A to a temperature of 600–650 °C, the temperature being monitored by a Pt/Pt–13%Rh thermocouple situated at the centre of the furnace. The products were collected in a U-shaped trap cooled in liquid nitrogen. The whole system was maintained at a pressure of 1–2 × 10^{-3} Torr by an Edwards Model E2M5 high capacity rotary oil pump, the pressure being measured by a Pirani gauge situated between the cold trap and the pump. Under these conditions the contact time in the hot zone was estimated to be ≈10 ms.

After the material had all sublimed, the products were recovered directly from the cold trap and analysed by ^1H and ^{13}C NMR spectroscopy and GC–MS, the identity of the products being determined by comparison with authentic samples. Yields were determined by calibration of the ^1H NMR spectra by adding an accurately weighed quantity of a solvent such as CH_2Cl_2 and comparing integrals, a procedure estimated to be accurate to ±10% or, for products such as benzonitrile which did not show a distinctive NMR signal, from the GC integrals.

Pyrolysis of 5a. 5a (0.10 g, 650 °C) gave a yellow oil. Careful analysis of the ^{13}C and ^1H NMR spectra and GC–MS showed eleven compounds to be present: but-1-ene **16a** (13%), benzyl isocyanate **17** (2%), dibenzylurea **18** (24%), 4-ethyl-2-phenyl-4,5-dihydrothiazole **21a** (5%), 2-phenylthiazole **23a** (3%), benzonitrile (19%), bibenzyl (10%), *N*-benzylidenebenzylamine (5%), benzaldehyde (2%), toluene (4%) and propanal (2%).

Pyrolysis of 5b. 5b (103 mg, 650 °C) afforded a yellow oil in the cold trap. Analysis of the ^{13}C and ^1H NMR spectra and GC–MS showed eleven compounds to be present: 3-methylbut-1-ene **16b** (12%), dibenzylurea **18** (10%), 4-isopropyl-2-phenyl-4,5-dihydrothiazole **21b** (4%), 2-phenylthiazole **22b** (4%), 4-isopropyl-2-phenylthiazole **23b** (4%), benzonitrile (16%), bibenzyl (6%), *N*-benzylidenebenzylamine (7%), benzaldehyde (2%), toluene (1%) and 2-methylpropanal (5%).

Pyrolysis of 5c. 5c (118 mg, 650 °C) afforded a yellow oil at the furnace exit and in the cold trap. Analysis of the ^{13}C and ^1H NMR spectra and GC–MS showed the oil to contain nine products: allylbenzene **16c** (18%), dibenzylurea **18** (15%), 4-benzyl-2-phenyl-4,5-dihydrothiazole **21c** (3%), 2-phenylthiazole **22c** (8%), 4-benzyl-2-phenylthiazole **23c** (2%), bibenzyl (12%), benzonitrile (7%), benzaldehyde (4%) and toluene (5%).

Pyrolysis of 5d. 5d (120 mg, 600 °C) afforded a yellow oil in the cold trap. The ^{13}C and ^1H NMR spectra showed a large number of compounds to be present, but identification proved inconclusive. GC–MS analysis showed a major product with *m*/*z* 83 (C_5H_9N) but examination of the ^{13}C NMR spectrum showed that the signals for the likely product, 3,4-dihydro-5-methyl-2*H*-pyrrole **27** were absent.

Synthesis of authentic samples of FVP products

Preparation of 3-methylbut-1-ene 16b. The FVP of isoamyl acetate (2.5 g, 19 mmol, 750 °C, 7.0 × 10^{-3} Torr) afforded 3-methylbut-1-ene (0.2 g, 15%); δ_H 5.8–5.75 (1 H, m), 5.0–4.85 (2 H, m), 2.28 (1 H, m) and 0.98 (6 H, d, *J* 8); δ_C 146.0 (CH), 111.1 (CH_2), 32.0 (CH) and 22.0 (2 CH_3).

Flash vacuum pyrolysis of benzyl isocyanate 17. The FVP of benzyl isocyanate (0.20 g, 650 °C, 1.0 × 10^{-3} Torr) produced no change in the starting compound. Upon standing overnight the liquid solidified to afford dibenzylurea **18** (0.18 g, 99%); δ_H 7.4–7.1 (10 H, m), 6.5 (2 H, br s) and 4.25 (4 H, d, *J* 4); $\delta_C(CD_3SOCD_3)$ 158.1 (CO), 140.7 (2 4^{ry}), 128.1 (4 CH), 126.9 (4 CH), 126.5 (2 CH) and 42.9 (2 CH_2).

