Photochemical Synthesis of Tricyclic β-Lactams and their Isomerization to β-Thiolactones

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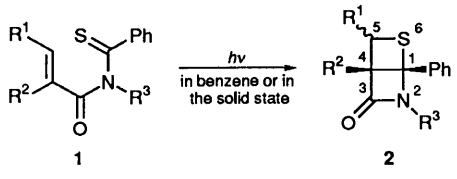
The photochemistry of cyclic *N*-(α,β-unsaturated carbonyl)-thionocarbamates and -dithiocarbamates has been studied. Photolysis of a benzene solution of 3-(methacryloyl)thiazolidine-2-thione gave 4-methyl-2,9-dithia-6-azatricyclo[4.3.0.0^{1,4}]nonan-5-one (a tricyclic-β-lactam) (30%) and 2-(3'-methyl-2'-oxothietan-3'-yl)-2-thiazoline (a β-thiolactone) (30%). Irradiation of 3-(2'-methylbut-2-enoyl)thiazolidine-2-thione, 3-(methacryloyl)oxazolidine-2-thione, and 3-(2'-methylbut-2-enoyl)oxazolidine-2-thione gave the corresponding β-lactams (33–67%), whereas that of the six-membered compounds, 3-(methacryloyl)- and 3-(2'-methylbut-2-enoyl)tetrahydro-1,3-oxazine-2-thione, led to β-thiolactones (33–66%). The ring transformation of this new ring system (thietane-fused penams and oxapenams) to β-thiolactones was confirmed by the fact that, on pyrolysis, the β-lactams gave the corresponding β-thiolactones in quantitative yield.

Considerable ingenuity has been demonstrated over many years in devising syntheses of the β-lactam system, the core element of penicillin and cephalosporin antibiotics, much effort having also been expended in the preparation of simple β-lactams.[1] Also, the photochemical behaviour of thiocarbonyl compounds has received much attention since it differs from that of the corresponding carbonyl derivatives, the mechanistic and synthetic features being of particular interest.[2] The Paterno–Büchi reaction of thioamides[3] and cyclic thioimides[4] are examples of this. Recently we reported the photochemical synthesis of thietane-fused β-lactams **2** involving intramolecular [2 + 2] cyclization of acyclic *N*-(α,β-unsaturated carbonyl)-thiobenzamides **1** (Scheme 1).[5] The substituent on the 1-



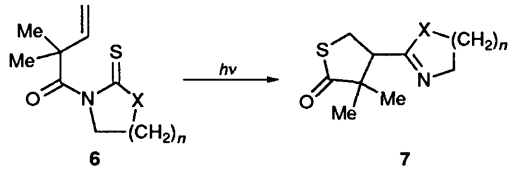
1 **2**

Scheme 1

position of the β-lactams was limited to aryl groups because of the stability of the starting materials **1**. In this study of the photochemistry of monothioimides, we have discovered that irradiation of *N*-(α,β-unsaturated carbonyl)-thionocarbamates and -dithiocarbamates gave new β-lactam systems, thietane-fused penams and oxapenams. Furthermore, the ring transformation of these new ring systems to β-thiolactones has also been studied.

All the *N*-acyl cyclic dithiocarbamates **3a**, **b** and thionocarbamates **3c–f** were obtained by condensing α,β-unsaturated carboxylic acid chlorides with the corresponding cyclic dithiocarbamates or thionocarbamates in the presence of triethylamine.† A benzene solution of 3-(methacryloyl)thiazolidine-2-thione **3a** in a Pyrex vessel when irradiated under an argon atmosphere with the UV light from a 1 kW high-pressure mercury lamp until the starting material had disappeared, gave 4-methyl-2,9-dithia-6-azatricyclo[4.3.0.0^{1,4}]nonan-5-one **4a** (30%) and 2-(1'-methyl-2'-oxothietan-3'-yl)-4,5-dihydrothiazole **5a** (30%).

The structure of **4a** was inferred from the results of elemental analysis and spectral data.‡ The IR spectrum of **4a** exhibits absorption at 1755 cm^{-1} attributable to the carbonyl bond of the four-membered lactam. The ^{1}H NMR spectrum shows an ABq at δ 3.03 and 3.60 assignable to the methylene protons of the thietane ring and the absence of olefinic protons. The ^{13}C NMR spectrum exhibits two singlet peaks at δ 84.3 (1-C) and 69.8 (4-C), and a triplet at 31.3 (3-C). No signals which could be attributed to the thiocarbonyl and olefinic group carbons were observed. The structure of **5a** was determined by a comparison of spectral data for 2-(5',5'-dimethyl-4'-oxothiolan-3'-yl)-4,5-dihydrothiazole **7** which was obtained from a photoreaction of *N*-(2',2'-dimethylbut-3'-enoyl)thiazolidine-2-thione **6** (see Scheme 2) and the structure of **7** was unequivocally



6 **7**

X = S, O, or CH_2
n = 1 or 2

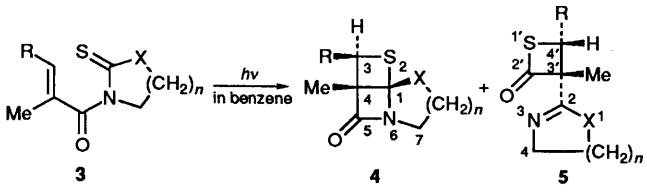
Scheme 2

established by X-ray crystallographic analysis.[6] The IR spectrum of **5a** exhibits absorption at 1755 cm^{-1} derived from the β-thiolactone carbonyl group whereas that of **7** was shown at 1720 cm^{-1}. For the ^{1}H and ^{13}C NMR spectra, peaks attributable to the 4,5-dihydrothiazole entity are

† Since all *N*-acyl dithiocarbamates **3a**, **b** and thionocarbamates **3c–f** were unstable, they were used as soon as possible without purification after removal of the solvent and precipitated Et_3N·HCl from the reaction mixture of thionourethane or dithiourethane, Et_3N and α,β-unsaturated carboxylic acid chloride. The crude materials were used for the photochemical step and the yields of β-lactams **4** and β-thiolactones **5** were determined on the basis of the amount of corresponding thionocarbamates and dithiocarbamates.

‡ The assignments were performed by 2D proton–carbon correlation experiments.

Table 1 Photolysis of *N*-(α,β-unsaturated carbonyl)-dithiocarbamates **3a**, **b** and -thionocarbamates **3c–f**



3 **4** **5**

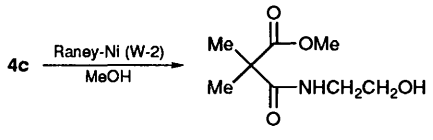
				Yield (%)[a]	
3	R	X	*n*	**4**	**5**
a	H	S	1	30	30
b	Me	S	1	67	0
c	H	O	1	44	0
d	Me	O	1	33	0
e	H	O	2	0	33
f	Me	O	2	0	66

[a] Isolated yields.

identical with those of compound **7**. The ^{1}H NMR spectrum for the β-thiolactone group showed an ABq at δ 2.95 and 3.69 attributable to 4′-H, and the ^{13}C NMR exhibits a triplet at δ 28.8 (4′-C) and two singlets at 78.1 (1′-C) and 192.0 (s, 2′-C=O).

The photolysis of other five-membered compounds **3b–d** gave the corresponding β-lactams **4b–d** (Table 1), whereas that of the six-membered compounds, *N*-acyl-tetrahydro-1,3-oxazine-2-thione **3e** and **3f**, provided the β-thiolactones **5e**, **f** in which the corresponding β-lactams **4e**, **f** were not detected.