4,5-Dihydrothiazoles 21 and thiazoles 22 and 23. The 4,5-dihydrothiazoles **21a**–**c** were prepared, as previously described,[10] by acylation of the appropriate amino alcohol **7** with benzoyl chloride to give **24** followed by treatment with P_2S_5. These were then used to obtain the 2,4-disubstituted thiazoles **22a**, **23b** and **23c** by treatment with sulfur.[10]

2-Phenylthiazole **23a** was prepared by the method of Lawson and Searle,[16] as a colourless oil (25%), bp (oven temp.) 160 °C at 1.0 Torr (lit.,[16] 267–279 °C at 760 Torr); δ_H 7.95–7.90 (2 H, m), 7.81 (1 H, d, *J* 3), 7.35–7.30 (3 H, m) and 7.20 (1 H, d, *J* 3); δ_C 168.2 (4^{ry}), 143.6 (CH), 133.5 (4^{ry}), 129.9 (CH), 128.9 (2 CH), 126.5 (2 CH) and 118.7 (CH).

Preparation of *N*-benzylidenebenzylamine. Benzaldehyde (5.43 g, 51.2 mmol) was added to a stirred solution of benzylamine (5.48 g, 51.2 mmol) in toluene (150 cm^3). Heating under reflux for 1 h using a Dean–Stark separator followed by evaporation

of the solution, afforded a yellow oil which was Kugelrohr distilled to yield *N*-benzylidenebenzylamine (9.0 g, 90%) as a colourless oil, bp (oven temp.) 175 °C at 0.5 Torr (lit.,[21] 200–202 °C at 10–20 Torr); δ_H 8.25 (1 H, s), 7.7 (2 H, m), 7.35–7.1 (8 H, m) and 4.7 (2 H, s); δ_C 162.6 (CH), 140.1 (4^{ry}), 136.9 (4^{ry}), 131.4 (CH), 129.3 (2 CH), 129.2 (2 CH), 129.0 (2 CH), 128.7 (2 CH), 127.7 (CH) and 65.6 (CH_2).

Preparation of 3,4-dihydro-5-methyl-2*H*-pyrrole 27. An ethereal solution of methyllithium (1.4 M; 37.5 cm^3, 50 mmol) was cooled to −20 °C and a solution of *N*-vinylpyrrolidin-2-one (5.0 g, 45 mmol) dissolved in diethyl ether (50 cm^3) was added dropwise over a period of 2 min. The mixture was stirred for a further 2 min at −20 °C and then 1 M hydrochloric acid (70 cm^3) was added and the mixture stirred for an additional 2 min. The organic layer was separated and extracted with dilute hydrochloric acid, the combined aqueous layers were washed with diethyl ether and then treated with aqueous sodium hydroxide until pH 10 was reached. The imine was extracted with CH_2Cl_2 and the extracts combined, dried, evaporated and Kugelrohr distilled to afford 3,4-dihydro-5-methyl-2*H*-pyrrole (1.83 g, 49%) as a colourless oil, bp (oven temp.) 50 °C at 14 Torr (lit.,[22] 103–105 °C at 760 Torr); δ_H 3.38 (2 H, m), 2.10 (2 H, t, *J* 9), 1.66 (3 H, s) and 1.50 (2 H, quintet, *J* 9); δ_C 174.7 (4^{ry}), 61.1 (CH_2), 38.7 (CH_2), 23.0 (CH_2) and 19.7 (CH_3).

Photolysis of 5c

A solution of **5c** (20 mg) in [$^2H_6$]acetone (0.5 cm^3) in a dry NMR tube was irradiated with a 100 W medium pressure mercury lamp. After 10 days the NMR spectra showed the dissolved material to be completely unchanged but a small crystal (≈2 mg) had been deposited which was found to be 2-*benzylamino*-3-*phenylpropane*-1-*sulfonic acid* **28** (Found: C, 61.7; H, 6.4; N, 4.5. $C_{16}H_{19}NO_3S{\cdot}0.4H_2O$ requires C, 61.5; H, 6.4; N, 4.5%); $\delta_H(CD_3SOCD_3)$ 9.4–9.2 (1 H, br s), 9.2–9.0 (1 H, br s), 7.6–7.4 (5 H, m), 7.4–7.2 (5 H, m), 4.5–4.3 (2 H, m), 3.65 (1 H, m), 3.35 (1 H, half AB pattern of d, *J* 20, 15), 2.90 (1 H, half AB pattern of d, *J* 20, 10), 2.70 (1 H, half AB pattern of d, *J* 15, 10) and 2.65 (1 H, half AB pattern of d, *J* 15, 4), $\delta_C(CD_3SOCD_3)$ 136.0 (4^{ry}), 132.0 (4^{ry}), 129.5 (2 CH), 129.3 (2 CH), 129.0 (CH), 128.8 (2 CH), 128.6 (2 CH), 127.0 (CH), 56.5 (CH), 48.8 (CH_2), 47.5 (CH_2) and 35.2 (CH_2).

Acknowledgements

We thank Zeneca Pharmaceuticals and SERC for a Case studentship (D. P. A.) and the Royal Society for a Warren Research Fellowship (R. A. A.).

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Paper 7/00521K
Received 22*nd January* 1997
Accepted 25*th March* 1997