Furthermore, the structure of the β-lactams **4** was supported by the fact that desulfurization of the β-lactam **4c** by Raney Ni (W-2) in methanol gave **8** (Scheme 3). Formation of compound



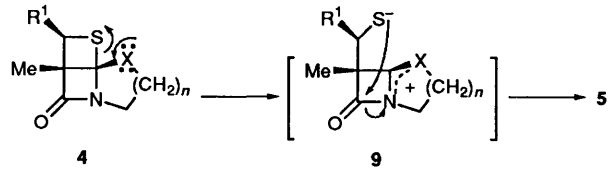
8

Scheme 3

8 is explainable in terms of the initial nucleophilic addition of methanol at the 1-position of the β-lactam **4c** followed by cleavage of the C(O)–N bond and desulfurization.

In order to determine the configuration of both β-lactams and β-thiolactones obtained from the tigloyl derivatives **1b**, **d**, **f**, an NOE study was carried out. Irradiation of the 3-methyl doublet at δ 1.54 of the β-lactam **4b** resulted in an increase in the area of both the 3-H methine quartet and the 4-methyl singlet at δ 4.15 and 1.28, respectively. Alternatively, irradiation of the 3-H methine quartet gave an increase in the 3-methyl singlet, but led to no observable NOE for the 4-methyl singlet resonance. Furthermore, irradiation of the 4-methyl singlet gave an increase in the 3-methyl doublet resonance but there was an absence of NOE between it and the 3-H methine quartet resonance. From these results, a *syn* configuration was assigned to the 3-Me and 4-Me of the β-lactams **4b**. The *anti* configuration of **5b** was also determined on the basis of an NOE experiment. Enhancement was shown for both 3′-Me singlet and 4′-Me doublet resonances when the 4′-H quartet was irradiated. Irradiation of the 3′-Me singlet gave an increase in the 4′-H methine resonance, but led to no observable NOE effect for the 4′-methyl doublet resonance. The *syn* configuration for **4d** and *anti* for **5d** and **5f** were also determined in a manner similar to that described above.

As mentioned above, we have already reported the photochemical reaction of **6** followed by a similar rearrangement to provide **7** (Scheme 2).* It is reasonable to presume that the β-thiolactone **5** is a secondary product from the primary photoproduct, the β-lactam **4**. In fact, when a dry toluene solution of **4a** or **4b** was heated under reflux for 4 h under a nitrogen atmosphere, **5a** or **5b** was obtained quantitatively. It is concluded that the transformation of β-lactams **4** to the β-thiolactones **5** involves the zwitterionic intermediate **9**, whereas the mechanism by way of a homolytic cleavage or a concerted process is also plausible (Scheme 4). We were unsuccessful in



4 **9**

Scheme 4

attempts to trap the intermediate by dipolarophiles such as dimethyl maleate or furan, since the thiolactone **5b** was formed, as in the absence of them, when **4b** was used for the reaction.†

Finally, the photolysis of various *N*-(α,β-unsaturated carbonyl)-thionocarbamates **3a**, **b** and -dithiocarbamates **3c–f** gave new β-lactam systems, thietane-fused penams **4a**, **b** and oxapenams **4c**, **d**, and β-thiolactones **5a–f**. Ring-opening, which reveals the angle strain in the tricyclic β-lactams, is facilitated by the electron-donating effect of the two heteroatoms adjacent to the thietane ring. The present reaction provides a useful synthetic route to new β-lactam systems, thietane-fused penams and oxapenams. Furthermore, the ring transformation of these new ring systems to β-thiolactones was also studied.

Experimental

IR spectra of $CDCl_3$ solutions were recorded with a Shimadzu IR-420 spectrophotometer. ^{1}H and ^{13}C NMR spectra of $CDCl_3$ solutions were recorded with JEOL FX-270 and GSX-500 spectrometers, respectively; *J*-values are given in Hz. An Eikosya 1 kW high-pressure Hg lamp was used in the irradiations. Silica gel (Merck, Kieselgel 60, 230–400 mesh) was used for flash chromatography.

Preparation of N-(α,β-*Unsaturated Carbonyl*)-*dithiocarbamates* **3a**, **b** *and* -*thionocarbamates* **3c–f**.—To a cold (0 °C) stirred solution of the thionourethane or dithiourethane (3.0 mmol), Et_3N (3.6 mmol) and THF (30 cm^3) under N_2 was added dropwise the α,β-unsaturated carboxylic acid chloride (3.6 mmol). The mixture was stirred for 2 h at room temperature after which it was evaporated under reduced pressure. A mixture of solvents (benzene–hexane, 1:1; 50 cm^3) was added to the residue to precipitate the Et_3N·HCl which was then filtered off through a Celite 545 column. The filtrate was evaporated under reduced pressure to provide the *N*-acyl-dithiocarbamates **3a**, **b** and -thionocarbamates **3c–f**, since these were unstable they were used as soon as possible without further purification. The crude products were used for the

* A similar rearrangement has been reported for aminothietane generated by intermolecular 2 + 2 cycloaddition of indolethione and alkenes.[7]

† It is known that dimethyl maleate is one of the most reactive dipolarophiles for 1,3-dipolar cycloaddition.[8]

photochemical step and the yields of β-lactams and β-thiolactones were determined on the basis of the amount of the corresponding thionocarbamates and dithiocarbamates.

3-*Methacryloylthiazolidine*-2-*thione* **3a**: ν_{max}/cm^{-1} 1700; δ_H 2.06 (d, *J* 0.9, 3 H, 2'-Me), 3.3–3.4 (m, 2 H, 5-CH_2), 4.3–4.4 (m, 2 H, 4-CH_2), 5.47 (m, 1 H, 3'-H) and 5.59 (d, *J* 0.6, 1 H, 3'-H); δ_C 18.8 (q, 2'-Me), 29.8 (t, 5-C), 55.9 (t, 4-C), 122.5 (t, 3'-C), 140.1 (s, 2'-C), 172.7 (s, C=O) and 201.6 (s, C=S).

3-(2'-*Methylbut*-2-*enoyl*)*thiazolidine*-2-*thione* **3b**: ν_{max}/cm^{-1} 1700; δ_H 1.79 (d, *J* 7.2, 3 H, 3'-Me), 1.90 (d, *J* 1.1, 3 H, 2'-Me), 3.39 (dd, *J* 7.2 and 7.4, 2 H, 5-CH_2), 4.37 (dd, *J* 7.2 and 7.4, 2 H, 4-CH_2) and 6.35–7.45 (m, 1 H, 3'-H); δ_C 13.0 (q, 3'-Me), 14.5 (q, 2'-Me), 29.7 (t, 5-C), 56.2 (t, 4-C), 128.6 (s, 2'-C), 137.3 (d, 3'-C), 173.3 (s, C=O) and 201.6 (s, C=S).

3-*Methacryloyloxazolidine*-2-*thione* **3c**: ν_{max}/cm^{-1} 1680 and 1640; δ_H 2.09 (dd, *J* 1.1 and 1.65, 3 H, 2'-Me), 4.17 (dd, *J* 8.0 and 8.3, 2 H, 5-CH_2), 4.59 (dd, *J* 8.0 and 8.3, 2 H, 4-CH_2), 5.47 (d, *J* 1.65, 1 H, 3'-H), and 5.53 (s, 1 H, 3'-H); δ_C 19.3 (q, Me), 47.3 (t, 4-C), 67.1 (t, 5-C), 122.0 (t, 3'-C), 139.5 (s, 2'-C), 172.1 (s, C=O) and 185.9 (s, C=S).

3-(2'-*Methylbut*-2-*enoyl*)*oxazolidine*-2-*thione* **3d**: ν_{max}/cm^{-1} 1680 and 1640; δ_H 1.80 (d, *J* 7.0, 3 H, 3'-Me), 1.86 (d, *J* 1.1, 3 H, 2'-Me), 4.1–4.2 (m, 2 H, 5-CH_2), 4.5–4.6 (m, 2 H, 4-CH_2) and 6.3–6.5 (m, 1 H, 3'-H); δ_C 13.3 (q, 3'-Me), 14.7 (q, 2'-Me), 47.5 (t, 4-C), 67.0 (t, 5-C), 128.5 (s, 2'-C), 136.3 (d, 3'-C), 172.7 (s, C=O) and 186.4 (s, C=S).

3-*Methacryloyl-tetrahydro*-1,3-*oxazine*-2-*thione* **3e**: ν_{max}/cm^{-1} 1700 and 1630 cm $^{-1}$; δ_H 2.09 (d, *J* 0.7, 3 H, 2'-Me), 2.2–2.3 (m, 2 H, 5-CH_2), 3.70 (t, *J* 6.9, 2 H, 4-CH_2), 4.43 (t, *J* 5.5, 2 H, 6-CH_2), 5.50 (m, 1 H, 3'-H), and 5.64 (d, *J* 0.6, 1 H, 3'-H); δ_C 18.7 (q, Me), 21.5 (t, 5-C), 44.3 (t, 4-C), 68.4 (t, 6-C), 121.8 (t, 3'-C), 140.9 (s, 2'-C), 174.2 (s, C=O) and 188.9 (s, C=S).

3-(2'-*Methylbut*-2-*enoyl*)-*tetrahydro*-1,3-*oxazine*-2-*thione* **3f**: ν_{max}/cm^{-1} 1680 and 1640; δ_H 1.82 (d, *J* 7.0, 3 H, 3'-Me), 1.94 (d, *J* 1.1, 3 H, 2'-Me), 2.2–2.3 (m, 2 H, 5-CH_2), 3.66 (t, *J* 6.8, 2 H, 4-CH_2), 6.4–6.5 (m, 1 H, 3'-H); δ_C 12.6 (q, 3'-Me), 14.6 (q, 2'-Me), 21.2 (t, 5-C), 44.5 (t, 4-C), 68.2 (t, 6-C), 133.2 (s, 2'-C), 136.9 (d, 3'-C), 174.3 (s, C=O) and 187.7 (s, C=S).

General Procedure for the Photolysis of the N-*Acyl-dithiocarbamates* **3a**, **b** *and -thiocarbamates* **3c–f**.—A benzene solution of **3a–f** in a Pyrex vessel under Ar was irradiated at 15 °C with the UV light from a 1 kW high-pressure mercury lamp until the starting material had disappeared (*ca.* 4–6 h in all cases). The residue obtained by concentrating the reaction mixture was purified by flash chromatography (eluent: benzene–EtOAc, 10:1–3:1). The crystalline products were recrystallized from Et_2O–hexane.

4-*Methyl*-2,9-*dithia*-6-*azatricyclo*[4.3.0.0^{1,4}]*nonan*-5-*one* **4a**: m.p. 97.5–99 °C; ν_{max}/cm^{-1} 1755; δ_H 1.36 (s, 3 H, 4-Me), 3.03 and 3.60 (ABq, *J* 11, 2 H, 3-CH_2), 3.0–3.4 (m, 3 H, 8-CH_2 and 7-CH) and 3.9–4.2 (m, 1 H, 7-CH); δ_C 14.7 (q, 4-Me), 31.3 (t, 3-C), 39.8 (t, 8-C), 43.5 (t, 7-C), 69.8 (s, 4-C), 84.3 (s, 1-C) and 172.7 (s, 5-C=O) (Found: C, 44.7; H, 4.85; N, 7.5. Calc. for $C_7H_9NOS_2$: C, 44.89; H, 4.84; N, 7.47%).

2-(3'-*Methyl*-2'-*oxothietan*-3'-*yl*)-4,5-*dihydrothiazole* **5a**: b.p. 60 °C (10 $^{-3}$ Torr); ν_{max}/cm^{-1} 1755 and 1610; δ_H 1.71 (s, 3 H, 3'-Me), 2.95 and 3.69 (ABq, *J* 8.8, 2 H, 4'-CH_2), 3.36 (t, *J* 7.8, 2 H, 5-CH_2) and 4.28 (t, *J* 7.8, 2 H, 4-CH_2); δ_C 22.2 (q, 3'-Me), 28.8 (t, 4'-C), 33.8 (t, 5-C), 64.0 (t, 4-C), 78.1 (s, 3'-C), 168.2 (s, 2-C) and 192.0 (s, 2'-C=O) (Found: C, 45.15; H, 4.85; N, 7.3. Calc. for $C_7H_9NOS_2$: C, 44.89; H, 4.84; N, 7.47%).

(syn)-3,4-*Dimethyl*-2,9-*dithia*-6-*azatricyclo*[4.3.0.0^{1,4}]*nonan*-5-*one* **4b**: m.p. 71–72 °C; ν_{max}/cm^{-1} 1755; δ_H 1.28 (s, 3 H, 4-Me), 1.45 (d, *J* 7.0, 3 H, 3-Me), 3.1–3.2 (m, 3 H, 8-CH_2 and 7-CH), 4.0–4.1 (m, 1 H, 7-CH) and 4.15 (q, *J* 7.0, 1 H, 3-CH); δ_C 9.5 (q, 4-Me), 18.5 (q, 3-Me), 39.6 (t, 8-C), 40.0 (d, 3-C), 43.4 (t, 7-C), 64.4 (s, 4-C), 72.4 (s, 1-C), and 173.7 (s, 5-C=O) (Found: C, 47.8; H, 5.6; N, 7.0. Calc. for $C_8H_{11}NOS_2$: C, 47.73; H, 5.50; N, 6.95%).

4-*Methyl*-9-*oxa*-2-*thia*-6-*azatricyclo*[4.3.0.0^{1,4}]*nonan*-5-*one* **4c**: m.p. 67–68 °C; ν_{max}/cm^{-1} 1755; δ_H 1.36 (s, 3 H, 4-Me), 3.03 and 3.60 (ABq, *J* 11, 2 H, 3-CH_2), 3.0–3.4 (m, 3 H, 8-CH_2 and 7-CH) and 3.9–4.2 (m, 1 H, 7-CH); δ_C 14.7 (q, 4-Me), 31.3 (t, 3-C), 39.8 (t, 8-C), 43.5 (t, 7-C), 69.8 (s, 4-C), 84.3 (s, 1-C) and 172.7 (s, 5-C=O) (Found: C, 49.35; H, 5.4; N, 8.2. Calc. for $C_7H_9NO_2S$: C, 49.12; H, 5.30; N, 8.18%).

(syn)-3,4-*Dimethyl*-9-*oxa*-2-*thia*-6-*azatricyclo*[4.3.0.0^{1,4}]-*nonan*-5-*one* **4d**: m.p. 64–65 °C; ν_{max}/cm^{-1} 1765; δ_H 1.26 (s, 3 H, 4-Me), 1.44 (d, *J* 7.0, 3 H, 3-Me), 3.2–3.25 (m, 1 H, 7-CH), 3.8–3.9 (m, 1 H, 7-CH), 3.92 (q, *J* 7.0, 1 H, 3-CH), 4.0–4.2 (m, 1 H, 8-CH) and 4.4–4.45 (m, 1 H, 8-CH); δ_H 7.24 (q, 4-Me), 18.2 (q, 3-Me), 36.8 (d, 3-C), 42.3 (t, 7-C), 73.8 (s, 4-C), 74.1 (s, 8-C), 98.0 (s, 1-C) and 178.1 (s, 5-C=O) (Found: C, 52.0; H, 6.0; N, 7.6. Calc. for $C_8H_{11}NO_2S$: C, 51.88; H, 5.99; N, 7.56%).

2-(3'-*Methyl*-2'-*oxothietan*-3'-*yl*)-4,5-*dihydrooxazine* **5e**: ν_{max}/cm^{-1} 1750 and 1660; δ_H 1.61 (s, 3 H, 3'-Me), 1.85–1.92 (m, 2 H, 5-CH_2), 2.74 and 3.59 (ABq, *J* 8.2 Hz, 2 H, 4'-CH_2), 3.44 (t, *J* 5.9, 2 H, 4-CH_2), and 4.23 (t, *J* 5.5, 2 H, 6-CH_2); δ_C 20.8 (q, 3'-Me), 21.6 (t, 5-C), 27.6 (t, 4'-C), 42.3 (t, 4-C), 65.5 (t, 6-C), 78.8 (s, 3'-C), 156.1 (s, 2-C) and 193.1 (s, 2'-C=O) [Found: *m/z* (FAB), 186.0580. Calc. for $C_8H_{12}NO_2S$ (MH^+): 186.0589].

(anti)-2-(3',4'-*Dimethyl*-2'-*oxothietan*-3'-*yl*)-4,5-*dihydrooxazine* **5f**: ν_{max}/cm^{-1} 1755 and 1660; δ_H 1.58 (s, 3 H, 3'-Me), 1.62 (d, *J* 6.8, 4'-Me), 1.85–1.95 (m, 2 H, 5-CH_2), 3.40 (q, *J* 6.8, 1 H, 4'-CH), 3.4–3.5 (m, 2 H, 4-CH_2) and 4.20–4.25 (m, 2 H, 6-CH_2); δ_C 18.1 (q, 3'-Me), 20.9 (q, 4'-Me), 21.6 (t, 5-C), 40.4 (d, 4'-C), 42.2 (t, 4-C), 65.1 (t, 6-C), 77.3 (s, 3'-C), 155.9 (s, 2-C) and 192.8 (s, 2'-C=O) [Found: *m/z* (FAB) 200.0744. Calc. for $C_9H_{14}NO_2S$ (MH^+): 200.0745].

Desulfurization of **4c** *by Raney Ni*.—To a mixture of methanol and Raney Ni (W-2) was added a methanol solution of the β-lactam **4c** and the mixture was stirred for 1 h. The Raney Ni was filtered off and the filtrate was evaporated under reduced pressure to provide a residue. This was subjected to silica gel column chromatography (eluent: benzene–EtOAc, 4:1) to afford *methyl* 2,2-*dimethyl*-N-(2-*hydroxyethyl*)*malonamate* **8** (38%); ν_{max}/cm^{-1} 3400 (NH), 3250 (OH), 1725 (C=O) and 1640 (C=O); δ_H 1.49 (s, 6 H, 2,2-Me_2), 2.1 (br, 1 H, OH), 3.73 (s, 3 H, CO_2Me), 3.87 (t, *J* 9.2, 2 H, CH_2NH) and 4.29 (t, *J* 9.2, 2 H, CH_2OH); δ_C 23.4 (q, 2,2-Me_2), 44.1 (s, 2-C), 52.5 (q, CO_2Me), 54.2 (t, CH_2NH), 67.9 (t, CH_2OH), 169.4 (s, C=O) and 173.8 (s, C=O) [Found: *m/z* (FAB), 190 (MH^+). Calc. for $C_8H_{16}NO_4$: 190].

Thermal Rearrangement of **4b** *to* **5b**.—A toluene solution (5 cm^3) of **4b** (100 mg) was refluxed for 4 h under N_2 after which the reaction mixture was subjected to column chromatography on silica gel, to give a quantitative yield of (anti)-2-(3',4'-*dimethyl*-2'-*oxothietan*-3'-*yl*)-4,5-*dihydrothiazoline* **5b**; ν_{max}/cm^{-1} 1755 and 1610; δ_H 1.59 (d, *J* 7.0, 3 H, 4'-Me), 1.71 (s, 3 H, 3'-Me), 3.2–3.4 (m, 2 H, 5-CH_2), 3.54 (q, *J* 6.8, 1 H, 4'-CH) and 4.2–4.4 (m, 2 H, 4-CH_2); δ_C 18.2 (q, 4'-Me), 22.9 (q, 3'-Me), 33.6 (t, 5-C), 41.2 (d, 4'-C), 64.5 (t, 4-C), 78.1 (s, 3'-C), 167.9 (s, 2-C) and 192.7 (s, 2'-C=O) [Found: *m/z* (EI), 201.0277. Calc. for $C_8H_{11}NOS_2$ (M^+): 201.0288].

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